Platinum Reduction Study on Pt/C Electro-catalysts for PEMFC

M.L. Hernandez-Pichardo[1,*], R. Gonzalez-Huerta[2], P. del Angel[3], E. Palacios-Gonzalez[3], M. Tufiño-Velazquez[4]
and J.C. Sánchez-Ochoa[1]

[1]Instituto Politécnico Nacional-ESIQIE. Laboratorio de Investigación de Fisicoquímica y Materiales, UPALM, 07738, México, D. F.
[2]Instituto Politécnico Nacional -ESIQIE, Laboratorio de Electrocatálisis, UPALM, 07738 D.F. México, D.F.
[3]Instituto Mexicano del Petróleo, Dirección de Investigación y Posgrado, Eje Central L. Cárdenas 152, 07730, México, D. F.
[4]Instituto Politécnico Nacional-ESFM, Laboratorio de Física Avanzada, UPALM, 07738 D.F. México, D.F.

Abstract: *Platinum reduction on Pt/C catalysts was studied on samples prepared by the impregnation method using different Pt precursors and reducing agents such as ethanol, sodium borohydride and ethanol-UV light (photo-assisted reduction), in order to compare the efficiency of the different reducing agents. The influence of the reduction level of the platinum species on the electrochemical behavior of these catalysts has been determined. The catalysts were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and linear and cyclic voltammetry. The results show that the reduction level depends mainly on the platinum precursor. Moreover, it was found that the higher electrochemical activity was found using catalysts reduced with ethanol, whereas by using $NaBH_4$ as the reducing agent, the total reduction of the platinum precursor is very difficult in same synthesis conditions. The analysis of the XPS results shows that samples reduced with ethanol presented the lower PtO_x/Pt reduction ratio.*

1. INTRODUCTION

Many research efforts on proton exchange membrane fuel cells (PEMFCs) are aiming at the development of catalysts with enhanced electrocatalytic activity and low cost. Nevertheless, the most widely used catalysts in PEMFCs are Pt-based nanocomposites, and although the Pt nanoparticles are incorporated into carbon support materials, the high cost of platinum increases the total cost of the cells. The deposit of the metallic phase on the catalyst surface is a critical step in the synthesis of the catalytic materials. Thus, the development of improved electrocatalysts with higher platinum dispersion is still a challenging issue. The impregnation method is one of the most commonly used techniques to fabricate catalysts, due to the ease of preparation. High-surface-area carbon black can be impregnated with catalyst precursors by mixing both in an aqueous solution. Following the impregnation step, a pretreatment is required to reduce the platinum precursor to its metal-

lic state. As reduction occurs after the impregnation step, the nature of the support and the reducing agent plays a crucial role in controlling particle size [1].

It is well known that the catalytic activity of metal nanoparticles depends on their shape and size among others parameters such as the dispersion on the support [2]. Several methods have been employed to obtain Pt/C nanocomposites [1-4], by using different reducing agents such as ethylene glycol [1,3], formic acid [2], hydrazine hydrate [4] and sodium borohydride solutions [5], among others. In general, it has been found that Pt nanoparticles were uniformly dispersed in different supports by using these methods of reduction; however, a comparative study of the different reducing agent is needed. Thus, in this work different reducing agents of platinum over Vulcan XC-72 were tested, modifying the preparation parameters such as: platinum precursor, reducing agent, and platinum content, in order to find the relation between the reduction extent and the electrochemical activity [6-8].

*To whom correspondence should be addressed: Email: mhernandezp@ipn.mx
Phone: (+) 52 55 57 29 60 00; Fax.: (+) 52 55 86 27 28

2. EXPERIMENTAL

2.1. Electrocatalysts synthesis

The Pt/C electrocatalysts were prepared by the impregnation method using two different precursors: platinum (II) acetylacetonate (AA), $Pt(C_5H_7O_2)_2$ and hexachloroplatinic acid (HA), $H_2PtCl_6xH_2O$. The platinum solutions were impregnated over Vulcan XC-72 carbon; with nominal platinum contents of 10% or 20% wt Pt. Three different reducing agents were used: chemical reduction with ethanol (RE), chemical reduction with sodium borohydride (RB) and photo-assisted reduction with ethanol (PE).

The catalysts were prepared by the impregnation of the platinum precursor solution on the carbon, with ethanol or an aqueous solution of NaBH$_4$ respectively. Then, the mixture was stirred during 1 h at room temperature; afterwards the product was washed, filtered and dried at 110 °C for about 2 h. Finally, the samples were treated at 400 ºC in nitrogen.

The Pt/C-PE catalysts were also reduced by the photochemical deposition of Pt using a UV-vis lamp of 80 W during 3 h. The carbon was dispersed into an ethanol solution of the platinum precursor; the suspension was ultrasonically irradiated with 25 KHz of power during 15 min at room temperature and stirred vigorously by a magnetic stirrer during 1 h. The suspension was poured into the photo-reactor and the sample was irradiated for 3 h. Finally the product was washed and dried at 70 °C by about 2 h.

2.2. 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$_2$SO$_4$ aqueous solution electrolyte. The electrochemical measurements were performed using a Potentiostat (EG&G PAR 263A). All electrochemical experiments were conducted at room temperature. The working electrode was a glassy carbon disk with a 5 mm diameter (0.19 cm^2). Glassy carbon and reference hydrogen electrodes were used as the counter and the reference electrode. The catalytic ink was prepared by dispersing 1 mg of catalyst in 8μL of Nafion® and 60 μL of ethyl alcohol in an ultrasound bath for 15 min. A drop containing 8 μL of catalyst ink was deposited onto the working electrode surface and dried at atmospheric conditions. Cyclic voltammetry (CV) was used to activate the electrodes. The CV measurements were developed in a nitrogen-saturated electrolyte from 0.0 to 1.2 V (NHE) at 50 mV s^{-1} until a steady state voltamperogram was reached; approximately 20 cycles were necessary. Linear current–potential curves (LV) were recorded from open circuit potential (E$_{op}$) to 0.2 V (NHE) in oxygen-saturated electrolyte at a different rotating speed from 100 to 2500 rpm. Current density was normalized with platinum content.

2.3. Physicochemical characterization

Pt distribution and local contents were studied by scanning electron microscopy (SEM) using a Nova-200 Nanolab Dual Beam Microscope, with a resolution of 1.1 nm. This equipment has coupled an X-ray Si (Li) ultrathin window energy dispersive spectrometer (EDS) from EDAX, to detect low atomic number elements from the beryllium onwards; and it is also able to carry punctual and global microanalysis. The X-ray diffraction patterns were obtained in a PANalytical X Pert PRO diffractometer fitted with a Cu
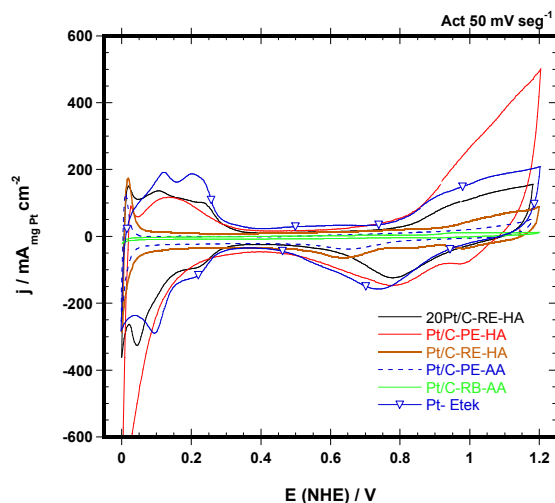

Figure 1. Cyclic voltammetry of Pt/C catalysts prepared from the different reducing agents and precursors, in O$_2$ free 0.5 M H$_2$SO$_4$ solution.

tube. And the XPS spectra of the catalysts were recorded on a K-Alpha Thermo Scientific 180 apparatus after excitation with a monochromatic Al K radiation. Calibration of the energy position of an XPS peak was performed by using the binding energy of carbon 1s peak at 284.8 eV.

3. RESULTS AND DISCUSSION

Five different Pt/C electrocatalysts were studied and they are described in Table 1. The cyclic voltammetry characterization of the platinum electrodes prepared with these catalysts was performed in a nitrogen-purged 0.5 M H$_2$SO$_4$ solution, at a 50 mV s^{-1} scan rate. In this experiment, the electrodes were submitted to 20 cycles in order to obtain reproducible voltammograms. Current density was normalized with platinum content (mA$_{mgPt}$ cm^{-2}). Figure 1 shows cyclic voltammograms of all the samples prepared from different reducing agents and precursors, the Pt-Etek electrode (commercial catalysts 10%Pt/C) was included for comparison purposes. Curves of 20Pt/C-RE-HA and Pt/C-PE-AA show typical characteristics of Pt-Etek, e.g., hydrogen adsorption and desorption regions are between 0.0 and 0.30 V (NHE), Pt oxidation starts at 0.80 V (NHE), and reduction of Pt oxide film is around 0.80 V (ENH). In comparison, Pt/C-RE-HA and Pt/C-PE-AA electrodes show low current densities; hydrogen region is thus attenuated due to a probable reduced distribution of the surface actives sites. We

Table 1. Catalysts prepared with different synthesis parameters.

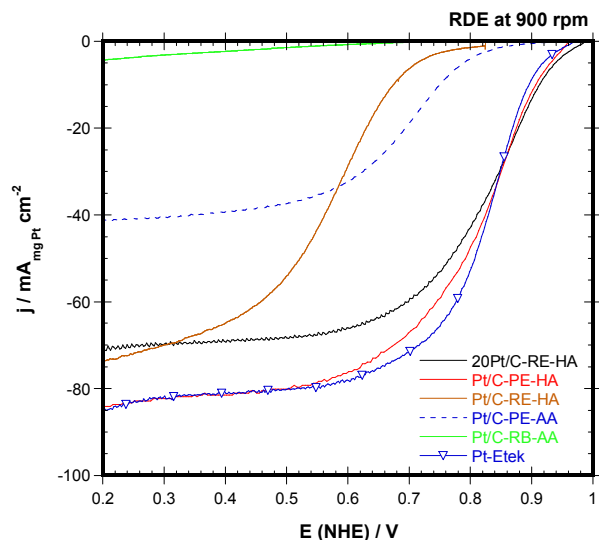| Catalyst	Pt (% wt)	Pt Precursor	Reducing Agent
Pt/C-RB-AA	10	$Pt(C_5H_7O_2)_2$ (AA)	Sodium Borohydride (RB)
Pt/C-PE-AA	10	$Pt(C_5H_7O_2)_2$ (AA)	Photo-assisted-Ethanol (PE)
Pt/C-PE-HA	10	$H_2PtCl_6xH_2O$ (HA)	Photo-assisted-Ethanol (PE)
Pt/C-RE-HA	10	$H_2PtCl_6xH_2O$ (HA)	Ethanol (RE)
20Pt/C-RE-HA	20	$H_2PtCl_6xH_2O$ (HA)	Ethanol (RE)

Figure 2. Lineal voltammetry of Pt/C catalysts prepared from the different reducing agents and precursors, in O_2 0.5 M H_2SO_4 solution.
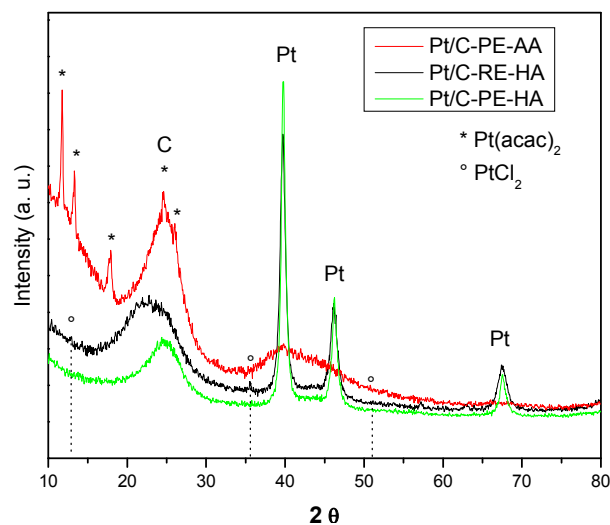

Figure 3. XRD patterns of the catalysts prepared by photo-assisted reduction (PE) and chemical reduction (RE) with ethanol.

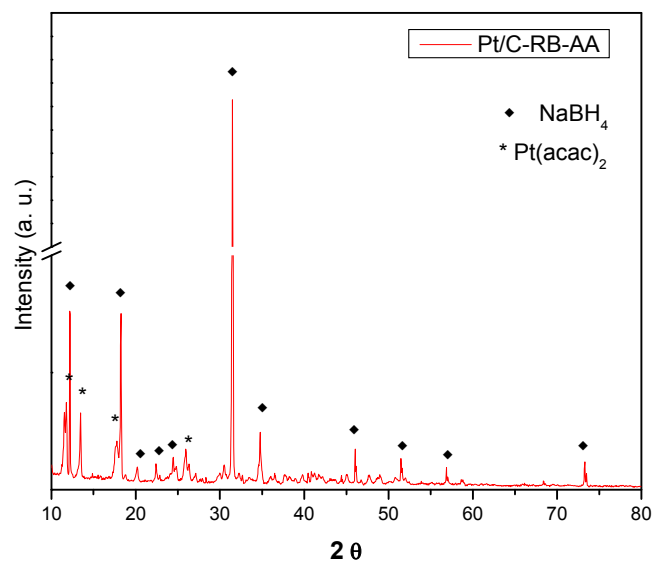Figure 4. XRD pattern of the catalyst prepared by chemical reduction with sodium borohydride (RB).

can also observe in Pt/C-PE-HA and Pt/C-RE-HA samples prepared from hexachloroplatinic acid a shoulder current at around 1 V (NHE). This is presumably due to the solvent present into the samples, however it is also possible that residual $PtCl_2$ was reduced during cyclic voltammetry and being the responsible the high current density and this reduction peak. Finally, It is noticeable that the cyclic voltammogram of the electrode prepared with Pt/C-RB-AA, catalyst synthesized by chemical reduction with sodium borohydride, has no catalytic activity, the current density is very low, and this electrode does not show platinum electrochemical behavior. This indicates that platinum was not reduced in the synthesis process. Pt/C-RB-AA material will not work as a catalyst for the ORR.

Figure 2 displays the ORR activity of Pt/C samples in O_2-saturated 0.5M H_2SO_4 at a rotating speed of 900 rpm at 25 °C. As observed in the figure, the ORR in the activation region is more favorable in 20Pt/C-RE-HA electrode than Pt/C-PE-AA and Pt-Etek electrodes. As showed in previous paragraph Pt/C-RE-HA and Pt/C-PE-AA show lower catalytic activity, and Pt/C-RB-AA has no catalytic activity.

The characterization results by XRD of these catalysts are shown in Figures 3 and 4. Figure 3 shows the catalysts with 10% Pt prepared by photo-assisted reduction using hexachloroplatinic acid (PE-HA) and platinum acetylacetonate (PE-AA), as well as the catalyst prepared by chemical reduction with ethanol (RE-HA). All catalysts present the broad diffraction peak at 2Ө = 25 degrees related with the diffraction of the turbostratic structure of Vulcan carbon; as well as the diffraction lines at 2Ө = 39.8, 46.2 and 67.5 degree, indicating the presence of platinum reflections (111), (200) and (220), respectively. It is noticeable that the catalysts synthesized by using hexachloroplatinic acid present a higher reduction level than the catalyst synthesized with $Pt(C_5H_7O_2)_2$, although some signals of $PtCl_2$ were found in the Pt/C-RE-HA catalyst, indicating an incomplete reduction of the HA. It is also observed that the pho-

tochemical deposition with platinum acetylacetonate is not sufficient for the total reduction of the platinum at these conditions, and the diffraction signals corresponding to the precursor are still obtained. This indicates that the reduction of the platinum acetylacetonate requires more severe synthesis conditions, such as higher time of irradiation.

The comparison of the synthesis method indicates that the synthesis of samples by chemical reduction with ethanol (RE) and photoassisted reduction with ethanol (PE) generates catalysts with similar structures and comparable broadness indicating similar crystallite size 11.6 and 16.1 nm, respectively (measured with respect to intensity for the main diffraction line using Scherrer equa-
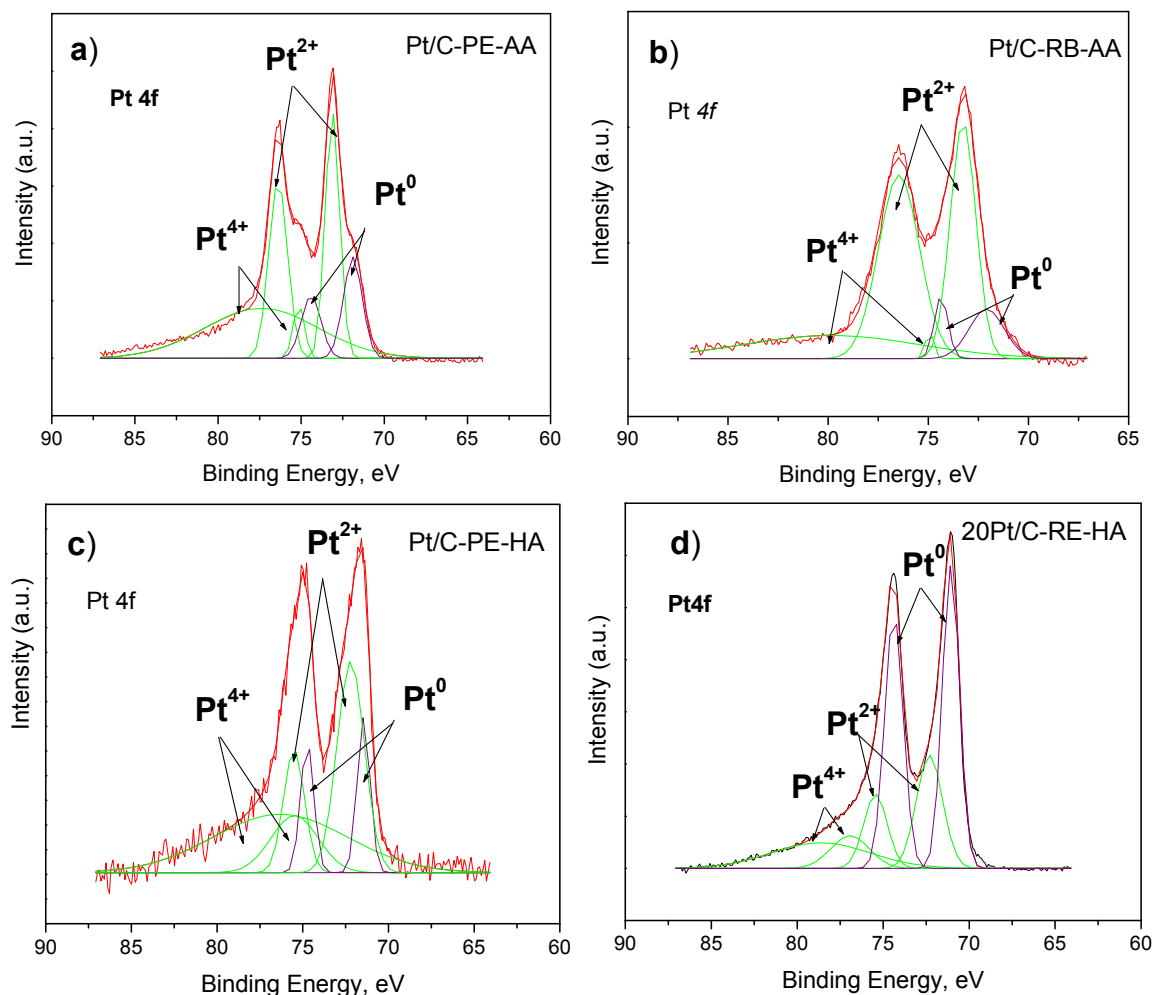
Figure 5. XP spectra of the Pt 4f region of the catalysts: a) Pt/C-PE-AA, b) Pt/C-RB-AA, c) Pt/C-PE-HA and d) 20Pt/C-RE-HA.

tion and the half width of the characteristic peak of each XRD pattern). However, it is noted a higher intensity of the Pt signals in the case of the Pt/C-PE-HA catalyst, which do not present additional peaks of other platinum phases, confirming a better reduction in comparison with the other catalysts.

Figure 4 shows the diffraction pattern of the sample prepared by chemical reduction with sodium borohydride (Pt/C-RB-AA). It is showed that this synthesis conditions are inefficient, since the signals observed correspond to the precursor (AA), as well as the reducing agent used ($NaBH_4$).

Figure 5 shows the Pt-4f X-ray photoelectron spectra of some of the catalysts. The spectra were deconvoluted in components with binding energies between 71.1-79.8 eV and the relative intensities (%) were used to calculate the PtO_x/Pt ratio, which represents the ratio between the unreduced Pt species and the metallic platinum. It can be seen that all the samples present the three oxidation states, corresponding to the PtO_2, PtO and Pt indicating an incomplete reduction of the platinum precursor, being that oxygen chemisorptions easily occurs on the surface of the Pt clusters [9].

The individual analysis of these spectra confirms that the catalysts prepared from hexachloroplatinic acid (HA) generate a higher

reduction of the platinum precursor. This result was confirmed by XPS, since the peak fitting of the Pt 4f band yielded a higher relative intensity of the component, which centered at about 74.4 eV, and 71.1 eV corresponds to metallic platinum [1,6]. The reduction of platinum is reflected in the PtO_x/Pt ratio, a lower ratio indicates a higher content of metallic platinum. Table 2 shows the results of the binding energies and relative intensities of platinum surface species used to calculate this ratio. It was found that the 20Pt/C-RE-HA and Pt/C-PE-AH catalyst presented the lower ratio confirming the higher Pt reduction by using this synthesis conditions. It was also found that the sample prepared by chemical reduction presents a higher concentration of unreduced platinum species that could include those corresponding to Pt (II) acetylacetonate, and therefore higher PtO_x/Pt ratio, that could explain the relative shift to higher bending energy.

These results agree with the cyclic voltammetry results, given that the catalysts with lower PtO_x/Pt ratio also presents the higher electrochemical activity; however, is interesting that samples with similar electrochemical behaviors, such as Pt/C-RE-HA and Pt/C-PE-HA do not present similar reduction ratios. So it can be inferred that this relationship is not proportional and could also depend on
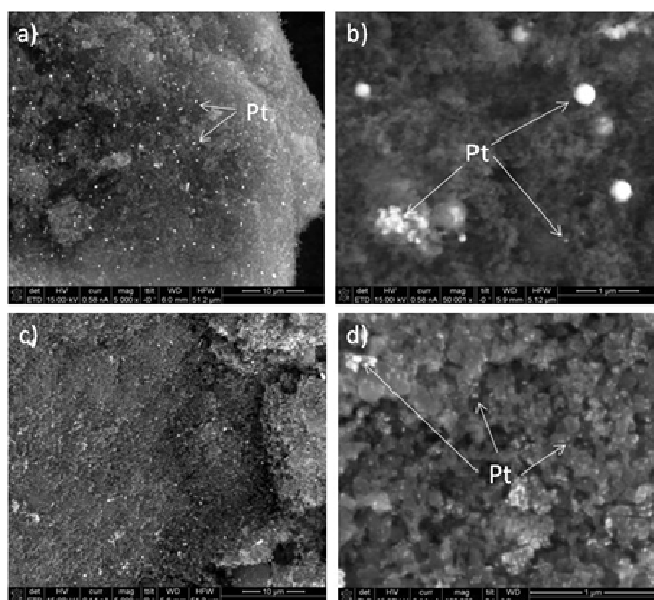
Figure 6. SEM micrographs of the samples: a) Pt/C-PE-HA image at low magnification, b) Pt/C-PE-HA image at high magnification shows different Pt size, the larger particles are around 250 nm and the smaller around 30 nm, c) 20Pt/C-RE-HA image shows a homogeneous distribution of Pt with very small particles, d) a higher magnifications shows Pt particles lower than 20 nm.

the distribution and availability of the active sites on the electrode surface.

Finally, Figure 6 shows the SEM images for the samples with higher activity: Pt/C-PE-HA (Figure 6a-b) and 20Pt/C-RE-HA (Figure 6c-d).The morphology shows a rough surface with a uniform distribution of elemental platinum on both catalysts. The comparison between particle sizes indicates that the 20Pt/C-RE-HA sample presents lower particle size (around 20 nm and smaller) with uniform distribution on the support, despite its higher platinum content, which is in part responsible for the higher electrochemical activity. This behavior can be attributed to the high concentration of metallic platinum and uniform distribution of the Pt nanoparticles on the carbon surface. In contrast, Pt/C-PE-HA sample shows a broad particle size distribution, from very small particles of around 30 nm to large particles of around 250 nm (Figure 6b), which explains the lower electrochemical activity between these catalysts.

4. CONCLUSION

This work shows the dependence of the Pt^0 formation on the reducing agent and the platinum precursor. The results indicate that the electrocatalytic activity depends on the distribution and availability of the metallic platinum particles on the carbon surface, the higher the Pt^0 the better electrochemical response. The results also show that by changing the reducing agent and the platinum precursor, the electrochemical activity of Pt/C catalysts could be modified. It was found the catalysts prepared by using hexachloroplatinic acid were easier to reduce to the Pt^0 than those synthesized with platinum acetilacetonate, however, the reducing agent also modified the physical and electrochemical properties of Pt/C catalysts.

5. ACKNOWLEDGMENTS

REFERENCES

[1] H. Huang, H. Chen, D. Sun and X. Wang, J. Power Sources, 204, 46 (2012).

[2] D. Wang, Y. Liu, J. Huang and T. You, J. Colloid Interf. Sci., 367, 199 (2012).

[3] M. Wang, F. Xu, H. Sun, Q. Liu, K. Artyushkova, E.A. Stach and J. Xie, Electrochim. Acta, 56, 2566 (2011).

[4] E. Yoo, T. Okada, T. Akita, M. Kohyama, I. Honma and J. Nakamura, J. Power Sources, 196, 110 (2011).

[5] J.J. Salvador-Pascual, V. Collins-Martínez, A. López-Ortíz and O. Solorza-Feria, J. Power Sources, 195, 3374 (2010).

[6] B. Ruiz-Camacho, M.A. Valenzuela, J.A. Pérez-Galindo, F. Pola, M. Miki-Yoshida, N. Alonso-Vante, R.G. González-Huerta, J. New Mat. Electrochemical Systems, 13, 183 (2010).

[7] L. Timperman, Y.J. Feng, W. Vogel, N. Alonso-Vante, Electrochimica Acta, 55, 7558 (2010).

[8] R.G. González Huerta, M.A. Valenzuela, R. Vargas García, N. Alonso-Vante, M. Tufiño Velázquez and B. Ruiz-Camacho, J. New Mat. Electrochemical Systems 15, 123 (2012).

[9] A.S. Arico, A.K. Shukla, H. Kim, S. Park, M. Min, V. Antonucci, Appl. Surf. Sci., 172, 33 (2001).

Table 2. Binding energies and relative intensities of platinum surface species.

Catalyst	Pt(IV)				Pt (II)				Pt^0				PtO_x/Pt
	BE* (eV)	%	BE* (eV)	%	BE* (eV)	%	BE* (eV)	%	BE* (eV)	%	BE* (eV)	%	
Pt/C-RB-AA	79.8	20.1	76.5	36.7	75.0	1.1	73.3	29.5	74.4	4.1	71.9	8.5	6.94
Pt/C-PE-AA	77.4	34.9	76.4	20.3	75.1	3.7	73.1	21.8	74.4	7.5	71.9	11.7	4.20
Pt/C-PE-HA	77.3	34.6	75.5	11.3	75.4	11.9	72.2	25.6	74.7	7.6	71.5	8.9	2.01
20 Pt/C-RE-HA	78.6	13.7	76.9	6.81	75.5	9.48	72.3	16.2	74.4	25.8	71.1	28.1	0.86

BE*: Bending Energy (eV).