EVALUACIÓN DE LA ELECTRODEPOSICIÓN DE RUTENIO SOBRE PLATINO

EVALUATION OF THE ELECTRODEPOSITION OF RUTHENIUM ON PLATINUM

Felia Zambrano de Volpe[1], Olga P. Márquez[2*], Jairo Márquez P.[2]
[1]Universidad de Oriente, Núcleo Anzoátegui, Departamento de Ingeniería Química
Puerto La Cruz 6001, Anzoátegui - Venezuela
[2]Universidad de Los Andes, Facultad de Ciencias, Departamento de Química
Laboratorio de Electroquímica, Grupo de Energía y Petróleo
Mérida 5101 – Venezuela; Email: olgamq@gmail.com

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RESUMEN

Se discute la preparación y caracterización de electrodos bimetálicos PtRu de diferentes composiciones, realizados mediante deposición, a subpotencial, de nanopartículas de Rutenio sobre un sustrato de Platino policristalino. Estos electrodos se prepararon mediante voltametría cíclica y cronoamperometría, con el fin de optimizar las condiciones de preparación, así como para comparar su actividad con la del electrodo de Pt no modificado.

Palabras clave: Electrodos modificados, Electrodeposición, Electrodo Platino/Rutenio, Electrocatalizadores.

ABSTRACT

The preparation and characterization of PtRu bimetallic electrodes of different compositions, performed at underpotential deposition of Ruthenium nanoparticles on a polycrystalline Platinum substrate, is discussed. These electrodes were prepared by cyclic voltammetry and chronoamperometry, in order to optimize the preparation conditions, as well as to compare their activity with that of the unmodified Pt electrode.

Key words: Modified electrodes, Electrodeposition, Platinum/Ruthenium Electrode, Electrocatalysts.

Felia Zambrano de Volpe: Ingeniera Química, graduada en la Universidad de Oriente. Profesora de la Universidad de Oriente, núcleo Anzoátegui. Realizó estudios doctorales en la Universidad de Los Andes, en el Postgrado de Eletroquímica Fundamental y Aplicaa (PEFAP). Su interés en investigación es Electroquímica y Electrocatálisis.
Olga P. Márquez: Ph.D. en Electroquímica (Univ. de Southampton, U.K.), licenciada en Química (UCV-ULA), miembro del personal docente y de investigación de la Facultad de Ciencias-ULA. E-mail: olgamq@ula.ve.
Jairo Márquez: Ph.D. en Electroquímica (Univ. de Southampton, U.K.), licenciado en Química (UCV-ULA), miembro del personal docente y de investigación de la Facultad de Ciencias-ULA. E-mail: jamar@ula.ve.

Introduction

Great Interest in the electro catalytic properties of Ruthenium has increased in recent years, due to its use in the preparation of bimetallic electrodes, in particular Platinum-based electrodes, as high activity electrocatalysts in fuel cells. The electrocatalytic properties of these bimetallic electrodes depend on the preparation conditions of the electrode surface, the morphology and the chemical composition of the deposit. The role that each of these variables plays in electrocatalytic processes is not yet well defined; because of the different oxidation states of Ruthenium, the electrochemical characteristics of Ruthenium deposited on Platinum are much more complex than those of other noble metals.[1-3]

Several studies on the electrochemical and electrocatalytic properties of Ruthenium / Platinum electrodes have been reported in the literature.[4-8] Some electrodes can be considered as Ruthenium electrodes since the electrodeposited Ruthenium layer is thick enough to completely cover the Platinum surface. Some authors used a Platinum electrode coated with Ruthenium adatoms as Ru/Pt electrocatalyst, thus improving the activity of the Platinum electrode by adsorbed Ru.[9]

Although it is recognized that the electrodeposition of Ruthenium on Platinum is more complex than on other noble metals, it has been one of the most used to modify the electrocatalytic properties of Platinum since it satisfies the requirement of forming surface species containing oxygen at low potentials and it is also stable in acidic media. This is why the oxidation of methanol over PtRu bimetallic catalysts has been and continues to be the subject of a great variety of papers published in the literature. Several mechanisms have been proposed to explain the catalytic effect of these materials, one of the most widely accepted being the bifunctional mechanism.[10,11]

This mechanism states that Pt dissociatively adsorbs methanol by chemisorption while Ruthenium activates water and provides preferential sites for OH adsorption at low potentials. The electrode prepared at underpotentials is more stable, and Ru always increases the electrocatalytic activity of Pt since the current densities obtained for the Ru/Pt system are always higher than those obtained on pure Pt.

This fact was attributed to a synergistic effect between the deposited metal and the substrate, which can be explained by the electronic interactions due to the proximities between the Pt and Ru atoms. Contrary to the results reported in literature regardingo PtRu alloys prepared by codeposition, Watanabe and co-workers[12] prepared PtRu alloys supported on Pt black that exhibit extremely high catalytic activity for methanol oxidation, obtaining a current density of 200 mA/cm^2 at 400 mV and a limiting current above 1A/cm^2, when the Ru:Pt ratio is 1:1. Iwasita and co-workers[13] studied the activity of different types of PtRu catalysts: Ru evaporated on Pt (111) in ultra high vacuum (UHV), Ru adsorbed on Pt (111) prepared with and without Hydrogen reduction. The authors justified the formation of small Ru islands when Ru is spontaneously deposited.

Although the PtRu system is the best catalyst for the electro-oxidation of methanol, continuous efforts are being made to improve the performance of this catalyst by incorporating a third metal that exhibits the characteristic of easily forming oxides and thus improving the oxidative desorption of CO. A Pt / Ru alloy catalyst, highly resistant to CO poisoning has been reported by Seol-Ah Lee and co-workers[14] the superior performance of Ru/Pt alloy catalys[15] might be attributed to the synergistic effect of P-doped Ru sites and Pt sites, which significantly improves the alkaline hydrogen evolution reaction kinetics.

Experimental

Reagents

All solutions used were prepared from commercial reagents of high purity and without prior purification, using ultapure Millipore water from 18 MΩ. The supporting electrolyte was prepared from H_2SO_4 (Riedel de Häen 95-97 %) and $HClO_4$ (Riedel de Häen 70 %); salts containing the metal ions RuCl3 (Sigma, pa.) and $PdCl_2$ (Sigma, pa.) Methanol (Aldrich,99.93 %).

Cell, electrodes and equipment

Figure 1 shows the three electrode, two compartmens cell used in this work. A 0.222 cm^2 Pt disk was used as the working electrode, while the counter elecctrode was a 8 mm diameter Pt disk. All measurements were made against a Hg/Hg_2SO_4 (MSE), reference electrode.

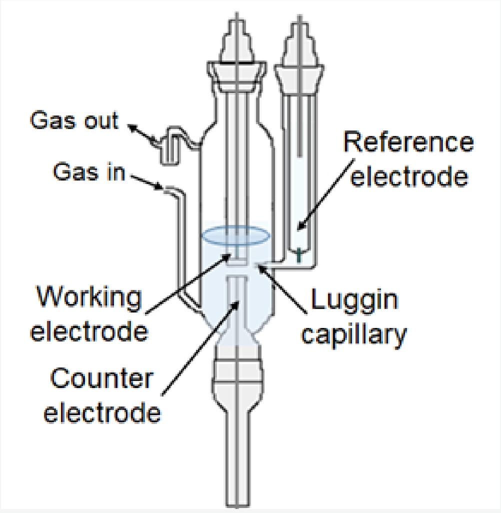


Figure 1.-Three electrode two compartment lectrochemical cell.

A BAS EPSILON potentiostat was used for the electrochemistry experiments. The morphological studies were made using a S-2500 Hitachi scanning electron microscope.

Procedure

Ruthenium electrodeposition was performed by cycling the potential, at different concentrations of $RuCl_3$ within the range 10^{-6}—10^{-3} M in 0.5 M H_2SO_4 using chronoamperometry, following the nucleation and growth process.

Before each experiment, the the working electrode was cleaned and polished with alumina 1: 0.3 and 0.05 µm, washed with plenty of ultrapure water and finally placed in an ultrasonic bath for 20 min. The metal electrodeposition was made at room temperature (≈25 °C).

Results and discussion

Figure 2 shows the voltammetric behavior of a Pt disk in a solution containing 1x10^{-4} M $RuCl_3$ at a sweep rate of 100 mV/s^{-1}.

The presence of Ruthenium ions on the response of bare platinum, decreases the

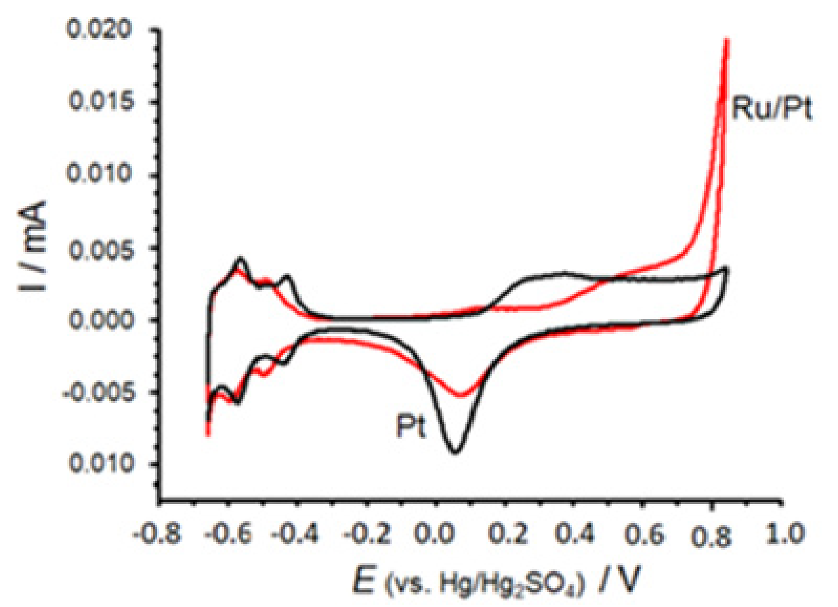


Figure 2.- Cyclic voltammetry of — 0.5 M H2SO4 and —10^{-4} M $RuCl_3$ at a Platinum electrode. √ = 100 mV/s^{-1}.

current in the Hydrogen evolution region, probably due to a block of some active sites on the Pt surface. During the anodic scan, a small wave at +0.10 V vs. MSE is observed which can be attributed to formation of oxygenated Ruthenium species; in addition, the formation of Platinum oxides is inhibited. In the cathodic scan, a decrease in the electrical charge associated with the reduction of Platinum oxides and an increase in current in the double layer region is observed, which could be associated to the beginning of Ruthenium deposition. After modifying the Pt electrode, its stability was tested in 0.5 mol/L H_2SO_4. It is evident, from the voltammetries that a sharp increase in current occurs around 0.7 V vs. MSE, which matches the expected potential for the oxidation of RuO_2, according to the reaction:

$$RuO_2 + 2H_2O \rightleftarrows RuO_4 + 4H^+ + 4e^- \qquad (1)$$

Coverage of Ruthenium on Platinum

Hydrogen adsorption on Platinum is affected by the amount of Ruthenium deposited on the surface due to the high amount of active sites occupied by Ruthenium. Fig. 3 shows the response of the Ru/Pt electrode in H_2SO_4, where it is clearly seen how the Hydrogen desorption current peaks decrease as the amount of Ru on the surface increases, thus inhibiting Hydrogen adsorption on Pt. A plot of the coverage (θ) versus $RuCl_3$ concentration allows a better appreciation of this result. This coverage is related to the substrate sites occupied by metal adatoms (N_M^S)and to the total number of substrate sites (N^S) by equation 2:

$$\theta = \frac{N_M^S}{N^S} = \frac{Q_H^S - Q_H^M}{Q_H^S} \qquad (2)$$

Where Q_H^S the charge required to oxidize Hydrogen adsorbed on the Platinum electrode and Q_H^M the charge required to oxidize Hydrogen adsorbed in the presence of metal adatoms.

It can be seen, from figure 3, that the coverage of Ruthenium, associated to the metal charge, increases with the concentration of $RuCl_3$ up to a maximum concentration value from which it decreases, indicating an oversaturation of the Platinum active sites by the metal being deposited. The maximum coverage was obtained at 6.53 x10^{-4} mol/L. Above this concentration, the tendency is to obtain a bulk Ru electrode rather than a Ru-Pt bimetallic electrode.

Figure 4 shows the response of a platinum electrode modified with Paladium, in H_2SO_4. An additional evaluation was performed by introducing Palladium to the binary catalyst, the results of which will be discussed in a later work, although it can be advanced the information that the electrodes modified

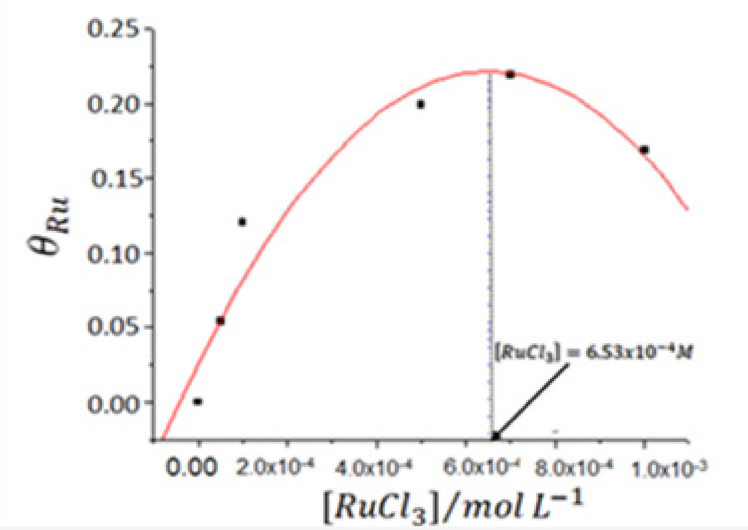


Figure 3.- Variation of Ruthenium coverage with concentration of $RuCl_3$

with different coatings of Ruthenium, Palladium and Ruthenium-Palladium, are being evaluated in the oxidation reaction of methanol in a cell with one compartment and three electrodes, at different temperatures (these studies are in progress and will be published later). The interesting thing about the addition of Palladium is its great capacity to absorb Hydrogen that is evident. In figures 4 and 5, where it can be observed: an increase of the charge in the Hydrogen zone.

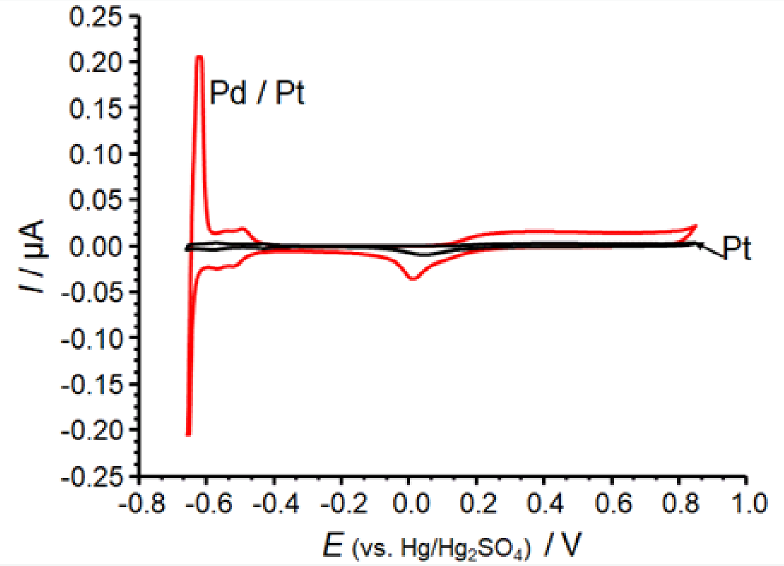


Figure 4.- Cyclic voltammetry of — 0.5 M H2SO4 and —10^{-4} M $PdCl_2$ at a Platinum electrode. √ = 50 mV/s^{-1}

Figure 5 shows the response of a platinum electrode modified by codeposition de Ruthenium and Paladium, in H_2SO_4.

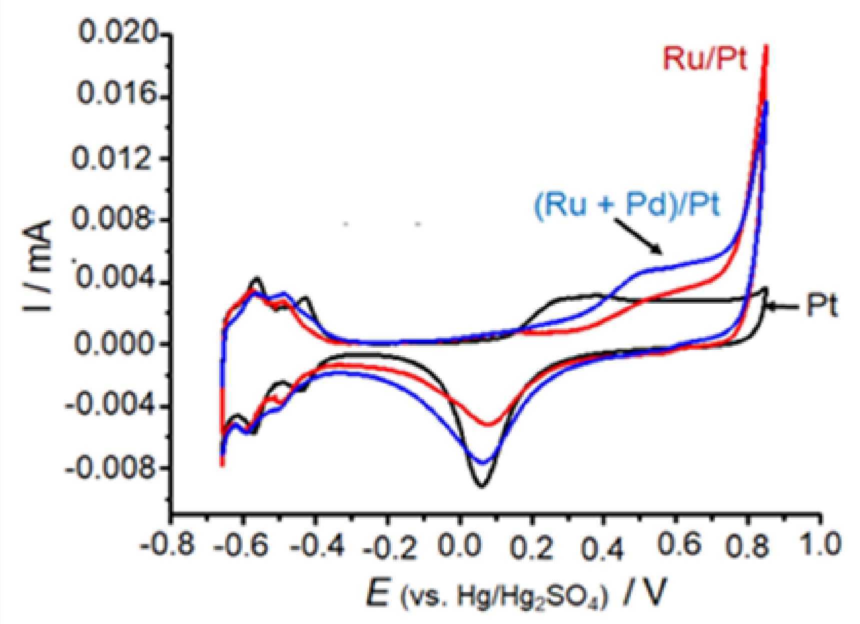


Figure 5.- Cyclic voltammetry of — 0.5 M H2SO4, —10^{-4} M $RuCl_3$,—(10^{-4} M $RuCl_3$+ 10^{-4} M $PdCl_2$), at a Platinum electrode. √ = 50 mV/s^{-1}

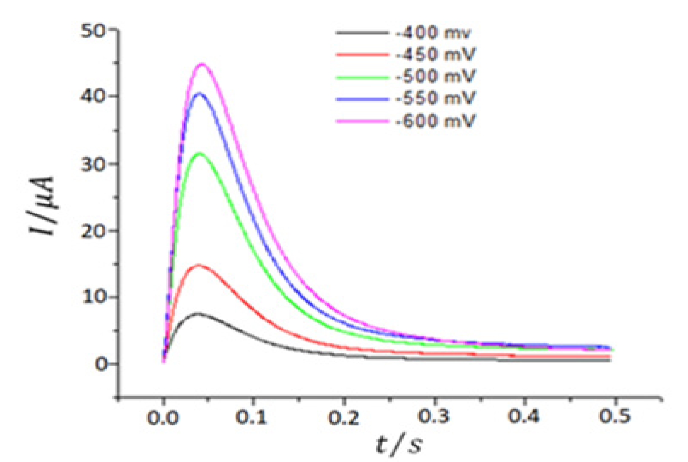


Figure 6.- Current transients for the deposition of Ru on Pt from 5x10^{-5}M $RuCl_3$ in 0.5 M H_2SO_4, Represented by equation 3

Chronoamperometry

Chronoamperometry is the most widely used electrochemical technique for the study of the early stages of formation of a metallic phase. In addition, these current transients contain relevant information about the nucleation and growth mechanism. In the early stages of the process the current is closely related to the morphological changes occurring on the electrode surface which is a product of nuclei formation and growth. Figure 6 shows the family of current transients obtained during the electrodeposition of Ruthenium on Platinum at different potential pulses.

$$I(t) = \frac{nFAD^{1/2}C}{\pi^{1/3}t^{1/2}} \qquad (3)$$

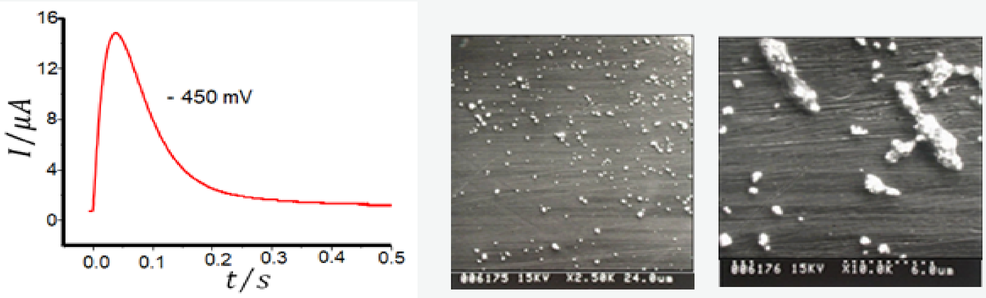
where D is the diffusion coefficient, nF is the molar charge of the deposited species, C is the concentration at the electrode Surface, which is given by equation 4 and A is the working electrode área.

$$C = C_0\left[1 - exp\left(\frac{nF\eta}{RT}\right)\right] \qquad (4)$$

where C_0 is the concentration of the bulk solution, T is the absolute temperature. R is the universal gas constant and n is the overpotential.The transient shape shows that the charge transfer process is very fast, therefore, the Ruthenium nucleation time is very short so that the currents due to the nucleation and growth process are overlapped with the doublé ayer charging process.

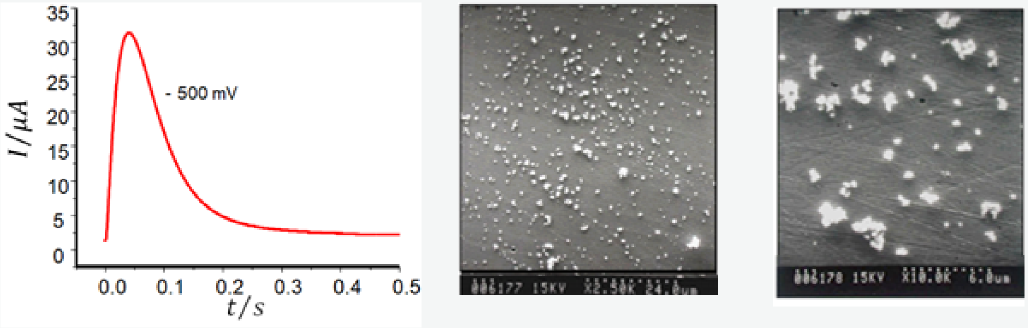
Characterization of the electrodes by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX).

Figures 7 - 9 show SEM images corresponding to the electrodeposition of Ruthenium on Platinum from 5x10^{-5} M $RuCl_3$ in 0.5 M H_2SO_4, under the conditions indicated therein.



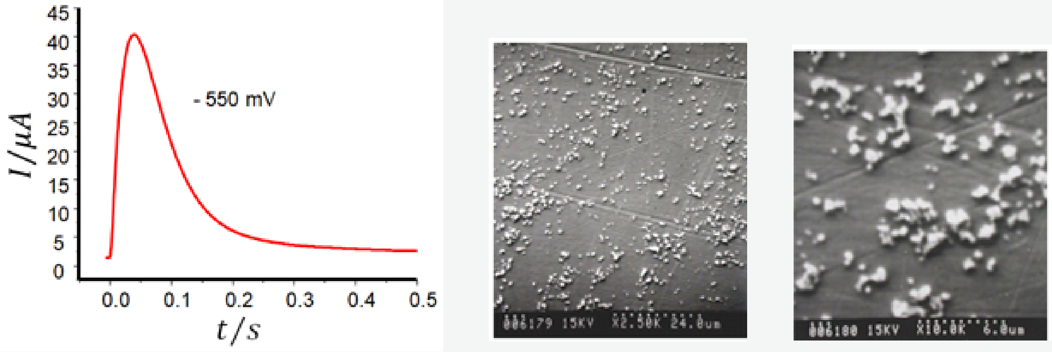
(a) (b) (c)

Figure 7.- (a) Curr ent transient for Ru deposition on Pt at -450 mV, SEM of Ru deposits at different magnifications: (b) 2.50K, (c) 10.0K.



(a) (b) (c)

Figure 8.- (a) Current transient for Ru deposition on Pt at -500 mV, SEM of Ru deposits at different magnifications: (b) 2.50K, (c) 10.0 K



(a) (b) (c)

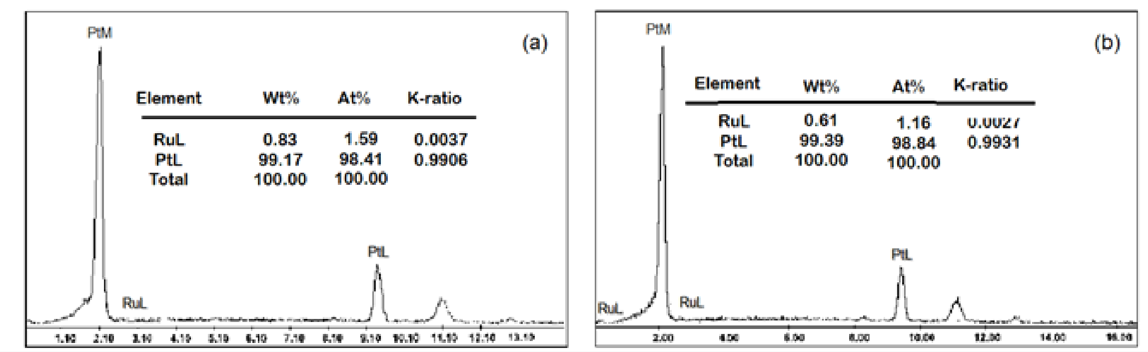
Figure 9.- (a) Current transient for Ru deposition on Pt at -550 mV, Scanning electron micrographs of Ru deposits at different magnifications: (b) 2.50K, (c) 10.0K

An analysis of the images reveals the simultaneous formation and growth of Ruthenium nuclei; this indicates that the electrodeposition process occurs by instantaneous nucleation because the growth centers appear over a limited number of active sites during the initial stages of the process. EDX spectra of Ru deposits on Pt at different deposition potentials are shown in figure 10.

Processing of images obtained by scanning electron microscopy

The term image processing is used to describe the operations performed on the micrographs of the deposits to make them more accessible for quantitative analysis.

This processing involves several stages,



(a)

Element	Wt%	At%	K-ratio
RuL	0.83	1.59	0.0037
PtL	99.17	98.41	0.9906
Total	100.00	100.00	

(b)

Element	Wt%	At%	K-ratio
RuL	0.61	1.16	0.0027
PtL	99.39	98.84	0.9931
Total	100.00	100.00	

Figure 10.-EDX spectra of Ru deposits on Pt at different deposition potentials. (a) -550mV (b) -500 mV. $[RuCl_3] = 5x10^{-5}$ M.

such as: (1) Image acquisition, (2) Image digitization, (3) Thresholding operations and (4) Measurements.

As mentioned above, the images were acquired by scanning electron microscopy and then digitized. With the operations threshold, an image characterized by a distribution of intensity levels within a binary image is obtained. This allows a better visualization and selection of the microstructural elements necessary to perform the measurements of interest.

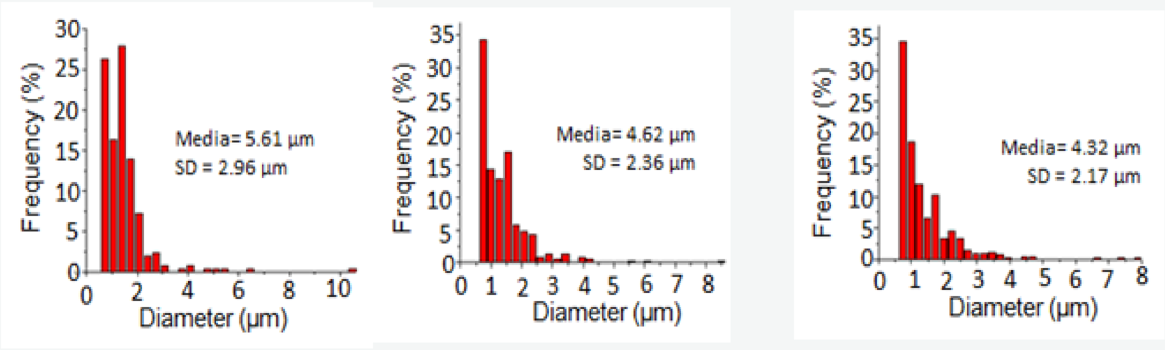
By means of this procedure, the image obtained allows to visualize the population of elements with characteristic geometries that appear with certain probability. This shows that the population of elements in the microstructure can be characterized by some specific property of its geometry which is generally size and/or shape. As the elements that constitute the analyzed microstructure differ in size and shape it can be inferred that these parameters are random variables and, therefore, the geometry of these elements in the microstructure can be described in terms of a probabilistic function. That function defines the probability of finding an element of a given shape and/or size, which is equal to the relative number of these in the studied microstructure.

Since these two parameters can be analyzed independently, size was chosen as a characteristic measure to describe the geometry of the particles and is reported as a linear dimension. According to ISO 9276, the size of an irregular particle is referred to as the equivalent diameter, which is defined as the diameter of a sphere having the same physical or geometrical properties as the irregular particle.

A convenient way to represent the data obtained from the particle size distribution in a microstructure is by means of a bar chart, i.e. a histogram. In it, the independent variable, in this case the diameter, is plotted on the abscissa axis and the dependent variable characterizing the quantity is plotted on the ordinate axis. The respective histograms are shown in Figure 11, these represent the graphical analysis of the size distribution data of the Ruthenium particles deposited on Platinum, at different deposition potentials.

It can be deduced from the histograms that the particle size distribution of Ruthenium is stochastic in nature (the term stochastic is used to emphasize the fact that the geometry of the particles shows a degree of randomness), therefore its description can be made based on the principles of probability theory rather than statistical mathematics. This allows us to characterize the geometry of the particles by a set of parameters that measure the trend of the particles in the total population, such as: the mean, the standard deviation (SD), the variance (SD2), and the coefficient of variation (CV).

Based on this, at different deposition potentials there is a certain probability of finding particles of different diameters, which is reflected in the frequency distribution obtained. The parameters that characterize the Ruthenium particle size distribution are shown in Table 1. It is observed that the



-450 mV (from figure 7) -500 mV (from figure 8) -550 mV (from figure 9)

Figure 11.- Histograms showing the particle size and distribution from figures 7-9

central tendency in this distribution does not vary significantly from -450 mV, which is ratified by the values of standard deviation and the coefficient of variation that measure the degree of dispersion of the data around the mean. This trend suggests that the equivalent diameter of each individual particle does not increase significantly with respect to the mean, which allows to confirm, once again, that the model used represents with good approximation the process, describing with good approximation the process of Ruthenium nucleation on the Platinum surface.

Another important feature highlighted in the figures is the effect that the deposition potential has on the density and morphology of the Ruthenium nuclei. This can be seen more clearly in the higher magnification images, where it is observed that the formation of the new phase occurs through the incorporation of adatoms into the growth centers, which may lead to a transition from a 2D to a 3D process. This matches the previous prediction obtained by the application of the theoretical model.

The modified electrodes were analyzed by energy dispersive X-ray spectroscopy (EDX) showing the presence of Ruthenium, as shown in Figure 10. These EDX spectra indicate that Ruthenium is present on the surface of the electrode, also showing signals corresponding to Platinum; this confirms the formation of a PtRu bimetallic electrode, i.e., Ruthenium is deposited as microparticles and does not cover the entire surface of the substrate. It should be noted that at -400 mV and -450 mV Ruthenium could not be quantified because the amount deposited is below the detection limits of the equipment.

Table 1.-. Values of the mean, standard deviation (SD), standard error of the mean (SE), coefficient of variation (CV) and variance (SD^2) for the particle size distribution of Ru on Pt.

E (mV)	**Number of particles**	**Media** (μm)	**SD** (μm)	**SE** (μm)	**SD^2** ($μm^2$)	**CV**
-400		8,24	4,55	0,83	20,70	0,55
-450	252	5,61	2,96	0,54	8,76	0,53
-500	348	4,62	2,36	0,43	5,57	0,51
-550	428	4,32	2,17	0,39	4,71	0,50

Conclusion

The results obtained in this research, serve as support for the study of electrocatalysis, using ternary and quaternary electrocatalysts, starting from the binary one reported here, capable of improving the conditions for the oxidation of low molecular weight alcohols and the hydrogen evolution reaction, for example, by varying the relative composition of a solution containing a mixture of Ruthenium and Platinum salts, using potentiostatic techniques under diffusional conditions.[16]

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