

Modified graphite electrodes as catalysts for electroreduction of hydrogen peroxide

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The adsorption behaviour and electrocatalytic activity of compact graphite electrodes, modified only with microquantities of palladium or with a mixture of (Pd+Au), have been studied in the reaction of electroreduction of hydrogen peroxide. The influence of the following factors has been investigated: composition of the promoter, pH and temperature of the working ambience on the electrocatalytic activity of the series of modified graphites at potentials of 0 and –50 mV (vs. Ag/AgCl). The electrode modified with microquantities of (Pd+Au) mixed in a proportion of 70:30% exhibits optimal operational characteristics (electrode sensitivity, linear concentration area and low background currents).

Key words: modified graphite electrodes, hydrogen peroxide, electroreduction

INTRODUCTION

Research aimed at developing methods for detecting hydrogen peroxide is of great importance at present. On the one hand, this is connected with the wide application of hydrogen peroxide in various spheres of industry (food processing, textile, cosmetic, pharmaceutical industries and medicine), and on the other hand, it is an interim product both of environmental processes and biochemical reactions. Most of the known enzymes-oxydoreductases (e.g. glucose oxidase, xanthine oxidase, etc.) catalyze chemical transformations of their typical substrates, whereby hydrogen peroxide is produced beside the reaction product. The working principle of most amperometric biosensors is based on the detection of hydrogen peroxide generated in the enzyme oxidation of the substrate.

Monitoring hydrogen peroxide through reliable, expeditious and economical methods is of great significance for many processes. Spectrophotometric [1–3], enzyme [4], thermo-optic [5], hemiluminiscent [6, 7] and other techniques and devices are used to detect and monitor it. Analyses thus made are quite time-consuming, they are influenced by the analytes accompanying the hydrogen peroxide, and require very expensive reagents. Electroanalytical methods, with their long linear area of concentration dependence and fast response, are very appropriate. They are based on direct reduction or oxidation of hydrogen peroxide. Electrooxidation of hydrogen peroxide, however, is carried out at potentials, at

which most of the components of the real samples (biological liquids, food, pharmaceutical, ecological samples) are co-oxidized as well, which substantially increases the quantitative determination of the substrate. That is why, a lot of research is aimed at searching of alternatives for improving the selectivity of the electrochemical detection of H₂O₂. A widely applicable strategy is the application (immobilization) of catalytically active substances on the surface of the electrode, such as metals, their oxides or complexes, enzymes, etc. [8–37]. The electrodes, thus modified, are included in electrochemical systems, based on registering the current generated in the electroreduction of hydrogen peroxide, and the process occurs at working potentials of about 0 mV (vs. Ag/AgCl). At such potentials the typical components of biological liquids, such as ascorbic acid, uric acid, glutathione, etc., are electrochemically inactive.

The detection of hydrogen peroxide has been experimented with various modified electrodes: gold [8, 9], platinum [10], gold-palladium composite electrodes [11], electrodes of various kinds of carbon materials – graphite [12, 15], glass-graphite [13, 14, 17, 24], carbon-paste electrodes [14, 15, 18–20], etc. Improvement of the selectivity of the electrochemical signal of hydrogen peroxide with these electrodes is achieved by using various catalytically active modifying components: transitional metals and their oxides [12–14]; platinum metals dispersed separately [15, 21], mixed with other platinum metals [8, 16, 17], in polymer films [10], together with Prussian Blue [22]; thiol and Nile Blue [9], etc. Especially popular in recent years

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have been the investigations for electroanalytical detection of H_2O_2 by using micro- and nanostructured carbon films containing metal particles, such as platinum, nickel, copper, iridium and silver [23–25]. Most of the research on developing modified graphite electrodes is focused on their inclusion in electro- and bioelectrochemical systems, based on the electroreduction of H_2O_2 . Peroxidase of horseradish [26–29] and other vegetable peroxidases [29–31], immobilized mainly on carbon transducers, as well as some hem-containing proteins [31–34] are of interest because they are efficient catalysts of electroreduction of H_2O_2 at working potentials of about 0 mV (vs. Ag/AgCl, in neutral solutions) where the obstructing influence of by-analytes is eliminated. Despite the high selectivity and sensitivity of these biosensors, the low operational stability of the biocomponent makes them more suitable for the construction of single-use elements.

Micro- and nanostructured graphites with metals from the platinum group are alternative electrocatalysts for the electroreduction of H_2O_2 at low working potentials [35], at which the interfering substances do not undergo electrochemical transformations [36]. In addition, their good characteristics (they can be stored for about a year and yet continue to have sufficient electrocatalytic activity [35, 36], high operational stability in a wide pH range and a simple preparation procedure) make them promising electrocatalysts in developing amperometric sensors on the basis of electroreduction of H_2O_2 [37]. The aim of this work is to investigate the electrocatalytic activity of graphite electrodes modified only with microquantities of Pd or with a mixture of (Pd+Au) in the reaction of H_2O_2 electroreduction.

EXPERIMENTAL

Inert pads of graphite type GMZ with a geometric surface $S = 1.6\text{--}1.8\text{ cm}^2$ ($0.7 \times 0.7 \times 0.3\text{ cm}$) were used. The structural characteristics of graphite are as follows: specific surface $0.8\text{ cm}^2 \cdot \text{g}^{-1}$, density $1.56\text{--}1.70\text{ g} \cdot \text{cm}^{-3}$ and porosity 20–25%. The graphite pads were kindly provided by Prof. Bogdanovskiy, the State University of Moscow, Russia. The graphite pads were modified with microquantities of platinum metals – sole palladium or palladium and gold mixed in the ratios (Pd:Au) 90:10%, 70:30%, 50:50%. The catalytically active components were deposited in a potentiostatic regime ($E_r^{\text{deposit}} = +0.05\text{ V}$ vs. reversible hydrogen electrode) by a brief electrolysis ($t_{\text{deposit}} = 10\text{ s}$) from the following elec-

trolyte: Pd from 2% $\text{PdCl}_2 + 0.1\text{ M HCl}$ and (Pd+Au) from 2% $\text{PdCl}_2 + 2\% \text{HAuCl}_4 + 0.1\text{ M HCl}$ in the above ratios (Pd:Au). The electrodes will be further denoted in the text as electrodes type A, B, C and D as follows:

Graphite modified with individual Pd (electrode type A);

Graphite modified with (Pd+Au) mixed in the ratio 90:10% (electrode type B);

Graphite modified with (Pd+Au) mixed in the ratio 70:30% (electrode type C);

Graphite modified with (Pd+Au) mixed in the ratio 50:50% (electrode type D).

All electrochemical measurements were performed in a three-electrode cell with separated compartments (working volume 12–15 mL). An Ag|AgCl electrode was used as a reference electrode, and platinum wire – as a counter electrode. The electrochemical setup also involved a bipotentiostat, type BiPAD (TACUSSEL, Villeurbanne, France); a generator, type EG-20 (Elpan, Lubawa, Poland); a digital voltmeter, type 1AB105 (ZPU, Pravets, Bulgaria); XY-Recorder (VEB, Messapparatewerk, Schlotheim, GDR); a thermostat UH (VEB MLW Prüfgeräte-Werk, Medingen, Germany); a pH-meter OP-208 (Radelkis, Budapest, Hungary). The solutions were bubbled with argon during the measurements.

RESULTS AND DISCUSSION

Adsorption capacity and characteristics of the energy state of hydrogen, hemisorbed on the surface of modified graphite electrodes

The pure graphite pads, which do not contain metal phase have no hydrogen maxima of the potentiodynamic I - E curves (Fig. 1a and 1b, curves 1). At the same time, on the anodic potentiodynamic I - E curves of the graphites containing microquantities of Pd and (Pd+Au) in various proportions (electrodes type A, B, C, D) peaks in the desorption of hydrogen are fixed. By integrating the area under the respective peaks in the range from -490 to -240 mV (vs. Ag/AgCl), and turning off the electricity for the purely graphite pads (the background current), the amount of electricity Q_{H}^0 , necessary for taking away the adsorbed hydrogen, was determined. From the value of Q_{H}^0 , provided the monolayer of H_{ads} is formed at $E = -640\text{ mV}$ (vs. Ag/AgCl) to which a charge of $210\text{ }\mu\text{C} \cdot \text{cm}^{-2}$, the real surface of the electrodes was determined (Table 1).

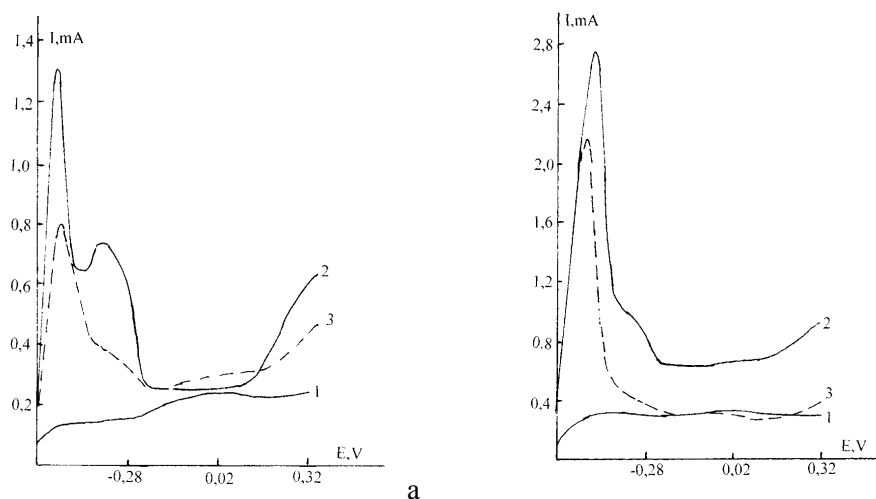


Fig. 1. a. Anodic potentiodynamic I - E curves of graphite electrode (curve 1); graphite electrode modified with Pd (curve 2) and graphite electrode modified with (Pd:Au 70:30%) (curve 3); background electrolyte 0.1 M phosphate-citrate buffer, pH 7.0; reference electrode Ag/AgCl; $V = 10 \text{ mV}\cdot\text{s}^{-1}$; b. Anodic potentiodynamic I - E curves of graphite electrode (curve 1); graphite electrode modified with (Pd:Au 90:10%) (curve 2) and graphite electrode modified with (Pd:Au 50:50%) (curve 3); background electrolyte 0.1 M phosphate-citrate buffer, pH 7.0; reference electrode Ag/AgCl; $V = 10 \text{ mV}\cdot\text{s}^{-1}$.

Table 1. Adsorption characteristics – real surface S_{real} and values of the desorption potentials of hydrogen $E_{\text{H}}^{\text{des}}$ for modified graphite electrodes in phosphate-citrate buffer, pH 7.0; temperature 25°C.

| Electrode type | $Q_{\text{H}}^0 \times 10^3, \text{C}$ | | $S_{\text{real}}, \text{m}^2$ | | $E_{\text{H}}^{\text{des}}, \text{V}$ (vs. Ag/AgCl) | |
|----------------|----------------------------------------|--------------|-------------------------------|--------------|-----------------------------------------------------|----------------------|
| | freshly prepared | After ageing | freshly prepared | After ageing | 1 st peak | 2 nd peak |
| type A | 10.71 | 9.66 | 51 | 46 | -0.52 | -0.37 |
| type B | 3.94 | 3.26 | 18.76 | 15.52 | -0.45 | -0.30 check |
| type C | 8.51 | 4.95 | 40.88 | 23.57 | -0.43 | - |
| type D | 1.91 | 1.6 | 9.08 | 7.62 | -0.48 | - |

The adsorption capacity of the modified graphites is considerably dependent on the microaddition of Au to the catalytically active component – the microquantities of palladium. It decreases with the increase of the Au additive to the microquantities of Pd (Table 1), both for the freshly produced electrodes and for the electrodes after ageing. In comparison to the electrode modified only with Pd microquantities (type A), in the case of the graphite, modified with a mixture of (Pd+Au) microquantities in the ratio 50:50% (type D) Q_{H}^0 , respectively the real surface (S_{real}), is reduced 6 times. S_{real} of the modified graphites (types A, B, C and D) after ageing of 3–4 weeks is reduced as a result of recrystallization. The data provided in Table 1 show that depending on the type of the modifying component the decrease of S_{real} after ageing varies. For the type A electrode (modified with microquantities of Pd only) it is only 10%, whereas for the electrodes of types B, C and D (modified with Pd+Au mixtures) the decrease is as follows: for electrodes types B and D the decrease of S_{real} is 16–17%, and for electrode type C – 42%.

The energy spectrum of hydrogen adsorption of the electrodes under survey also depends on whether they have been modified with microquantities of Pd only or with microquantities of (Pd+Au). On the anodic potentiodynamic curve (Fig. 1a, curve 2) of the graphite modified with palladium microquantities only (type A), two peaks are observed which correspond to two forms of adsorbed hydrogen – weakly linked at a potential of -0.52 V, and strongly linked at a potential of -0.37 V. With the change of the composition of the modifying catalytically active component of Pd microquantities only to (Pd+Au) mixture (in different proportions), the second form of adsorbed hydrogen disappears. On the potentiodynamic curve of the type B electrode (Fig. 1b, curve 2), only one hydrogen maximum can be seen at a potential of -0.45 V, and a check at a potential of -0.30 V. This check of the I - E curves for the electrodes type C (Fig. 1a, curve 3) and type D (Fig. 1b, curve 3) disappears, that is, they are characterized by only one form of adsorbed hydrogen – for type C at a potential of -0.43 V, and for type D at a potential of -0.48 V.

A comparison of the values of the potentials of hydrogen desorption $E_{\text{H}}^{\text{des}}$ for the electrode type A with those for the electrodes types B, C and D, shows that the modification of graphite with microquantities of (Pd+Au) mixed in different proportions, leads to a shift of $E_{\text{H}}^{\text{des}}$ in anode direction, that is for electrodes types B, C and D, the energy of the bond Pd – H is increased.

Electrocatalytic activity of modified graphites

Figure 2 shows the polarization curves of the electroreduction of hydrogen peroxide on graphite electrodes modified with microquantities of Pd only, and with (Pd+Au) mixture (electrodes types A, B, C and D) in the potential range of -300 to $+250$ mV (vs. Ag/AgCl). In this potential region, cathode currents of electroreduction of hydrogen peroxide have been registered only for the four modified graphite electrodes, whereas for the purely graphite pad (empty squares) and for graphite modified only with microquantities of gold (crosses) such currents have not been observed.

The polarization curves presented for the electrodes type A, B, C and D show intervals of potential where the current hardly varies (a “plateau region”). These plateau regions are strictly dependent on the type of catalytically active component (microquantities of Pd alone, or Pd combined with Au in the ratios – 90:10%, 70:30%, and 50:50%).

For the graphite electrode modified only with microquantities of Pd (type A, empty triangles), the plateau region is from -50 to $+50$ mV; for the electrode type B (solid squares) this range is from -100 to $+150$ mV, and for the type D graphite (asterisks) – from -50 to $+150$ mV. Type C electrode (empty circles) is characterized by a wider plateau from around -150 mV to around $+150$ mV.

For all types of modified graphites, the dependence of the electrode signal (cathode current) on the

concentration of the hydrogen peroxide was investigated at two potentials from the range of the plateau – 0 mV and -50 mV in buffer solutions at pH 7.0 and 8.4. The electrode signal, which increases linearly with the substrate concentration (calibration graph, $n = 3$), and the sensitivity (determined as the slope of the linear part, dI/dC), depend on the nature of the catalytically active component, deposited on the graphite (Table 2).

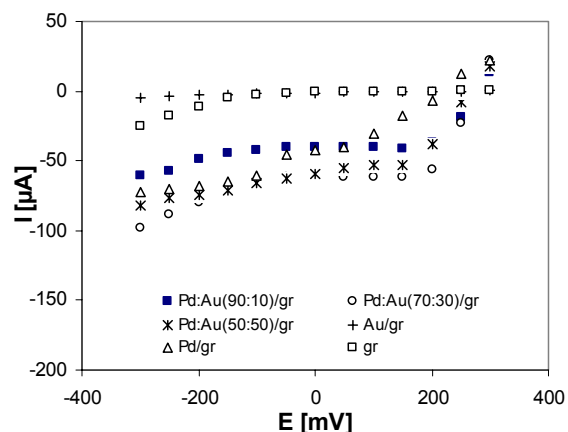


Fig. 2. Steady-state current as a function of potential applied at modified graphites when 0.1 mM H_2O_2 is present; electrodes: Δ - type A; \blacksquare - type B; \circ - type C; $*$ - type D; background electrolyte 0.1 M phosphate-citrate buffer, pH 7.0; reference electrode Ag/AgCl; temperature 25°C .

For all four types of modified graphite, the sensitivity increases as the potential becomes more negative. The signal obtained at -50 mV is higher than that registered at 0 mV, as follows: for electrode type A it is 1.5 times higher (in phosphate-citrate buffer, pH 7.0); for electrodes types B and C – 1.2 times (both in phosphate-citrate buffer, pH 7.0, and for phosphate buffer pH 8.4); for electrode type D – 1.4 times (in phosphate-citrate buffer, pH 7.0) and 1.7 times (in phosphate buffer, pH 8.4).

Table 2. Basic operational characteristics of graphite electrodes modified with microquantities of Pd or mixture of (Pd+Au) during hydrogen peroxide electrochemical reduction; temperature 25°C ; phosphate-citrate buffer pH 7.0 and phosphate buffer pH 8.4.

| Potential, mV (vs. Ag/AgCl) | Electrode sensitivity, $\mu\text{A}\cdot\mu\text{M}^{-1**}$ | | | | Linear range, μM^{***} | | | |
|-----------------------------|-------------------------------------------------------------|---------------|---------------|---------------|-----------------------------------|--------------------|---------------------|---------------------|
| | Electrode type | | | | Electrode type | | | |
| | A | B | C | D | A | B | C | D |
| -50 | 0.56 | 0.30 0.27* | 0.86 0.81* | 0.34 0.30* | 10–500 | 10–750 10–1130* | 10–1270 10–1270* | 10–840 10–680* |
| 0 | 0.38 | 0.25 0.25* | 0.71 0.71* | 0.24 0.18* | 10–500 | 10–520 10–1270* | 10–830 10–1270* | 10–1130 10–1060* |

* Phosphate buffer pH 8.4;

** The electrode sensitivity was determined as the slope of the linear portion of the calibration graph;

*** The linear portion of the calibration graph.

The range of linearity of the electrode signal also depends on the applied potential for electroreduction of hydrogen peroxide (Table 2). For electrodes types B and C, the linearity of the signal, as well as the sensitivity, increases as the potential moves in cathode direction, that is, at -50 mV, whereas for the type D electrode this dependence is the opposite – the linear part of the calibration graph is shorter at -50 mV (up to $840 \mu\text{M}$) compared with potential 0 mV (up to $1130 \mu\text{M}$) (in phosphate-citrate buffer, pH 7.0). For this electrode in phosphate buffer, pH = 8.4 for potentials -50 mV and 0 mV, the range of linearity of the signal is up to $680 \mu\text{M}$ and up to $1060 \mu\text{M}$, respectively. For the graphite modified only with microquantities of Pd (type A) the linearity of the signal does not depend on the applied potential.

From the data on the main operational characteristics of graphite electrodes (Table 2), it is evident that the highest sensitivity ($dI/dC = 0.86 \pm 0.02 \mu\text{A} \cdot \mu\text{M}^{-1}$) in the electroreduction of H_2O_2 is exhibited by the modified graphite of type C at applied potential of -50 mV. The same electrode is also characterized by the longest linear range on the calibration graph at -50 mV (up to $1270 \mu\text{M}$). At potential of -50 mV for electrode type C the lowest background currents are also registered.

At potentials from the plateau region, the effect of the temperature on the electrode response of modified graphites has been investigated. Temperature-kinetic investigation at potentials 0 , -50 and -100 mV in Arrhenius coordinates ($\lg I$ vs. $1/T$) for electrode type C shows that the lines corresponding to different potentials of polarization have the same slope (not shown). The values of the activation energy E_a and its independence on the potential of polarization show that the rate of electroreduction of H_2O_2 on all four types of modified graphite is limited by the concentration polarization. This type of polarization can be caused either by a delay of the supply of H_2O_2 to the electrode or by the slow course of a purely chemical reaction (homogeneous or heterogeneous), which precedes its own electrochemical act.

The comparative study of the data from Table 2 and Table 3 shows that: 1) electrodes of types A and

C, which are characterized by equal values of the activation energy, in the reaction of electroreduction of H_2O_2 exhibit quite different activity (electrode sensitivity in $\mu\text{A} \cdot \mu\text{M}^{-1}$), and 2) for electrodes of the types D and B, a great difference in the activation energy is observed, but there are no noticeable changes in the electrode sensitivity. These discrepancies between E_a and activity can be explained by the values of the pre-exponential factor Z_0 (Table 3), which were determined from the equation $I = Z_0 \cdot e^{E_a/RT}$. The electrodes catalysts change the rate of the reaction by influencing either the value of E_a or the value of Z_0 . The activation energy is proportional to the productivity of the active centres, and Z_0 is proportional to the number of active centres on a unit of surface. Modified graphites of the types A and C change the rate of the process by affecting mainly the value of Z_0 (Table 3) – the more active electrode (type C) is distinguished by a greater number of active centres. When the electrodes are arranged in the order – B, C, A and D, from the data shown in Table 3 it is evident that both the values of E_a and Z_0 decrease at the same time. This phenomenon is known as “compensation effect”, in which the pre-exponential factor is a linear function of the activation energy, that is, $\ln Z_0 = \alpha \cdot E_a + \beta$ (Fig. 3). In the compensation effect, the decrease of the number of active centres is accompanied by an increase in the productivity and a decrease in the activation energy.

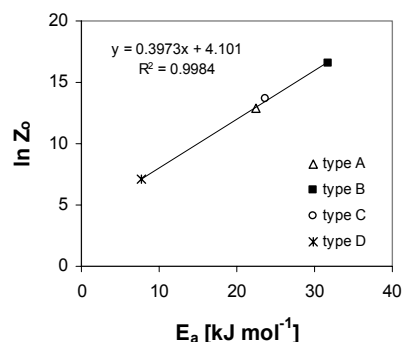


Fig. 3. $\ln Z_0$ as a function of activation energy E_a at applied potential -100 mV (Ag/AgCl); phosphate-citrate buffer pH 7.0; temperature 25°C .

Table 3. Values of the activation energy E_a and the pre-exponential factor Z_0 for modified graphite electrodes; applied potentials -50 and -100 mV (vs. Ag/AgCl); phosphate-citrate buffer pH 7.0; temperature 25°C .

| Electrode type | Potential, mV (vs. Ag/AgCl) | | | | | | | |
|----------------|-------------------------------------------|-----------|--------------------------------------|-------------------|-------------------------------------------|-----------|--------------------------------------|-------------------|
| | -50 | | | | -100 | | | |
| | E_a , $\text{kJ} \cdot \text{mol}^{-1}$ | $\ln Z_0$ | $Z_0 \times 10^{-6}$, μA | r^2 | E_a , $\text{kJ} \cdot \text{mol}^{-1}$ | $\ln Z_0$ | $Z_0 \times 10^{-6}$, μA | r^2 |
| type A | 24.23 ± 1.3 | 13.58 | 0.79 | 0.92 ₂ | 22.51 ± 1.3 | 12.92 | 0.41 | 0.98 ₁ |
| type B | 30.59 ± 1.3 | 16.19 | 10.75 | 0.92 ₁ | 31.68 ± 1.3 | 16.61 | 16.33 | 0.89 ₃ |
| type C | 23.78 ± 1.3 | 13.74 | 0.92 | 0.98 ₂ | 23.61 ± 1.3 | 13.71 | 0.90 | 0.98 ₄ |
| type D | 7.23 ± 1.3 | 7.06 | $1.16 \cdot 10^{-3}$ | 0.98 ₄ | 7.65 ± 1.3 | 7.11 | $1.23 \cdot 10^{-3}$ | 0.99 ₅ |

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МОДИФИЦИРАНИ ГРАФИТОВИ ЕЛЕКТРОДИ КАТО КАТАЛИЗАТОРИ ЗА ЕЛЕКТРОРЕДУКЦИЯ НА ВОДОРОДЕН ПЕРОКСИД

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(Резюме)

Изучени са адсорбционното поведение и електрокаталитичната активност на компактни графитови електроди модифицирани само с микроколичества от паладий или със смес от (Pd + Au) в реакцията електро-редукция на водороден пероксид. Изследвано е влиянието на състава на промотора, рН и температурата на работната среда върху електрокаталитичната активност на серията модифицирани графити при потенциали 0 mV и -50 mV (Ag/AgCl). Модифицираният с микроколичества на смес от (Pd + Au) в съотношение 70:30% електрод показва оптимални операционни характеристики (електродна чувствителност, линейна концентрационна област и ниски фонове токове).