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Oxygen Reduction Reaction on Pt/C Catalysts Prepared by Impregnation and Liquid Phase Photo-Deposition

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Abstract: *Pt/C catalysts supported on carbon (5 wt.% Pt) synthesized by photo-deposition and impregnation methods were electrochemically evaluated in the oxygen reduction reaction. Platinum nanoparticles were prepared by photo-irradiation of Pt precursors (H_2PtCl_6 and $C_{10}H_{14}O_4Pt$) with UV-irradiation (365 nm) at room temperature. The photo-reduction of H_2PtCl_6 to metallic platinum ($Pt^{4+}\rightarrow Pt^{2+}\rightarrow Pt^0$) was faster than $C_{10}H_{14}O_4Pt$ ($Pt^{2+}\rightarrow Pt^0$) at the same operation conditions. The Pt/C samples were characterized by XRD, EDS, H_2 chemisorption, TEM, cyclic and linear voltammetry techniques. XRD and TEM/EDS studies showed that Pt particles synthesized with $C_{10}H_{14}O_4Pt$ by the photo-deposition method were smaller with a higher dispersion on carbon than those prepared with H_2PtCl_6. A similar behavior was found when the impregnation method is used. The platinum particle size was smaller with $C_{10}H_{14}O_4Pt$ as compared to H_2PtCl_6 precursor. The Pt/C catalyst synthesized with $C_{10}H_{14}O_4Pt$ by the photo-deposition method displayed a catalytic activity in the oxygen reduction reaction comparable to a commercial 10 wt. % Pt/C, ETEK catalyst.*

Keywords: Platinum nanoparticles, Liquid photo-deposition, Impregnation, Oxygen reduction.

1. INTRODUCTION

The polymer electrolyte fuel cells (PEMFC) are devices capable of directly converting the stored chemical energy of a fuel into electricity more efficiently than internal combustion engine without CO_x emission gases, due to their high efficiency and friendliness to the environment PEMFC have attracted huge interest in recent years. Platinum (Pt) nanoparticles supported on carbon Vulcan (CV) are commonly used in hydrogen/oxygen fuel cells as electrodes supports for both the anode and the cathode [1-3]. Carbon is a common choice for supporting nanosized electrocatalyst particles in PEMFC due to its large area, high electrical conductivity and pore structures [4]. Several features are essential for electrocatalysts in order to be used in a PEMFC, namely, high catalytic activity for hydrogen oxidation (anode), oxygen reduction reaction (cathode), resistance to poisoning by CO and good electrical conductivity to allow the electron transfer to the catalytic sites [5-6]. At the present time, one of the most important challenges of the PEMFC for the widespread commercial use is to reduce the cost of the electrocatalyst by reducing the platinum loading as low as 0.04 mg cm^{-2} or less [6-7]. Furthermore, the lifespan or stability of the electrocatalyst is a significant factor for improving the performance and durability of the PEMFC. Nowadays, several approaches to increase corrosion resistance of electrocatalysts have been studied [4, 7-10].

The preparation of catalysts is a fundamental step to obtain the desired activity, selectivity and life time for a specific reaction [11]. The reduction of Pt catalyst loading can be achieved through new different routes of synthesis of Pt nanoparticles as the liquid phase photo-deposition method (LPPD) [12-13]. The LPPD is a facile and low cost technique carried out at room temperature employing inorganic or organic precursors [14].

Considering that currently the Pt electrocatalyst is the material with the highest activity for both electrochemical reactions (anodic and cathodic) in a PEMFC, we report results concerning the synthesis of different Pt/C catalysts of nanometer particle size. In this work, we studied two synthesis routes a) LPPD method and b) impregnation method, using as Pt precursors: H_2PtCl_6 and

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$C_{10}H_{14}O_4Pt$. The structural and electrochemical characterization was carried out by XRD, EDS, H_2 chemisorption, TEM and cyclic and linear voltammetry. The results showed a significant enhancement of electrochemical activity due to the use of Pt/C catalysts prepared by LPPD with $C_{10}H_{14}O_4Pt$ as Pt source.

2. EXPERIMENTAL

2.1. Materials

Carbon Vulcan (XC-72®) with a surface area of ca. 183 m^2 g^{-1} was used as supports of platinum. An aqueous H_2PtCl_6 solution 0.005 M (SPEX Standard) and platinum acetyl acetonate ($C_{10}H_{14}O_4Pt$) $Pt(acac)_2$ (Aldrich) were used as precursors of platinum (Pt). A commercial catalyst 10 wt.% Pt/C-Etek was measured for comparison purposes. Absolute ethanol (J.T. Baker) and chromatography grade, nitrogen were used as dissolvent and to purge the solutions before and during the irradiation, respectively.

2.2. Catalysts preparation

Four catalysts of Pt supported on carbon Vulcan (5 wt.% Pt) were prepared by two methods: a) LPPD technique, and b) impregnation method. In both methods, two platinum precursors: H_2PtCl_6 and $C_{10}H_{14}O_4Pt$, were used. The obtained Pt/C catalysts were coded as indicated in the Table 1, i.e., I=Impregnation, P=Photo-deposition, ClPA=Chloro Platinic Acid and AA= Acetyl Acetonate.

2.2.1. Synthesis of Pt/C by liquid phase photo-deposition method

The Pt/C-P-ClPA and Pt/C-P-AA electrocatalysts were prepared from an aqueous solution of platinum precursor of H_2PtCl_6 and $C_{10}H_{14}O_4Pt$, respectively. The synthesis process followed in this work was recently reported by us [15]. The platinum aqueous solution (5×10^{-4} M) was prepared with an excess of ethanol (1:3) in a glass photo-reactor. Nitrogen gas was bubbled into the solution during 10 min with vigorous stirring to remove the dissolved oxygen. Under this condition the solution was irradiated with a black light lamp (Tecno Lite®) of 20 W with the main wavelength at 365 nm, at 25ºC for 10 h. Carbon Vulcan support was added to the solution, which was continuously irradiated for 24 h. Then, the solution was heated in an oven at 100 ºC overnight to remove the solvent by evaporation. The dry powder samples obtained were heat treated at 350ºC for 1 h in a flowing mixture of 5% O_2 – 95% He in order to eliminate the impurities and the organic compounds of the precursors used. Finally these samples were reduced in a flowing mixture of 10% H_2–90% Ar at 500ºC, 1 h. Depending on the chemical precursor nature; the photo-reduction of Pt precursors can be formulated as follows:

a) H_2PtCl_6 [16-17]

$$PtCl_6^{2-} + CH_3CH_2OH \xrightarrow{N2,\ hv} PtCl_5^{2-} + Cl^- + CH_3CH_2O\circ + H^+ \quad (1)$$

$$PtCl_5^{2-} + CH_3CH_2O^o \longrightarrow PtCl_4^{2-} + CH_3CH_2 = O + HCl \quad (2)$$

$$PtCl_4^{2-} + 4H^+ \longrightarrow Pt^{2+} + 4Cl^{1-} + 4H^+ \longrightarrow Pt^0 + 4HCl \quad (3)$$

b) $C_{10}H_{14}O_4Pt$ [13]

$$Pt(acac)_2 + CH_3CH_2OH \xrightarrow{N2,\ hv} Pt(acac) + Hacac + CH_3\dot{C}HOH \quad (4)$$

$$Pt(acac) \longrightarrow Pt^0 + \dot{acac} \quad (5)$$

$$\dot{acac} + CH_3CH_2OH \longrightarrow Hacac + CH_3\dot{C}HOH \quad (6)$$

$$2CH_3\dot{C}HOH \longrightarrow CH_3CH_2OH + CH_3CH=O \quad (7)$$

2.2.2. Synthesis of Pt/C by impregnation method

For comparison Pt/C-I-ClPA and Pt/C-I-AA electrocatalysts were also prepared by incipient wetness impregnation method (IWI) [18] using a platinum aqueous solution (0.5×10^{-4} M) of H_2PtCl_6 and $C_{10}H_{14}O_4Pt$, respectively. The platinum precursor solution was prepared at the identical conditions described above with an excess of ethanol (1:3). The IWI technique was carried by placing the carbon into contact with an excess of platinum precursor solution with stirring during 2 h at 25ºC, followed by heating in air atmosphere at 100 ºC overnight to remove the solvent.

The Pt/C-I-ClPA and Pt/C-I-AA samples were thermally treated at the same oxidation- reduction conditions used in the Pt/C catalysts prepared by the photo-deposition method.

2.3. Characterization techniques

X-ray diffraction (XRD) patterns were collected on a Bruker D8 AXS equipment using a Cu anode (K_α, λ = 1.5406 Å) and a Bragg-Brentano configuration. The angle 2θ was varied from 37 to 50º with 2°/min and 35 kV.

EDS analysis were obtained on a FEI XL-30 SEM (Sirion) operated at 5 KeV. The dry samples obtained after the irradiation were dispersed by ultrasound in ethanol and the resulting suspension was

Table 1. Code and characteristics of Pt/C electrocatalyst synthesized through Liquid Phase Photo-Deposition (P) and impregnation (I) methods with different sources of platinum.

Catalyst	Precursor of platinum	*Average particle size of Pt (nm)	*Pt dispersion (%)	**Pt content (wt %)	***Average particle size of Pt (nm)
Pt/C-I-C1PA	H_2PtCl_6	36.7	3.1	4.5	-
Pt/C-P-ClPA	H_2PtCl_6	10.4	10.8	4.1	5.1
Pt/C-I-AA	$C_{10}H_{14}O_4Pt$	30.0	5.3	4.0	-
Pt/C-P-AA	$C_{10}H_{14}O_4Pt$	5.2	21.5	3.7	3.6

*Estimated by H_2 chemisorptions ** Estimated by EDS technique *** Estimated by TEM analysis

deposited onto a copper mesh and dried at ambient conditions before analysis.

The H_2 chemisorption (pulse method) test was performed to determine the average active particle size and metal dispersion (defined as the number of Pt surface atoms/number of total Pt atoms). This analysis was carried out by applying calibrated pulses of H_2 to the sample using an Autochem II 2920 equipment (Micromeritics) with a thermal conductivity detector (TCD). Prior to measurements, the samples were thermally treated as mentioned above. The sample is exposed to a H_2 volume (0.274 cm3) and certain amount of gas reacts with the active sites. The amount of H_2 chemisorbed is obtained by the difference between the total amounts of reactant gas injected, the amount that eluted from the sample and the number of pulses of H_2. The Pt dispersion was then calculated on the basis of a 1:2 H_2 to Pt adsorption. The average diameters of Pt clusters and Pt dispersion values were estimated assuming spherical Pt particles from Eq. (8) and (9), respectively.

$$PS = \frac{6}{\rho\left(\frac{W}{GMW}\right)x\left(6.023x10^{23}\right)x(SA)} \tag{8}$$

$$D = \left(\frac{VxSF}{SWx22414}\right)GMW * 100 \tag{9}$$

Where PS is the particle size, ρ metal density (g/cm^3), W sample weight (g), SA specific surface area (per gram of metal) GMW gram molecular weight (g/g-mole), D is the percent of dispersion, V sorbed volume (cm^3), SF stoichiometry factor, SW sample weight (g). The dispersion word is referred to the distribution of active sites.

Particle size distribution was obtained from micrographs of high resolution TEM. These images were obtained using a JEOL-JEM-2200 field emission operated at 200 kV. The samples were prepared with the carbon supported catalyst (< 1mg) in methanol and dispersing by ultrasound 5 min. Thereafter, a drop of the solution was placed over a carbon coated Cu grid (300 mesh) and dried at room temperature. An additional thermal treatment was performed during 20 min under an infrared lamp (250 W) until 150º C was attained.

2.4. Electrochemical measurements

The electrochemical measurements were performed by using the conventional three-electrode array single compartment cell. A platinum mesh was used as the counter electrode and Hg/Hg_2SO_4/0.5M H_2SO_4 (MSE = 0.680 V/NHE) as the reference electrode. All potentials are referred to NHE. Glassy carbon disk RDE0008 with a cross-sectional area of 0.196 cm^2 was used as a support for the thin films and used as an ink-type working electrode. This thin film was deposited from a solution prepared by adding 8 µL of a resulting suspension from a sonicated mixture of 60 µL of an alcoholic solution containing 6 µL of 5wt% Nafion (Du Pont, 1000 EW) and 1mg of Pt catalyst. The estimated amount of catalyst on the glassy carbon electrode surface was about 0.61 mg cm^{-2}.

Rotating disk electrode (RDE) experiments were performed in a Pine MSRX rotation speed controller to connect a Potentiostat/Galvanostat (EG&G Mod. 263A). Electrochemistry Software 4.3 (EG&G PARC) was used to analyze the responses. A 0.5 M H_2SO_4 electrolyte (pH= 0.3) was prepared from distilled water. The working electrode was activated in an oxygen free electrolyte, by scanning the cyclic potential in a region between 1.7 V/NHE to 0.0 V/NHE at 100 mV s^{-1} and 40 cycles. Thereafter, the acid electrolyte was saturated with pure oxygen and maintained on the electrolyte surface during the RDE experiments. Hydrodynamic experiments were performed in the rotation rate range of 100-2500 rpm at 5 mV s^{-1}. Between RDE measurements, the acid electrolyte was saturated with pure oxygen for 5 min to obtain the stable open circuit potential. The current density was calculated using the geometric surface area.

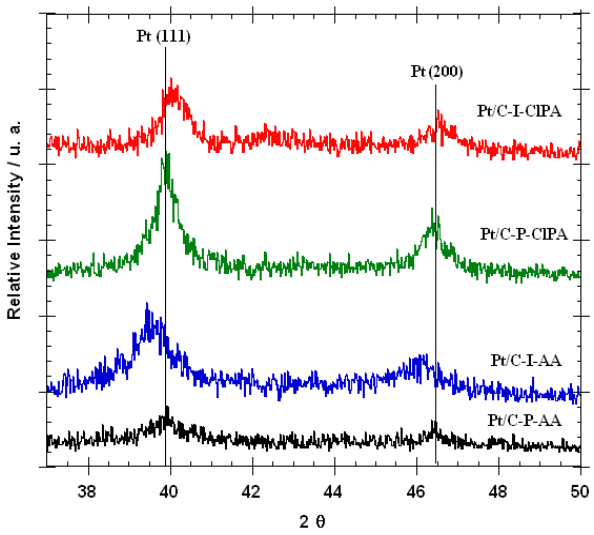

Figure 1. X ray diffraction patterns of the Pt/C electrocatalysts prepared by photo-deposition and impregnation methods using H_2PtCl_6 y $C_{10}H_{14}O_4Pt$ as Pt precursors.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Figure 1 shows the X-ray diffraction patterns of the catalysts Pt/C-P-ClPA, Pt/C-P-AA, Pt/C-I-ClPA and Pt/C-I-AA prepared by photodepositon and impregnation methods with different precursors (H_2PtCl_6 and $C_{10}H_{14}O_4Pt$). Two peaks at 39.8º and 46.2º corresponding to the (111) and (200) reflections of platinum were identified. The diffraction patterns of Pt/C electrocatalysts prepared by photo-deposition technique (Pt/C-P-ClPA and Pt/C-P-AA) indicated that a higher peak intensity is obtained when H_2PtCl_6 is used as Pt precursor compared to $C_{10}H_{14}O_4Pt$ precursor. This behavior can be explained by the higher kinetic rate of photo-reduction of H_2PtCl_6 precursor compared to $C_{10}H_{14}O_4Pt$ [15]. In the case of Pt/C prepared by impregnation method a similar behavior was found. However, in the samples prepared by impregnation method, it was found a shift in peak position of Pt/C-I-ClPA and Pt/C-I-AA catalysts. In the literature, this behavior is related to presence of structural defects as vacancies or dislocacions, in the solid aggregate [20]. Using $C_{10}H_{14}O_4Pt$ as Pt source by the photo-deposition technique gives rise to a smaller crystallite size of Pt than the impregnation method.

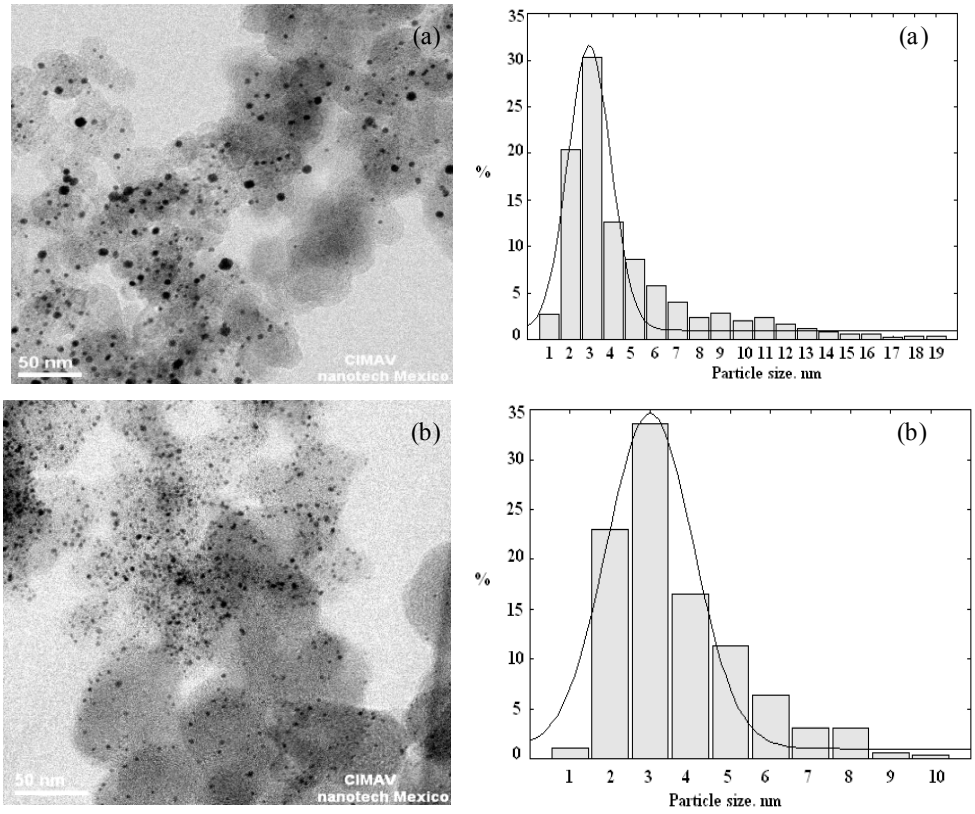

Figure 2. TEM micrographs and particle size distribution of a) Pt/C-P-CIPA and b) Pt/C-P-AA catalyst prepared by photo-deposition method.

3.2. H_2 chemisorption

The platinum dispersión of Pt/C samples, pepared by photo-depositon and impregnation were evaluated by H_2 chemisoption and EDS techniques, results are reported in Table 1. Assuming spherical Pt particles, the Pt/C-P-AA and Pt/C-P-ClPA catalysts prepared by photo-depostion method delivered the lowest average particle size (5.25 and 10.4 nm) as compared to Pt/C samples prepared by impregnation. The Pt/C-I-AA and Pt/C-I-ClPA catalysts showed an average particle size of 30 and 36.7 nm, respectively. The values of particle size was estimated by Eq. (8) taking into account only the surface atoms that react with the H_2. The Pt dispersion calculated by Eq. (9) was between 3 to 21.5 %. The EDS results indicated that Pt/C samples, prepared by impregnation and LPPD methods, have an average Pt mass loading of 3.7 and 4.5 wt.% (see Table 1).

3.3. Transmission electronic microscopy

TEM micrographs of platinum supported on carbon prepared by photo-deposition method are shown in figure 2. According to the figure 2(a), a large size of Pt/C-P-CIPA particles causes a non-uniform distribution over carbon, whereas a high homogeneity and distribution can be observed in Pt/C-AA catalyst (fig. 2b). 90% of Pt/C-P-CIPA particles are between 2 and 10 nm and the same percentage is over 2 to 6 nm for Pt/C-P-AA catalyst; this relatively large distribution of Pt particles could be associated with the kinetics rate of photochemical reduction of platinum precursor in previous studies [15]. The mean particles size is between 5.1 and 3.6 nm (Pt/C-P-CIPA and Pt/C-P-AA, respectively) with a spherical or globular morphology (Table 1). Faceted particles where found at bigger size.

3.4. Electrochemical results

Cyclic voltammetry has become a technique for initial electrochemical studies of new system and has proven very useful in obtaining information about stability in the reaction media and distribution of the actives sites on the electrode surfaces. Figure 3 presents cyclic voltammogram (CV) of Pt/C-I-CIPA, Pt/C-P-CIPA, Pt/C-I-AA, Pt/C-P-AA and Pt/C-Etek (used as reference) in outgassed 0.5M H_2SO_4 at 100 mV s^{-1} in the range from 0.0 to 1.70 V at 25 ºC. All the samples were measured using powder of the same weight to prepare the corresponding ink of the same volume. The curves of Pt/C-I-AA and Pt/C-P-AA show typical characteristics of Pt, e.g., hydrogen adsorption and desorption are between 0.0 and 0.30 V, Pt oxidation starts at 0.80 V, and reduction of Pt oxide film is centered at 0.60 V. In comparison, Pt/C-I-CIPA and Pt/C-P-CIPA show lower current densities. The hydrogen region is thus attenuated due to a probable reduced distribution of the surface actives sites. According to TEM micrographs the larger size of Pt/C-P-CIPA particles, cf. figure 2(a), causes a non-uniform distribution over carbon, while a high homogeneity and best distribution

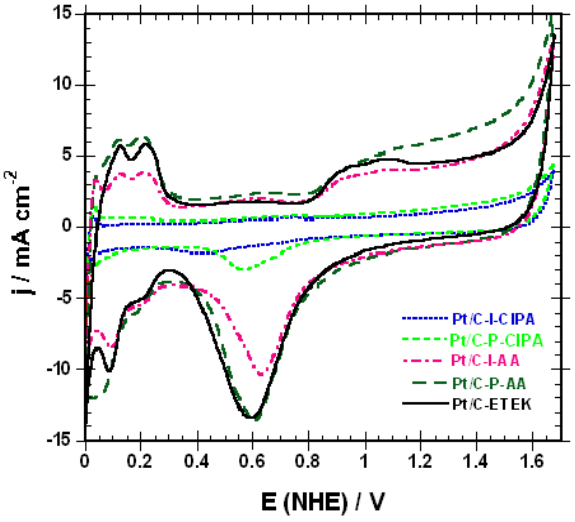

Figure 3. Cyclic voltammograms of Pt/C electrocatalyst synthesized by impregnation and photo-deposition methods.
Data recorded in out gassed 0.5M H_2SO_4 at 25 °C. Scan rate of 100 mV s^{-1}.

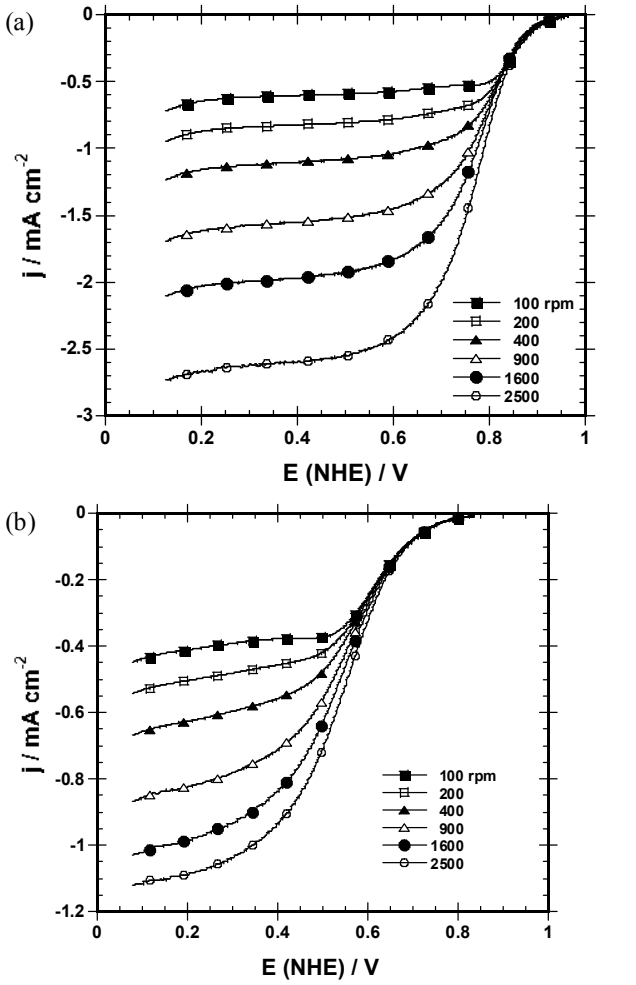

Figure 4. Current–potential curves of oxygen reduction at a) Pt/C-P-AA and b) Pt/C-I-ClPA catalyst in 0.5M H_2SO_4 saturated with oxygen at different rotation rates. Currents recorded at 5mV s^{-1}.

could be observed in Pt/C-P-AA catalyst.

The oxygen reduction reaction, (ORR) depends strongly on the hydrodynamic conditions, the Figure 4 shows the polarization curves of (a) Pt/C-P-AA and (b) Pt/C-I-ClPA electrodes at different rotation rates in oxygen saturated 0.5M H_2SO_4 solution at 25 ºC. In the Figure 4(a) the main characteristic in the polarization curve is the defined charge transfer control, mixed and mass transfer regions. The open circuit potential (E_{oc}) is 0.96 V; it is a typical value of Pt electrodes. A charge-transfer kinetics control with rotation rate-independent current is observed in the range of 0.96–0.80 V/NHE, and at more cathodic potentials, between 0.80 V/NHE and 0.70 V/NHE, mixed charge transfer and mass transport become significant. At potentials < 0.70 V the observed current density is due to mass transport and dependent on the rotation rate. It was considered that the increase in the limiting current is associated with the increase of oxygen diffusion through the electrode surface. On Pt/C-P-AA, the oxygen reduction is fast enough that at high overpotentials a current plateau is observed [21-22]. On the other hand, the ORR on the Pt/C-I-ClPA sample (Figure 4(b)) the open circuit potential attains only 0.83 V. Thus indicating that this sample possesses a lower oxygen adsorption capacity than Pt/C-P-AA sample, with a further consequence of an ill-defined mass transfer region.

During the electrochemical process, the electron transfer and the mass transport are two consecutive processes being one of them the rate determining step. The overall current density, j, is a contribution of the kinetic current density, j_k, the limited current density, j_d, and the diffusion current density due the oxygen diffusion through the Nafion film, j_f. The oxygen diffusion current density cannot be considered significant when a thin film is deposited on the electrode surface and hence not expected to do an important contribution in the overall current density, especially when only 8µL of catalyst ink is deposited on the electrode surface. The kinetic current is proportional to the intrinsic activity of the catalyst according to Eq. (11).

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \qquad (11)$$

$B=0.2nFCD^{2/3}n^{-1/6}$, where 0.2 is a constant used when ω is expressed in rpm, C is the oxygen concentration in the electrolyte (1.1×10^{-6} mol/cm^{-3}), D is the oxygen diffusion coefficient in a sulfuric acid solution (1.4×10^{-5} cm^2 s^{-1}), and n is the kinematic viscosity of the sulfuric acid (1.0×10^{-2} cm^{-2} s^{-1}).

Figure 5 shows the mass transfer corrected Tafel plots for Pt/C-I-CIPA, Pt/C-P-CIPA, Pt/C-I-AA, Pt/C-P-AA and Pt/C-Etek. The mass transfer corrected Tafel plots, for the first-order reaction kinetics, were obtained in the mixed activation-diffusion region, calculated from Eq. (12).

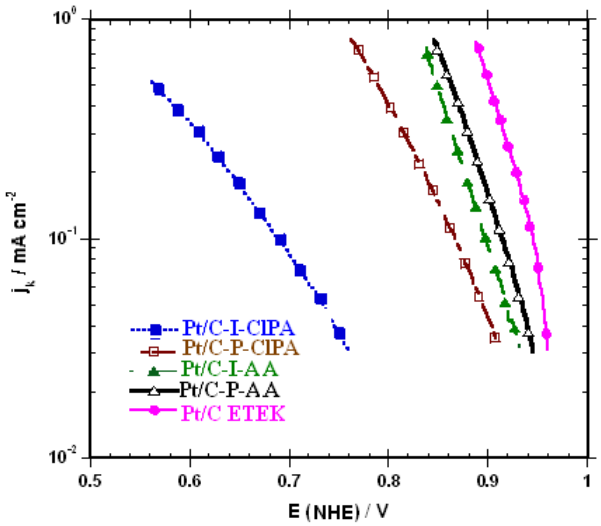

Figure 5. Mass transfer corrected Tafel plots deduced from RDE analysis of oxygen-saturated 0.5 M H_2SO_4 at 25°C

Table 2. Electrokinetic parameters deduced from Tafel plots in H_2SO_4 at 25 °C

Electrocatalyst	E_{oc} (NHE) / V	-b V dec^{-1}	α	Potential / V j =0.1 mA cm^{-2}
Pt/C-I-CIPA	0.83	0.127	0.46	0.69
Pt/C-P-CIPA	0.95	0.118	0.49	0.86
Pt/C-I-AA	0.96	0.074	0.79	0.90
Pt/C-P-AA	0.96	0.073	0.79	0.92
Pt ETEK	0.96	0.070	0.82	0.95

$$i_k = i\frac{i_d}{i_d - i} \qquad (12)$$

where $i_d/(i_d - i)$ is the mass transfer correction. The diffusion-limited density current i_d, was deduced from the Koutecky–Levich plots [19].

Table 2 summarizes all the kinetic parameters deduced for the ORR on the Pt/C electrocatalysts in 0.5M H_2SO_4 at 25°C. Pt/C-I-CIPA and Pt/C-P-CIPA samples show a Tafel slope around -0.120 V dec^{-1}, while Pt/C-I-AA and Pt/C-P-AA the Tafel slope is ca. -0.070 V dec^{-1}. The enhancement of the electrocatalytic activity of Pt/C-I-AA catalyst is attributed to the effect of Pt precursor, it is evident that $C_{10}H_{14}O_4Pt$ (AA) is a better Pt precursor than H_2PtCl_6 (CIPA), since it generates homogeneity and uniform distribution of Pt particles over carbon while CIPA generates larger Pt particles size with a non-uniform distribution over carbon according to the TEM micrographs. Table 2 depicts also the corresponding potential attained at 0.1 mA cm^{-2}. As one can see the Pt/C-P-AA compound has the highest potential at this current density, and would be considered as the best from the four electrocatalyst synthesized for the ORR in the acid electrolyte at 25 °C though it shows a potential of 30 mV lower than Pt-Etek. Therefore, it can be concluded that the photo-reduction method generates the best ORR catalyst.

4. CONCLUSIONS

Nanoparticles of Pt supported on carbon were synthesized by impregnation and liquid phase photo-deposition methods. The use of different Pt precursors (H_2PtCl_6 and $C_{10}H_{14}O_4Pt$) in both methods influences the metal particle size distribution and electrocatalytic activity. A smaller average particle size of Pt deposited on carbon was found by impregnation and photo-deposition methods when $C_{10}H_{14}O_4Pt$ is used as platinum precursor as compared to H_2PtCl_6 source. It was also observed that the liquid phase photo-deposition method gives a high homogeneity and uniform distribution of Pt particles using $C_{10}H_{14}O_4Pt$ as platinum precursor, while H_2PtCl_6 generates larger Pt particle size with a non-uniform distribution compared with the results obtained by the impregnation method. The smallest metal particle (3.6 nm) size was obtained in the Pt/C-P-AA sample prepared by photo-deposition method and $C_{10}H_{14}O_4Pt$ as Pt source. The electrocatalytic activity of Pt/C-I-CIPA, Pt/C-P-CIPA, Pt/C-I-AA and Pt/C-P-AA in the oxygen reduction reaction in acid medium demonstrated that the Pt/C-P-AA shows the highest potential necessary to reach the same current density.

5. ACKNOWLEDGMENTS

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