Ethanol Tolerant Catalyst Based in Platinum and Silver in Graphene

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Abstract. In this work, the use of the electrochemical deposit PtAg on the glassy carbon modified with graphene (PtAg/G) is proposed. The electrochemical test (Rotatory Disc Electrode, RDE) showed a better performance to reduce oxygen for PtAg/G compared to a similar material obtained in Vulcan carbon (PtAg/V). The reduction potential is around 0.82 V versus RHE in PtAg/G compared to 0.77 V versus RHE in PtAg/V. The PtAg/G has a smaller particle size, this was attributable to the better distribution of active graphene sites.

1. Introduction
The Oxygen Reduction Reaction (ORR) is an interesting reaction because it shows a big sensibility to electrode surface and the presence to others adsorbent species. Another important factor in the investigations is the size of the catalyst particles, demonstrating that nano-sized materials offer high performance due to the greater active area they present,[1] however, the electrocatalytic activity of the materials does not only depend on the size of the particle, but also the nature of the support and the method of preparation; There are several methods of synthesis stories such as sol-gel, sputtering, chemical pyrolysis among others.

Some studies suggest that the ORR activity depends strongly on the intrinsic catalytic activity of the metal, crystallographic orientation of the active phase, metal support interaction and morphology of the catalytic phase and support.[2] It is well known that the Pt is the most promising electro catalyst for the ORR since it presents good activity and chemical stability under the operating conditions,[3] but, it has some drawbacks such as high cost, obtaining in pure state, it is easily poisoned [4] by what its electrocatalytic activity decreases with time. Some other studies focus on demonstrating the use of the bi-metallic compounds as a solution for the poisoning, so, PtAg is the proposed material.

2. Experimental

2.1 Preparation of electrodes
The glassy carbon electrode was modified by a transferring catalytic ink. The ink was obtained by dispersing the support (3.0 mg Graphene) in isopropyl alcohol (440 μL, 99.9%) and further addition of Nafion® solution (42 μL, 5 wt.% Ion Power). Basically, mixture was made by sonication for 20 min. for the first graphene and isopropyl mixture to form a homogeneous suspension, after, it was added the Nafion® and put in sonication for 20 min. 2 μL is deposited with the help of a micropipette on the glassy
carbon support, covering the geometric area (0.0706 cm²), in the form of a thin layer obtaining a thin and homogeneous film.

2.2 Synthesis of catalysts
In a first step a layer of Vulcan carbon or graphene was placed over a glassy carbon electrode. This layer was prepared in isopropyl alcohol with Nafion®. The glassy carbon electrode was used as working electrode in an electrochemical cell with three electrodes, also was used a Calomel KCl sat reference electrode (E = 0.197 V / NHE), and an auxiliary graphite electrode. As an electrolyte, a 0.5 M H₂SO₄ solution, prepared with deionized water. The catalyst was made in two steps the first consisted in a Pt deposit by chronoamperometry at a potential of 0.04 V vs NHE and the second step is the Ag deposit by the same technique at a potential of 0.55 V vs NHE.

2.3 Electrochemical characterization
All RDE measurements were conducted by a potentiostat/galvanostat BioLogic, in a three-electrode cell at room temperature. A Calomel electrode saturated with KCl, and a graphite electrode were used as the reference electrode and counter electrode, respectively. The working electrode was prepared using a glassy carbon disc, which was previously polished with alumina powder (0.05 μm) and washed with deionized water. The catalyst thin film was formed on the surface of glassy carbon (GC) electrode by transferring catalytic ink (2 μL) and air-drying. All experiments were performed in alkaline media (1M KOH saturated with oxygen).

3. Results and discussion

3.1. RDE measurements
The Figure 1 shows a comparison for the ORR of all the synthetized catalysts under similar experimental conditions. Also shows the experiments that were made in the solution of 1M KOH saturated with Oxygen, at speeds of 100, 400, 900, 1600 and 2500 rpm, for the materials PtAg/V (Vulcan) and PtAg/G (Graphene) respectively.

From the curves, it was observed that the starting potential of the RRO for PtAg/V is 0.77 V vs RHE. On the other hand, for the PtAg/G catalyst the RRO starts at 0.82 V vs RHE. When the bimetallic compounds were evaluated, a 0.05 V difference was observed between PtAg/V and PtAg/G. This change is caused by the silver layer, which affects the catalytic activity of platinum.

![Figure 1. RDE Voltammetry from ORR in 1M KOH + O₂ for a) PtAg/Vulcan and b) PtAg/G (ν= 5 mV s⁻¹)](image)
Limit current densities were used to construct the Levich graphs, which are shown in Figure 2. The theoretical graphs for the RRO by transfer of two and four electrons were calculated using the Levich equation.

\[ |i_L| = 0.62nFD^{2/3}v^{-1/6}D^{-1/6}C \]  

(1)

The electrochemical characterization shows that the materials studied are active towards the ORR, preferably proceeds by a global multielectronic transfer of 4 e\(^-\) (direct route) for the formation of water. Also, the activity towards the ORR shows a relationship with the particle size.

1. **DIRECT ROUTE**

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

\[ \text{E}^0(\text{O}_2/\text{H}_2\text{O}) = 1.229 \text{ V} \]

2. **INDIRECT ROUTE**

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{E}^0(\text{O}_2/\text{H}_2\text{O}_2) = 0.267 \text{ V} \]

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

\[ \text{E}^0(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.77 \text{ V} \]

![Figure 2](image_url)

**Figure 2.** Determination of n electrons transferred for the ORR in the synthesized materials.

### 3.2. Ethanol tolerance tests

The Figure 3 shows the linear voltammetry experiments for PtAg/V and PtAg/G respectively. It shows that, in the absence of Ethanol (EtOH), both catalysts promote RRO. However, when ethanol is added to the system, for the PtAg/V system a decrease in the limit current is showed, as well as a negative displacement in the Open Circuit Potential (OCP) of the system. This could be attributed to a competition between the RRO and the ethanol oxidation reaction (EOR). Therefore, the EOR is more favorable over PtAg/V than the RRO. As the ethanol concentration increases, the negative change in the OCP increases, as does the anodic current. The oxygen reduction potential is up to 250 mV lower than the system without ethanol.
However, in the case of the compound PtAg/G it is observed that it maintains its activity towards the ORR even when the ethanol is present. The OCP of the system practically remained unchanged regardless of the concentration of ethanol, and anodic currents are not observed in the curves, therefore, it is evident that the EOR is not promoted on this material. When the highest concentration was added, the oxygen reduction potential decreased only 13 mV with respect to the system without ethanol.

Tolerance properties are conferred by the Ag coating, however, it is evident that, although the Ag was deposited in the same way with the Vulcan support, Graphene showed that the increase of active sites helped a greater displacement of Ag on the support, for which better results were obtained.

![Figure 3. Linear Voltammetries of the ORR in the presence of EtOH at 1600 rpm at KOH 1M + O2 (sat) to a) PtAg/V and b) PtAg/G (V= 5 mVs⁻¹)](image)

3.3. SEM results

SEM experiments were carried out to observe the shape, size and dispersion of the synthesized PtAg nanoparticles over the support (Figure 4). The average PtAg particle size for the PtAg/V and PtAg/G catalysts were 378 and 230 nm, respectively.

In addition, a good dispersion was achieved over the Vulcan and Graphene as can be observed in Figure 4a and 4b respectively. SEM images indicate that the catalyst is composed almost by spherical nanoparticles in both cases, but it can be observed that the graphene modifies mainly the surface of the glassy carbon, it is a sign to increase significantly the active sites.
4. Conclusions

The electrochemical deposit is an effective synthesis method that allows to obtain nanometric Pt electrocatalysts for the ORR, being at 0.62 V vs RHE the optimal potential to obtain electrocatalysts with the best electrocatalytic activity. It is intended that the addition of the second material improves the electrocatalytic activity of Pt towards the ORR, due to diffusional and electronic effects.

Graphene provides more active sites than Vulcan support, thus increasing almost twice the current response with deposits of materials separately, however, tests with the bimetallic compound show a closeness to the currents provided by the Vulcan but with an improvement in their OCP potentials.

5. References:

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