Bulgarian Chemical Communications, Volume 45, Special issue A (171 – 178) 2013

Electrochemical characteristics and structural specifics of carbonaceous electrodes, modified with micro- and nanodeposits of platinum metals

T. M. Dodevska[1], E. G. Horozova[2*], N. D. Dimcheva[2]

[1] *University of Food Technologies, Department of Inorganic Chemistry and Physical Chemistry,*
26 Maritsa Blvd., Plovdiv 4002, Bulgaria
[2] *P. Hilendarski University of Plovdiv, Department of Physical Chemistry*
24 Tsar Asen St., Plovdiv 4000, Bulgaria

Received March 22, 2013; revised May 13, 2013

For a series of graphite and glassy carbon electrodes, modified with micro- and nanodeposits of (Pd+Pt) and (Pd+Au) mixtures in varied proportions of the catalytically active components, surface topography of the modified electrodes has been studied with atomic force microscopy (AFM). It has been established that, catalytic activity of the modified electrodes in the reduction of H_2O_2 depends on the specific nature and structure of the metal phase, electrochemicaly deposited on the carbonaceous carrier. Moreover, the specifics of the structure, morphology of the metal deposits as well as their surface coverage has been shown to dramatically depend on the type of catalytically active components (nature and ratio of the two metals in the modifying mixture) and the nature of the carbonaceous matrix (type, porosity and surface condition).

Key words: modified electrodes, nanoparticles, electocatalysis, electroreduction of hydrogen peroxide, AFM studies

INTRODUCTION

The reaction of electroreduction of hydrogen peroxide is of current significance to modern electrochemical science and technology [1-5]. The rate and selectivity of this reaction to a great extent determine the working basic characteristics of a series of amperometric biosensors of the first generation, applied in the selective quantitative analysis of various analytes in medicine, food industry, ecology and other spheres.

The rate of the reaction electroreduction of hydrogen peroxide, as well as its selectivity, depends on the used electrocatalysts, the best of which are platinum metals. Due to their high price, limited availability and insufficient specific activity, the modern trends in developing electrocatalysts are connected with reducing their use to the minimum and, at the same time, achieving a significant catalytic effect. In connection with this, these studies are aimed at developing electrocatalysts on the basis of micro- and nanosized multi-component systems (binary and trimetal catalytic phases) [6-21].

Fundamental and applied research in the field of platinum electrocatalysts shows that their catalytic activity depends on their nature, on the nature of their surface layer, on their structure and specific surface. All these factors can be utilized by optimizing the conditions and methods for obtaining them. By choosing a suitable type of carrier, composition and proportion of the components in the modifying mixture and the method of obtaining, new electrocatalysts with an enhanced catalytic activity and stability can be obtained. Such a research method aimed at obtaining new, inexpensive modified carbon electrodes for selective reduction of hydrogen peroxide was applied by us. Based on the advantages of carbon materials (chemical inertness, wide working range of potentials, low cost, etc.), our research in recent years has shown that porous graphite (porosity of 20 – 25%) and glassy carbon, electrochemically modified with nano- and microquantities of mixtures in different proportions of (Pd + Pt) and (Pd + Au), are effective electrocatalysts for the reduction of H_2O_2 at low working potentials – 0 and -50 mV (vs. Ag/AgCl) [14-21]. The modification of the carbonaceous materials in the above-mentioned studies was conducted while modeling the conditions for obtaining – deposit time of the catalytically active

---

* To whom all correspondence should be sent:
E-mail: horozova@uni-plovdiv.bg

phase 10 s and deposit potential of -50 mV (in relation to a reversible hydrogen electrode). An inexpensive method, not requiring costly equipment, was used to obtain nanosized metal coating, namely electrodeposition. In all these publications the prospective application of the developed peroxide electrodes as a basis for creating first-generation amperometric biosensors has been demonstrated, as well. The carbon materials, thus modified, show the following positive characteristics: presence of high electrocatalytic activity in the reduction of H_2O_2 in a wide range of potentials – from 250 to -250 mV (vs. Ag/AgCl); simplified procedure of obtaining; high working stability in a wide pH range; sufficient electrocatalytic activity for a long period of time – for over a year, etc.

It is evident from the stated above that the main way of influencing the electrocatalytic activity of the electrodes is the choice of suitable conditions, procedure and method of obtaining. The improvement of the methods of obtaining electrocatalysts with the specified properties and the understanding of the nature of their catalytic activity require not only electrochemical tests but also investigation of the structure of their surface layer.

With reference to this, the aim of this study, which is a follow-up of our previous studies referred to above [14-21], is to investigate the surface morphology of the modified carbon electrodes and to compare the structural data with the results from their electrocatalytic activity in the target reaction – the reduction of H_2O_2. On this basis, the main factors ensuring the increase of the electrochemical activity and stability of the obtained modified carbonaceous electrodes are to be identified.

EXPERIMENTAL

Materials

Two types of inert carbon matrices were used as carriers:

1. Graphite of the GMZ type with S_{geom} = 1.7 cm^2 and with the following structural characteristics: specific surface of 0.8 $cm^2.g^{-1}$; density of 1.6 – 1.7 $g.cm^{-3}$; porosity of 20 – 25 %.
2. Glassy carbon with S_{geom} = 1.35 cm^2.

Modification of the electrode surface

The electrochemical modification of the carbon matrixes with nano- and microquantities of mixtures of (Pd + Pt) and (Pd + Au) was performed as follows: the catalytically active components are deposited in a potentiostatic mode E_r = 0.05 V (in relation to a reversible hydrogen electrode) via a brief electrolysis (10 s) from the following electrolytes: mixture (Pd + Pt) of 2% $PdCl_2$ + 2% H_2PtCl_6 + 0.1 M HCl (in the following proportions Pd:Pt 50:50; Pd:Pt 70:30; Pd:Pt 90:10, volumetric parts); mixture (Pd + Au) of 2% $PdCl_2$ + 2% $HAuCl_2$ + 0.1 M HCl (in the following proportions Pd:Au 50:50; Pd:Au 70:30; Pd:Au 90:10, volumetric parts).

Apparatuses and determining polarization dependencies

A standard three-electrode glass cell with separate electrode spaces and a working volume of 11 – 15 cm^3, reference electrode – Ag/AgCl (1M KCl) and a counter electrode – a platinum wire, was used for the electrochemical tests. The electrode sensitivity was determined as the relation of the stationary current (I_s) to the substrate concentration (C).

For the purpose, the concentration polarization dependencies of the stationary current are established: the working electrode – modified graphite or glassy carbon is placed in the working space of the electrochemical cell containing 11 cm^3 0.1M phosphate-citrate buffer with a pH = 7.0 at 25^0C. It is connected to the electrochemical system comprising the following apparatus modules: bipotentiostat Bi-PAD (TACUSSEL, France), generator EG 20 (Elpan, Lubawa, Poland) and a recording device of the XY type (VEB, Messapparatewerk; Scholtheim, Germany).

The methods of determining the concentration polarization dependencies of the stationary current is described in studies [14-21].

Surface structure of the modified electrodes

Detailed information about the topography of the modified electrode surface was obtained by applying the method of atomic-force microscopy (AFM). The surface structure of the modified carbonaceous electrodes was investigated using an atomic-force microscope AFM (Anfatec Instruments, Germany).

RESULTS AND DISCUSSION

Electrochemical characteristics of the modified carbonaceous electrodes in the reaction of electroreduction of H_2O_2

The electrochemical reduction of hydrogen peroxide on the modified carbonaceous electrodes proceeds by the following equation:

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$$

The dependence of the current of electroreduction from the concentration of H_2O_2 is linear, allowing its quantitative determination. The ratio of the current to the concentration of H_2O_2, which is determined from the linear portion of the concentration polarization curve, gives the sensitivity of the electrode.

The ratio between the components (in volumetric and molar %) of the electrolyte mixtures of (Pd + Pt) and of (Pd + Au), used for modifying the matrixes of graphite and glassy carbon is shown in Table 1. This table also presents the electrochemical characteristics (electrode sensitivity and linearity of the signal) of the investigated electrodes in the reaction of hydrogen peroxide electroreduction.

The investigated catalytic systems (Table1) are based on the element Pd. Pd is relatively inexpensive (approximately 2.5 times cheaper than Pt) and therefore it is a very promising electrocatalyst. The graphite and glassy carbon modified with nano- and microquantities of pure Pd are characterized by the following electrochemical properties in the electroreduction of H_2O_2: for Pd/C – electrode sensitivity of 0.56 $\mu A.\mu M^{-1}$ and linearity of the signal of up to 500 μM, and for Pd/GC – 0.26 $\mu A.\mu M^{-1}$ sensitivity and up to 500 μM linearity of the signal [21].

The increase of the electrocatalytic activity of Pd was achieved by introducing microquantities of Pt and of Au in the modifying mixture (Table1). The microadditions of 13 molar % of Pt and 18 molar % of Au to the main element in the mixture (Pd) result in a 1.5 increase of the electrode sensitivity of graphite modified with a mixture of (Pd + Pt) (electrode №2) and with a mixture of (Pd + Au) (electrode №5). The addition of 25 molar % of Pt to Pd doubles the electrode sensitivity of the graphite modified with a mixture of (Pd + Pt) (electrode №3). The glassy carbon matrix modified by 6 and 34 molar % of microquantities of Au to Pd exhibits electrocatalytic activity which is approximately 1.4 times as high as that of electrode Pd/GC. In the three investigated series of modified graphite, the microadditions of Pt and Au to Pd in all molar percentages shown in Table 1 result in an improvement of the linear range of concentration dependence of the signal, as compared with electrodes Pd/C and Pd/GC.

The data provided in Table 1 shows that modified glassy carbon electrodes (series III) exhibit a lower electrode sensitivity in the quantitative determination of H_2O_2 as compared to modified graphite. This fact is probably due to the structural peculiarities of glassy carbon, which is known to be characterized by an exceptionally uniform, homogeneous, almost flawless outer surface. The reasons for the lower activity of this series of catalysts can be summed up as follows: 1/ substantial reduction of S_{real} of modified glassy carbon during the specific processes of re-crystallization, occurring after the deposition of the metal phase; 2/ mechanical loss of part of the deposition; 3/ resistance of the glassy carbon material.

In conclusion, the modified graphite electrode of the type Pd:Au (82 molar % : 18 molar %) exhibits the best electrochemical characteristics among all the investigated electrodes – it has the highest sensitivity (0.86 $\mu A.\mu M^{-1}$) and the longest linearity range of the calibration graph (up to 1270 μM).

AFM (atomic-force microscopy) of the surface of modified carbonaceous electrodes

The surface structure of modified carbonaseous electrodes was examined by applying the method of AFM. Fig. 1 shows AFM-images of the surface of graphite modified with mixtures of (Pd + Pt). It can be seen that there is a substantial difference in the relief of the electrode surface depending on the content of the microaddition of Pt to Pd in the modifying mixture. When a metal phase (Pd + Pt), in which the Pt content is at least 4 molar per cent, is deposited on the graphite, an electrode (№1) with the lowest sensitivity (0.22 $\mu A.\mu M^{-1}$) is obtained. The AFM – image of the surface of this catalyst (Fig. 1a) clearly shows different in size dendrites (60 – 400 nm), densely populated with unclearly shaped fine-grained formations.

When the Pt content in the modifying mixture is increased to 13 molar per cent, the metal phase of (Pd + Pt) is deposited on the graphite (electrode №2) mainly in the form of metal islands (Fig. 1b). Fine, parallel plates, forming compact plateau-like, sharp-edged structures, can clearly be seen in the said image. In the periphery of these plateaus, there are fine formations, under 50 nm in size. This type of metal deposition exhibits the highest electrode sensitivity – 0.82 $\mu A.\mu M^{-1}$ of all the electrodes in series I. When a metal phase (Pd + Pt) with an even higher Pt content – 25 molar per cent, is deposited, the surface of the electrocatalyst (electrode №3) is densely strewn with a multitude of different in size oval formations (20 – 120 nm). The metal deposition with this structure also shows a relatively high electrode sensitivity in the electroreduction of H_2O_2 – 0.62 $\mu A.\mu M^{-1}$.

Table 1. Composition of the electrochemical bath (in volume and molar %), electrode sensitivity (I_s/C) and linearity range of the electrocatalytic electrodes responce at the reduction of H_2O_2; temperature 25 ^{0}C; 0.1M phosphate-citrate buffer pH = 7.0; E = - 0.05 V(vs.Ag/AgCl, 1M KCl).

Electrode №	Type of matrix	Bath composition			Electrode sensitivity µA.µM^{-1} at E=-0.05V	Linearity range, µM
		modifying components	volume %	molar %		
1	graphite	Pd:Pt (series I)	90:10	96:4	0.22	up to 400
2			70:30	87:13	0.82	up to 600
3			50:50	75:25	0.62	up to 500
4	graphite	Pd:Au (series II)	90:10	94:6	0.30	up to 750
5			70:30	82:18	0.86	up to 1270
6			50:50	66:34	0.34	up to 840
7	glassy carbon	Pd:Au (series III)	90:10	94:6	0.35	up to 980
8			70:30	82:18	0.19	up to 1020
9			50:50	66:34	0.36	up to 760

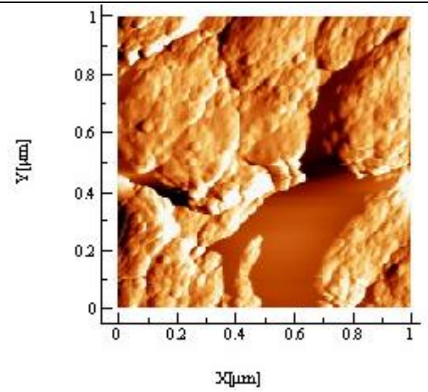

Fig. 1a

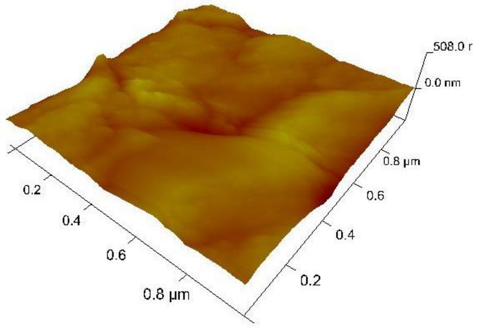

Fig. 1a, 3D

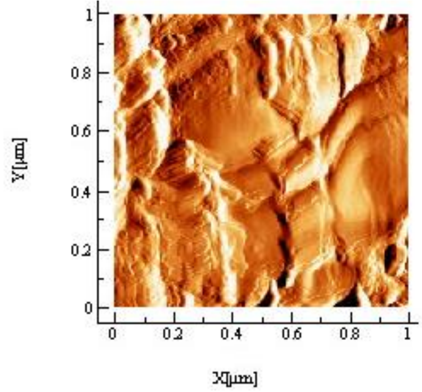

Fig. 1b

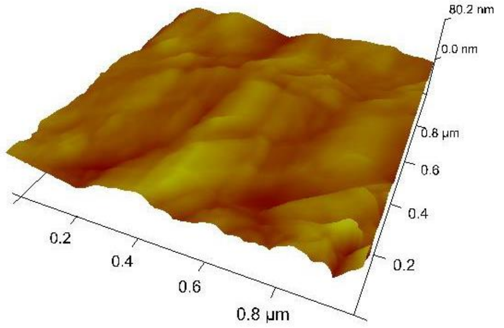

Fig.1b, 3D

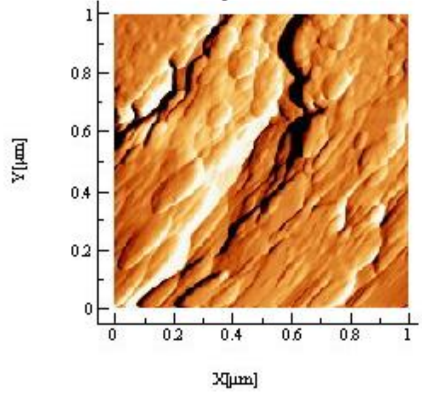

Fig. 1c

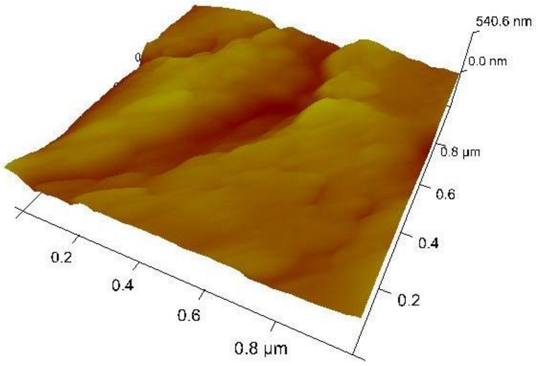

Fig. 1c, 3D

Fig. 1. AFM images of the surface morphology of modified graphites: a) 96%Pd:4%Pt/C; b) 87%Pd:13%Pt/C; c) 75%Pd:25%Pt/C (ratio of the modifying components in molar %).

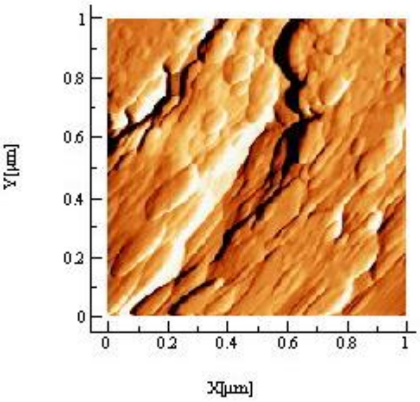

Fig. 2a

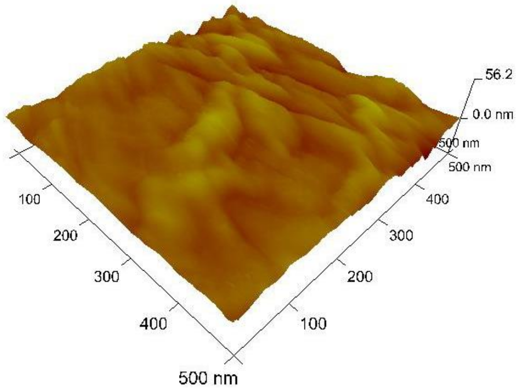

Fig. 2a, 3D

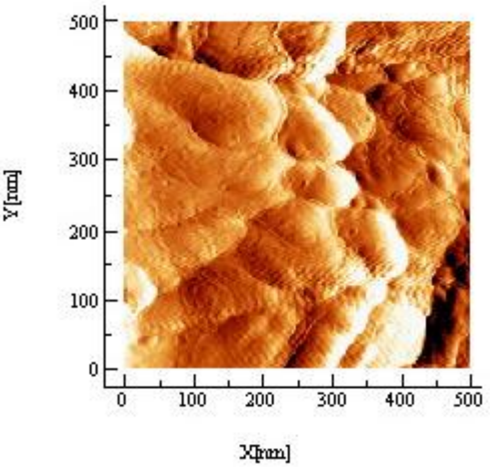

Fig. 2b

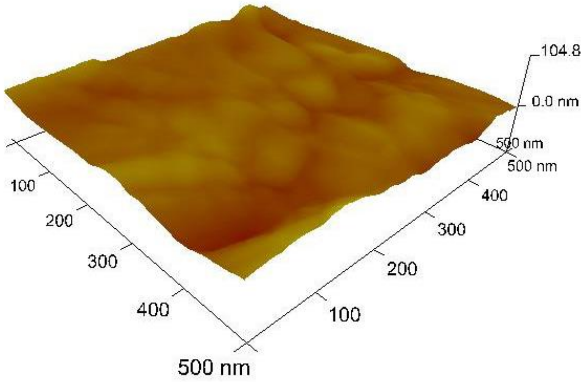

Fig. 2b, 3D

Fig. 2. AFM images of the surface morphology of modified graphites: a) 82%Pd:18%Au/C; b) 66%Pd:34%Au/C (ratio of the modifying components in molar %).

The AFM – images presented in Fig. 1b and Fig. 1c differ in the size and shape of the insular formations of the deposited metal phase. On electrode №2 (Fig.1b) they are smaller in size and have sharper building components – a structure which probably contributes to the higher activity of this electrode, as compared to that of electrode №3 (Fig.1c).

The microadditions of Au to Pd in the modifying mixture radically change the surface morphology of the depositions of (Pd + Au) on the same graphite carrier (Fig. 2). The topography of the surface of the graphite thus modified significantly differs from that of the ones discussed so far (Fig. 1).

With electrode №5, where 18 molar per cent of Au were added to Pd (Fig. 2a) and electrode №6, where 34 molar per cent of Au were added to Pd (Fig. 2b), different in size formations are observed on the surface. These formations are ribbed, probably as a result of the gradual overlaying of the metal phase. With electrode №5 (Fig. 2a) the deposition (Pd + Au) is visibly with clusters which are smaller in size and sharper in shape, both in the periphery of the islands and in their inner part, as compared to electrode №6 (Fig. 2b). On the basis of the observations of the structure of electrode №5 it can be concluded that the smaller content of the Au microaddition (18 molar per cent) to Pd results in the formation of a structure with the highest electrocatalytic activity in the quantitative determination of H_2O_2 (electrode №5 of series II is the most active one – Table 1).

Fig. 3 shows the AFM images of the surface of depositions of the same modifying mixture (Pd + Au), but on another carbonaceous matrix – glassy carbon. With electrode №7, in which the Au addition to Pd is only 6 molar per cent, the image of the surface is specific and does not resemble any of the ones discussed so far. Two forms of deposition

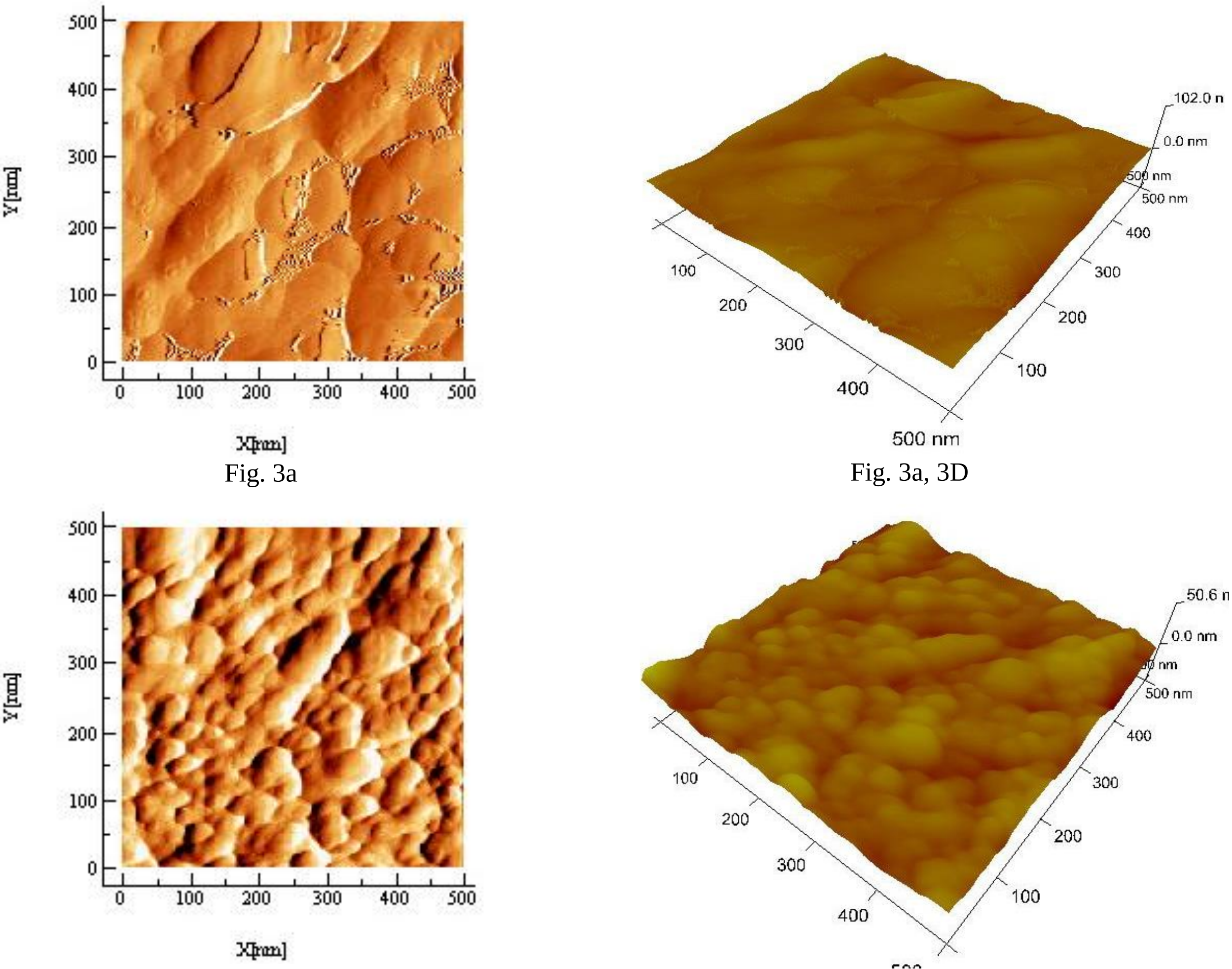

Fig. 3a

Fig. 3a, 3D

Fig. 3b

Fig. 3b, 3D

Fig. 3. AFM images of the surface morphology of modified glassy carbon electrodes: a) 94%Pd:6%Au/GC; b) 66%Pd:34%Au/GC (ratio of the modifying components in molar %).

are clearly identifiable (Fig. 3a): light plates tightly covering the protruding areas of the matrix, and a multitude of well-shaped grains, approximately and less than 10 nm in size. Most of these fine grains are grouped in structures resembling chains, situated in the grooves of the relief, with an insignificant number of them clearly separated.

In the deposition of a metal phase (Pd + Au), in which the Au content is much higher – 34 molar per cent (electrode №9), the surface of the electrocatalyst (Fig. 3b) is very different from that in Fig. 2b, which shows the deposition of the same modifying mixture but on a different carrier – graphite. With electrode №9 the metal phase is deposited evenly on the glassy carbon, forming grains of the same type (Fig. 3b). The grains in this metal formation are less than 50 nm in size, and vary within relatively narrow range (from 10 to 50 nm).

The comparative examination of Fig. 2b and Fig. 3b, showing AFM images of metal depositions of the same modifying component (Pd + Au) (66 molar %: 34 molar %), but on different carbon matrixes, proves that the nature of the carbon material also has a significant effect on the structure of the deposited active phase. While the structures observed on the graphite matrix (Fig. 2b) are ribbed, most probably following the morphology of the carrier itself, with the glassy carbon matrix (Fig. 3b) the granular formations are distinctly shaped and distributed across the whole visible surface.

CONCLUSION

The presented AFM images of the surface of the modified carbonaceous electrodes provide sufficient grounds to conclude that the catalytic activity of the electrocatalysts upon the electrochemical reduction of H_2O_2 depends both on the type of the catalytically active modifying component (nature and ratio between the two platinum metals) and on the nature of the carbon matrix, with the following being established:

- the optimal catalytic activity in the target reaction shows the deposits on graphite of the catalytically active phase, in which the content of the main element Pd is approximately 85 molar per cent, regardless of the nature of the second modification component (Pt or Au), and forms structures with similar in size and shape;
- the substitution of Au microaddition for Pt in the modification electrolytic solution (while preserving the percentage of the principal component Pd) results in deposits on graphite distinguished for their ribbed formations; the graphites modified by (Pd + Au) deposits are characterized by about twice as long linear range of concentration dependence of the amperometric signal;
- the modification by the same mixture (Pd + Au) (66 molar % : 34 molar %) of various carbonaceous materials (glassy carbon and graphite) produces electrocatalysts with practically the same catalytic activity, despite the notable defferences in the structure of the deposited catalytic phase.

Acknowledgments: *Financial support from the Bulgarian National Science Fund (grant DDVU – 02/38) and University of Food Technologies Research Fund (grant 5/12–N) is gratefully acknowledged.*

REFERENCES

1. R. Cretu, D. Gligor, L. Muresan, I. Popescu, L. M. Muresan, *J. Appl. Electrochem.*, **36**, 1327 (2006).
2. A. Eftekhari, *Microchim. Acta*, **141**, 15 (2003).
3. J. Li, R. Yuan, Y. Chai, T. Zhang, X. Che, *Microchim. Acta*, **171**, 125 (2010).
4. R. Pauliukaite, S.B. Hočevar, E. A. Hutton, B. Ogorevc, *Electroanalysis*, **20**, 47 (2008).
5. P. A. Fiorito, V. R. Gonçales, E. A. Ponzio, S. I. de Torresi, *Chem. Commun. (Camb.)*, **3**, 366 (2005).
6. X. Luo, A. Morrin, A. Killard, M. Smith, *Electroanalysis*, **18**, 319 (2006).
7. O. Niwa, *Bull. Chem. Soc. Jpn*, **78**, 555 (2005).
8. P. Yang, W. Wei, C. Tao, B. Xie, X. Chen, *Microchim. Acta*, **162**, 51 (2008).
9. S. Hrapovic, Y. Liu, K. B. Male, J. H. Luong, *Anal. Chem.*, **76**, 1083 (2004).
10. M. Yang, Y. Yang, Y. Liu, G. Shen, R. Yu, *Biosens. Bioelectron.*, **21**, 1125 (2006).
11. I. Gurrappa, L. Binder, *Sci. Technol. Adv. Mater.*, **9**, 043001-12 (2008).
12. A.E. Alvarez, D. R. Salinas, 2nd Mercosur Congress on Chemical Engineering – Brasil, report 808, (2005).
13. J. Hrbac, V. Halouzka, R. Zboril, K. Papadopoulos, T. Triantis, *Electroanalysis*, **19**, 1850 (2007).
14. N. Dimcheva, E. Horozova, Z. Jordanova, *Z. Naturforsh.*, C, **57**, 883 (2002).
15. N. Dimcheva, E. Horozova, Z. Jordanova, *Z. Naturforsch.*, C, **57**, 705 (2002).
16. T. Dodevska, E. Horozova, N. Dimcheva, *Anal. Bioanal. Chem.*, **386**, 1413 (2006).
17. E. Horozova, T. Dodevska, N. Dimcheva, *Journal of the University of Chemical Technology and Metallurgy*, **43**, 59 (2008).
18. E. Horozova, T. Dodevska, N. Dimcheva, *Bioelectrochemistry*, **74**, 260 (2009).
19. T. Dodevska, E. Horozova, N. Dimcheva, *Central European Journal of Chemistry*, **8**, 19 (2010).
20. E. Horozova, T. Dodevska, N. Dimcheva, *International Journal of Electrochemistry*, Article ID 697698, 8 pages ; doi: 10.4061/2011/697698 (2011).
21. T. Dodevska, PhD Thesis, UFT, Plovdiv, 2011.

ЕЛЕКТРОХИМИЧНИ ХАРАКТЕРИСТИКИ И СТРУКТУРНИ ОСОБЕНОСТИ НА ВЪГЛЕРОДНИ ЕЛЕКТРОДИ, МОДИФИЦИРАНИ С МИКРО- И НАНООТЛОЖЕНИЯ ОТ ПЛАТИНОВИ МЕТАЛИ

Т. М. Додевска[1], Е. Г. Хорозова[2], Н. Д. Димчева[2]

[1]*Университет по хранителни технологии, катедра „Неорганична химия и физикохимия“, Пловдив 4002*
[2]*Пловдивски университет „Паисий Хилендарски“, катедра „Физикохимия“, Пловдив 4000*

Постъпила на 22 март, 2013 г.; Коригирана на 13 май, 2013 г.

(Резюме)

Повърхностната топография на серия от графитови и стъкловъглеродни електроди, модифицирани с микро- и нанооотложения от смеси (Pd + Pt) и (Pd + Au) в различни съотношения на каталитично-активните компоненти, беше изследвана с атомна силова микроскопия (AFM). Установи се, че каталитичната активност на модифицираните електродите в реакцията на редукция на H_2O_2 зависи от спецификите в природата и структурата на металната фаза, електрохимично отложена върху въглеродния носител. Особеностите в структурата и морфологията на металните отложения, както и степента на заселеност на електродната повърхност, се определят от вида на каталитично-активните компоненти (природа и съотношение на двата метала в модифициращата смес) и природата на въглеродната матрица (тип, порьозност и състояние на повърхността).