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Oxygen Reduction Performance of Pt/TiO_2-C Electrocatalyst prepared by Two-step Chemical Vapor Deposition

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Abstract: *The low durability of Pt/C electro-catalysts in polymer electrolyte membrane fuel cells (PEMFC), e.g., as a result of carbon oxidation to CO_2 in an acid medium, has been recognized as one of the most important hindrances to long-term stability. In this work, Pt electrocatalysts supported on TiO_2-carbon and Vulcan carbon were prepared by the chemical vapor deposition method. The physical and electrochemical properties of Pt/TiO_2-C and Pt/C electrocatalysts were investigated by the characterization techniques of XRD, TEM, CO stripping and cyclic and linear voltammetry. The prepared materials were electrochemically evaluated in the oxygen reduction reaction (ORR) in an acid medium at room temperature. The XRD results show crystalline fcc platinum formation. The mean particle size is between 2 and 4 nm with a spherical morphology. Pt/TiO_2-C electrocatalysts showed a higher electrochemical active surface area and better activity results for the ORR compared with the Pt/C samples. The addition of TiO_2 to the conventional Pt/C catalyst modifies the electronic properties affecting the oxygen adsorption and improving the catalytic activity for the oxygen reduction reaction.*

Keywords: Pt nanoparticles, TiO_2, CVD, Oxygen reduction, Fuel cells

1. INTRODUCTION

The demand for energy is increasing in our modern society. The dependence on oil-based fuels for transportation is the major cause of air pollution in the growing urban areas of the world. This fact has generated strong motivation to find alternative sources of efficiently generated clean energy [1]. Polymer electrolyte fuel cells (PEMFCs) are devices capable of directly converting the stored chemical energy of a fuel into electricity more efficiently than an internal combustion engine and without CO_x emission gasses. Currently, one of the most important challenges for PEMFCs in terms of facilitating their widespread commercial use is to improve the performance and durability of the electrocatalyst by developing novel carbon-based catalyst-support materials [2-3]. Several features are essential for electrocatalysts to be used in a PEMFC, namely, high catalytic activity for hydrogen oxidation (anode) and the oxygen reduction reaction (cathode), resistance to organic molecules (methanol and formic acid) and CO poisoning and good electrical conductivity to allow electron transfer to the catalytic sites [4]. Platinum nanoparticles supported on carbon are commonly used in hydrogen/oxygen fuel cells as electrodes for both the anode and the cathode. Pt-based bimetallic catalysts (e.g., Pt-Fe, Pt-Ni and Pt-Co) for the oxygen reduction reaction (ORR) have been reported to reduce the cost of the catalyst [5]. In terms of durability, the supporting materials should possess a good compromise between the electric conductivity and corrosion resistance. Several approaches to increase the corrosion resistance of electrocatalysts have been studied [6-7]. More stable supporting carbon structures have been designed by the addition of conducting oxides (TiO_2, SnO_2, WO_3, NbO_2, etc.) to create oxidation-resistant catalyst-supports [8-13]. The contact of TiO_2 with Pt is likely to minimize particle agglomeration and therefore maintain control of the nanostructure of the metal catalyst-support [14]. A titanium dioxide-carbon support is an interesting composite material to use in

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fuel cells due to its high stability and durability in environments requiring PEM cathode performance (high-potential and acidic environments) [15]. The metal-support interaction modifies the electronic and stability properties of the catalytic center (ligand effect), thus improving the electrochemical activity for the oxygen reduction reaction (ORR) compared with Pt/C [16-17].

The preparation of catalysts is a fundamental step toward obtaining the desired activity, selectivity and lifetime [18]. Several methods of synthesis have been investigated to increase the activity of the conventional Pt/C electrocatalyst for PEMFCs. To improve on the advantages identified in previous research, in this work, we investigate the two-step chemical vapor deposition (CVD) technique as an alternative synthesis methodology to prepare Pt/C and Pt/TiO_2-C samples as active and stable electrocatalysts for PEMFCs. The use of this technique produces well-dispersed nanoparticles ranging from 1 to 20 nm, depending on their chemical nature and deposition conditions, which have been defined for different powdered substrates [19]. The preparation of supported catalysts by two-step CVD consists of a first step involving precursor vapor absorption on the support particles followed by a thermal treatment to obtain the active particles [20].

2. EXPERIMENTAL

2.1. Materials

Platinum acetyl acetonate [(CH_3-COCHCO-CH_3)$_2$Pt] (Aldrich), carbon (Vulcan XC-72) and TiO_2 rutile nanopowder were the precursors for the Pt/TiO_2-C and Pt/C electrocatalyst preparation involving the two-step CVD method, a technique called vapor-phase impregnation-decomposition [20].

2.2. Catalyst preparation

A thermal horizontal tube quartz reactor was used for the two-step CVD method. For the 10 wt.% Pt/5 wt.% TiO_2-C (CVD) preparation, the organic platinum precursor, the titanium and the carbon support were mechanically mixed at room temperature with a 10:5:85 weight ratio before impregnation. The mixed powders were heated at 473 K for 10 min using a total pressure of 4.5 torr; these conditions evaporated the platinum precursor. Then the impregnated Pt precursor was moved to a higher temperature zone heated to 523 K in a N_2 atmosphere (100 mL min^{-1}) for 10 min inside the tube reactor to achieve precursor decomposition and to produce Pt nanoparticles on the TiO_2-C nanocomposite [21]. The sample containing 10 wt.% Pt/C (CVD) was synthesized using the same conditions mentioned above for the two-step CVD method using a 10:90 (Pt:C) weight ratio.

The 10 wt.% Pt/C (CR) electrocatalyst synthesized by a carbonyl chemical route was prepared for comparison purposes. The 10% Pt/C (CR) shows similar electrocatalytic activity to the 10% Pt/C commercial sample (Pt Etek) [16]. The Pt/C (CR) sample was prepared following the synthesis methodology previously reported [22-23]. Table 1 shows the labeling and classification of platinum electrocatalysts prepared by the two-step chemical vapor deposition and carbonyl route.

2.3. Physical characterization

The X-ray diffraction (XRD) patterns of the prepared platinum base electrocatalysts were collected on Bruker D8 AXS equipment using a Cu anode (K_a, λ=1.5406 Å) and a Bragg-Brentano configuration. The angle 2θ was varied from 30 to 90° at 0.2° min^{-1} and 35 kV. The particle size distribution and the surface morphology of the platinum electrocatalysts were obtained with Transmission Electron Microscopy (TEM) using a JEOL-JEM-2200 field emission microscope operated at 200 kV. The dried samples (Pt/C and Pt/TiO_2-C) were prepared by dispersion in ethanol by ultrasound, and the resulting suspension was deposited onto a cooper mesh and dried at ambient conditions before the TEM analysis.

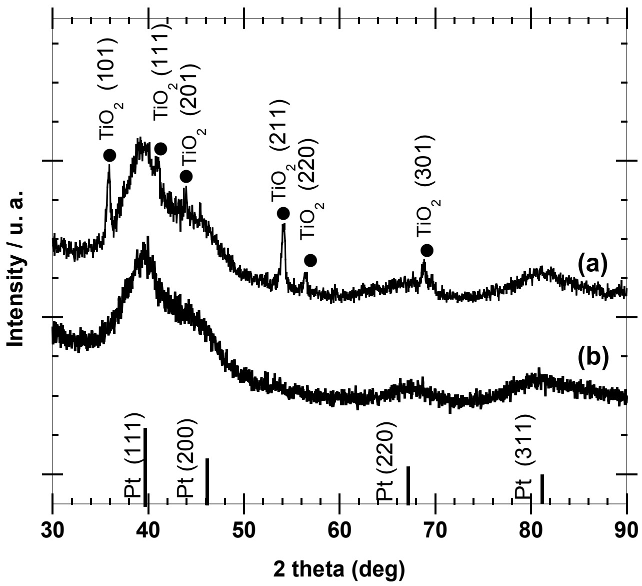

Figure 1. X-ray diffraction patterns of (a)10 wt.% Pt/ 5 wt.% TiO_2-C and (b)10 wt.% Pt/C electrocatalysts prepared by the two-step chemical vapor deposition method. (•) refers to reflections from the TiO_2 rutile phase.

2.4. Electrochemical measurements

A conventional single three-electrode test electrochemical cell was used in the electrochemical experiments. All of the electrode potentials in this work are related to a normal hydrogen electrode (NHE) in a 0.5 M H_2SO_4 aqueous solution electrolyte. The rotating disk electrode (RDE) measurements were performed using a Potentiostat (EG&G PAR 263A) and a Pine MSRX rotation speed controller. All electrochemical experiments were conducted at room temperature. The working electrode was a glassy carbon disk with a 3 mm diameter (0.071 cm^2). Glassy carbon and reference hydrogen electrodes were used as the counter and the reference electrode. The catalytic ink was prepared by dispersing 10 mg of catalyst in 250 mL of Nafion® and 1250 µL of distilled water in an ultrasound bath for 1 h. A drop containing 3.0 mL of catalyst ink was deposited onto the working electrode surface and dried under a nitrogen atmosphere. Cyclic voltammetry (CV) was used to characterize the electrocatalyst surface and to obtain the electrochemical surface area (EAS H_{upd}) [24]. The CV measurements were developed in a nitrogen-saturated electrolyte from 0.05 to 1.2 V at 50 mV s^{-1} until a steady-state voltammogram was reached; approximately 20 cycles were necessary.

Steady-state polarization curves were obtained with the RDE at

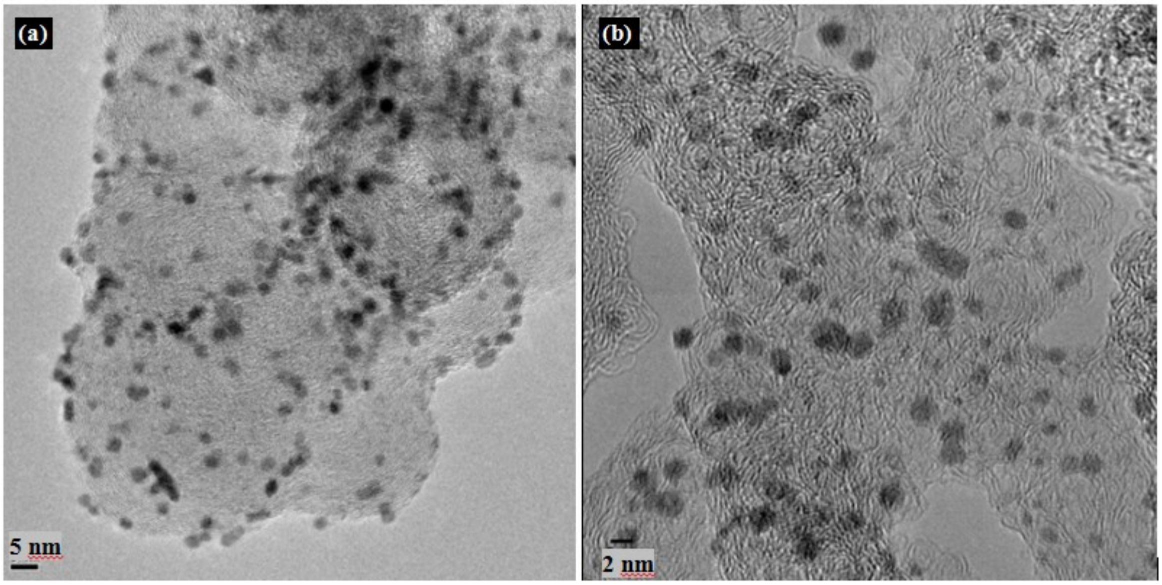

Figure 2. Transmission Electron Microscopy (TEM) graphs for (a) 10 wt.% Pt/5 wt.% TiO$_2$-C and (b) 10 wt.% Pt/C electrocatalysts prepared by the two-step chemical vapor deposition method.

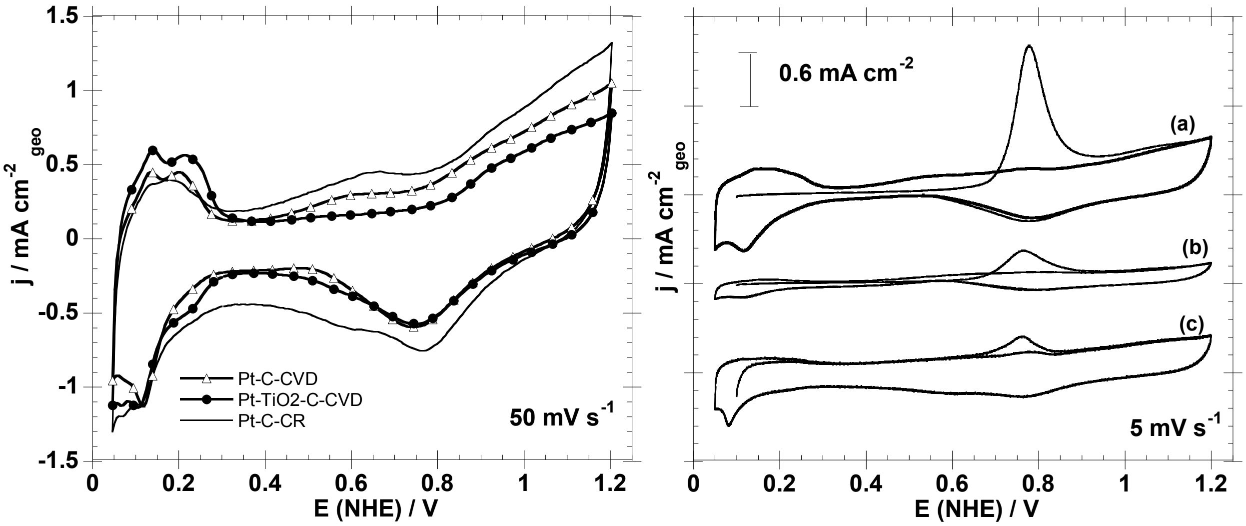

Figure 3. left: Cyclic voltammetry and right: CO tripping for (a) 10 wt.% Pt/ 5 wt.% TiO$_2$-C and (b) 10 wt.% Pt/C electrocatalysts prepared by the two-step chemical vapor deposition compared with (c) 10 wt.% Pt/C-CR catalyst synthesized by the carbonyl route in 0.5 M H_2SO_4 electrolyte at room temperature.

several rotation speeds (200 to 2500 rpm at 5 mV s^{-}1) to evaluate the ORR kinetic parameters, and the experiments were recorded in the potential range between 0.2 and 1.0 V (NHE) using the acid electrolyte saturated with pure oxygen and maintained on the electrolyte surface during the RDE tests. The current density was calculated using the geometric surface area.

The platinum active surface area (EAS H_{upd}) was estimated by obtaining the charge of hydrogen desorption in the potential range from 0.05 to ~0.3 V (NHE) and assuming that hydrogen is only adsorbed on Pt sites with 210 μC corresponding to 1 cm^2 of exposed area. The double-layer charging currents were subtracted from the total voltammetry currents to obtain the H desorption charge [24-25]. The CO stripping technique was used to calculate a complementary electrochemical active surface area (EAS CO). Using the CO gas as a model molecule, the quantity of CO charge desorbed was calculated using the same sample quantity. For the CO stripping technique, the electrode potential was held at 0.1 V/NHE, and CO was bubbled for 5 min. Thereafter, the CO was removed by purging the electrolyte with argon for 15 min. Two cycles were performed from 0.05 V to 1.2 V/NHE at 5 mV s^{-1} to quantify the area under the curve [26].

3. RESULTS AND DISCUSSION

3.1. Physical characterization results

3.1.1. Structural analysis

Fig. 1 shows the X-ray diffraction patterns of (a) Pt/TiO_2-C (CVD) and (b) Pt/C (CVD) electrocatalysts prepared by two-step chemical vapor deposition. In the materials prepared, the face-centered cubic (*fcc*) structure of platinum is identified. The attenuated diffraction peaks of Pt found at 2θ values of 39.8º, 46.2º, 67.4º and 81.2º were ascribed to the (111), (200), (220) and (311) planes. These results were in agreement with the Pt standard JCPDS 04-0802. The presence of some reflections at 2θ values of 36.1°, 41.2°,44.0°, 54.3°, 56.6° and 69° (indicated by solid circles in Fig. 1) can be ascribed to the (101), (111) (210), (211), (220) and (301) planes of rutile-phase TiO_2. The position of the Pt diffraction peaks remained constant. A shift in the peaks position was not observable, indicating that there was no Pt-Ti alloy formation [27, 28].

3.1.2. Morphology

Figure 2 shows TEM images of (a) Pt/TiO_2-C (CVD) and (b) Pt/C (CVD) electrocatalysts prepared by the chemical vapor deposition method. According to the micrographs, both materials had a similar morphology, with uniform distribution on the TiO_2-C nanocomposite and carbon substrates. The mean particle size is between 2 and 4 nm, with a spherical or globular morphology.

3.2. Electrochemical characterization results

3.2.1. Cyclic voltammetry measurements

The left side of Figure 3 shows the corresponding cyclic voltammogram (CV) curves in a nitrogen-purged 0.5 M H_2SO_4 solution at 25 °C on the Pt/C (CVD) and Pt/TiO_2-C (CVD) electrocatalysts compared with the Pt/C (CR) sample. The voltammogram curves of platinum-based electrocatalysts prepared by two-step chemical vapor deposition and the carbonyl route show the fingerprint electrochemical characteristics of platinum and confirm the observations made above with respect to the crystalline size and the dispersion of the catalysts on the oxide-carbon nanocomposite and carbon support. Between 0.05 and 0.3 V/NHE, hydrogen adsorption-desorption is observed. The Pt/TiO_2-C electrocatalysts presented good definition of hydrogen adsorption-desorption as a function of the particle size, crystallographic faces and the Pt electronic density caused by the metal-substrate interaction. On the anodic sweep above 0.8 V/NHE, an oxide film is formed on the surface of the platinum materials. The oxide film is removed during the cathodic sweep by the oxide reduction; between 0.3 and 0.6 V/NHE, the double-layer region is located. The electrochemical surface area (EAS) is an important parameter in the characterization of PEMFC electrocatalysts and electrodes. The EAS H_{upd} can be calculated from CV data (Fig. 3, left) using a charge of 0.21, which corresponds to the charge required to oxidize a monolayer of adsorbed hydrogen on Pt [29-30]. The EAS H_{upd} resulting data are shown in Table 1.

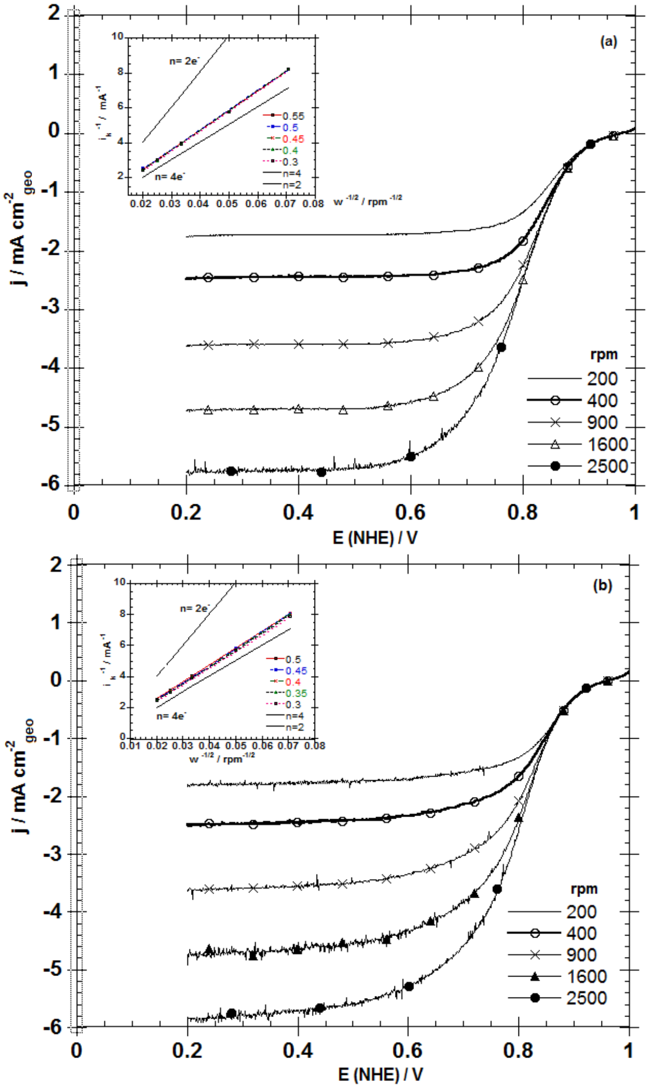

Figure 4. ORR-polarization curves for (a)10 wt.% Pt/ 5 wt.% TiO_2-C (CVD) and (b) 10 wt.% Pt/C (CR) electrocatalysts in saturated oxygen-electrolyte in 0.5 M H_2SO_4 at different rotation rates from 200 to 2500 rpm. Currents were recorded at 5 mV s^{-1}. T=25°C. The inset shows the corresponding Koutecky-Levich plot at various electrode potentials.

3.2.2. CO stripping

The right side of Figure 3 shows the CO oxidation curves corresponding to Pt/TiO_2-C (CVD) and Pt/C catalysts prepared by both methodologies. The two cyclic voltammograms were recorded in CO-free solution after adsorbing CO at 0.1 V (NHE) to saturation coverage. The CO stripping voltammetry is characterized by a sharp peak centered at 0.75 V (NHE) for the three materials synthesized. To compare the EAS (H_{upd}) obtained from hydrogen desorption curves, the electrochemical active surface area from the CO oxidation curves (EAS_{CO}) was calculated using the value of 0.420 mC cm^{-2} of charge, which is required to oxidize a monolayer of CO adsorbed on Pt (Table 1). The EAS_{CO} of the Pt-/TiO_2-C (CVD) material was higher than that of the Pt/C (CVD) and Pt/C (CR) samples. The charge available to oxidize carbon monoxide (CO stripping) increases by increasing the Pt loading on the substrate; this means that more metallic surface active sites are available to CO oxidation. Therefore, the oxidation charge depends on the particle size, the particle distribution and the quantity of surface parti-

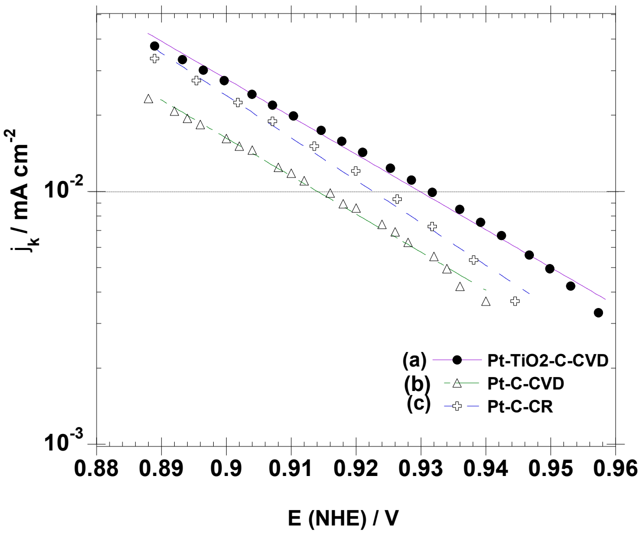

Figure 5. Mass-transfer–corrected Tafel plot deduced for the RDE analysis on (a) Pt/TiO$_2$-C (CVD) and (b) Pt/C (CVD) electrocatalysts prepared by the two-step chemical vapor deposition compared with (c) Pt/C (CR) prepared by the carbonyl route.

cles [26, 31]. The peak oxidation position of CO onto Pt-/TiO2-C is in apparent contradiction with earlier results [16]. The reason for this is the lack of Pt selectivity onto the oxide sites.

3.2.3. ORR electrochemistry

Figure 4 displays the ORR-polarization curves for (a) Pt/TiO$_2$-C (CVD) and (b) Pt/C (CR) electrocatalysts in saturated oxygen-electrolyte in 0.5 M H_2SO_4 at different rotation rates from 200 to 2500 rpm at room temperature. In Figure 4(a), the main characteristics of the polarization curve are the defined charge transfer control (0.96-0.85 V/NHE), the mixed-diffusion limiting currents (0.85-0.6 V/NHE) and the mass transfer region (0.2-0.6 V/NHE). An explanation of the increase in the limiting current could be associated with the increase of molecular oxygen diffusion through the electrode surface. A similar shape of the polarization curves was observed for the Pt/C (CR) electrocatalysts in Figure 4 (b). The inset in Figure 4 represents the inverse current density (i^{-1}) as a function of the inverse of the square root of the rotation rate ($\omega^{-1/2}$), corresponding to a Koutecky-Levich (K-L) plot for (a) Pt/TiO$_2$-C (CVD) and (b) Pt/C (CR) samples at various electrode potentials. The linearity of the K-L plots indicates first-order kinetics with respect to molecular oxygen [32, 33]. For all of the samples, a similar K-L slope of 98-112 mA^{-1} rpm$^{1/2}$ was obtained. The theoretical slope of 100.7 mA^{-1} rpm$^{1/2}$ was calculated for the four-electron process, indicating that the ORR on Pt nanoparticles catalyst at different potentials follows the four-electron pathway leading to water [15, 23].

Figure 5 shows the mass transfer–corrected Tafel plots deduced for the RDE analysis on (a) Pt/TiO$_2$-C (CVD) and (b) Pt/C (CVD) electrocatalysts prepared by two-step chemical vapor deposition compared with those of (c) Pt/C (CR) prepared by the carbonyl route. The Tafel slope at a high current density has a value of 60 mV decade^{-1}, as expected for a first electron transfer rate-determining step. Table 1 summarizes the kinetics parameters deduced for the ORR on the Pt-TiO$_2$-C and Pt-C electrocatalysts.

The interaction of the Pt with -oxide substrate shows that at 0.01 mA cm^{-2}, the cathode overpotential decreases by approximately 20 mV for the ORR on Pt/TiO$_2$-C in relation to the Pt/C samples. These results indicated that Pt dispersed onto a TiO$_2$-C support exhibits high catalytic activity compared with traditional Pt/C for the oxygen reduction reaction in a sulfuric acid solution. The different values depended on the adsorption energy of the oxygen and mean that the transfer of the first electron to the adsorbed oxygen is the rate-determining step of the ORR kinetic reaction.

4. CONCLUSION

Platinum nanoparticles supported on TiO$_2$-C and carbon were prepared by a two-step chemical vapor deposition method. Their electrochemical activity in the ORR reaction was compared with that of a Pt/C catalyst prepared by the carbonyl route. The Pt/TiO$_2$-C electrocatalysts showed an enhancement of their electrocatalytic activity for the ORR compared with the conventional Pt/C catalyst due to the presence of TiO$_2$. The electronic changes are related to the incorporation and interaction between Pt-Ti that promotes a ligand effect on the platinum electronic properties and an increase in the oxygen reduction. The present study demonstrates that the chemical vapor deposition method is an effective alternative method for the preparation of nanometric platinum electrocatalysts with a homogeneous dispersion on different substrates.

5. ACKNOWLEDGEMENTS

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Table 1. Pt/TiO$_2$-C and Pt/ C electrocatalysts synthesized by two-step chemical vapor deposition.

Catalysts[a]	Koutecky-Levich slope (mA^{-1} rpm$^{1/2}$)	EAS$_{CO}$ (cm^2)	EAS H$_{upd}$ (cm^2)	-b mV dec^{-1}	E@0.01 mA cm^{-2} (V/NHE)
10wt.%Pt/5wt.%TiO$_2$-C (CVD)	112.1	4.1	0.90	67	0.93
10wt.%Pt/C (CVD)	98.2	0.87	0.71	66	0.91
10wt.%Pt/C (CR)	106.9	0.75	0.76	60	0.92

[a] CVD=chemical vapor deposition method of synthesis. The Pt/C-CR reference catalyst was prepared by carbonyl route (CR).

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