

# Highly Methanol Tolerant Cathode Based on PtAg for Use in Microfluidic Fuel Cell

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**Abstract.** In the present work, a methanol tolerant cathode catalyst was developed through the electrodeposition of bimetallic nanoparticles PtAg on a glassy carbon electrode using potentiostatic and voltammetric techniques. The resulting particles were characterized by Scanning Electron Microscopy (SEM) and electrochemical techniques. According to the SEM study the synthesized nanoparticles have semi-spherical shape and their average diameter is 100 nm. This material shows catalytic activity to the oxygen reduction reaction with high tolerance to methanol.

## 1. Introduction

The development of microdevices has encouraged the quest for power sources able to operate for long time with a low operation cost [1]. In this sense, microfluidic fuel cells ( $\mu$ FFCs) are an attractive alternative for power supplies because can operate using co-laminar flow of fuel [2-5] and oxidant electrolytes without a physical barrier to separate the two half-cells. The main components and functions related to the electrochemical reactions are located in a single microfluidic channel. In this microfluidic channel, the mixing of two parallel streams is minimal, nonetheless, if a reactant crossover exists, the performance of the cell is affected [6]. This situation has motivated the development of new catalysts that allow using them in conjunction with a single reactants stream in order to simplify behavior and cell design.

The purpose of this work is developing a PtAg/C bimetallic catalyst, prepared by electrodeposition (a rapid and low cost technique), with high tolerance to methanol in order to apply it in a flow methanol  $\mu$ FFC.



## 2. Experimental

### 2.1. Materials

Electrodeposits of Pt and Ag were carried out by chronoamperometry technique from two aqueous solutions, the first one containing 5 mM  $K_2PtCl_4$  + 0.5 M  $H_2SO_4$ , while the second one contains 5 mM  $AgNO_3$  + 0.5 M  $H_2SO_4$ . The plating baths were prepared using analytic grade reagents with deionized water. The working electrode was a glassy carbon tip provided by BAS<sup>TM</sup> with 0.071 cm<sup>2</sup> of area. The exposed surface was polished with alumina 0.05  $\mu$ m. A graphite bar was used as counter electrode. The reference electrode was an Hg/HgSO<sub>4</sub> electrode. All the potentials here reported are referred to the SCE. The electrochemical experiments were carried out with a VSP Biologic potentiostat/galvanostat.

### 2.2. Synthesis of PtAg/GC catalyst

In order to study the electrochemical behavior of platinum and silver, cyclic voltammetry was carried out in the 1.35 to -0.05 V potential range at different scan rates. PtAg/GC catalyst was obtained in two consecutive steps. In the first one, Pt particles were synthesized by applying a pulse of 0.27 V during 10 seconds from solution 1. After that, the electrodes were washed with deionized water and then introduced in the solution 2 in order to proceed with the second step of the synthesis. Electrodeposition of Ag onto Pt particles was carried out by applying a potential pulse of 0.54 V during 30 seconds from solution 2. Pt/GC particles were also synthesized, with the only purpose of compare them with the PtAg/GC particles, following the procedure above described. The electrodeposits were characterized by SEM and EDS using a JEOL JSM 6510LV.

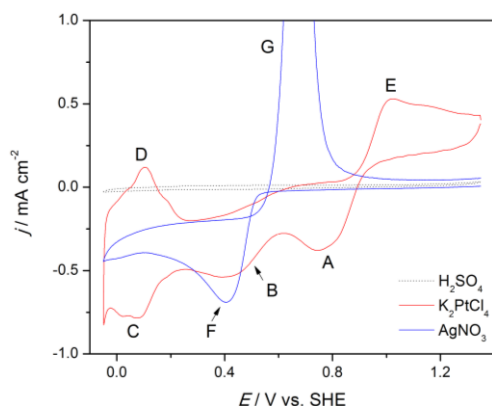
### 2.3. Electrochemical characterization and evaluation of catalysts

Performance of modified electrodes was studied in both acidic (0.5 M  $H_2SO_4$ , J. T. Baker 99.7%) and basic (0.3 M KOH, J. T. Baker 87%) media using cyclic voltammetry. Evaluation of Pt/GC and PtAg/GC materials in the ORR was conducted in basic media under oxygen atmosphere in hydrodynamics conditions. The catalysts were tested in absence and presence of different concentrations (up to 5 M) of methanol. Linear sweep voltammetry at a scan rate of 5 mV s<sup>-1</sup> was used for the evaluation.

## 3. Results and discussion

### 3.1. Electrochemical deposition of PtAg particles on glassy carbon

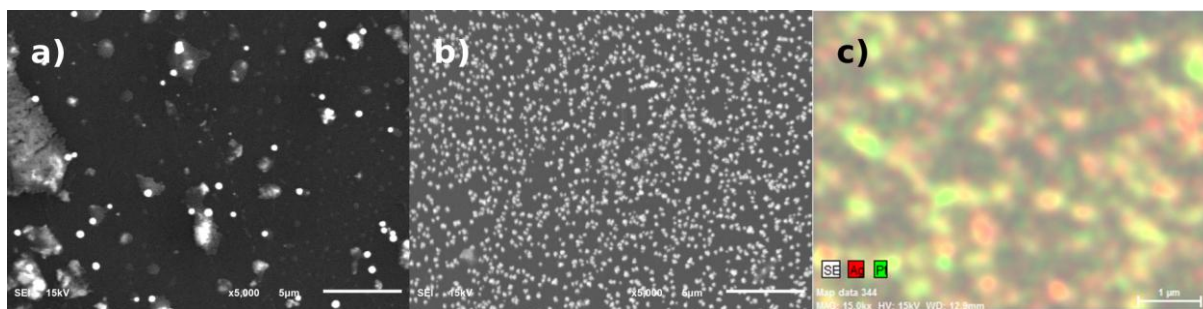
A typical cyclic voltammogram of 5 mM  $K_2PtCl_4$  in 0.5 M  $H_2SO_4$  is shown in Fig. 1. During the potential scan in cathodic direction, 3 peaks, A, B and C were recorded at 0.767, 0.415 and 0.080 V respectively. Peak A is associated with hydrogen adsorption process and peak B to the hydrogen reduction at underpotential conditions. Peak C is related to Pt reduction. During the inverse potential scan, peaks D and E may be associated with the dissolution of platinum deposited at the direct scan. Also, in Fig. 1 it is shown the cyclic voltammogram of 5 mM  $AgNO_3$  + 0.5 M  $H_2SO_4$ . During the cathodic scan, a peak is observed at 0.435 V, associated with the reduction of silver. In the inverse potential scan, the peak G is associated with the dissolution of silver. Additionally, it is shown the voltammogram obtained only from supporting electrolyte; note that there are not any electrochemical signals. Therefore, the peaks previously discussed are due to Pt and Ag.



**Figure 1.** Cyclic voltammetry for platinum and silver precursors ( $v = 50 \text{ mV s}^{-1}$ )

### 3.2. Characterization of Pt/GC and PtAg/GC particles

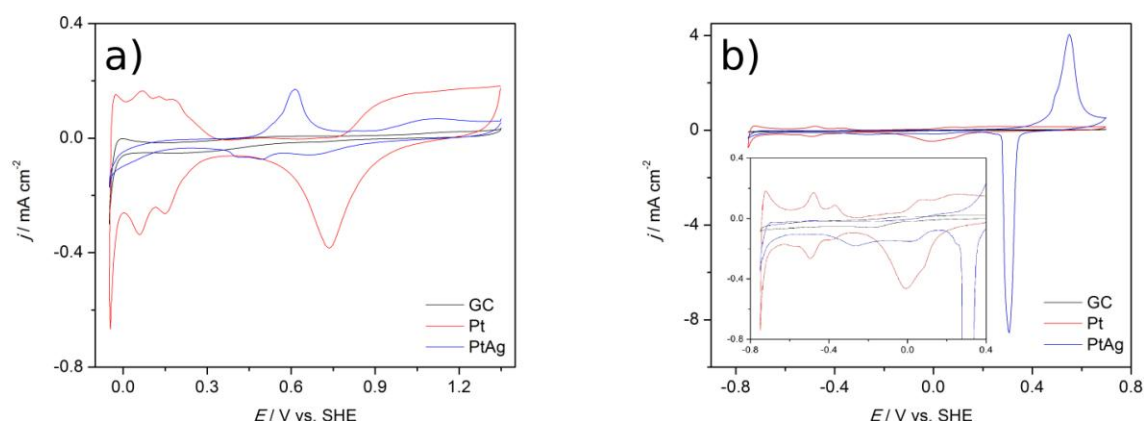
Figure 2a and 2b show SEM micrographs of the Pt/GC and PtAg/GC deposits. In both cases, spherical particles (around 100 nm) are observed. The figure 2c shows the distribution of Pt (green) and Ag (red) in the PtAg/GC sample. It is also possible to observe the presence of both metals homogeneously distributed onto the glassy carbon surface.



**Figure 2.** Scanning electron micrography of a) Pt/GC and b) PtAg/GC at 5,000X c) PtAg/GC element mapping at 15,000 X

### 3.3. Electrochemical characterization of Pt/GC and PtAg/GC catalyst

Figure 3 shows the cyclic voltammograms of the Pt/GC and PtAg/GC electrodes. For Pt/GC, in H<sub>2</sub>SO<sub>4</sub> 0.5 M, observe the reduction of platinum oxide at 0.75 V and the hydrogen adsorption/desorption zone at a potential value lower than 0.3 V, but these signals disappear in the PtAg/GC system. This can be attributed to the masking induced by the silver covering. This phenomenon is also observed in alkaline media (KOH 0.3 M). However, it is important to mention that the peaks recorded were associated with formation and reduction of silver oxides.



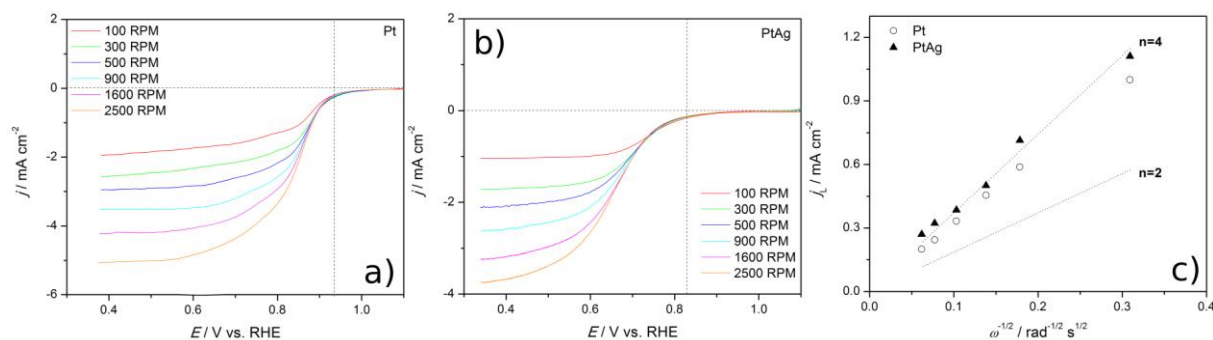
**Figure 3.** Cyclic voltammograms for bare GC, Pt/GC and PtAg/GC a) acid media and b) alkaline media.

### 3.4. Evaluation of Pt/GC and PtAg/GC catalysts in the ORR

The activity of synthesized catalysts towards oxygen reduction reaction was studied by linear sweep voltammetry in hydrodynamic conditions. Polarization curves were obtained from 0.3 M KOH in an oxygen-saturated atmosphere in the rotation rate range [100 - 2500] rpm. The results for Pt/GC and PtAg/GC are shown in the figure 4a and 4b, respectively. The onset potential of the ORR for Pt is 0.93 V vs. RHE, while the onset potential for PtAg/GC is 0.80 V vs. RHE. This negative shift is due, probably to the Ag layer on Pt, which reduces its catalytic activity. From the polarization curves, the disk-limiting current density was used to construct the Levich plot [7], shown in Fig 4c. The theoretical plots for the transfer of two and four electrons for the ORR were calculated using the Levich equation (Eq. 2).

$$i_L = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_0 \quad \text{Eq. 2}$$

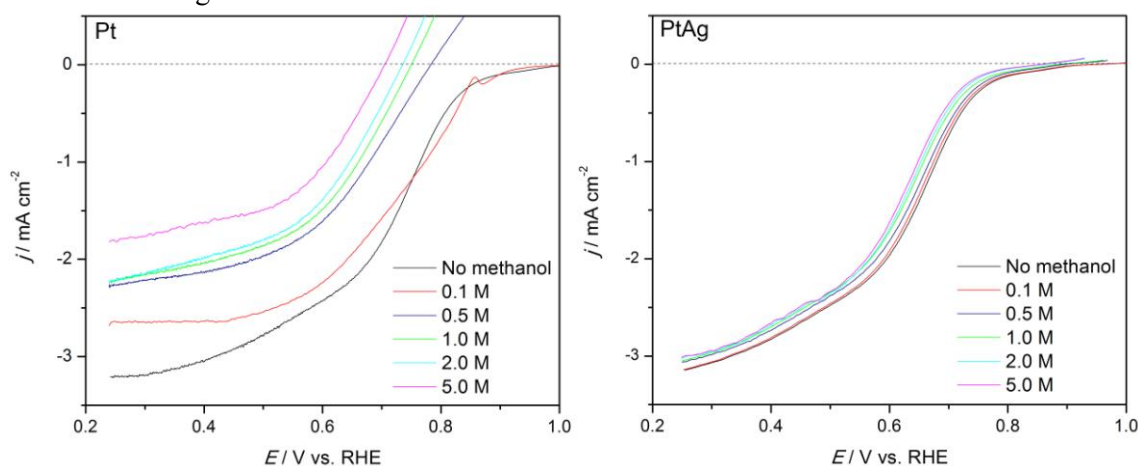
where  $i_L$  is the limiting current (A),  $n$  is the total number of electrons transferred,  $F$  is the Faraday constant ( $96485.34 \text{ C mol}^{-1}$ ),  $A$  is the area of the electrode ( $\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $\omega$  is the rotation rate ( $\text{rad s}^{-1}$ ),  $\nu$  is the kinematic viscosity ( $\text{cm}^2 \text{ s}^{-1}$ ) and  $C_0$  is the concentration in bulk ( $\text{mol cm}^{-3}$ ). By comparison of the experimental and theoretical plots, it is demonstrated that both catalysts show consistent behavior with a four-electron transfer mechanism.



**Figure 4.** Oxygen Reduction Reaction on a) Pt, and b) PtAg. c) Levich plot for both catalysts.

### 3.5. Oxygen Reduction Reaction in presence of Methanol.

The electrochemical behavior of the catalysts for the ORR in presence of methanol was also evaluated in a rotating rate of 1600 RPM. The methanol concentration used are 0.1, 0.5, 1.0, 2.0 and 5 M. The evaluation was carried out through polarization curves, which are shown in Figure 5. In absence of methanol, both catalysts promote the ORR. However, when methanol is added, in the case of Pt/GC a decrease in the cathodic current is observed, due to the competition between ORR and methanol oxidation reaction (MOR) processes [5], resulting in anodic currents. Also, it can be observed that at the higher methanol concentration, it is obtained the larger negative shift in the onset potential of the ORR, becoming up to 200 mV in comparison to the system where methanol is not added. On the other hand, the PtAg/GC catalyst keeps its catalytic activity towards the ORR regardless of the concentration of methanol. No anodic currents are observed with the PtAg/GC catalyst, which means that no methanol oxidation reaction occurs. Additionally, the shift on the onset potential of the ORR is 20 mV when the highest concentration of methanol is added.



**Figure 5.** Oxygen reduction in presence of Methanol on Pt/GC and PtAg/GC at 1600 rpm.

### Conclusions

A bimetallic PtAg/GC material was obtained by electrochemical technique. This material shows a high methanol tolerance, above 5.0 M in alkaline media. Hence, this material is a promising candidate, in order to avoid the crossover effect in methanol fuel cell, and for using in microfluidic fuel cell.

### Acknowledgement

Abrego-Martínez acknowledges to CONACYT for a postgraduate scholarship. Mendoza-Huizar gratefully acknowledges financial support from the Universidad Autónoma del Estado de Hidalgo.

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