

## Nanoparticles of Pt and Ag-Pt Synthesized by Ultrasonic for Oxygen Reduction Reaction

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### ABSTRACT

This paper presents the synthesis of nanoparticles of Pt, Ag and Pt-Ag using ultrasonic irradiation at room temperature. The metal nanoparticles were supported on carbon substrates. A concentration study of alcohol was carried out to determine the kinetics of reduction metallic using UV-vis spectroscopy. The materials synthesized (Pt/C, Ag/C and Pt-Ag/ C) were evaluated on the oxygen reduction reaction (ORR) for be applied as cathodes in a Proton Exchange Membrane Fuel Cell (PEMFC). The electrochemical evaluation of the materials synthesized was performed using a cyclic and linear voltammetry technique in acidic medium and room temperature conditions. The kinetic reaction study indicates that the higher alcohol concentration favors the reduction of the metal precursor. Preliminary results demonstrate that the bimetallic electrocatalyst exhibits greater catalytic activity for the ORR compared to the monometallic sample. Pt-Ag/C electrocatalyst can be used as a cathode in a fuel cell.

*Keywords:* Ag-Pt electrocatalyst, ultrasonic, oxygen reduction reaction, fuel cells



## 1. Introduction

Fuel cells are promising technologies due to their high energy density and low pollutant emission compared to conventional power sources [1]. Recent advances in polymer anion exchange membranes have led to increasing studies of alkaline fuel cells (AFCs). AFCs have advantages over traditional proton exchange membrane fuel cell (PEMFCs) due to improved kinetics in the alkaline media where transition metals that are cheaper than Pt can be used without a significant penalty in activity [2]. One of the best advantages of this technology is the low or zero emission pollution. However, the high cost related with the use of electrocatalysts as Pt nanoparticles is one of the first problems. In the past decade, a number of studies have been carried out to Pt alloys with enhanced electrocatalytic performance toward oxygen reduction reaction (ORR) with respect to pure Pt [3-4]. Two kinds of effects, ie ligand and geometric effects are identified for improved the electrocatalytic activity of Pt alloys.

Recently, a series of nanostructured Pt-Ag catalyst with different load of Pt and Ag are been investigated in order to improve the electrocatalytic activity, especially in AFCs due to the alkaline medium. Also, is interesting to prove the Pt-Ag alloys in acid medium. The synthesis of Pt and Ag mono and bimetallic nanoparticles has been reported in several works previously with different methodologies as impregnation [5], chemical reduction [1,6], mechanical mixed [2], thermal method [7], photochemical method [8], etc. However, in most of them, either organic solvents, toxic reducing agents and stabilizers, which had potential environmental and biological risks, or more than one reactive step is required. Sonochemical method, since discovered, has been studied for yielding kinds of materials, especially noble metal nanoparticles. In the present work we present the preliminary results of the synthesis of Pt and Pt-Ag alloy via ultrasonic irradiation without adding any surfactant to be used as electrocatalysts in fuel cells. During the process, high temperature and pressure resulting from the broken of cavitation bubbles caused by ultrasonic irradiation is an important role. The metallic and bimetallic nanoparticles were supported on carbon Vulcan. We have mainly focused in this study on the effect of concentration of alcohols in the kinetic of the synthesis method and the effect on the activity of Pt-Ag electrocatalysts. The results show significant enhancement of electrochemical activity due to use of Ag in the conventional Pt/C catalysts compared to the commercial catalyst Pt/C.

## 2. Experimental

### 2.1 Synthesis of Pt and Pt-Ag nanoparticles

Carbon Vulcan was used as support of Pt nanoparticles and Pt-Ag alloys synthesized by ultrasonic technique. 20 mL  $\text{H}_2\text{PtCl}_6$  (Aldrich) solution ( $1 \times 10^{-3}$  M) and ethanol was mixed in ultrasonic bath at room temperature for 5 h in  $\text{N}_2$  atmosphere. Nitrogen was used to purge the solution before and during the irradiation. After, carbon Vulcan was added to solution and continued the sonication during 30 min. The reduction of  $\text{Pt}^{4+}$  to  $\text{Pt}^0$  was followed by UV-Vis absorption spectra recorded using a spectrophotometer (ThermoScientific) and quartz 3 mL cell before to added the carbon. 1:1 y 2:1 ratios of alcohol : solution were investigated for kinetic reaction rate. The band at 260 nm was sampling by UV-vis every 1 h during the process (0-6h). The solvent was removed by evaporation, then, it was dried in an oven at  $100^\circ\text{C}$  for 2 h. Two catalysts of Pt/C, Pt-Ag/C were synthesized using the method described before.



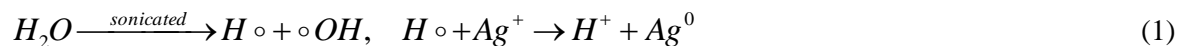
## 2.2 Electrochemical Characterization

The electrocatalytic properties of Pt and Pt-Ag catalysts supported on Vulcan carbon were examined at room temperature in a standard three-electrode cell. A platinum mesh was used as the counter electrode, and a standard saturated calomel electrode (SCE = 0.24 V) as the reference electrode. The potentials in this paper were related to the normal hydrogen electrode (NHE). Glassy carbon disk with a cross-sectional area of 0.19 cm<sup>2</sup> was used as a support for the thin films and used as an ink-type working electrode. The catalytic ink was prepared with 1 mg of catalyst, 25 µL of 5 wt% solution Nafion® (Du Pont, 1100 EW) and 125 µL of ultrapure water. For Rotating Disk Electrode experiments, 10 µL of this sonicated mixture were deposited on glassy carbon electrode (0.06 mg cat). Cyclic voltammetry (CV), in a nitrogen-saturated H<sub>2</sub>SO<sub>4</sub> 0.5 M electrolyte was performed to clean the electrode surface from 0.05 to 1.2 V/NHE at 50 mV s<sup>-1</sup>. 20 cycles were necessary to stabilize the system. Hydrodynamic experiments were recorded at oxygen atmosphere in the rotation range of 200, 400, 900, 1600 and 2500 rpm at 5 mV s<sup>-1</sup> from 1.0 to 0.2 V/NHE. All the electrochemical results of the materials synthesized were tested and compared with the commercial sample of Pt/C (10 wt. Pt).

## 3. Results

Figure 1 shows the UV-Vis spectrum of H<sub>2</sub>PtCl<sub>6</sub> as a function of ultrasonic time using (a) 1:1 and (b) 2:1 ratios of alcohol: solution. Both plots exhibit an absorption band located at 262 nm that can be attributed to ligand-to-metal charge transfer of PtCl<sub>6</sub><sup>2-</sup> complex [9]. After sonicated for 6 h the platinum precursor solution with alcoholic concentration of 1:1 as shown in Fig. 1-a. The same observation was found in the platinum solution with an alcoholic concentration of 2:1, Fig. 1-b. A higher concentration of alcohol helps to the kinetic of metal reduction by ultrasonic method. These results indicate that the ultrasonic reduction of H<sub>2</sub>PtCl<sub>6</sub> in water-alcohol solutions leads to the reduction of Pt<sup>4+</sup> to Pt<sup>0</sup> metal particles via Pt<sup>2+</sup> [10]. The coloration of solution changes from yellow to brown and no other color change was observed; therefore we assume that reduction to Pt<sup>0</sup> was obtained.

Fig. 2-a shows the UV-Vis spectrum of silver after sonicated for 7 h. The alcoholic concentration of solution was 2:1. An absorption band appears at a wavelength that varies between approximately 420-430 nm which is related to the Plasmon resonance of silver nanoparticles spherical and nearly spherical shape, respectively [11]. During the ultrasonic process, the alcohol acts as a reducing agent and the water molecules decompose to hydrogen radicals (H•) and hydroxyl radicals (•OH) under ultrasonic conditions, and then H• supplies electrons for the reduction of Ag<sup>+</sup>:



During the reaction, an increase of pressure is caused by the slight formation of oxygen produced by the following way:



That means, that the overall reaction can be written as:



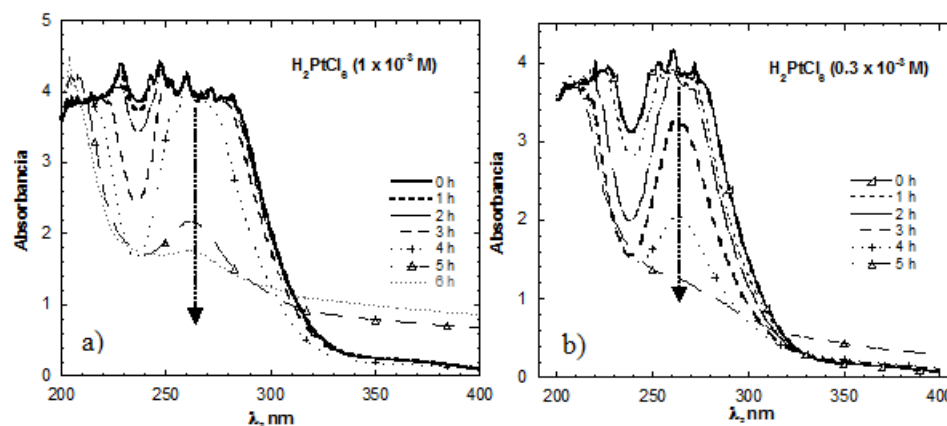


Fig. 1 UV-VIS spectra of absorption of  $\text{H}_2\text{PtCl}_6$  ( $\text{Pt}^{4+} \rightarrow \text{Pt}^{2+} \rightarrow \text{Pt}^0$ ) after sonication using a platinum precursor solution with a concentration of alcohol of a) 1:1 and b) 2:1.

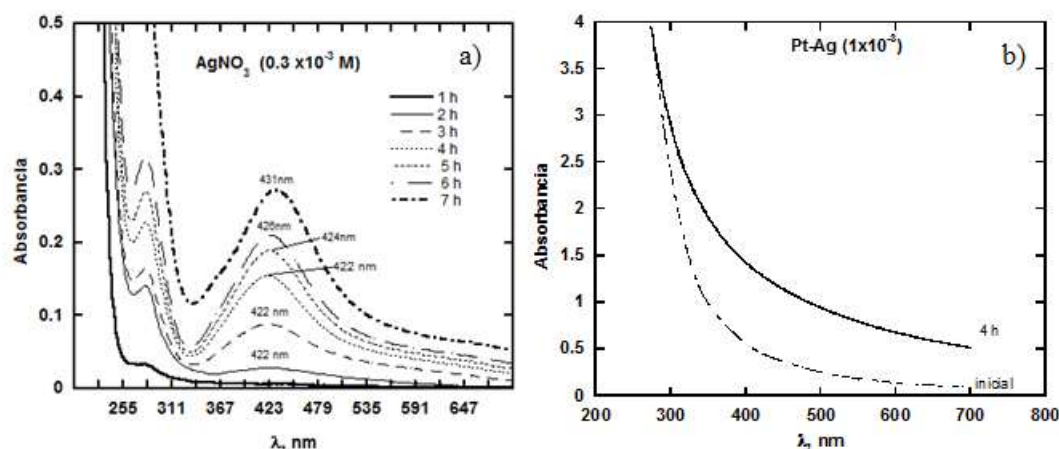


Fig. 2 UV-VIS spectra of absorption obtained as a function time during the ultrasonic of different alcohol:solution of a)  $\text{AgNO}_3$  ( $\text{Ag}^+ \rightarrow \text{Ag}^0$ ) and b)  $\text{H}_2\text{PtCl}_6\text{-AgNO}_3$

The UV-Vis absorption spectrum of the bimetallic catalysts Pt-Ag obtained using a  $\text{AgNO}_3$  and  $\text{H}_2\text{PtCl}_6$  alcoholic solution (2:1) before and after 4 h of sonicated is presented in Figure 2-b. The absorption band of Ag-Pt corresponding to the plasmon resonance around 200-400 nm does not appear. However, the absorption band increases after irradiation with ultrasound. According to those reported in the literature [11] this is related to the size of the nanoparticles because nanoparticles are less than 4 nm, which is reduced to a change of their electronic properties by which the spectrum is observed absorption. This



hypothesis would be confirmed by microscopy characterization studies to confirm the size of the nanoparticles.

CV curves measurements were recorded in the range of potential from 0.05 to 1.2 V/NHE. The results of Pt/C and Pt-Ag/C synthesized by sonication are presented in Fig. 3. The CV curve of commercial Pt/C Etek is also show of Fig 3 for comparison purposes. All shapes of the voltammograms are very similar and correspond to the typical voltammograms of Pt nanoparticles in acid medium [12].

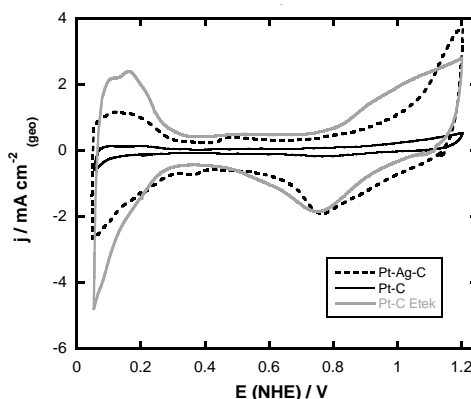


Fig. 3 Cyclic voltammetry of (—)Pt/C, (---)Pt-Ag/C and (—)Pt/C-Etekin 0.5 M H<sub>2</sub>SO<sub>4</sub>saturated with nitrogen at a scan rate of 50 mV s<sup>-1</sup> at RT with 20 cycles.

A rotating disk electrode (RDE) study of Pt/C, Pt-Ag/C and Pt/C Etek electrocatalysts to carry out the ORR are presented in Fig. 4. The typical curves on Pt nanoparticles en acid medium exhibit the three distinct regions characteristic: (I) the kinetic region, where the current,  $i_k$ , is independent of the rotation velocity; (II) the mixed control region, where the behavior is determined by kinetic as well as diffusion processes; and (III) the mass-transfer region, where the diffusion current,  $i_d$ , is a function of the rotation velocity [12]. One of the most important results in this study is that the polarization curves of Pt-Ag/C exhibit higher electrochemical activity than Pt/C and Pt/C Etek.

Fig.5 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/C, (b) Pt-Ag/C and c)Pt/C Etek samples at various electrode potentials. The linearity of the K-L plots indicates first-order kinetics with respect to molecular oxygen [3, 4]. For all of the samples, a similar K-L slope of 105-116 mA<sup>-1</sup> rpm<sup>1/2</sup> was obtained. The theoretical slope of 100.7 mA<sup>-1</sup> rpm<sup>1/2</sup> 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 [14].





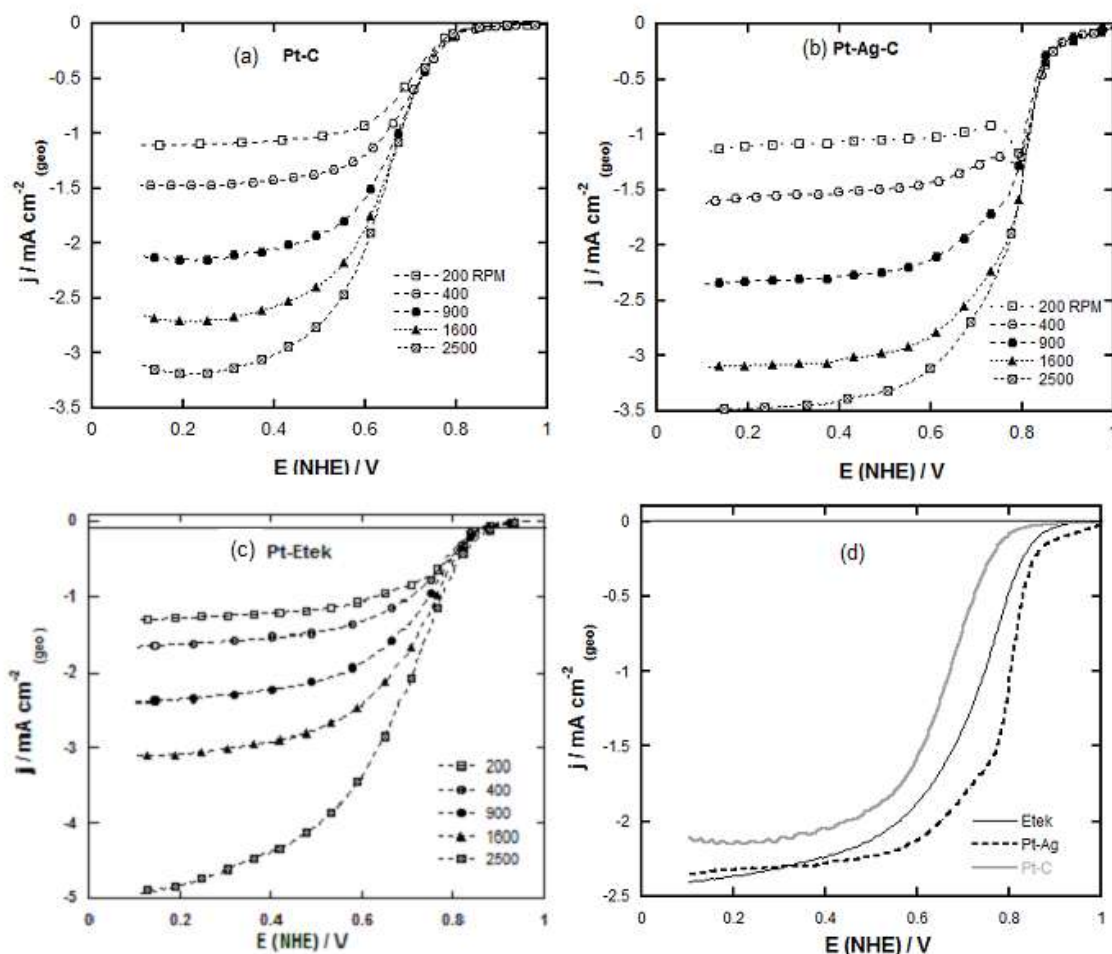


Figure 4. Oxygen reduction reaction (ORR) curves of a) Pt/C, b) Pt-Ag/C prepared by ultrasound compared to c) Pt/C Etek in  $0.5 \text{ M H}_2\text{SO}_4$  at different rotating speed. Scan rate of  $5 \text{ mV s}^{-1}$  at RT.

Fig. 6 shows the mass transfer-corrected Tafel plots deduced for the RDE analysis on (a) Pt/C and (b) Pt-Ag/C electrocatalysts prepared by ultrasonic compared with those of (c) Pt/C Etek commercial catalyst. The Tafel slope at a high current density has a value of  $60 \text{ mV decade}^{-1}$ , as expected for a first electron transfer rate-determining step. Table 1 summarizes the kinetics parameters deduced for the ORR on the Pt/C and Pt-Ag/C electrocatalysts. The interaction of the Pt with Ag shows that at  $0.9 \text{ V/ENH}$ , the cathode over-potential increases by  $83 \text{ mA/cm}^2$  in relation to the Pt/C samples. These results indicated that Pt alloyed to the Ag 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.



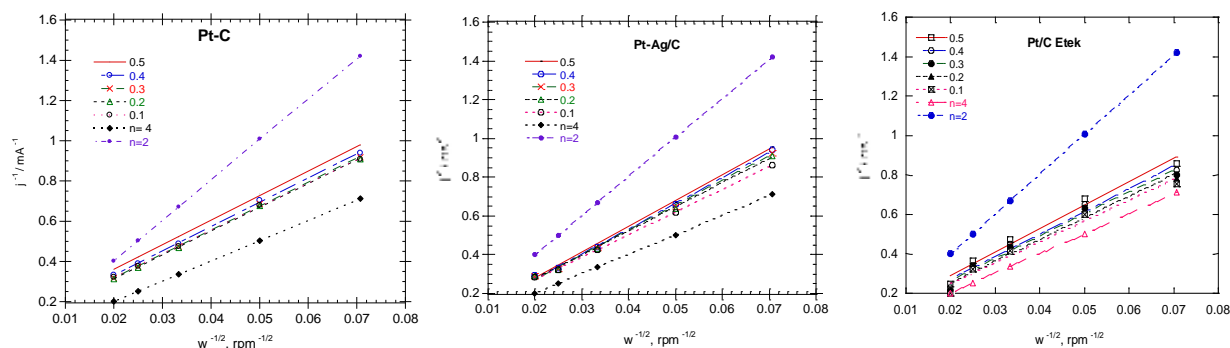


Figure 5. Koutecky-Levich (K-L) plot of a) Pt/C, b) Pt-Ag/C prepared by ultrasound compared to c) Pt/C Etek obtained of the data experiments of Fig. 4.

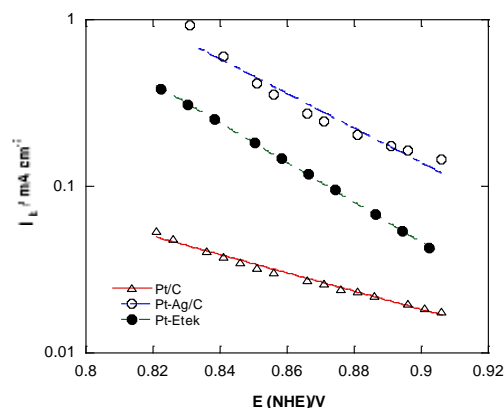


Figure 6. Mass-transfer-corrected Tafel plot deduced for the RDE analysis on a) Pt/C, b) Pt-Ag/C prepared by ultrasound compared to c) Pt/C Etek

Table 1. a) Pt/C and b) Pt-Ag/C electrocatalysts synthesized prepared by ultrasound compared

Catalyst	Koutecky-Levich slope ( $\text{mA}^{-1} \text{rpm}^{1/2}$ )	$\alpha$	$b$ ( $\text{mV dec}^{-1}$ )	$j_k$ at 0.9 V/NHE ( $\text{mA/cm}^2_{\text{Pt}}$ )
Pt/C	116.3	0.62	95	0.009
Pt-Ag/C	115.1	0.56	105	0.151
Pt/C Etek	106.9	0.53	110	0.068

#### 4. Summary and perspectives

Pt/C and Pt-Ag/C electrocatalysts were successfully synthesized by ultrasonic technique on friendly environmental conditions. According to the electrochemical results the activity of the bimetallic Pt-Ag catalyst synthesized has better electrocatalytic properties for to be used as fuel cell cathodes than Pt/C



synthesized at the same conditions as well as the commercial catalyst. The presence of Ag on the Pt structure modifies the electronic properties of Pt favorably to carry out the ORR. However, is important support this investigation with help of the physical characterization of the samples synthesized with electron microscopy and X-ray diffraction. Also, is necessary analysis the electrochemical behavior in basic medium for to be used as cathodes on an AFC.

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