

## Effect of glassy carbon properties on the electrochemical deposition of platinum nano-catalyst and its activity for methanol oxidation

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**Abstract:** The effects of the properties of glassy carbon on the deposition of platinum particles and the electrocatalytic activity of platinum supported on glassy carbon (GC/Pt) for methanol oxidation in alkaline and acidic solutions were studied. Platinum was potentiostatically deposited on two glassy carbon samples, thermally treated at different temperatures, which were either polished or anodically polarised in acid (GC<sub>OX-AC</sub>/Pt) and in alkali (GC<sub>OX-AL</sub>/Pt). Anodic polarisation of glassy carbon, either in alkaline or acidic solution, enhances the activity of both types of GC/Pt electrodes for methanol oxidation. The activity of the catalysts follows the change in the properties of the glassy carbon support upon anodic treatment. The specific activity of the GC<sub>OX-AL</sub>/Pt electrode for this reaction in alkali is increased only a few times in comparison with the activity of the GC/Pt one. On the other hand, the specific activity of the GC<sub>OX-AC</sub>/Pt electrode for methanol oxidation in acid is about one order of magnitude higher than that of the GC/Pt electrode. The role of the substrate on the properties of catalyst is discussed in detail.

**Keywords:** glassy carbon support, platinum catalyst, electrochemical properties, methanol electrooxidation, scanning tunneling microscopy (STM).

### INTRODUCTION

Owing to its physicochemical features, carbon is, in a variety of forms, extensively used as an electrode material in different electrochemical systems. Very often it is applied as a catalyst support. The physicochemical characteristics and surface chemistry of carbon<sup>1–4</sup> influence the properties of the support itself as well as of a catalyst. One of the most intensively studied systems is platinum catalyst supported on high area carbon. The electrocatalytic activity of these catalysts for

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methanol oxidation in acidic solutions, as well as the effects influencing their performance have been discussed in a number of papers<sup>5–17</sup> because of their possible application in fuel cells. It was noticed that the nature of the high area carbon support affected the structure of platinum deposits and thus their activity.<sup>7,8,13–15</sup> Nevertheless, particle size, distribution and loading of platinum were the focus of research and appeared to play a significant role in the electrocatalysis.<sup>7–17</sup> However, rather wide particle size distributions, agglomeration, Ohmic drops in the porous catalyst layers, possible different impurities in the carbon used for commercial Pt catalysts, *etc.*, could complicate the examination of the platinum particle activity. Therefore, glassy carbon was introduced into these studies.<sup>9–12,17</sup>

Glassy carbon is an inert material and when polished has a rather low surface area but it is porous and contains different functional groups. It is composed of aromatic ribbon molecules randomly oriented and tangled in a complicated manner and its physico-chemical properties are greatly influenced by the starting polymer and the temperature of carbonization.<sup>18,19</sup> Studies have shown that the double layer charge (*i.e.*, activity) of glassy carbon depends not only on the properties of the material determined by the temperature of thermal treatment but also on the mechanical, chemical or electrochemical pretreatment.<sup>19–22</sup> The degree of electrochemical activation depends not only on the potential and time of polarization but also on the pH of the solution applied in the electrochemical treatment.<sup>22</sup> It was shown earlier that the properties of glassy carbon, determined by the factors mentioned above, greatly influenced silver deposition on glassy carbon<sup>23</sup> as well as platinum electrodeposition and its electrocatalytic activity for methanol and formic acid oxidation in acidic solution.<sup>24–25</sup> However, these effects of GC have not been thoroughly studied so far. Using material prepared from the same polymer but treated at different temperatures, as well as using mechanical and different electrochemical pretreatments enables the examination of the influence of the physico-chemical properties of this material on metal deposition and the properties of the obtained catalyst.

In the present work, a comprehensive study of the effects of the properties of glassy carbon on the electrodeposition of platinum particles and on their activity for methanol oxidation in alkaline and acidic solution is presented.

#### EXPERIMENTAL

Platinum was deposited on the following samples of glassy carbon (GC) (Sigradur – Sigr, Elektrographite, GmbH, Germany):

- sample GC-K (thermally treated at 1000 °C),
- sample GC-G (thermally treated at 2500 °C).

The GC electrode surfaces were refreshed before each deposition of platinum, by abrasion with emery paper of decreasing grain size followed by polishing with alumina of 1, 0.3 and 0.05 µm particle size. The final cleaning of the electrodes was performed in high purity water (Millipore 18 MΩ) in an ultrasonic bath.

The electrochemical treatment of the previously polished electrodes was the same as in Ref. 22 *i.e.*, anodic polarisation in 1 M NaOH at 1.41 V vs SCE for 35, 95 and 625 s, or in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 2.25 V for 95 s. These supports were designated as GC<sub>OX-AL</sub> and GC<sub>OX-AC</sub>, respectively.

Before each deposition of platinum, a cyclic voltammogram of the GC electrode was recorded (potential range  $-1.2$  V to  $0.4$  V, sweep rate  $50$  mV/s in  $0.1$  M NaOH solution and potential range  $-0.4$  V to  $1.2$  V, sweep rate  $50$  mV/s in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution) to ensure that the GC surface was clean and free of Pt from the previous experiment.

Platinum was electrodeposited on a GC disc electrode (geometric area  $A_{\text{GC}} = 0.21$  cm<sup>2</sup>) by the potential step method in deoxygenated  $0.5$  M  $\text{H}_2\text{SO}_4 + 6$  mM  $\text{H}_2\text{PtCl}_6$ . The potential perturbation from  $-0.2$  V to  $0.1$  V was applied after  $0.5$  s at the initial potential. Platinum was deposited under the same conditions in each experiment but with loadings ( $w_{\text{Pt}}$ ) of  $18 \pm 1$   $\mu\text{g}/\text{cm}^2$  (partly covered surface) and  $67 \pm 2$   $\mu\text{g}/\text{cm}^2$  (completely covered surface). The amount of platinum was estimated from the integrated charge measured from the  $I-t$  transient response corrected for the charging of the glassy carbon. After deposition, the electrode was thoroughly rinsed with high purity water and transferred to a cell containing  $0.1$  M NaOH or  $0.5$  M  $\text{H}_2\text{SO}_4$ .

A polycrystalline Pt electrode, used for comparison, was prepared by polishing and cycling the potential between the hydrogen and oxygen evolution potentials.

The electrocatalytic activity of GC/Pt and Pt electrodes for methanol oxidation was studied in  $0.1$  M NaOH +  $0.5$  M  $\text{CH}_3\text{OH}$  and  $0.5$  M  $\text{H}_2\text{SO}_4 + 0.5$  M  $\text{CH}_3\text{OH}$  solutions. Methanol was added to the solution while holding the electrode potential at  $-0.95$  V in sodium hydroxide or at  $-0.2$  V in sulfuric acid. Cyclic voltammetry at a sweep rate of  $50$  mV/s and  $1$  mV/s was used to determine the basic voltammograms and activity of the catalysts, respectively.

The reagents used were of p.a. purity, and the solutions ( $1$  M NaOH,  $0.1$  M NaOH and  $0.5$  M  $\text{H}_2\text{SO}_4$ ) were prepared with high purity water. The electrolytes were purged with purified nitrogen prior to each experiment.

All electrochemical experiments were performed at room temperature in a standard three-electrode three-compartment glass cell. The counter electrode was a Pt wire, while a bridged saturated calomel electrode (SCE) was used as the reference. All the potentials are given *versus* the SCE. The electronic equipment in all of the experiments consisted of a PAR Model 273 potentiostat and a Philips Model 8033 X-Y recorder.

GC/Pt electrodes, with polished supports and supports previously oxidized in  $1$  M NaOH or in  $0.5$  M  $\text{H}_2\text{SO}_4$ , were characterized at room temperature in air by the AFM (Atomic Force Microscopy) and STM (Scanning Tunnelling Microscopy) techniques. The structural characterization was performed with a NanoScope E (Digital Instruments, USA) microscope. AFM observations were carried out in the height mode using NanoProbes silicon nitride cantilevers with a force constant of  $0.06$  N/m. STM images were obtained in the height mode using a Pt-Ir tip (set-point current,  $i_t$ , from  $1$  to  $2$  nA, bias voltage,  $V_b = -300$  mV).

## RESULTS

### *Microscopic characterization*

The AFM and STM techniques were used for structural characterization of platinum deposited on a polished glassy carbon support, GC/Pt (A), on a GC support oxidized in  $0.1$  M NaOH for  $95$  s,  $\text{GC}_{\text{OX-AL}}/\text{Pt}$  (B), and on a GC support oxidized in  $0.5$  M  $\text{H}_2\text{SO}_4$  for  $95$  s,  $\text{GC}_{\text{OX-AC}}/\text{Pt}$  (C) (Figs. 1 and 2). The STM images of polished and electrochemically treated GC electrodes were presented previously.<sup>22,26</sup> The AFM images of GC/Pt electrodes reveal the topography of glassy carbon substrates with platinum deposited on the surface in the form of large 3D agglomerates of lateral size ranging from  $100$  to  $600$  nm, regardless of the treatment of the sample (Fig. 1). The corresponding height profiles and particle size distributions of GC/Pt and  $\text{GC}_{\text{OX}}/\text{Pt}$  electrodes (Fig. 1) show that anodic polarization of the GC prior to Pt deposition, either in alkali or in acid, generally leads to the formation of smaller Pt ag-

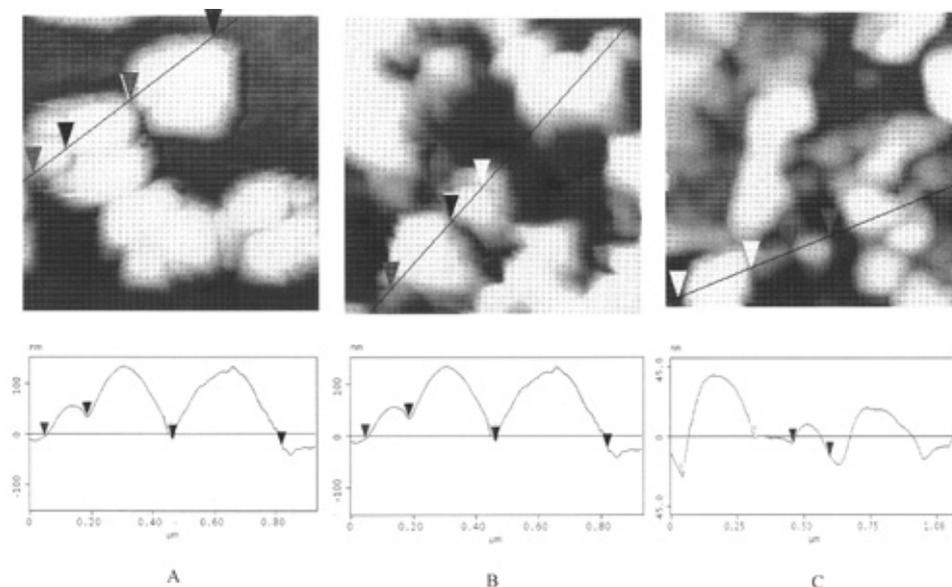


Fig. 1. AFM Images of GC-G/Pt (polisher support – A), GC-G<sub>Ox-AL</sub>/Pt (GC support oxidized at 1.41 V vs SCE for 95 s –B) and GC-G<sub>Ox-AC</sub>/Pt (GC support oxidized at 2.25 V vs. SCE for 95 s – C)  $w_{Pt} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ .

glomerates. It was found that the predominant Pt agglomerates on a polished GC support are  $487 \pm 106$  nm (Fig. 1A), on a support oxidized in alkali  $466 \pm 103$  nm (Fig. 1B) and on GC oxidized in acid  $234 \pm 87$  nm (Fig. 1C).

The STM topographic images, the corresponding height profiles and particle size distributions of all the examined GC/Pt electrodes display the internal structure of the Pt agglomerates (Fig. 2). Regardless of the GC substrate, each of them consists of spherical nanoparticles of platinum on a scale of 4–22 nm. Analyses of the images from different parts of the samples show that the predominant Pt particle size on GC/Pt is  $8.9 \pm 1.6$  nm (Fig. 2A). The Pt particle size decreases with oxidative treatment. Hence, for a GC<sub>Ox-AL</sub>/Pt electrode, it is  $8.4 \pm 2.9$  nm (Fig. 2B) and for GC<sub>Ox-AC</sub>/Pt,  $7.4 \pm 1.6$  nm (Fig. 2C).

#### *Electrochemical characterization*

Platinum was deposited on two different samples of glassy carbon (GC-K and GC-G) under the same conditions. The samples were either polished or anodically polarized in 1 M NaOH or 0.5 M H<sub>2</sub>SO<sub>4</sub> prior to Pt deposition.

Typical cyclic voltammogram of GC/Pt and GC<sub>Ox-AL</sub>/Pt electrodes in 0.1 M NaOH are shown in Fig. 3. The voltammograms are similar with those for polycrystalline platinum or Pt supported on high area carbon (Pt-C/GC).<sup>5,26</sup> The region of hydrogen adsorption/desorption ( $-0.9 \text{ V} < E < -0.6 \text{ V}$ ) followed by reversible OH<sup>-</sup> adsorption ( $-0.6 \text{ V} < E < -0.3 \text{ V}$ ) and irreversible oxide formation ( $E > -0.3 \text{ V}$ ) can be distinguished at both the GC supported Pt catalysts. The potential values of all

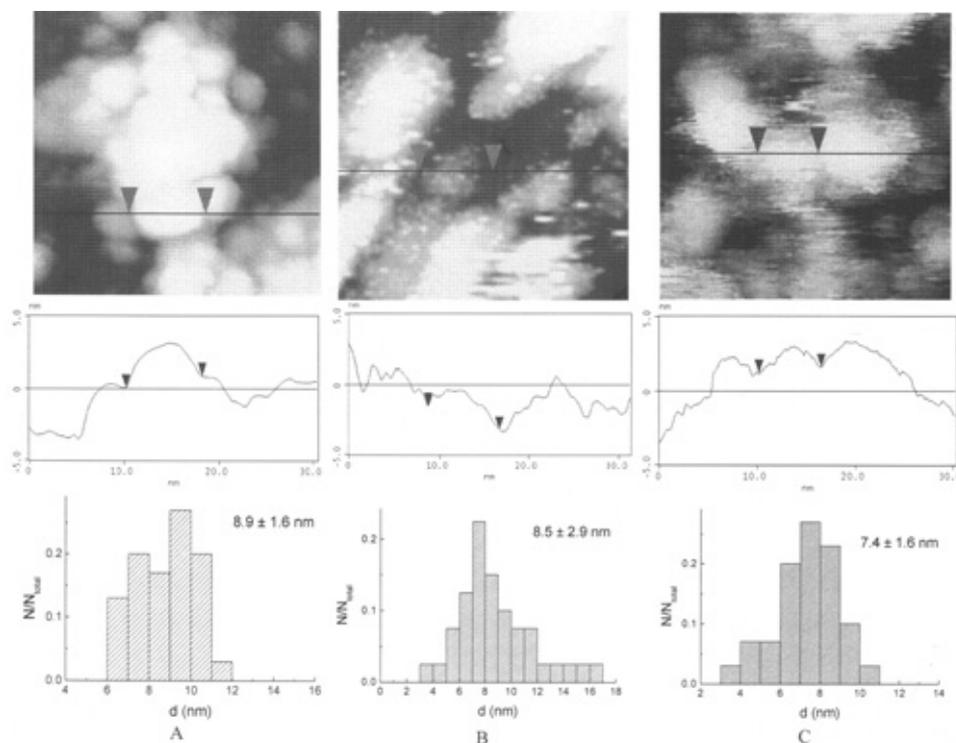


Fig. 2. STM Images of GC-C/Pt (polished support – A), GC-G<sub>Ox-AL</sub>/Pt (GC support oxidized at 1.41 V vs. SCE for 95 s – B) and GC-G<sub>Ox-AC</sub>/Pt (GC support oxidized at 2.25 V vs. SCE for 95 s – C)  $w_{Pt} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ .

the anodic and cathodic peaks remain the same for the electrodes with a polished support, regardless of the type of GC sample. However, both hydrogen peaks are shifted  $\approx 20$  mV more anodically while potential of oxide reduction is shifted some  $\approx 20$  mV towards more negative values when the GC had been previously oxidized.

Cyclic voltammograms of GC-G/Pt and GC-G<sub>Ox-AC</sub>/Pt electrodes recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution are presented in Fig. 4. The cyclic voltammogram for the GC-G/Pt electrode (polished support – Fig. 4A) resembles the voltammogram for a polycrystalline Pt electrode<sup>11</sup> and even more for a Pt-C/GC electrode<sup>5</sup> in the same solution, with a well defined hydrogen adsorption/desorption region ( $-0.2 \text{ V} < E < 0.15 \text{ V}$ ) and a region of surface oxidation at higher potentials. The cyclic voltammogram for the GC-G<sub>Ox-AC</sub>/Pt electrode (oxidized support – Fig. 4B) practically resembles the one for oxidized glassy carbon.<sup>22</sup> The redox peak at 0.4 V is related to the redox reaction of functional groups (quinones/hydroquinones) on the carbon surface in acidic solution for an oxidized, bare glassy carbon support.<sup>19,21,22</sup> The presence of platinum could only be seen from the difference between the voltammograms for GC-G<sub>Ox</sub> and GC-G<sub>Ox-AC</sub>/Pt in the potential region between  $-0.2 \text{ V}$  and  $0.1 \text{ V}$ , corresponding to hydrogen adsorption/desorption. However, the shapes

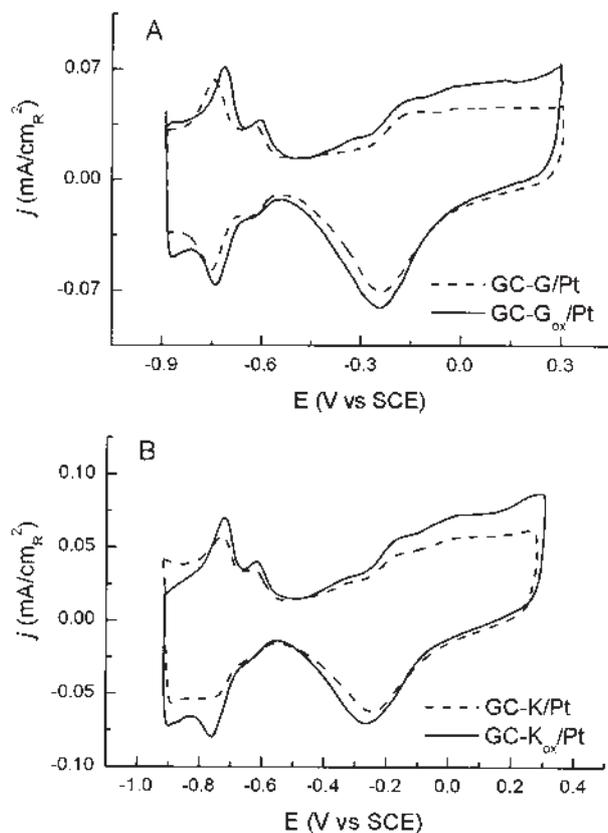


Fig. 3. Cyclic voltammograms of (A) GC-G/Pt and GC-G<sub>OX-AL</sub>/Pt and (B) GC-K/Pt and GC-K<sub>OX-AL</sub>/Pt electrodes in 0.1 M NaOH ( $w_{Pt} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ , GC support oxidized at 1.41 V vs. SCE for 95 s, sweep rate 50 mV/s).

of the voltammograms for GC<sub>OX-AC</sub>/Pt electrodes with a support previously oxidized in acidic solution strongly depend on the time and potential of the anodic polarization of the glassy carbon. Hence, if GC is oxidized at the same potential but for a shorter time, the CV for GC<sub>OX</sub>/Pt reveals the presence of characteristic peaks for both Pt and oxidized glassy carbon.<sup>24</sup>

The real surface area of platinum deposit ( $A_{Pt}$ ) was estimated using H adsorption/desorption coulometry measured by cyclic voltammetry (the integrated part of the CV was in the potential range from  $-0.95$  V to  $-0.55$  V in 0.1 M NaOH and from  $-0.2$  V to 0.15 V in 0.5 M H<sub>2</sub>SO<sub>4</sub>, with a correction for double layer charging) or from the difference in the charge between GC<sub>OX</sub>/Pt and GC<sub>OX</sub> measured by cyclic voltammetry (in the same potential regions as mentioned above) with a correction for double layer charging for polycrystalline Pt. In the case of the electrode with the support oxidized in acid, only the second procedure was possible. In all other cases, the  $A_{Pt}$  values, calculated in both ways, differed by less than 5%. The specific catalyst area ( $S_{Pt}$ ) was calculated from the equation  $S_{Pt} = (A_{Pt})/(A_{GC}, w_{Pt})$ . The values of  $A_{Pt}$  and  $S_{Pt}$  for all the electrodes and the double layer charge of the corresponding GC substrate are given in Table I. The double layer charge of GC increases with oxidative treatment and

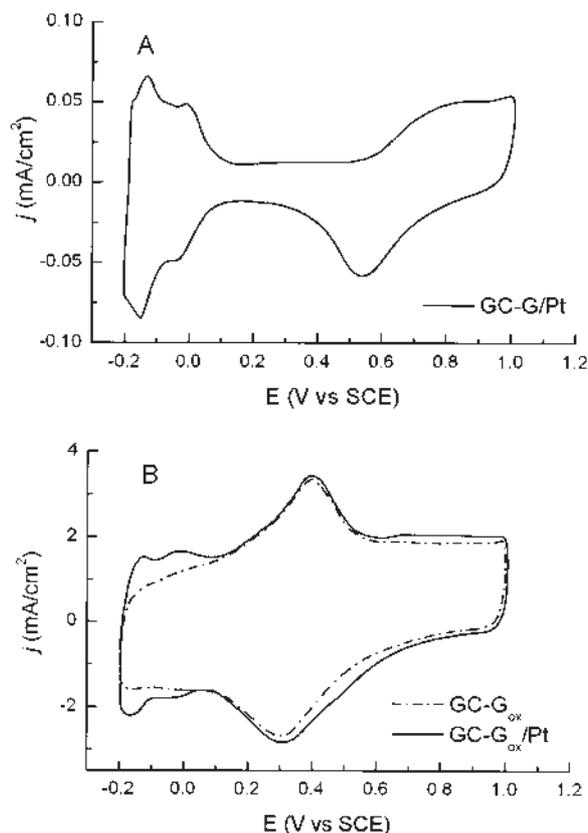


Fig. 4. Cyclic voltammograms of (A) GC-G/Pt and (B) GC-G<sub>OX-AC</sub>/Pt and GC<sub>OX-AC</sub> electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $w_{Pt} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ , GC support oxidized at 2.25 V vs. SCE for 95 s, sweep rate 50 mV/s).

this increase is higher after treatment in acidic solution. Regardless of the treatment, the GC-K electrode had a higher charge in comparison with the GC-G electrodes. The real surface area was larger for the catalysts at oxidized supports and increased with loading. In addition, the ( $A_{Pt}$ ) of platinum on a GC-K support were higher regardless of the pretreatment of the GC sample compared with those for GC-G/Pt electrodes with the same loading both for polished and oxidized supports. The platinum particles deposited on oxidized GC supports have a higher  $S_{Pt}$  in comparison with those on polished supports for the same type of GC.

TABLE I. Double layer charge of GC and the real Pt surface area  $A_{Pt}$  (cm<sup>2</sup>) and specific catalyst area  $S_{Pt}$  (m<sup>2</sup>/g) of GC/Pt electrodes

|                                | GC-K                                   |               |  |               | GC-G                                   |               |  |               |
|--------------------------------|--|---------------|--|---------------|--|---------------|--|---------------|
|                                | $w = 18 \pm 1 \mu\text{g}/\text{cm}^2$ |               | $w = 67 \pm 2 \mu\text{g}/\text{cm}^2$ |               | $w = 18 \pm 1 \mu\text{g}/\text{cm}^2$ |               | $w = 67 \pm 2 \mu\text{g}/\text{cm}^2$ |               |
|                                | Polished <sup>1</sup>                  | OX-AL<br>95 s |
| $q^{1*}$<br>mC/cm <sup>2</sup> | 0.39                                   | 0.64          | 0.43                                   | 0.67          | 0.29                                   | 0.59          | 0.27                                   | 0.61          |
| $A_{Pt}$ /cm <sup>2</sup>      | 0.38                                   | 0.56          | 0.87                                   | 1.79          | 0.26                                   | 0.45          | 0.74                                   | 1.36          |

TABLE I. Continued

|   | GC-K                                   |               |  |               | GC-G                                   |               |  |               |
|---|--|---------------|--|---------------|--|---------------|--|---------------|
|   | $w = 18 \pm 1 \mu\text{g}/\text{cm}^2$ |               | $w = 67 \pm 2 \mu\text{g}/\text{cm}^2$ |               | $w = 18 \pm 1 \mu\text{g}/\text{cm}^2$ |               | $w = 67 \pm 2 \mu\text{g}/\text{cm}^2$ |               |
|   | Polished <sup>I</sup>                  | OX-AL<br>95 s |
| $S_{\text{Pt}}/(\text{m}^2/\text{g})$       | 10.6                                   | 14            | 6.4                                    | 12.5          | 7.2                                    | 12.2          | 5.4                                    | 9.4           |
| $q^{\text{II}*}$<br>$\text{mC}/\text{cm}^2$ |  |               |  |               | Polished <sup>II</sup>                 |               | OX-AC 95 s                             |               |
|   |  |               |  |               | 0.19                                   | 20.86         |  |               |
| $A_{\text{Pt}}/\text{cm}^2$                 |  |               |  |               | 0.25                                   | 0.39          |  |               |
| $S_{\text{Pt}}/(\text{m}^2/\text{g})$       |  |               |  |               | 7                                      | 10.3          |  |               |

I: Electrode used in 0.1 M NaOH; II: electrode used in 0.5 M H<sub>2</sub>SO<sub>4</sub>; I\*: potential range from -0.95 V to 0.3 V vs. SCE; II\*: potential range from -0.25 V to 1 V vs. SCE

### Methanol oxidation

The influence of the type of GC and its pretreatment on the properties of electro-deposited platinum particles and the electrocatalytic activity of the GC/Pt electrodes was studied in the methanol oxidation reaction in alkaline and acidic solutions.

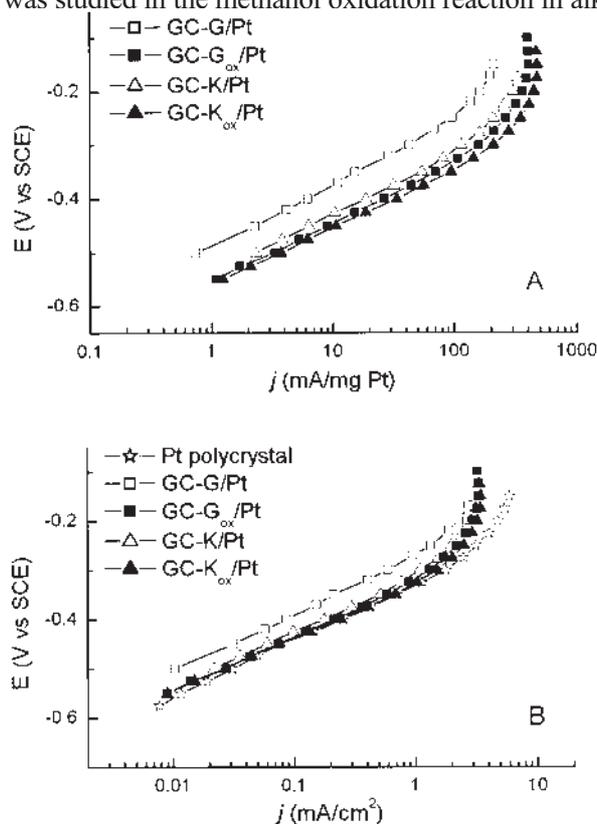


Fig. 5. Steady state polarization curves for the oxidation of 0.5 M CH<sub>3</sub>OH in 0.1 M NaOH at GC/Pt with polished supports and GC<sub>OX-AL</sub>/Pt with oxidized supports. ( $w_{\text{Pt}} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ , GC supports oxidized at 1.41 V vs. SCE for 95 s, sweep rate 1 mV/s; A—mass activity and B—specific activity scale).

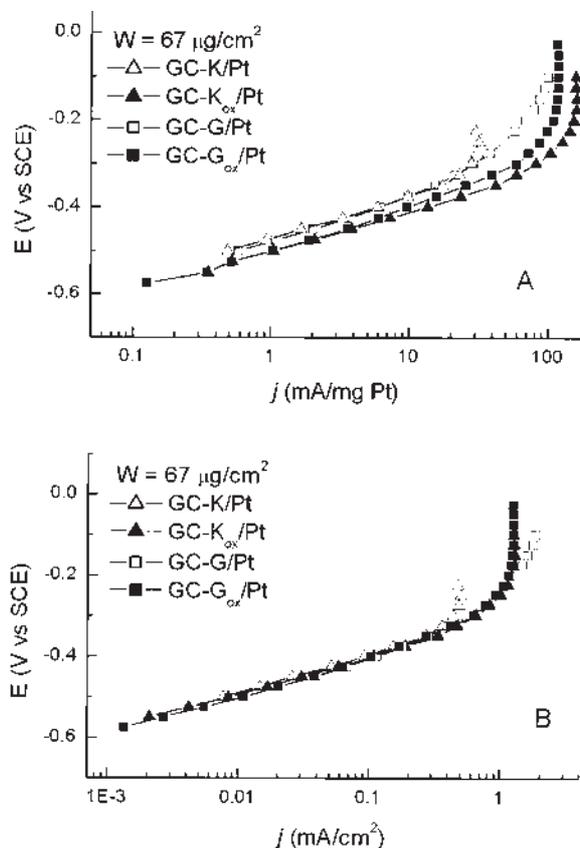


Fig. 6. Steady state polarization curves for the oxidation of 0.5 M  $\text{CH}_3\text{OH}$  in 0.1 M NaOH at Pt deposited on GC-G and GC-K polished and oxidized supports (GC support oxidized at 1.41 V vs. SCE for 95 s;  $w_{\text{Pt}} = 67 \pm 2 \mu\text{g}/\text{cm}^2$ ; A—mass activity and B—specific activity scale).

Figure 5 shows the Tafel plots for both the GC-G/Pt and GC-K/Pt electrodes with a polished and oxidized GC support on the mass activity scale (Fig. 5A) and on the specific activity scale (Fig. 5B). The results were compared with those for a smooth Pt electrode. Well-defined, straight lines with a Tafel slope of approximately  $110 \pm 10 \text{ mV}/\text{dec}$  were obtained for all GC/Pt electrodes, regardless of the type or pretreatment of the GC. However, the Pt catalysts on different types of polished or oxidized supports have different activities. The Pt deposits on either polished or oxidized GC-K samples were more active than those on GC-G supports, which have a specific activity close to the smooth Pt. The Pt catalyst at the GC-G glassy carbon has a lower activity than smooth Pt if the substrate is polished and almost the same activity when the substrate is oxidized. Consequently, this means that Pt on both polished or oxidized GC-K support is a better catalyst for methanol oxidation than Pt on the GC-G support.

In order to examine further whether the difference in activity between GC-G/Pt and GC-K/Pt electrodes could be related to the different properties of the support, electrodes with a loading that should completely cover the surface of the GC substrate were also studied. Tafel plots for both GC/Pt electrodes (polished and oxi-

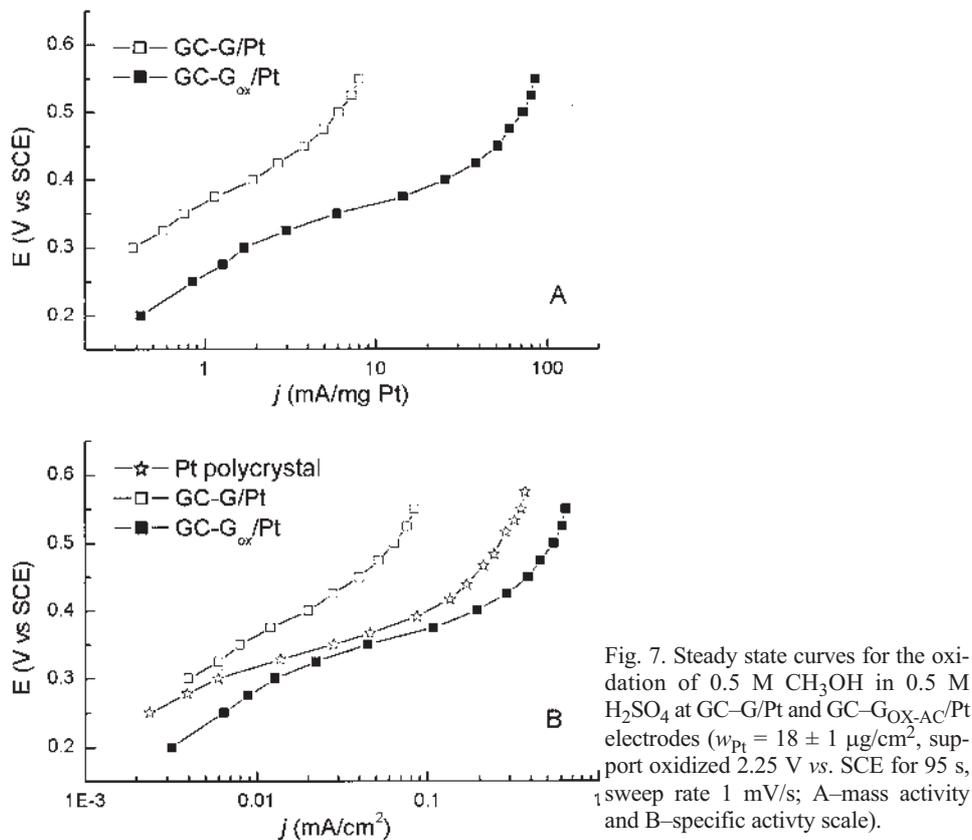


Fig. 7. Steady state curves for the oxidation of 0.5 M CH<sub>3</sub>OH in 0.5 M H<sub>2</sub>SO<sub>4</sub> at GC-G/Pt and GC-G<sub>OX-AC</sub>/Pt electrodes ( $w_{Pt} = 18 \pm 1 \mu\text{g}/\text{cm}^2$ , support oxidized 2.25 V vs. SCE for 95 s, sweep rate 1 mV/s; A—mass activity and B—specific activity scale).

dized GC support) with a high loading, on the mass activity scale (A) and on the specific activity scale (B), are presented in Fig. 6. There is no significant difference in the activity either between the electrodes with polished, or between the electrodes with oxidized substrates when the whole support surface is covered with Pt. The fact that the activities are practically the same for all the studied electrodes clearly indicates the influence of the support on the Pt deposition and thus, on the activity of the catalyst obtained. These results suggest that further study should be focused on the region of low loading.

The GC substrates were oxidized for different times in order to examine the effect of the time of electrochemical pretreatment. The results presented in Table II show that the activity of the electrodes for methanol oxidation changed, being higher or lower depending on the time of substrate oxidation, following always the changes in the properties of the GC support.

The effect of the support was also examined in methanol oxidation in sulfuric acid. In this case, only the GC-G/Pt and GC-C<sub>OX-AC</sub>/Pt electrodes were used. The G type of GC was chosen because the study in alkaline solution (Fig. 5) showed more significant differences in the activity depending on the treatment of the G compared to

the K type. Figure 7 shows the Tafel plots for GC-G/Pt and GC-G<sub>OX-AC</sub>/Pt electrodes on a mass activity scale (A) and on a specific activity scale (B). Inspection of this Figure clearly reveals that the activity of GC-G<sub>OX-AC</sub>/Pt electrode in the oxidation of methanol is about one order of magnitude higher than that of GC-G/Pt.

TABLE II. Parameters and activity for methanol oxidation of GC/Pt electrodes with a loading  $w = 18 \pm 1 \mu\text{g}/\text{cm}^2$  with GC supports oxidized in 1 M NaOH prior to Pt deposition

| Pretreatment of GC/Pt | GC double layer charge* $q/\text{mC cm}^{-2}$ | Pt surface area $A_{\text{Pt}}/\text{cm}^2$ | Specific activity# $j/\text{mA cm}^{-2}$ |
|-----------------------|---|---|--|
| GC-K Electrode        |   |   |  |
| Polished              | 0.39  | 0.38  | 1.09                                     |
| Oxidized 35 s         | 0.55  | 0.44  | 1.32                                     |
| Oxidized 95 s         | 0.64  | 0.56  | 1.51                                     |
| Oxidized 625 s        | 0.59  | 0.66  | 1.25                                     |
| GC-G Electrode        |   |   |  |
| Polished              | 0.29  | 0.26  | 0.58                                     |
| Oxidized 35 s         | 0.40  | 0.32  | 0.68                                     |
| Oxidized 95 s         | 0.59  | 0.45  | 1.32                                     |
| Oxidized 625 s        | 0.48  | 0.35  | 1.04                                     |

\*: Potential range from  $-0.95 \text{ V}$  to  $0.3 \text{ V}$  vs. SCE; #: current for oxidation of  $0.5 \text{ M CH}_3\text{OH}$  in  $0.1 \text{ M NaOH}$  at  $-0.3 \text{ V}$  vs. SCE from the polarization curve recorded at  $1 \text{ mV/s}$

## DISCUSSION

AFM and STM images (Figs. 1 and 2) showed that during electrochemical deposition Pt forms agglomerates of similar morphology composed of spherical Pt particles with sizes ranging from a few nm to a few tens of nm, regardless of the nature of the GC support. After oxidation of the GC (prior to Pt deposition), smaller agglomerates are formed (Fig. 1) and, thus, the real surface area, as well as the specific surface area of the GC<sub>OX</sub>/Pt electrodes increase (Table I), while the Pt particle diameter decrease compared with catalysts on polished supports (Fig. 2). The activity of the GC<sub>OX</sub>/Pt electrodes for methanol oxidation increases (Figs. 5 – 7). The enhancement in activity is much higher than the increases of  $A_{\text{Pt}}$  and  $S_{\text{Pt}}$  or the decrease of the particle size, and depends on the type of the support. The effect of the support, attributed to the physico-chemical properties and surface chemistry of GC, influences the properties of the Pt deposits and, consequently, the methanol oxidation reaction.

The GC samples used in this work were obtained from the same polymer resin but thermally treated at different temperatures. Glassy carbon treated at lower temperature during carbonisation (GC-K) consists of randomly oriented imperfect parallel layers of ribbon molecules, resulting in a higher porosity and lower order of the structure and, thus, in more defects on the surface.<sup>20</sup> Contrary, the GC-G type, treated at a higher temperature is composed of ribbon molecules with region of perfect linearity and, thus, has a highly ordered structure and low porosity.<sup>20</sup> Anodic

polarisation of GC, either in alkali or in acid, based on the analysis of the dependence of voltammetric charge, as well as of the dependence of the morphological changes of the electrode surface on the time of oxidation, proceeds through three stages in the electrochemical activation process.<sup>22</sup> It starts with the oxidation of surface active sites, which are presumably defects of the graphite structure (discontinuities in the basal plane) and functional groups formed. When all of surface active sites have been oxidized, electrolyte penetration through the domains of the graphitic structure of the GC becomes more intense and leads to the growth of a graphite–oxide layer, which is followed by the destruction of the surface and, eventually, when the graphite–oxide layer fills up the space between the graphitic molecules, to exfoliation of the material. After this third stage, freshly exposed domains of the graphitic structure are in contact with the electrolyte and the graphite–oxide layer commences to thicken again, until a new exfoliation occurs. The real surface area of the electrode and the double layer charge increase (I and II stage) and then decrease (III stage) in the course of the electrochemical treatment. The degree of these changes depends not only on the potential and time of polarisation, but also, very much, on the pH of the solution. The oxidation of GC is more intense in acidic than in alkaline solution and, therefore, the increase in the double layer charge (Table I and Ref. 22) and in roughness is larger after oxidation in acidic solutions than in alkaline solutions.<sup>22</sup> This is most probably because in an alkaline solution, the electrolyte does not penetrate through the graphite structure and, therefore, the oxidation occurs only on the external surface of the glassy carbon, thereby leading to a peeling of the very fine particles, which results in the appearance of fine pits on the surface, a relatively small increase of the surface roughness and double layer charge. On the other hand, in acidic solution, the electrolyte penetrates deeper through the graphite structure and the growth of the oxide layer leads to the appearance of cracks on the surface and, with further oxidation (longer time), exfoliation of bigger or smaller flakes of the material. As a result of this, the rate of the oxidation depends on the degree of order in structure of the GC, being higher for GC–K than for GC–G. The type K of glassy carbon is more porous and the electrolyte can penetrate deeper through the sample, facilitating its fast oxidation. Due to this, but also to the weaker bonds between the ribbon molecules as a consequence of the less ordered structure, intense peeling occurs even before all the available free space is filled with graphite oxide. Therefore, upon oxidation, the GC–K sample goes through the different stages faster although the increase in charge is slower in comparison with that of the GC–G type, as the number of active centres formed is lower.<sup>22</sup>

Oxidation of the active sites and growth of the graphite–oxide layer leads to changes in the fraction of surface functional groups. Previous results<sup>22</sup> of an XPS examination of polished and electrochemically treated GC–K and GC–G glassy carbon showed the highest percentage of phenolic, followed by carbonyl and the lowest percentage of carboxyl group on both polished surfaces. With electrochemical treatment, the number of these functional groups increases and this increase

depends on the conditions used during activation (pH of the solution, potential and time of oxidation), reflecting in a change of the double layer charge. Hence, if the samples are oxidised in alkali, the fraction of carbonyl and carboxyl groups increases, with a somewhat higher increase in the carboxyl ones, but, in general, the increase in the graphite–oxides is rather modest. Also a higher fraction of oxygen-containing functional groups on the surface and thus a higher double layer charge (activity), in alkaline solution was found for both the polished and oxidised GC–K sample in comparison with the GC–G one.<sup>22</sup> On the other hand, upon oxidative treatment in acidic solution, the amount of functional groups is rather high, with the highest increase in the fraction of phenolic group and much lower for carbonyl and carboxyl groups.<sup>22,25</sup> These different functional groups, *i.e.*, oxide species on the surface, are acidic sites on carbon.<sup>27,28</sup> They are adsorption sites for the catalyst precursor<sup>29,30</sup> and they also decrease the hydrophobicity of carbon, making its surface more accessible for the precursor.<sup>4</sup> Changes in the surface oxides can alter the mean particle size of Pt deposits and also influence their intrinsic activity, due to different metal–support interactions.<sup>31</sup> Platinised carbons with different functional group characteristics were examined by X-ray photoelectron spectroscopy (XPS).<sup>31</sup> Signals found on the XPS spectrum were assigned to zerovalent Pt, PtO (Ref. 31) *i.e.*, Pt(OH)<sub>2</sub> (Ref. 32) and PtO<sub>2</sub> (Ref. 31). Based on the shift in their binding energies in comparison with bulk Pt a significant metal–support interaction was also suggested.<sup>33</sup> The intensity of the signals depended on the acidic or basic character of the carbon–support. It was concluded that acidic groups on the carbon promote a coverage of oxygen-containing species on platinum and such a catalyst is more active for methanol oxidation.<sup>31</sup>

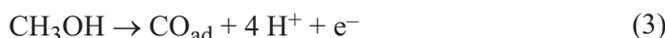
Based on the above explanations,<sup>4,22,30</sup> a higher percentage of acidic groups on the GC surface leads to a better adsorption of Pt precursor and a better dispersion of Pt on the surface. The result is a higher specific surface area, smaller particle size and a larger real surface of the platinum deposit. These conditions are more completely fulfilled at the less ordered, polished or oxidised, GC–K, *i.e.*, GC–K/Pt and GC–K<sub>OX-AL</sub>/Pt electrodes (Table I, Fig. 2). Thus, a Pt catalyst on polished or oxidised GC–K supports has a higher activity for methanol oxidation (Figs. 5 and 6). On the other hand, the higher is the fraction of acidic functional groups on GC, the stronger is the metal–support interaction and the higher is the fraction of Pt(OH)<sub>2</sub> in the catalyst.<sup>31</sup> The higher coverage with oxygen-containing species of Pt catalysts on oxidised GC leads to the higher activity of the GC<sub>OX</sub>/Pt electrodes in alkaline and acidic solutions (Figs. 5 and 7).

In order to elucidate the influence of the properties of the Pt deposit on methanol oxidation, this reaction will be briefly discussed. It is well known that oxygen-containing species (OH species) are one of the active intermediates in methanol oxidation. They are generated by discharge of water in acidic solution (Eq. 1) and (Eq. 2).

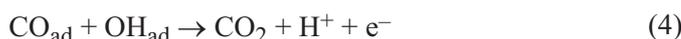




or by discharge of  $\text{OH}^-$  anions in alkaline solution (Eq. 2) and react with  $\text{CO}_{\text{ad}}$  produced by methanol dehydrogenation (Eq. 3):



giving  $\text{CO}_2$  in a Langmuir–Hinshelwood type of reaction (Eq. 4):<sup>34</sup>



The Tafel plots presented in Figs. 5 and 7 also show that the increase in activity upon oxidation of the substrate in alkaline is lower in comparison with the increase of activity of the catalyst oxidized in acidic solution. The increase in the fraction of acidic groups on GC oxidized in alkali is much lower than on GC oxidized in acid at the corresponding potential for the same time, especially in the case of phenolic groups.<sup>22</sup> This fact could be the reason for the modest increase (2 – 4 times) in activity for methanol oxidation on Pt supported on  $\text{GC}_{\text{OX-AL}}$  in comparison with a polished substrate and for the remarkable increase of almost one order of magnitude for the  $\text{GC}_{\text{OX-AC}}$ /Pt electrode.

On the other hand, Pt itself, due to its ability to adsorb OH species at significantly lower potentials in alkaline than in acidic solutions, is more active in methanol oxidation in alkaline than in acidic solutions. Therefore, the enhanced coverage of Pt with OH species caused by oxidative treatment of the support should not affect the activity of a Pt catalyst in alkali (Fig. 5) as much as in acid solutions Fig. 7.

The results presented, show that the properties and the activity of Pt catalyst supported on glassy carbon follow the changes of the GC properties upon its oxidation. Data from Table II support this conclusion. Namely, as already mentioned, GC–K electrodes are more readily activated during anodic polarization but GC–G electrodes undergo a more severe change.<sup>22</sup> When anodically polarized in alkaline solution, both GC electrodes exhibit, after an initial slight increase in the double layer charge at the beginning of oxidation, a small initial decrease prior to a continuous but very slow increase in activity, within the polarization times considered.<sup>22</sup> Table II shows that the  $\text{GC–K}_{\text{OX}}$ /Pt electrode is more active for the same time of substrate oxidation in comparison with  $\text{GC–G}_{\text{OX}}$ /Pt which, on the other hand, exhibits higher changes in activity. Also, after an initial increase, both electrodes exhibit a small decrease of activity due to the prolonged time of substrate oxidation following, as can be seen, changes in the double layer charge of their supports.

The influence of the support on the properties of the catalyst is also confirmed by the results presented in Fig. 6, showing no difference between the electrodes examined either with a polished or with an oxidized support when the whole surface of the electrode is covered with the catalyst, due to high loading of Pt. In this case, the upper layers of Pt are deposited on Pt, not on GC and the influence of the metal–support interaction diminishes, leading to a similar coverage of Pt with oxygen-containing species and thus a negligible difference in the activity between the electrodes examined.

The activity of a carbon supported Pt catalyst could also be influenced by the Pt particle size. The enhanced rates for methanol oxidation on smaller nanoparticles are attributed to the decreased CO poisoning caused by a reduced number of the ensembles of two adjacent Pt sites needed for CO adsorption, *i.e.*, due to the "ensemble effect".<sup>35</sup> However, this effect is pronounced only at very small particles ( $d$  smaller than 4 nm). STM images (Fig. 2) show smaller Pt particles on GC<sub>OX</sub>/Pt electrodes than on GC/Pt. However, on all samples, the particle diameters are significantly larger than 4 nm. Therefore, the contribution of diminishing particle size upon electrochemical treatment of the support, *i.e.*, "particle size effect", could not considerably influence the activity of the GC<sub>OX</sub>/Pt, although this point should not be completely disregarded.

One of the possible roles of a GC substrate in the activity of GC/Pt electrodes is that OH-like functional groups on the glassy carbon participate in the oxidation of the adsorbed intermediate species formed in methanol dissociation.<sup>14</sup> This possibility should be examined further.

#### CONCLUSION

The results obtained by studying the oxidation of methanol in acid and alkaline solutions on GC/Pt electrodes with differently treated GC substrates can be summarized as follows:

Analysis of the STM images show that the Pt particle sizes decrease with oxidative treatment, from  $8.9 \pm 1.6$  nm at GC/Pt to  $8.4 \pm 2.9$  nm and  $7.4 \pm 1.6$  nm at GC<sub>OX-AL</sub>/Pt and GC<sub>OX-AC</sub>/Pt, respectively.

Both thermal treatment and electrochemical pretreatment of the substrate play a role in the deposition of platinum and, consequently, in the activity of GC/Pt catalysts. Platinum electrodeposited on GC-K glassy carbon, thermally treated at a lower temperature, was more active for methanol oxidation in alkaline solution than Pt electrodeposited on GC-G, prepared at a higher temperature.

The activity of the catalyst for this reaction follows the change in the properties of the glassy carbon upon oxidation. Oxidation of a GC substrate in alkaline solution, prior to Pt deposition, enhances a few times the activity of the resulting GC/Pt electrode for methanol oxidation compared with a polished support. Oxidation of a GC substrate in acid solution, prior to Pt deposition, however leads to a remarkable increase in the activity of the resulting GC<sub>OX-AC</sub>/Pt electrode for methanol oxidation in acidic solution.

The increase of activity is associated with a higher fraction of acid functionalities in the treated substrate, *i.e.*, to a higher coverage with OH-like species in the Pt deposit. The "particle size effect" does not play an important role on the increase of activity because the decrease in particle size upon electrochemical treatment of the support is not significant.

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## ИЗВОД

ЕФЕКАТ ОСОБИНА СТАКЛАСТОГ УГЉЕНИКА НА ЕЛЕКТРОХЕМИЈСКИ  
НАТАЛОЖЕН ПЛАТИНСКИ НАНО-КАТАЛИЗАТОР И ЊЕГОВУ  
АКТИВНОСТ У ОКСИДАЦИЈИ МЕТАНОЛА

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Испитиван је утицај особина подлоге од стакластог угљеника на таложње платинских честица и електрокаталитичку активност тако добијене електроде (GC/Pt) у реакцији оксидације метанола у киселој и алкалној средини. Платина је потенциостатски таложена на два узорка стакластог угљеника, термички третирана на различитим температурама, који су полирани или анодно поларизовани у киселом GC<sub>OX-AC</sub>/Pt или алкалном (GC<sub>OX-A</sub>/Pt) раствору. Анодна поларизација стакластог угљеника било у киселини или у алкалији пре таложња платине доводи до повећања активности оба типа GC/Pt електрода за реакцију оксидације метанола. Активност Pt катализатора прати промене у особинама подлоге од стакластог угљеника које настају услед анодне поларизације. Специфична активност GC<sub>OX-AL</sub>/Pt електрода у оксидацији метанола у алкалним растворима повећава се само неколико пута у односу на активност катализатора на полираној подлози (GC/Pt). Са друге стране, специфична активност GC<sub>OX-AC</sub>/Pt електрода у оксидацији метанола у киселим растворима у поређењу са активношћу GC/Pt електрода већа је практично за цео ред величине. У раду је такође детаљно дискутована улога подлоге на особине катализатора.

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