Food Science and Applied Biotechnology

e-ISSN: 2603-3380

Journal home page: www.ijfsab.com
<https://doi.org/10.30721/fsab2018.v1.i1>

Research Article

Amperometric sensing of hydrogen peroxide using glassy carbon electrode modified with rhodium

Yanna Lazarova¹ and Totka Dodevska¹✉

¹ University of Food Technologies, Department of Organic chemistry and Inorganic chemistry

Abstract

Following our previous studies on the catalytic activity of electrochemically deposited on glassy carbon Rh electrocatalyst towards the reduction of hydrogen peroxide (H₂O₂), the electrochemical behaviour of the modified electrode was studied by means of cyclic voltammetry and chronoamperometry at pH-values from 5.0 to 9.0. The modified electrode exhibited a rapid, sensitive and reproducible response for the quantitative determination of H₂O₂ at low applied potential. Amperometry carried out at constant potential of 0 V (vs. Ag/AgCl, 3M KCl) at pH 6.0 (25 °C) gave the following operational parameters: detection limit of 4 μM, linear dynamic range 0.01 – 5.5 mM and electrode sensitivity of 377 μA mM⁻¹ cm⁻².

Keywords: amperometric sensor, rhodium, electrodeposition, hydrogen peroxide reduction

Abbreviations:

GC – glassy carbon
CV – cyclic voltammetry
RSD – relative standard deviation

✉ Corresponding author: Totka Mihaylova Dodevska, Associate Professor, PhD; Department of Organic chemistry and Inorganic chemistry, Technological Faculty, University of Food Technologies, 26 Maritsa Blvd., Plovdiv 4002, Bulgaria, +35932603679, E-mail: dodevska@mail.bg

Article history:

Received 16 October 2017
Reviewed 18 January 2018
Accepted 19 January 2018
Available on-line 14 March 2018

<https://doi.org/10.30721/fsab2018.v1.i1.4>

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Introduction

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. Rh shows outstanding catalytic properties in various reactions such as the reduction of nitrate and nitrite ions (Casella et al. 2014), hydrogenation of CO, CO₂, alkenes and arenes (García et al. 2014; Park et al. 2007), C-C cross-coupling (Kanaru et al. 2009), decomposition of methane and some oxidation reactions (Ortiz et al. 2006; Horozova et al. 2008; Yuan et al. 2010; Sathe et al. 2011). Rh is an excellent catalyst in (NO)_x removal (Beyer et al. 2010), 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.

In our previous studies it was established that the electrochemical behaviour of the Rh-modified electrodes significantly depends on the nature of the carbonaceous carrier (Dodevska et al. 2016). In the target reaction (reduction of H₂O₂) the electrode based on glassy carbon possesses more than two-fold higher catalytic activity in comparison with the modified spectroscopic graphite. In the present work we studied Rh-modified glassy carbon, developed by using simple electrochemical deposition method, as a sensing element in the amperometric detection of H₂O₂ – industrially and biologically relevant analyte. H₂O₂ is used as an oxidizing and bleaching agent in the pharmaceutical, cosmetic, textile and paper industries; in the food industry H₂O₂ is used in the artificial aging of wines and as a sterilizing agent in the dairy industry; in medicine the excess of H₂O₂ in human body is associated with oxidative stress, aging, cancer and progressive neurodegenerative diseases. Moreover, the development of effective materials with defined operational parameters for quantitative determination of H₂O₂ at low potentials is relevant not only for the establishment of amperometric analysis of H₂O₂, but also for developing selective first generation biosensors.

Materials and Methods

The working electrode was a disc from glassy carbon (GC) with diameter of the working surface 3 mm and visible surface area of ca. 7.07 mm² (Metrohm). RhCl₃.nH₂O, HCl, H₂O₂ (30% (v/v) aqueous solution), Na₂HPO₄.12H₂O, NaH₂PO₄.2H₂O were purchased from Fluka. All chemicals used were of analytical grade. 0.1 M phosphate buffer solution (PBS) was made of sodium phosphates (monobasic and dibasic) dissolved in double distilled water with pHs 5.0 – 9.0 adjusted with H₃PO₄ 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 GC 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⁻¹. 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 H₂O₂ 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 H₂O₂ stock solution was freshly prepared before each measurement.

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 µm alumina slurry on a polishing cloth (LECO, USA), followed by sonication in double distilled water for 3 min.

After bath sonication, the electrode was rinsed with double distilled water and allowed to dry at room temperature for few minutes. The rhodium was electrodeposited onto the clean working surface of the GC electrode by means of CV – 1 cycle at a scan rate of 100 mV s^{-1} from electrolyte containing 2% RhCl_3 , dissolved in 0.1 M HCl . 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. The modified Rh/GC was subsequently rinsed twice with double distilled water, dried at ambient conditions and employed for the electrochemical studies.

Results and Discussions

Cyclic voltammetry (CV) was used to characterize the modified electrode. The presence of Rh deposits on the glassy carbon carrier was confirmed by the cyclic voltammogram, recorded in an electrolyte, H_2SO_4 . Fig. 1 shows the CV of modified electrode Rh/GC registered in 0.1 N H_2SO_4 in the potential range from -0.3 to 1.0 V at scan rate of 100 mV s^{-1} . The characteristics (i.e. the attribution of observed peaks) of the CV for Rh/GC in sulphuric acid are comparable as those of polycrystalline rhodium (Jerkiewicz et al. 1994) and electrodeposited mesoporous Rh film (Bartlett et al. 2003).

Figure 1. Cyclic voltammogram (CV) of modified electrode Rh/GC; supporting electrolyte 0.1 N H_2SO_4 (deaerated); scan rate of 100 mV s^{-1} ; reference electrode Ag/AgCl , 3 M KCl ; temperature 25°C .

According to the literature data (Jerkiewicz et al. 1994), different surface oxide films on Rh grow with increasing applied anodic potential. The formation of oxide film begins at around 0.2 V on the anodic scan. This process involves electrochemisorption of one monolayer of OH^- and leads to the formation of $\text{Rh}(\text{OH})$ species. At higher anodic potentials (at about 0.8 V) further oxidation and formation of $\text{Rh}(\text{OH})_3$ species occurs. Reversing the sweep direction towards more negative potentials (from 1.0 to -0.3 V) it can be observed that there is a single stripping peak associated to surface oxide reduction. The position of the stripping peak for Rh-electrodes is known to be sensitive to the anodic scan limit, acid concentration and the scan rate (Pallotta et al. 1981; Villard et al. 1997); under the chosen experimental conditions the stripping peak occurs at potential of 0.1 V.

Oxide formation proceeds in three distinguishable stages and the reduction in two steps, accordingly to the following oxide formation-reduction scheme:

Oxidation:

At potentials above 1.4 V (vs. RHE) authors (Jerkiewicz et al. 1994) proposed the formation of $\text{RhO}(\text{OH})$ species:

Reduction:

Continuing the cathodic scan, the current peak at -0.21 V is associated with the formation of a layer of adsorbed hydrogen at the electrode surface, which then is stripped from the surface at -0.13 V on the anodic scan.

The successful modification of the glassy carbon carrier is also evidenced by CV recorded in buffer

solution. The cyclic voltammograms of the bare GC electrode and of the rhodium-modified GC electrode were obtained in 0.1 M PBS with pH 7.0 (Fig. 2). No redox peak is observed on the CV of bare GC electrode (enlarged in inset plot). Compared with bare GC electrode, the background current of modified electrode is apparently larger, which indicates that the effective electrode surface area is significantly enhanced.

Figure 2. CVs of the bare glassy carbon electrode (red line) and of the rhodium-modified glassy carbon electrode (black line) recorded in 0.1 M PBS (pH 7.0); scan rate of 50 mV s^{-1} ; reference electrode Ag/AgCl, 3 M KCl; temperature 25°C .

In the next step, rhodium-modified GC was employed for the different scan rate studies in pH 7.0 PBS. Fig. 3a clearly shows that all the anodic and cathodic peak currents of Rh/GC increase linearly with respect to the scan rate in the range of $10 - 100 \text{ mV s}^{-1}$. In Fig. 3b is presented the plot of anodic and cathodic peak currents versus the scan rate. The linear regression equation (inset) for the anodic peak current was $I_{p,a} (\mu\text{A}) = 0.08561 \text{ v (mV s}^{-1}) + 0.94942$, $R^2 = 0.999$ and for the corresponding cathodic peak current was $I_{p,c} (\mu\text{A}) = -0.17968 \text{ v (mV s}^{-1}) - 6.20754$, $R^2 = 0.977$, respectively. The linear increase in the anodic and cathodic peak currents of modified Rh/GC electrode according to the scan rate illustrates that the proposed rhodium deposit was stable and exhibits surface controlled thin-layer electrochemical behavior. In order to obtain prior information about the catalytic activity of the electrode towards the electroreduction of hydrogen peroxide, an amperometric response was recorded

in the presence of 0.5 mM and 1.0 mM H_2O_2 at a constant potential of 0 V in buffer solutions with pH-values 5.0, 6.0, 7.0, 8.0 and 9.0.

Figure 3. (a) CVs of modified electrode Rh/GC in 0.1 M PBS (pH 7.0) at different scan rates (10, 20, 30, 40, 50, 75 and 100 mV s^{-1}); (b) Plot of peak currents versus the scan rate; reference electrode Ag/AgCl, 3 M KCl; temperature 25°C .

Cathode currents in presence of H_2O_2 , resulting from its electrochemical reduction, were observed in the whole investigated pH-range. Upon addition of H_2O_2 the Rh/GC electrode shows increasing reduction currents (staircase current response), corresponding to the electrochemical conversion of the analyte.

The background subtracted steady-state response ($I_s - I_o$) of the electrode, registered in this study, is presented in Fig. 4. As shown, the current response decreased rapidly in alkaline medium. With increasing the pH from 7.0 to 8.0, there was a

sharp decline in the electrode response. From the experimental data it is seen that lowering the intensity of the current is almost 70 %. The electrode response, registered at pH 9.0 is almost 88 % lower than that recorded at pH 7.0. At the same time, the lowering of the pH below 7.0, does not affect significantly the electrode response, and its value is very close to the one registered at pH 6.0 and pH 5.0.

Figure 4. Effect of pH on the response of modified electrode Rh/GC in presence of 0.5 mM H_2O_2 (black) and 1.0 mM H_2O_2 (red); applied potential of 0 V; electrolyte 0.1 M PBS; temperature 25°C.

The effect of the pH on the operational parameters, in terms of electrode sensitivity and linear dynamic range, of the modified electrode was also investigated. Fig. 5a shows the typical current-time ($I-t$) plot upon the successive injection of H_2O_2 in PBS with pH 6.0. A well-defined response was observed during the successive additions of 0.01 mM H_2O_2 , which evidences a stable and efficient catalytic property of rhodium. It can also be observed that the modified electrode responds rapidly to the changes of H_2O_2 concentration, producing steady-state signal within 8s. The corresponding calibration curve is presented in Fig. 5b. The linear response was proportional to the H_2O_2 concentration up to 5.5 mM (correlation coefficient of 0.987) with a sensitivity of 377 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of 4 μM (at a signal-to-noise ratio of 3). The reproducibility of the current signal for the modified electrode to 970 μM H_2O_2 was also examined in 0.1 M PBS (pH 6.0) – the relative standard deviation (RSD) was

calculated 3.7 % for five successive measurements (current responses were 35.25, 33.55, 36.60, 34.20 and 36.30 μA , respectively).

Figure 5. (a) Authentic record of the amperometric response of a modified electrode Rh/GC in 0.1 M PBS (pH 6.0) at potential of 0 V upon additions of 0.01 mM H_2O_2 ; b) Dependence of the amperometric response on the concentration of H_2O_2 , inset: electrode response at low concentration range (up to 0.25 mM H_2O_2).

The basic operational parameters of the modified electrode determined in 0.1 M PBS over pH range 5.0 – 9.0 at potential of 0 V, are provided in Table 1. The linear dynamic range of the electrode signal also differs as dependent on the pH value of the buffer solution – the linearity of the signal, as well as the sensitivity, decreases as the pH value increasing over 6.0. The same effect was observed when increasing the acidity of the background electrolyte – at pH 5.0 the dynamic range is shortened by 500 μM (up to 5.0 mM H_2O_2) as compared to pH 6.0.

The performance of the Rh/GC catalyst, developed in this study, was compared with other modified electrodes. In Table 2 we have summarized various H₂O₂ sensors, based on modified glassy carbon electrodes, with respect to the applied potential and the sensitivity. All data presented are recorded in supporting electrolyte buffer solution with pH in the range 6.0 – 7.5 in the H₂O₂ electroreduction mode. It can be seen that the proposed Rh/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.

Conclusions

The obtained rhodium-modified glassy carbon electrode exhibits fast and stable amperometric response, low detection limit (4 μ M) and wide linear range (0.01–5.5 mM) for H₂O₂ detection at low applied potential (0 V vs. Ag/AgCl). In addition, the working pH-range (5.0 – 7.0) and the high sensitivity of the electrode, makes it suitable transducer for studies with immobilized enzymes. The here presented catalyst provides a new approach to construct effective amperometric biosensor systems, based on oxidoreductases producing H₂O₂, for quantitative detection of biologically important compounds. Further experiments, such as the practical application of this modified electrode in real samples and the construction of biosensors, for high selective and sensitive bioanalysis, are underway.

Table 1. Operational parameters of modified electrode Rh/GC at various pH values; applied potential of 0 V; temperature 25°C.

pH	Sensitivity, μ A mM ⁻¹ cm ⁻²	R ²	Linearity, mM
5.0	366	0.989	5.0
6.0	377	0.987	5.5
7.0	337	0.982	4.3
8.0	96	0.987	4.0
9.0	40	0.981	2.7

Table 2. Comparison of the electrode sensitivity of amperometric sensors for H₂O₂ detection, based on modified glassy carbon electrodes, with the achieved in the present work.

Electrode modifier/(Electrode)	Applied potential, V	Electrode sensitivity, μ A mM ⁻¹ cm ⁻²	Reference
PtNW-CNT-CHIT/(GC)	-0.1 ^b	260	Qu et al. 2007
Co ₃ O ₄ nanowalls/(GC)	-0.2 ^a	80.74*	Jia et al. 2009
Ag/(GC)	-0.2 ^a	104.53*	Qin et al. 2011
PVA-MWCNTs-PtNPs/(GC)	0 ^a	122.63	Fang et al. 2012
Pd/PEDOT nanospheres/(GC)	-0.2 ^b	215.3	Jiang et al. 2013
Graphene-AgNPLs/(GC)	-0.5 ^a	183.5	Zhong et al. 2013
Rh/(GC)	0 ^a	377	This work

* Calculated from the data in paper;

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

^b Reference electrode: saturated calomel electrode (SCE) (0.242 V vs. SHE).

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