# Rhodium-modified carbonaceous electrodes: application to electrochemical sensing of hydrogen peroxide

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In this research, a fast, simple and reproducible procedure for electrochemical modification of carbonaceous carriers with rhodium has been reported. Rhodium was electrodeposited by means of cyclic voltammetry at various scan rates. The electrochemical behaviour in the electroreduction of  $H_2O_2$  of the graphite and glassy carbon electrodes, modified applying the here presented procedure, was studied using cyclic voltammetry and chronoamperometry at pH 7.0. The applicability of the modified electrodes for sensitive quantitative amperometric detection of hydrogen peroxide at low applied potentials (0 V and -0.1 V vs. Ag/AgCl, 3M KCl) has been demonstrated. As an optimized electrode, modified glassy carbon type Rh\_v100/GC exhibited excellent electrocatalytic performance – fast, stable and sensitive (493  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>) response, low detection limit (1.5  $\mu$ M H<sub>2</sub>O<sub>2</sub>) and wide linear range (up to 5.5 mM), making it one of the promising candidates for efficient non-enzymatic amperometric detection of H<sub>2</sub>O<sub>2</sub>.

Keywords: carbonaceous materials, rhodium, electrodeposition, hydrogen peroxide reduction, electrocatalyst.

# **INTRODUCTION**

In the development of efficient electrode-catalysts, it is particularly important to obtain on chemically inert electrically conductive carrier metal deposits with high specific catalytic activity in the target reaction. In this connection, dispersing the catalytically active phase onto the surface of solid carbonaceous carriers not only significantly reduces the cost of the produced catalysts but also repeatedly increases their activity.

The studies of the deposition of micro- and nanosized structures of rhodium (Rh) are motivated by the well-known catalytic activity of this metal and its extreme resistivity towards acids and bases, rendering Rh-structures broadly applicable and potentially aging resistant. Rhodium shows outstanding catalytic properties in various reactions such as the reduction of nitrate and nitrite ions [1], hydrogenation of CO, CO<sub>2</sub>, alkenes and arenes [2, 3], C-C cross-coupling [4], decomposition of methane and some oxidation reactions [5–8]. Rhodium is an excellent catalyst in (NO)<sub>x</sub> removal [9], so it is a common component of the three-way catalyst used for the simultaneous conversion of nitrogen oxides, CO and hydrocarbons in automobile exhausts.

It is well known that the catalytic properties of the metal deposits depend on the particles size and shape, and morphology of the metal phase onto the carrier surface. These parameters are determined both by the nature, physical characteristics and pretreatment of the carrier, as well as by the procedure for deposition. Numerous studies proved the electrodeposition as an attractive method for modifying various electrode materials. The great advantage of electrochemical techniques is the possibility of strict and accurate control allowing high reproducibility of the modification procedure. The required equipment is standard for any electrochemical laboratory and offers a wide range of possibilities electrodeposition to be performed in potentiostatic or potentiodynamic conditions as well as by applying pulse techniques.

Based on the above, the present study deals with the optimization of electrochemical procedure for obtaining stable rhodium deposits onto carbonaceous electrodes (glassy carbon and spectroscopic graphite). With aim to develop a non-enzymatic sensor for rapid and sensitive quantitative detection of  $H_2O_2$ , an industrially and biologically relevant analyte, the catalytic activity of the so-obtained modified electrodes in the reduction of  $H_2O_2$ 

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at potentials around and below 0 V (vs. Ag/AgCl, 3M KCl) was investigated. Hydrogen peroxide is used as an oxidizing and bleaching agent in the pharmaceutical, cosmetic, textile and paper industries; in the food industry  $H_2O_2$  is used in the artificial aging of wines and as a sterilizing agent in the dairy industry; in medicine the excess of  $H_2O_2$  in human body is associated with oxidative stress, aging, cancer and progressive neurodegenerative diseases. Moreover, the development of effective materials with pre-defined operational parameters for quantitative determination of  $H_2O_2$  at low potentials is relevant not only for the establishment of amperometric analysis of  $H_2O_2$ , but also for developing selective first generation biosensors.

# MATERIALS AND METHODS

## Materials

Two types carbonaceous carriers were used as working electrodes: 1/ disc from glassy carbon (GC) with diameter of the working surface 3 mm and visible surface area of *ca*. 7.07 mm<sup>2</sup> (Metrohm) and 2/ disc from spectroscopic graphite (Gr) with diameter of the working surface 5.6 mm and visible surface area *ca*. 25 mm<sup>2</sup> (RWO, Ringsdorf, Germany).

RhCl<sub>3</sub>.nH<sub>2</sub>O, HCl, H<sub>2</sub>O<sub>2</sub> (30% (v/v) aqueous solution), Na<sub>2</sub>HPO<sub>4</sub>.12H<sub>2</sub>O NaH<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O were purchased from Fluka. All chemicals used were of analytical grade. Phosphate buffer solution, 0.1 M, (PBS) was made of sodium phosphates (monobasic and dibasic) dissolved in double distilled water with pH adjusted with H<sub>3</sub>PO<sub>4</sub> and NaOH using a pH meter MS2006 (Microsyst, Bulgaria). Double distilled water was used to prepare aqueous solutions.

#### Apparatus and measurements

The electrochemical measurements were performed using computer controlled electrochemical workstation EmStat2 (PalmSens BV, The Nederland), equipped with PSTrace 2.5.2 licensed software, in a conventional thermostated three-electrode cell, including a working electrode (modified with rhodium electrode), an Ag/AgCl (3 M KCl) reference electrode, and a platinum auxiliary electrode.

All the electrochemical measurements were carried out at a temperature of 25°C. To remove oxygen, the background solution was purged with pure argon. Cyclic voltammograms (CVs) were recorded at scan rates from 10 to 100 mV s<sup>-1</sup>. Peak intensities of CVs were reported with baseline correction. The amperometric experiments (calibrations) were performed by successive addition of aliquots of  $3.10^{-2}$  M H<sub>2</sub>O<sub>2</sub> freshly prepared solution to background electrolyte (0.1 M PBS) in the cell (30 mL initial volume) with simultaneous registration of the current at a constant potential.

The experimental data were processed by software package 'OriginPro 8'.

## Electrochemical deposition of Rh

Before modification, the GC electrode surface was carefully polished with 0.3 and 0.5  $\mu$ m alumina slurry on a polishing cloth (LECO, USA), the graphite electrode was carefully polished to mirrorlike finish with emery paper with decreasing particle size (P800, P1200 and P2000). After polishing, the electrodes were sonicated in double distilled water for 3 min and allowed to dry at room temperature for few minutes. The rhodium was electrodeposited from electrolyte 0.1 M HCl, containing 2.0% RhCl<sub>3</sub>, by means of cyclic voltammetry. The electrode surface was seeded with rhodium particles when starting the cycle at -0.3 V, then the scan goes up to 0.9 and back to -0.3 V.

#### **RESULTS AND DISCUSSION**

In order to establish the effect of electrodeposition scan rate on the activity of the catalysts in electroreduction of  $H_2O_2$ , GC electrodes were modified at scan rates of 50, 100 and 200 mV s<sup>-1</sup>, respectively. To indicate the type of the modified electrode we take the following notation: Rh\_scan rate/GC (for example: GC modified by applying a rate of 50 mV s<sup>-1</sup> will be denoted in the text as Rh\_v50/GC).

The presence of Rh-deposits on the glassy carbon carrier was confirmed by CV, recorded in an electrolyte 0.1 M PBS (pH 7.0) Fig. 1 shows CVs

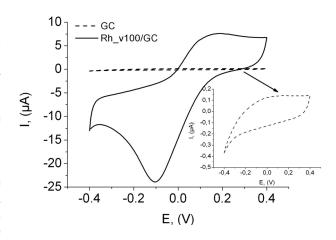
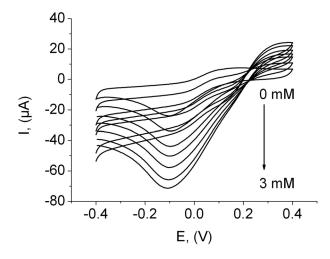


Fig. 1. CVs of the bare GC electrode (dash line) and of the modified Rh\_v100/GC electrode (solid line) recorded in 0.1 M PBS (pH 7.0); scan rate of 50 mV s<sup>-1</sup>.

of the unmodified GC electrode and modified electrode type Rh\_v100/GC, registered in the potential range from -0.4 to 0.4 V at scan rate of 50 mV s<sup>-1</sup>. No redox peak is observed on the CV of the bare GC electrode (enlarged in inset plot). Compared with bare GC electrode, the background current of the modified electrode is apparently larger, which indicates that the effective electrode surface area is significantly enhanced.

Further experiments were carried out to evaluate the electrocatalytic activity of the modified electrode Rh\_v100/GC in the electroreduction of  $H_2O_2$ . Fig. 2 presents CVs recorded in 0.1 M PBS



**Fig. 2.** CVs of modified electrode Rh\_v100/GC in 0.1 M PBS (pH 7.0) at scan rate of 50 mV s<sup>-1</sup> with increasing  $H_2O_2$  concentration (from inner to outer) 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM.

pH 7.0 at various concentrations of  $H_2O_2$ . When the concentration of  $H_2O_2$  in the electrolyte is increased from 0.5 to 3.0 mM, cathodic peak current at -0.1 V progressively increases. A plot of concentration vs. cathodic peak current exhibits a linear dependency over entire experimental range. This phenomenon indicates that the modified electrode not only reduces  $H_2O_2$ , but can also be used for amperometric determination of  $H_2O_2$ .

Chronoamperometry (CA) under stirred conditions as an electrochemical technique has a much higher current sensitivity than cyclic voltammetry. The performance of the modified electrodes regarding the sensing of  $H_2O_2$  was evaluated using CA according to detection limit, linear range, response time and stability. The amperometric response of the prepared electrodes was registered after successive additions of  $H_2O_2$  stock solution under potentials of -0.1 and 0 V.

Fig. 3A displays the authentic record of the signal of GC electrodes, modified at different scan rates, to successive concentration increments over 0.5 to 7.0 mM H<sub>2</sub>O<sub>2</sub> range. Cathode currents in presence of H<sub>2</sub>O<sub>2</sub>, resulting from its electrochemical reduction, were observed for the proposed electrochemical systems. Upon addition of H<sub>2</sub>O<sub>2</sub> the modified electrodes show increasing reduction currents (staircase current response), corresponding to the electrochemical conversion of the analyte. As can be seen electrodes type Rh v50/GC and Rh v200/ GC do not yield the desired response. Significant disadvantage of type Rh v200/GC being a high noise level, recorded even at relatively low H<sub>2</sub>O<sub>2</sub> concentrations. At the same time type Rh v50/GC exhibits much lower current response than the other two modified electrodes. Analogous results in the

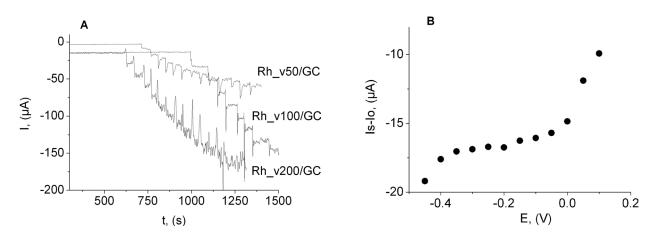
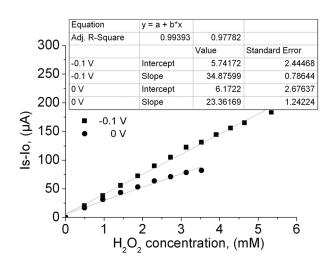


Fig. 3. A) Authentic record of the amperometric response at the modified electrodes type  $Rh_v50/GC$ ,  $Rh_v100/GC$  and  $Rh_v200/GC$  for successive additions of  $H_2O_2$  into stirred 0.1 M PBS (pH 7.0) at an applied potential of -0.1 V. B) The steady-state current as a function of potential applied at electrode type  $Rh_v100/GC$  when 0.5 mM  $H_2O_2$  is present.

analytical behavior of the three modified electrodes were obtained in the CA study at an applied potential of 0 V. Based on the observed, electrode type Rh\_v100/GC was used in further investigations. The polarization curve (Fig. 3B) over the potential range from -0.45 to 0.1 V, registered in 0.1 M PBS (pH 7.0) with 0.5 mM  $H_2O_2$  present, clearly shows interval of potentials where the cathodic current hardly varies (a "plateau region"). The plateau region for the modified electrode occurred between -0.4 and 0 V.

The background subtracted steady-state response ( $I_s$ - $I_0$ ) of the electrode in PBS (pH 7.0) is presented in Fig. 4. At an applied potential of -0.1 V the linear response was proportional to the  $H_2O_2$ concentration up to 5.5 mM (correlation coefficient



**Fig. 4.** Calibration plot for electrode type Rh\_v100/GC; 0.1 M PBS (pH 7.0); applied potentials: -0.1 V and 0 V.

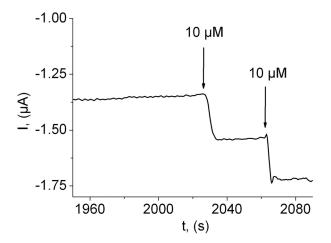


Fig. 5. Authentic record of the amperometric response of modified electrode Rh\_v100/GC upon additions of 10  $\mu$ M H<sub>2</sub>O<sub>2</sub> in 0.1 M PBS (pH 7.0); potential of 0 V.

of  $0.99_4$ ) with a sensitivity of 34.88  $\mu$ A mM<sup>-1</sup> (or 493  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>). At a potential of 0 V the linearity was up to 3.5 mM H<sub>2</sub>O<sub>2</sub> (0.97<sub>8</sub>) with a sensitivity of 23.36  $\mu$ A mM<sup>-1</sup> (330  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup>).

The modified electrode responded rapidly producing steady-state signal within 8 s. A well-defined current response was observed during the successive additions of 10  $\mu$ M H<sub>2</sub>O<sub>2</sub> (detection limit of 1.5  $\mu$ M at a signal-to-noise ratio of 3), which evidences a stable and efficient catalytic property of rhodium deposits (Fig. 5).

In order to assess the impact of type of carbonaceous carrier on the activity of the electrocatalysts, graphite electrode (Gr) has been modified using the same procedure for electrodeposition of Rh (denoted in text as type Rh v100/Gr). The chronoamperometric data at potential of 0 V suggest that the analytical detection of H<sub>2</sub>O<sub>2</sub> with a modified graphite Rh v100/Gr is distinguished by twice lower sensitivity (230 µA mM<sup>-1</sup> cm<sup>-2</sup>), short linear dynamic range (up to 2.8 mM), slower response (15 s), higher background current and noise (detection limit of 10  $\mu$ M). The probable reason for the observed differences in the electrochemical behavior of the two modified electrodes is highly porous surface of the graphite carrier, used for the development of catalyst type Rh v100/Gr.

The long-term operational stability and reproducibility of the signal of the modified electrode are essential for its applicability as a sensing element. In this connection, the reproducibility of the current signal for the electrode type Rh\_v100/GC to 0.5 mM H<sub>2</sub>O<sub>2</sub> at an applied potential of 0 V was examined. The relative standard deviation (RSD) was calculated to be 3.2% for 5 successive measurements (current responses were 16.8, 17.3, 15.9, 16.5 and 17.0  $\mu$ A, respectively).

Further, the reproducibility of the proposed procedure of electrodeposition of Rh was studied by analysis of the same concentration of  $H_2O_2$  (0.5 mM) using four equally prepared electrodes type Rh\_v100/GC. The electrodeposition procedure had good reproducibility with a RSD of 6.7%. Here, it should be noted the key role of the pre-treatment process of the electrode surface preceding the procedure of electrodeposition.

The modified electrode was stored in air over a 3 months period. During the first two weeks there was a gradual decrease to 87% of its initial current response, probably due to processes of recrystallization of the metal phase; after this period the electrode activity remained practically unchanged. The long-term stability of the electrode is in general comparable to the stability of other modified electrodes, applied for  $H_2O_2$  sensing: 85.3% after 1 week of storage [15], 87% (1 month) [16], 92% (3 weeks) [17]. Y. Lazarova, T. Dodevska: Rhodium-modified carbonaceous electrodes: application to electrochemical sensing...

Electrode modifier	E, V	Sensitivity, µA mM <sup>-1</sup> cm <sup>-2</sup>	Linear range, M	Detection limit, M	Ref.
Ag/NFM	-0.58ª	157.0	$1.0 \times 10^{-5} \sim 1.6 \times 10^{-2}$	4.0×10 <sup>-6</sup>	10
Ir <sup>IV</sup> Ox.H <sub>2</sub> O	-0.3ª	6.15°	5.0×10 <sup>-6</sup> ~1.5×10 <sup>-4</sup>	5.0×10 <sup>-6</sup>	11
GR-AuNPs	$-0.4^{a}$	3.0 <sup>d</sup>	$2.0 \times 10^{-5} \sim 2.8 \times 10^{-4}$	6.0×10 <sup>-6</sup>	12
PtNWs-CNTs-CHIT	-0.1 <sup>b</sup>	260.0	$1.0 \times 10^{-6} \sim 3.0 \times 10^{-2}$	_	13
Co <sub>3</sub> O <sub>4</sub> NWs	-0.2ª	80.74	up to 5.35×10 <sup>-3</sup>	1.0×10 <sup>-5</sup>	14
Ag	-0.2ª	104.53*	$5.0 \times 10^{-6} \sim 1.2 \times 10^{-2}$	5.0×10 <sup>-7</sup>	15
PVA/MWCNTs/PtNPs	$0^{a}$	122.63	2.0×10 <sup>-6</sup> ~3.8×10 <sup>-3</sup>	7.0×10 <sup>-7</sup>	16
Pd/PEDOT NSs	-0.2 <sup>b</sup>	215.3	up to 1.0×10 <sup>-3</sup>	2.84×10 <sup>-6</sup>	17
ERGO-AgNPLs	$-0.5^{a}$	183.5	2.0×10 <sup>-5</sup> ~1.0×10 <sup>-2</sup>	3.0×10 <sup>-6</sup>	18
Rh_v100/GC	-0.1ª	493.0	2.0×10 <sup>-6</sup> ~5.5×10 <sup>-3</sup>	1.5×10 <sup>-6</sup>	This
Rh_v100/Gr	$0^{a}$	230.0	$2.0 \times 10^{-5} \sim 2.8 \times 10^{-3}$	1.0×10 <sup>-5</sup>	work

Table 1. Comparison of the operational characteristics of amperometric sensors for  $H_2O_2$  detection, based on modified glassy carbon electrodes, with the achieved in the present work

\*Calculated from the data in paper;

<sup>a</sup> Reference electrode: Ag/AgCl, 3 M KCl (0.200 V vs. SHE);

<sup>b</sup> Reference electrode: saturated calomel electrode (SCE) (0.242 V vs. SHE);

° the unit is: nA  $\mu$ M<sup>-1</sup> cm<sup>-2</sup>;

<sup>d</sup> the unit is:  $\mu A \mu M^{-1} cm^{-2}$ .

NFM – nanofibrous membrane, GR – graphene, ERGO – electrochemically reduced graphene oxide, CNTs – carbon nanotubes, MWCNTs – multiwall carbon nanotubes, NPLs – nanoparticles, NWs – nanowalls, NSs – nanospheres, CHIT – chitosan, PVA – poly(vinyl alcohol), PEDOT – poly(3,4-ethylenedioxythiophene).

The performance of the Rh\_v100/GC catalyst, developed in this study, was compared with other modified electrodes. In Table 1 we have summarized various  $H_2O_2$  sensors, based on modified glassy carbon electrodes, with respect to the applied potential, sensitivity, linear dynamic range and limit of detection. All data presented are recorded in supporting electrolyte buffer solution with pH in the range 6.0-7.5 in the  $H_2O_2$  electroreduction mode. It can be seen that the proposed Rh\_v100/GC electrode shows an excellent sensitivity, several times higher than that obtained by using other glassy carbon electrodes modified with metal or metal oxide particles.

#### CONCLUSION

In conclusion, a fast, simple and reproducible procedure for electrochemical modification of carbonaceous carriers with rhodium has been demonstrated in this study. The graphite and glassy carbon electrodes, modified applying the presented procedure, were used for the electrocatalytic reduction of  $H_2O_2$  and their applicability for amperometric detection of  $H_2O_2$  in micromolar concentrations has been proven. The modified glassy carbon type Rh\_v100/GC exhibited excellent electrocatalytic performance – fast and stable response, low detection limit (1.5  $\mu$ M) and wide linear range (up to 5.5 mM) for H<sub>2</sub>O<sub>2</sub> detection at low applied potential (-0.1 V vs. Ag/AgCl, 3M KCl). The developed electrocatalyst provides a new approach to construct a highly sensitive and selective amperometric biosensors of first generation (based on hydrogen peroxide-producing enzymes) for quantitative detection of biologically important compounds. Further experiments, such as the practical application of this modified electrode as a transducer in the construction of glucose and L-lactate biosensors, are underway.

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# МОДИФИЦИРАНИ С РОДИЙ ВЪГЛЕРОДНИ ЕЛЕКТРОДИ: ПРИЛОЖЕНИЕ ЗА ЕЛЕКТРОХИМИЧНА ДЕТЕКЦИЯ НА ВОДОРОДЕН ПЕРОКСИД

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#### (Резюме)

Настоящото изследване представя бърза, семпла и възпроизводима процедура за електрохимично модифициране на въглеродни носители с родий. Електрохимичното поведение при електроредукция на  $H_2O_2$  на графитов и стъклографитов електрод, модифицирани чрез представената тук методика, е изучено чрез циклична волтамперометрия и хроноамперометрия при pH 7.0. Показана е приложимостта на модифицираните електроди за количествена амперометрична детекция на  $H_2O_2$  при ниски работни потенциали (0 V и –0.1 V vs. Ag/AgCl, 3M KCl). Модифицираният електрод тип Rh\_v100/GC, получен чрез електроотлагане на родий при определената като оптимална скорост на разгъване на потенциала (100 mV s<sup>-1</sup>), показва отлично поведение – бърз, стабилен и чувствителен отклик, нисък откриваем минимум (1.5  $\mu$ M  $H_2O_2$ ) на аналита и широка област на линейна зависимост на сигнала (до 5.5 mM), което го характеризира като подходящ трансдюсер за неензимна амперометрична детекция на  $H_2O_2$ .