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Platinum Reduction Study on Pt/C as Electro-Catalysts for PEMFC

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ABSTRACT

In this work different methods of the platinum reduction were tested, modifying the preparation parameters such as: Pt precursor, reducing agent, and synthesis conditions, in order to find the higher dispersion of the platinum nanoparticles over the support, as well as the optimal particle size. The catalysts were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and lineal and cyclic voltammetry. The results show that by using NaBH₄ as reducing agent the total reduction of the platinum precursor is not possible, and the electrocatalytic activity diminishes significantly, probably due to the formation of NaBO₂; whereas the higher activity was found by the reduction with hydrogen at 400 °C. The results of characterization by cyclic voltammetry show that catalyst prepared by photochemical deposition using hexachloroplatinic acid as like precursor of platinum has a high electrochemical activity, stability in acidic medium and a high distribution of the actives sites on the electrode surface. This means that this catalyst is considered as a possible candidate to be used as a cathode in the Membrane-Electrode Assembly (MEA) in a Proton Exchange Membrane Fuel cell (PEMFC).

Keywords: Photochemical deposition , chemical reduction, platinum catalysts.



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. The most widely used catalysts in PEMFCs are Pt-based nanocomposites, in which Pt nanoparticles are incorporated into carbon support materials. Due to the ease of preparation, impregnation is one of the most commonly used techniques to fabricate catalysts. High-surface-area carbon black can be impregnated with catalyst precursors by mixing the two in an aqueous solution. Following the impregnation step, a reduction step is required to reduce the catalyst precursor to its metallic state. As reduction occurs after the impregnation step, the nature of the support plays a crucial role in controlling particle size [1].

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 [1]. It is well known that the catalytic activity of metal nanoparticles depends on their shape and size among others parameters such as 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 borohydrate solutions [5], among others. In general, it has been found that Pt nanoparticles were uniformly dispersed on the different supports by using this methods of reduction, however, a comparative study of the different reducing agent is lacking. Thus, in this work different methods of the platinum reduction over Vulcan XC-72 were tested, modifying the preparation parameters such as: Pt precursor, reducing agent, and synthesis conditions, in order to find the higher dispersion of the platinum nanoparticles over the support.

2. Experimental

2.1 Electrocatalysts synthesis

The Pt/C electrocatalysts were prepared by the impregnation method using two different precursors, platinum (II) acetylacetonate $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ and hexachloroplatinic acid $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$. The platinum solutions were impregnated over Vulcan XC-72 carbon, with a nominal content of 10% wt. Pt. Three reduction methods were used: photochemical deposition (FD), chemical reduction with ethanol (RE) and chemical reduction with sodium borohydride (RQ).

The Pt/C-FD catalysts were prepared 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.

The catalysts prepared by chemical reduction were synthesized by Pt impregnation by mixing the Pt precursor with the reducing agent (sodium borohydride or ethanol). The solution was stirred with the respective portion of Vulcan

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XC-72 carbon during 1 h at room temperature; afterwards the product was washed. Finally, the slurry was filtered and dried at 110 °C for 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 H₂SO₄ 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 cm²). 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 8 μL 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.

2.3 Physicochemical characterization

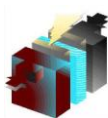
Pt and tungsten dispersion and local contents were studied by SEM using a Quanta™ 650 FEG Dual Beam Microscope, Field Emission Scanning Electron Beam. The X-ray diffraction patterns were obtained in a PANalytical X Pert PRO diffractometer fitted with a Cu tube. And the XPS spectra of the catalysts were 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 adventitious carbon 1s peak at 284.8 eV.

3. Results and discussion

The synthesized catalysts are described in Table 1. Cyclic Voltammetry (CV) has become a very popular technique for initial electrochemical studies of new system and has proved be very useful in obtaining information about stability in the reaction media and distribution of the actives sites on the electrode surfaces. The cyclic voltammetry characterization of the platinum electrodes was performed in a nitrogen-purged 0.5 M H₂SO₄ 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.

Table 1. Catalysts synthesized by different methods.

Catalyst	Pt Precursor	Synthesis Method
Pt/C-FD-AA	Pt(C ₅ H ₇ O ₂) ₂	Photochemical deposition (FD)
Pt/C-FD-AH	H ₂ PtCl ₆ xH ₂ O	Photochemical deposition (FD)
Pt/C-RE-AH	H ₂ PtCl ₆ xH ₂ O	Chemical reduction with ethanol (RE)
Pt/C-RQ-AA	Pt(C ₅ H ₇ O ₂) ₂	Chemical reduction with sodium borohydride (RQ)



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Figure 1 shows cyclic voltammograms of the samples prepared by photochemical deposition using acetylacetonate (Pt/C-FD-AA) and hexachloroplatinic acid (Pt/C-FD-AH) for comparison purposes. The Pt/C-FD-AH electrode presents definition in adsorption-desorption hydrogen region, which is characteristic in polycrystalline noble metals. Analysis at a more positive potential, corresponding to the anodic region, shows a well-defined hydroxide-adsorbed peak. Cathodic scan shows a reduction potential of the oxides formed during anodic sweep at 0.8 V. On the other hand, the Pt/C-FD-AA catalyst, Figure 1, shows a striking difference in the current magnitude in all potential scan. The Pt/C-FD-AA presents an expected low electrochemically active area in the hydrogen region as well as low oxygen reduction activity. The reduction peak of the oxides formed during anodic sweep shows a high displacement to cathodic potential at 0.65 V. In both catalysts we can observed the shoulder current at around 1V; it is presumably due to the solvent or precursor present into the samples.

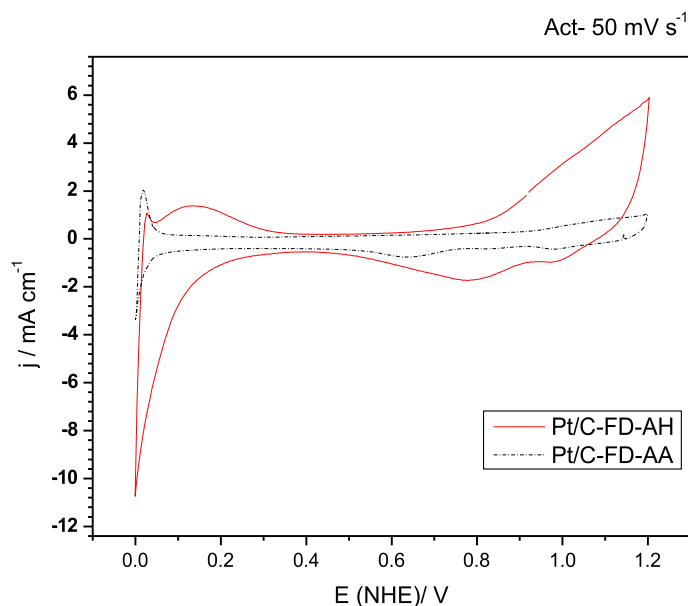


Figure 1. Cyclic voltammetry of Pt/C catalysts prepared by photodeposit using two different precursors, in O_2 free 0.5 M H_2SO_4 solution. Scan rate potential of 50 mV s^{-1} .

Figure 2 presents cyclic voltammograms of the Pt/C-RE-AH catalysts prepared by chemical reduction with ethanol, using hexachloroplatinic acid as like precursor of platinum; the Pt/C-RQ-AA catalysts prepared by chemical reduction with sodium borohydride using acetylacetonate like platinum precursor. The /C-RE-AH catalyst presents low definition in adsorption-desorption hydrogen region, but it shows a hydroxide-adsorbed region. Cathodic scan shows a reduction potential of the oxides formed during anodic sweep at 0.65 V. Pt/C-RQ-AA electrode has no catalytic activity, the current density is low, this electrode not show platinum electrochemical behavior. These catalysts show lower catalytic activity than catalysts synthesized by photo-chemical deposition.

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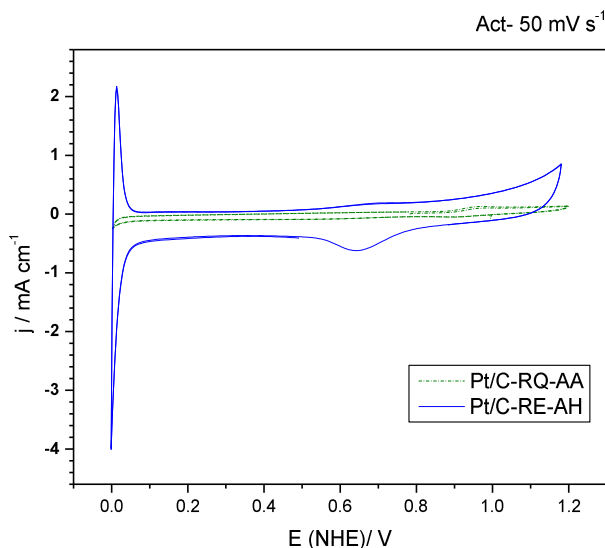


Figure 2. Cyclic voltammetry of Pt/C catalysts prepared by chemical reduction, with ethanol (RE) and with NaBH_4 (RQ), in O_2 free 0.5 M H_2SO_4 solution.

The characterization results by XRD are shown in Figures 3 and 4. It is observed that the catalysts prepared by photochemical deposition using hexachloroplatinic acid as well as the catalysts prepared by chemical reduction with ethanol generates a higher reduction of the platinum precursor; while the photochemical deposition with acetylacetonate is not sufficient for the total reduction of the platinum and the signals corresponding to the precursor are still obtained, which could indicate that the reduction of the acetylacetonate probably requires a higher time of irradiation. No peaks corresponding to the platinum oxides were observed.

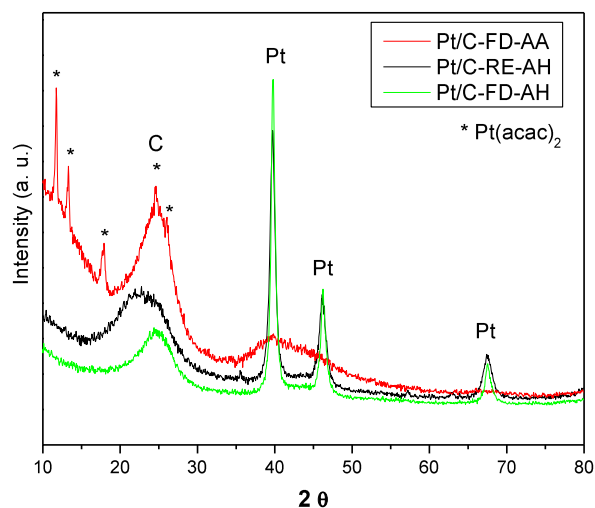


Figure 3. XRD patterns of the catalysts prepared by photochemical deposition (FD) and Chemical reduction with ethanol (RE).

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On the other hand, Figure 4 shows the diffractogram of sample prepared by chemical reduction with sodium borohydride (RQ). It is observed that this is the more inefficient method since the only signals observed correspond to the precursor, as well as the reducing agent used (NaBH_4).

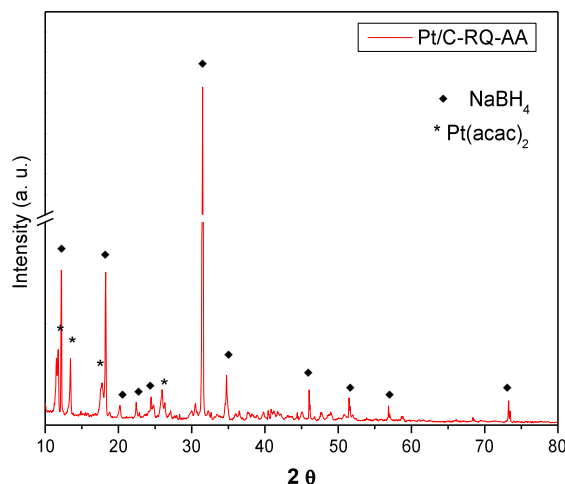


Figure 4. XRD patterns of the catalyst prepared by chemical reduction with sodium borohydride (RQ).

The results of the XPS are shown in Figures 5 and 6. Figure 5 shows a comparison of the three spectra of the samples prepared by the three synthesis methods. It is confirmed that the catalysts prepared by photochemical deposition using hexachloroplatinic acid as well as the catalysts synthesized by chemical reduction with ethanol generates a higher reduction of the platinum precursor as it was observed by XRD, since the peak fitting of the Pt 4f band yielded three components, which centered at 78.6 eV, 76.5 eV, 74.8 eV and 71.2 eV corresponding to platinum (IV), (II) an metallic platinum respectively [1].

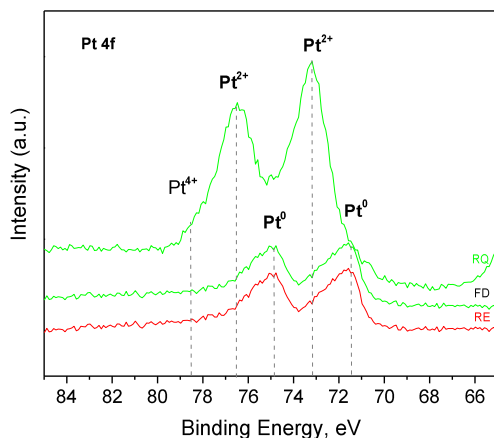


Figure 5. Comparison of the XP spectra of the Pt 4f region of the different catalysts.

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Figure 6 shows the individual study of the XP spectra of the three methods. It is observed that all the samples present the three oxidation states indicating an incomplete Pt reduction; however the sample prepared by chemical reduction present a higher concentration of Pt(II) which could correspond to PtO as well as to the not reduced platinum (II) acetylacetonate.

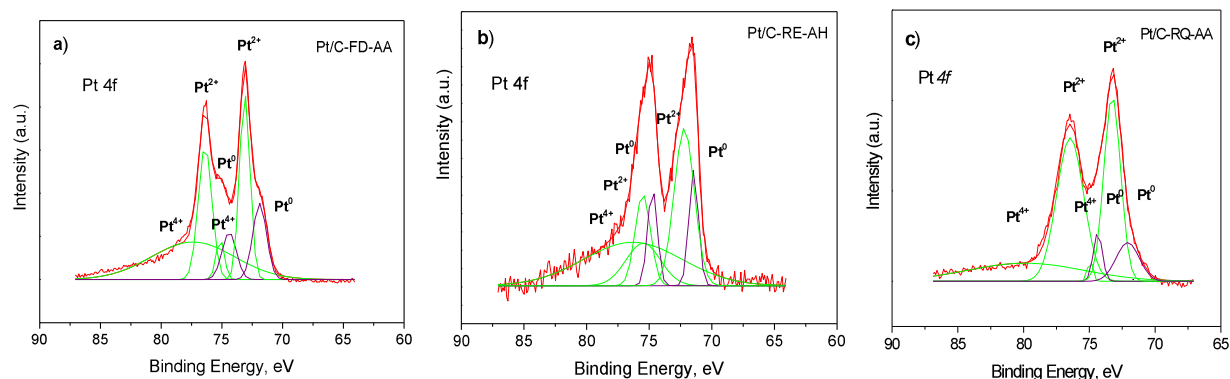


Figure 6. XP spectra of the Pt 4f region of the different catalysts: a) Pt/C-FD-AA, b) Pt/C-RE-AH and c) Pt/C-RQ-AA.

The reduction of platinum is reflected in the $(Pt^{4+}+Pt^{2+})/Pt^0$ ratio, it means that a lower ratio indicates a higher content of metallic platinum. Table 2 shows the results of the proportion and evolution of platinum surface nanostructures. It was found that the Pt/C-RE-AH catalyst presented the lower ratio confirming the higher Pt reduction by using this synthesis method.

Table 2. Proportion and evolution of platinum surface species.

Catalizador	Pt(IV)				Pt (II)				Pt ⁰				Pt ²⁺ /Pt ⁰
	BE*	%	BE*	%	BE*	%	BE*	%	BE*	%	BE*	%	
Pt/C-FD-AA	--	--	--	--	76.3	49.9	73.2	29.6	74.5	5.4	71.9	15.1	3.87
Pt/C-RE-AH	76.3	34.6	75.5	11.3	75.4	11.9	72.2	25.6	74.7	7.6	71.5	8.9	2.27
Pt/C-RQ-AA	--	--	--	--	76.5	51.2	73.2	36.3	74.4	4.2	71.9	8.3	7.00

BE*: Bending Energy (eV).

Finally, Figure 7 shows the SEM study and mapping images for the Pt/C-FD-AH sample, it shows a uniform distribution of elemental platinum. The platinum powder morphology shows a rough surface with agglomerates of well-defined spherical cluster with dimensions of about 50 to 100 nm.

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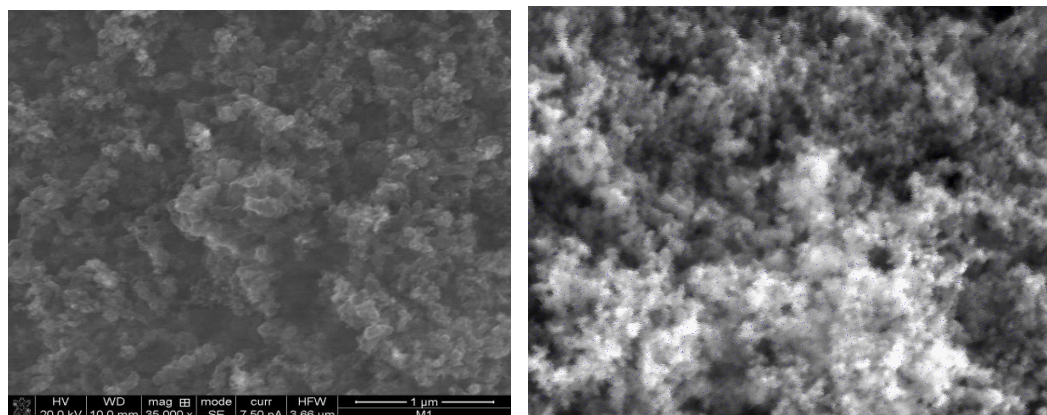


Figure 7. SEM micrographs of Pt/C- AH- FD- catalyst synthesized by the reduction method with ethanol and EDS analysis.

4. Conclusions

By changing the reducing agent and the platinum precursor, four Pt/C catalysts with different Pt morphologies were obtained. The electrocatalytic activities of the Pt/C nanocomposites were studied. It was found that the catalysts prepared by photochemical deposition shows higher catalytic activity than the other catalysts, which can be attributed to the high concentration of metallic platinum and uniform dispersion of the Pt nanoparticles on the carbon surface.

5. Acknowledgements

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6. References

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