Platinum particles electrodeposition on carbon substrates

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Abstract

Electrochemical deposition of platinum on different carbon substrates was applied to obtain supported submicroparticles to use as electrocatalysts for the oxidation of methanol in acid media. Particles with well-defined morphology and size can be obtained by this technique controlling electrodeposition potential and time. Glassy carbon and graphite fibers were used as substrates. Platinum particles were deposited from chloroplatinic acid solutions. Conventional electrochemical techniques were used to characterize supported platinum surface status. Particle size and catalyst mass were influenced by deposition potential and time. The application of double potential steps favored a more uniform dispersion of the particles and a general reduction in particle size. From specific surface area measurements particle diameters between 10 and 20 nm were estimated when glassy carbon was used as support. Differences in size and morphology were observed when Pt was deposited on graphite fibers. Notwithstanding using similar conditions, the particles on fibers were bigger and tending to coalesce. This behavior was ascribed to the highly hydrophobic surface of the fibers. The Pt deposits were tested as catalyst for electrochemical methanol oxidation. The Pt/GC electrocatalytic activity expressed as current per Pt mass was found to depend on the metal particle size, showing a decreasing activity when the catalyst diameter increase.

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1. Introduction

Direct methanol fuel cells (DMFC) have advantages over other fuel cells because methanol is easily prepared, handled and stored [1]. The key component of a DMFC is the membrane electrode assembly (MEA), which comprises a polymer electrolyte membrane, and catalyst coated porous electrodes for methanol oxidation (anode), and oxygen reduction (cathode). Generally, the membrane is Nafion®, or a similar perfluorosulfonic acid based polymer, the anode catalyst is pure Pt or a Pt-based alloy, the cathode catalyst is Pt black, and the electrodes are made of carbon fiber paper or carbon cloth.

The catalyst material most frequently used for the electrochemical oxidation of methanol in acid media consists of carbon-supported Pt particles (Pt/C). It is generally accepted that the rate-determining step is the oxidation of a methanol adsorbate by an adsorbed hydroxide species or activated water group [2–4]

\[ \text{C–OH} + \text{OH}_{\text{ads}} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \]  

(1)

In reason that the gaseous product CO₂ should be removed from the catalytic sites and the electrode pores, the anodes used for the methanol oxidation must have an open internal structure [5]. The choice of a suitable porous carbon support is a factor that may affect the performance of supported catalysts. Interactions between the catalyst and the carbon support have been identified which modify the catalyst activity [6].

Carbon fiber materials and carbon paper can be utilized as electrode support and diffusion layer, and as catalysts supports. These materials are widely used as electrodes in...
electrochemical reactors because the properties of graphite are combined with a three-dimensional flexible structure. The result is a large surface area, low cost, rugged, chemically resistant and versatile material for different electrochemical applications [7–9].

Platinum is deposited on the carbon support using the impregnation-reduction method, where reduction is effected chemically or electrochemically. The electrodeposition method of preparing Pt/C is advantageous in achieving greater selectivity in the placement of the platinum particles into the preformed electrode, but it have the drawback that after initial formation of a platinum particle, further deposition continues on the same particle resulting in increase of the size of the particle [10]. On the other hand, electrodeposition seems to be the only technique through which loadings in microgram range are achievable.

The purpose of this paper is to provide a better insight into the use of both graphite fiber multifilament electrodes and graphite fiber cloth as support of fuel cell platinum electrocatalysts. The conditions for the electrodeposition of Pt crystallites on graphite fibers are determined. The morphological and structural characteristics of these deposits are studied and compared with similar deposits obtained on glassy carbon. In addition, the electrocatalytic activity of these deposits for the methanol electro-oxidation in acid media is analyzed.

2. Experimental

For the preparation of supported Pt electrodes different materials were employed. Glassy carbon (GC) discs of 0.07 cm$^2$ exposed geometric area were polished with emery paper (grit 1200) and alumina of grade 1 and 0.3 μm before electrodeposition. Two types of electrodes were prepared from graphite fiber cloth. Graphite fiber bundles with a weight of 1 mg/cm length were cut of 2 cm length and fixed to a platinum plate using graphite paint. Hereafter, we will refer to these electrodes as fiber or GF electrodes. Larger electrodes were constructed of graphite cloth with a thickness of 0.1 cm and a specific surface area of 124 cm$^2$ cm$^{-3}$. Hereafter, we will refer to these electrodes as cloth or GFC electrodes. Before using, the fibers were cleaned by immersion in acetone, and afterward they were dried and impregnated with chloroplatinic acid solution during 15 min with strong nitrogen bubbling.

Electrochemical measurements were carried out in conventional glass cells at room temperature. The counter electrode was a platinum sheet, separated from the working electrode compartment by a porous glass diaphragm. A saturated calomel electrode located in a Luggin capillary served as the reference electrode (+0.241 V vs. RHE). All the potentials mentioned in this work are referred to this electrode. The electrolytes were aqueous solutions of 0.5 M H$_2$SO$_4$, 5 mM H$_2$PtCl$_6$, 0.5 M H$_2$SO$_4$, 2 mM H$_2$PtCl$_6$, 0.5 M H$_2$SO$_4$, 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$. An inert nitrogen atmosphere was maintained over the electrolyte. A PAR 273 potentiostat was used to run the experiments. Conventional electrochemical techniques, linear and cyclic voltammetry and chronoamperometry, were used.

The activity for methanol oxidation was measured in 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$ by applying a sweep at a scan rate of 100 mV s$^{-1}$, starting at 0 V. The activities expressed as current per unit mass were obtained from a voltammogram after reaching a repetitive electrode behavior.

Platinum was electrodeposited from x M H$_2$PtCl$_6$ solutions + 0.5 M H$_2$SO$_4$ (x = 2 and 5 mM) on glassy carbon (Pt/GC) and on graphite fibers (Pt/GF) and on graphite cloths (Pt/GFC) using chronoamperometry. To obtain platinum electrodeposits with different characteristics two potential vs. time step functions were applied: (a) starting from the rest potential a constant potential ($E_1$) was applied to the electrode for times ($t_1$) varying between 60 and 600 s; (b) two consecutive potential steps were used, the first step at $E_1 = -0.5 V$ for times ($t_1$) ranging from 0.2 to 5 s and the second step at $E_2 = 0 V$ for times $t_2$ between 60 and 600 s.

The amount of deposited platinum per cm$^2$ of the geometric area, $W$, was determined from the electrical charge, assuming that reduction of PtCl$_2$ complex to Pt was the sole reaction. The adimensional surface area of the platinum catalyst ($A$) was measured from the electrical charge used in hydrogen adsorption ($Q_{HI}$) from voltammograms obtained in 0.5 M H$_2$SO$_4$ between −0.25 and +0.5 V. Assuming that 1 cm$^2$ of smooth Pt requires 210 μC [11], $A = Q_{HI}/210A_g$, where $A_g$ is the geometric surface area of the electrode. Platinum deposits were also characterized by calculated values of their mass specific surface, $S$, in m$^2$ g$^{-1}$ ($S = 100 A/W$).

The morphological characterization of the electrodes was carried out using a scanning electronic microscope JEOL 100. The average diameter of platinum particles in nm, $d_p$, was calculated from the mass specific surface area, $S$, assuming a spherical shape of the particles by the equation: $d_p = 6000/\rho S$, where $\rho$ is platinum specific density (21.4 g cm$^{-3}$) [12].

3. Results and discussion

3.1. Pt/GC electrodes

Platinum electrodeposition begins at 0.4 V and the current due to the reaction increase when the potential shift to more negative values, becoming a mass controlled process at 0.15 V. Proton reduction begins near −0.25 V, and at lower potentials occurs simultaneously with platinum reduction. A summary of the results for Pt/GC electrodes prepared according to the two aforementioned methods are presented in Table 1.

The electrode potential has small effect on the mass specific surface area, but some decreasing is observed for potentials $E_2$ more negative than −0.2 V. These deviations can be attributed to the hydrogen adsorption charge that
introduces inaccuracies in determination of the electric charge used in the platinum electro-reduction [13]. The first 7 values in Table 1 have been prepared following the single step method, and in this case, the mass specific surface area increases in the first minutes of deposition but reaches values nearly constant approaching 300 s.

The last 10 values in the table were prepared following the double step method. When a short initial potential pulse at a very negative potential (−0.5 V) was applied to the electrode, higher surface areas were obtained that when a unique constant potential was used. The predominant factor is the length of the first step. This can be seen in Fig. 1, where the growth of platinum loading, surface area factor is the length of the first step. This can be seen in a unique constant potential was used. The predominant factor is the length of the first step. This can be seen in Fig. 1, where the growth of platinum loading, surface area factor is the length of the first step.

For example for \( t_1 = 60 \) s, crystallite sizes vary between 0.2 and 0.6 \( \mu m \). For longer deposition times the platinum particles exhibit scarce growth although more particles are observed.

Fig. 2 presents the SEM images of deposits obtained using the double pulse function. The results show that the application of a first short pulse at −0.5 V favors the formation of a greater quantity of nuclei, although the crystallites exhibit similar size and shape. When the total deposition time is close to 60 s, the crystallite size distribution determined from SEM images show values similar to the mean diameter calculated assuming a spherical geometry and smooth surface (Table 1). However, for longer times the SEM measured particle diameter are rather larger. STM studies give similar results and it seems probable that the particles observed by SEM are porous agglomerates and they may rather be envisaged as packed piles of nm-scale clusters than as massive crystallites with a rough surface [15].

Fig. 5 presents the histograms corresponding to the SEM images of Fig. 4. The histogram in Fig. 5(a) shows that the distribution of particle sizes is quite broad. Fig. 5(b) corresponds to the deposit obtained using double pulse and the shape shows a major quantity of smaller particles and a tail toward large particles.

![Fig. 1. Influence of \( t_1 \) on platinum loading, adimensional surface area and specific surface area, \( E_1 = -0.5 \) V, \( E_2 = 0 \) V, \( t_2 = 60 \) s.](image)

![Fig. 2. Dependency of the adimensional surface area \( A \) with platinum loading for essays obtained in the conditions of Table 1.](image)

![Table 1: Parameters of Pt electrodeposits on GC electrodes](image)
Fig. 3. Top-view SEM image of Pt/GC electrodes prepared by the method (a) from 0.5 M H₂SO₄ + 2 × 10⁻³ M H₂PtCl₆ at E₂ = 0 V. (a) t₁ = 0, t₂ = 300 s, (b) t₁ = 0, t₂ = 600 s.

Fig. 4. Top-view SEM image of Pt/GC electrodes comparing the particles obtained using different methods: (a) E₂ = 0 V, t₂ = 60 s, single-pulse method, (b) E₁ = −0.5 V, t₁ = 0.2 s, t₂ = 60 s, E₂ = 0 V, double-pulse method.

Fig. 5. Histograms showing size distributions of Pt particles in Pt/GC electrodes. Conditions correspond to the electrodes of Fig. 4: (a) E₂ = 0 V, t₂ = 60 s, single-pulse method, (b) E₁ = −0.5 V, t₁ = 0.2 s, t₂ = 60 s, E₂ = 0 V, double-pulse method.
3.2. Pt/GF and Pt/GFC electrodes

Platinum deposits on graphite fibers exhibit some differences with that obtained on glassy carbon. Table 2 shows the characteristic parameters determined for different Pt/GF and Pt/GFC electrodes. Comparing these results with those shown in Table 1, one can observe that the mass specific surface area is lower in these electrodes than at Pt/GC electrodes. Moreover, it has been found that the measured Pt surface area depends on the time used to impregnate the fibers previously to the metal electrodeposition. This behavior is ascribed to the highly hydrophobic surface of these fibers that difficult the impregnation with the electrolyte [16]. SEM micrographs in Fig. 6 correspond to Pt/GF prepared under different conditions. Fig. 6(a) is obtained using the single-pulse method. Comparing with the Pt/GC electrodes (Fig. 3(a)) less quantity of particles is observed but the crystallites have greater size. Moreover, a wide variation in particle size and the existence of agglomerates of several particles is observed.

The Pt deposits prepared by the two-pulse method exhibit a significant improvement in the platinum loading and the distribution of the particles on the fibers (Fig. 6(b)) when compared with the electrodes prepared by the single step method (Figs. 6(a)). The relative duration of both steps, have an effect on the characteristic of the Pt deposit. When the length of the first step $t_1$ is increased from 0.2 up to 5 s a more uniform dispersion of the metal on the fiber is observed. On the other hand, rising the second step duration $t_2$ only cause the growth of the particle size.

When platinum was deposited on graphite cloth, a marked improvement was observed. When results for both Pt/GF and Pt/GFC are compared (Table 2), higher specific surface areas are obtained with the cloth. This result is confirmed by the SEM images of the Pt deposits that show more uniform distribution and smaller particle size of the deposit obtained with the cloth.

The difference may be attributed to a more uniform current distribution in the graphite cloth electrode. The fiber electrodes are connected at the end to the platinum contact and consequently the current must pass through all the length of the electrode and the contact between the individual fibers may change. In contrast, in the cloth electrodes the strands are interwoven with a better contact between the fibers.

3.3. Electro-oxidation of methanol in sulfuric acid

Fig. 7 shows the current–potential curve of three electrodes of Pt deposited on different substrate in the methanol–sulfuric acid solution. The electro-oxidation of methanol starts ca. 0.1 V and the current increase is due to this reaction. After the current peak, a decrease in the

<table>
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<th>$E_1$/V</th>
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<th>$S_{GF}$/m$^2$ g$^{-1}$</th>
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![Fig. 6. Top-view SEM image of Pt/GF electrodes prepared from 0.5 M H$_2$SO$_4$ + 5 x 10$^{-3}$ M H$_2$PtCl$_6$: (a) $E_2 = 0$ V, $t_2 = 300$ s, (b) $E_1 = –0.5$ V, $t_1 = 1$ s, $E_2 = 0$ V, $t_2 = 300$ s.](image1)

![Fig. 7. Electro-oxidation of methanol at Pt/GC, Pt/GF and Pt/GFC electrodes in 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$. Platinum was deposited at the following conditions: $E_1 = –0.5$ V, $t_1 = 5$ s, $E_2 = 0$ V, $t_2 = 300$ s.](image2)
current is observed due to the formation of oxide in the platinum surface, which decreases the number of active sites on the electrode surface. The platinum deposits at the three electrodes were obtained in the same conditions. To compare the catalytic activity of significantly different electrodes the current is expressed per μg of platinum. The methanol oxidation current of Pt/GC and Pt/GF are much larger than that of Pt/GFC electrode. The better performance of the Pt supported on glassy carbon may be associated to the higher mass specific surface area, since the electrochemical reaction depends on the electrocatalyst surface area. The results of methanol electro-oxidation at electrodes prepared under different sets of conditions are summarized in Table 3. The specific catalytic activity of these electrodes is compared as a function of the specific current maximum shown in Fig. 7. Higher catalytic activity is measured for Pt/GC electrodes probably because not all the platinum deposited on the fibers is uniformly accessible to the reactants.

The variation of $i_{p}(GC)$ with the mass specific surface area is represented in Fig. 8. Although the points appears rather dispersed, the catalytic activity increases with the mass specific surface area, that correspond to a reduction in the particle size. Some authors have found that methanol oxidation reaction rate at Pt deposited on a carbon support is influenced by the particle size [3,17]. However, results are contradictory and different problems complicates interpretation of the results obtained using commercial catalysts, such us poisoning of metal, metal agglomerations, substrate–catalyst interaction, etc. Variations in the catalyst activity can be connected with a change in the bond strength of the methanol adsorbates with platinum particles, which is determined primarily by the structural properties of the deposits.

4. Conclusions

Platinum deposits at glassy carbon and graphite fibers and graphite cloths by electrodeposition exhibit differences that can be attributed to the geometry and the surface properties of the carbonaceous supports.

The application of short potential pulses at −0.5 V (ECS) during times variables from 0.2 to 5 s favors a more uniform dispersion of the particles and a general reduction in particle size. From mass specific surface area measurements particle diameters between 10 and 20 nm are estimated when glassy carbon is used as support. Differences in size and morphology are observed when Pt is deposited on graphite fibers. Nevertheless using similar conditions, the particles on fibers are bigger and show tendency to coalesce. This behavior was ascribed to the highly hydrophobic surface of the fibers.

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