

## Kinetic characterization of Prussian Blue-modified graphite electrodes for amperometric detection of hydrogen peroxide

RALUCA C. CRETU, DELIA M. GLIGOR, LAURA MURESAN, IONEL CATALIN POPESCU  
and LIANA M. MURESAN\*

Department of Physical Chemistry, Babes-Bolyai University, Str. Arany Janos, no. 11, 400028 Cluj-Napoca, Romania  
(\*author for correspondence, tel.: +40-264-595872, fax: +40-264-590818, e-mail: limur@chem.ubbcluj.ro)

Received 21 September 2005; accepted in revised form 10 March 2006

**Key words:** amperometric sensors, hydrogen peroxide, modified graphite electrodes, Prussian Blue

### Abstract

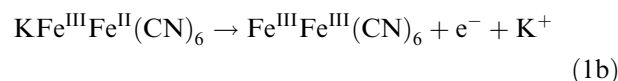
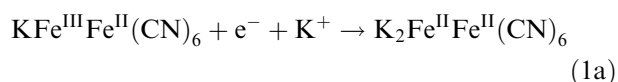
Prussian Blue-modified graphite electrodes (G/PB) with electrocatalytic activity toward  $\text{H}_2\text{O}_2$  reduction were obtained by PB potentiostatic electrodeposition from a mixture containing 2.5 mM  $\text{FeCl}_3$  + 2.5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  + 0.1 M  $\text{KCl}$  + 0.1 M  $\text{HCl}$ . From cyclic voltammetric measurements, performed in  $\text{KCl}$  aqueous solutions of different concentrations ( $5 \times 10^{-2}$ –1 M), the rate constant for the heterogeneous electron transfer ( $k_s$ ) was estimated by using the Laviron treatment. The highest  $k_s$  value ( $10.7 \text{ s}^{-1}$ ) was found for 1 M  $\text{KCl}$  solution. The differences between the electrochemical parameters of the voltammetric response, as well as the shift of the formal potential, observed in the presence of  $\text{Cl}^-$  and  $\text{NO}_3^-$  compared to those observed in the presence of  $\text{SO}_4^{2-}$  ions, points to the involvement of anions in the redox reactions of PB. The G/PB electrodes showed a good electrochemical stability proved by a low deactivation rate constant ( $0.8 \times 10^{-12} \text{ mol cm}^2 \text{ s}^{-1}$ ). The electrocatalytic efficiency, estimated as the ratio  $(I_{\text{cat}})_{\text{H}_2\text{O}_2}/(I_{\text{cat}})$ , was found to be 3.6 (at an applied potential of 0 mV vs. SCE;  $\Gamma = 5 \times 10^{-8} \text{ mol cm}^{-2}$ ) for a  $\text{H}_2\text{O}_2$  concentration of 5 mM, thus indicating G/PB electrodes as possible  $\text{H}_2\text{O}_2$  sensors.

### 1. Introduction

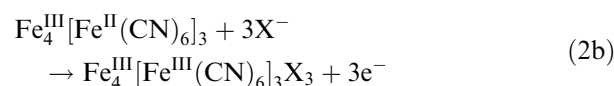
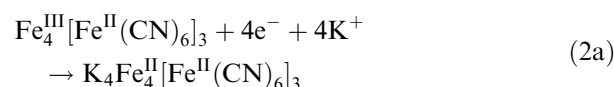
Prussian Blue (PB)-based amperometric sensors for hydrogen peroxide determination are very attractive because they offer the possibility of selective detection, by electroreduction in the presence of  $\text{O}_2$  [1]. PB has a high catalytic efficiency, comparable to that of biological catalysts [2] and, at the same time, allows a significant decrease in the applied electrode potential, avoiding the electrochemical interference in real samples. However, PB-modified electrodes still face some drawbacks especially with regards to long-term stability and sensitivity to pH changes [3].

There are indications that cycled PB films may be a mixture of two stoichiometries,  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$  called “insoluble PB” and  $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  called “soluble PB” [4, 5]. The electrochemical response of PB deposited on electrodes is controlled by the counterion motion through the film, necessary for charge compensation during the electrochemical process [4]:

“Soluble” form of PB [6]



“Insoluble” form of PB [7]



As can be seen, the electrochemical behavior of the two forms of PB is similar, but not identical, and involves the incorporation of alkali metal cations and probably the expulsion of water molecules. The degree of hydration strongly influences the electrochemical behavior of PB films and the film conductivity [8]. In the case of the “insoluble” form of PB, entrapment of anions has to be taken into consideration, but this aspect remains controversial [9]. Obviously, all these features should be involved in the electrochemical and

electrocatalytical behavior of PB-modified electrodes, being sources of their short and long time instability.

In this work, the effects of  $K^+$  ion concentration and of anions nature on the electrochemical characteristics of PB films electrodeposited on graphite electrodes was systematically investigated. From voltammetric measurements, under different experimental conditions, the number of transferred electrons and cations as well as the values of the heterogeneous rate constant for charge transfer were determined. The electrochemical stability and the electrocatalytic activity towards  $H_2O_2$  reduction of PB modified graphite electrodes (G/PB) were also studied. The analytical parameters of the  $H_2O_2$  sensors were estimated from voltammetric and amperometric calibrations.

## 2. Experimental

### 2.1. Reagents

$FeCl_3$  was purchased from Fluka and hydrogen peroxide from Merck (Darmstadt, Germany).

The supporting electrolyte was a 0.1 M KCl (Reactivul Bucharest) solution. The pH was adjusted using appropriate HCl solutions. All reagents were of analytical grade and used as received.

### 2.2. Preparation of the G/PB modified electrodes

Prior to surface modification, the graphite electrode (Ringsdorff-Werke, GmbH, Bonn-Bad Godesberg, Germany) of  $\sim 3$  mm diameter, was mechanically wet polished on fine (grit 400 and 600) emery paper (Buehler, Lake Bluff, In., USA). Electrodeposition of Prussian Blue films was accomplished potentiostatically at + 400 mV vs. SCE for 40 s, in a mixture containing 2.5 mM  $FeCl_3$  + 2.5 mM  $K_3[Fe(CN)_6]$  + 0.1 M KCl + 0.1 M HCl as described in [3]. The electrode was then carefully washed with water and transferred into a solution containing 0.1 M HCl and 0.1 M KCl, where it was electrochemically cycled between + 350 and -50 mV vs. SCE (38 cycles; potential scan rate, 50 mV  $s^{-1}$ ) until a stable voltammetric response was observed (results not shown). After that, the G/PB modified electrodes was washed with water and dried 1 h at 100°C.

### 2.3. Electrochemical measurements

Electrochemical measurements were performed using an electrochemical analyzer (Autolab-PGSTAT 10, Eco Chemie, Utrecht, The Netherlands) connected to a PC for potential control and data acquisition. Electrochemical deposition of PB onto the graphite electrode and voltammetric investigation of the G/PB modified electrode were carried out using a typical three-electrode electrochemical cell. The modified graphite electrode was used as working electrode, a platinum ring as

counter electrode and a saturated calomel electrode (SCE) as reference electrode.

For each electrode, the surface coverage ( $\Gamma$ , mol  $cm^{-2}$ ) was estimated from the under peak areas, recorded during the cyclic voltammetry (CV) measurements at low potential scan rate ( $v \leq 10$  mV  $s^{-1}$ ), and considering the surface redox valence equal to unity [10]. All presented results are the average of at least 3 identically prepared electrodes, if not otherwise stated.

Amperometric batch measurements for  $H_2O_2$  detection were carried out with the G/PB electrode at an applied potential of -50 mV vs. SCE and under constant magnetic stirring.

## 3. Results and discussion

### 3.1. Electrochemical behavior of G/PB electrodes

The cyclic voltammograms recorded during the preparation of G/PB modified electrodes (0.1 M KCl and 0.1 M HCl, pH 1) present two pairs of well-defined anodic and cathodic peaks (results not shown). In this work only the peak pair with the formal potential (estimated as the average of the cathodic and anodic peak potentials) [11] of  $\sim 0.150$  V vs. SCE was investigated, well-placed in the optimal potential domain for  $H_2O_2$  amperometric detection [12].

The electrochemical parameters of the G/PB modified electrode voltammetric response indicate the presence of a quasi-reversible couple ( $\Delta E_{peak} = 45$  mV and  $|I_{p,a}/I_{p,c}| = 1$ ;  $\Gamma = 2.5 \times 10^{-8}$  mol  $cm^{-2}$ ). The film initially formed by electrodeposition consists mainly of the "insoluble" form of PB. During potential cycling in KCl containing solution the film losses part of the Fe(III) (high spin iron) which is substituted by potassium ions and is converted into the "soluble" form [13]. Consequently, the number of electroactive sites within the film decreases and the electrical resistance of the film increases [8], as proved by the increase of peak separation ( $\Delta E_p$ ).

As predicted for a surface confined redox species [14], the cyclic voltammograms recorded for a given range of potential scan rates (0.01–20.4 V  $s^{-1}$ ) in KCl solutions of different concentrations (0.1 M, 0.5 M and 1 M) showed a linear dependence of peak current ( $I_p$ ) on electrode potential scan rate ( $v$ ) (Table 1). The deviations from linearity observed at high scan rates could be due to the contribution of diffusion to the voltammetric response.

The number of electrons involved in the redox process, estimated from the  $I_p$  vs.  $v$  dependence [11]:

$$I_p = [n^2 F^2 / 4RT] \Gamma A v \quad (3)$$

was found to be close to 1 (with an uncertainty below 25%), where  $A$  [ $cm^2$ ] is the electrode surface area,  $\Gamma$  [mol  $cm^{-2}$ ] is the surface coverage with adsorbed species; the other symbols have the usual meaning.

From the variation of peak potential with scan rate (Figure 1), using the treatment proposed by Laviron

Table 1. Linear regression parameters for the log I vs. log v dependence observed for G/PB modified electrodes. Experimental conditions: scan rate (0.01–0.8 V s<sup>-1</sup>; 0.01–6.4 V s<sup>-1</sup> and 0.01–10.24 V s<sup>-1</sup> for 0.1 M, 0.5 M and 1 M KCl solutions, respectively); starting potential, –50 mV vs. SCE

KCl conc./M	Slope		R/no. of experimental points		Surface coverage, $\Gamma/10^8 \text{ mol cm}^{-2}$
	oxidation	reduction	oxidation	reduction	
0.1	$0.70 \pm 0.01$	$0.62 \pm 0.01$	0.998/11	0.998/11	5
0.5	$0.69 \pm 0.01$	$0.63 \pm 0.01$	0.996/17	0.998/17	3
1	$0.68 \pm 0.02$	$0.63 \pm 0.01$	0.995/17	0.996/17	2

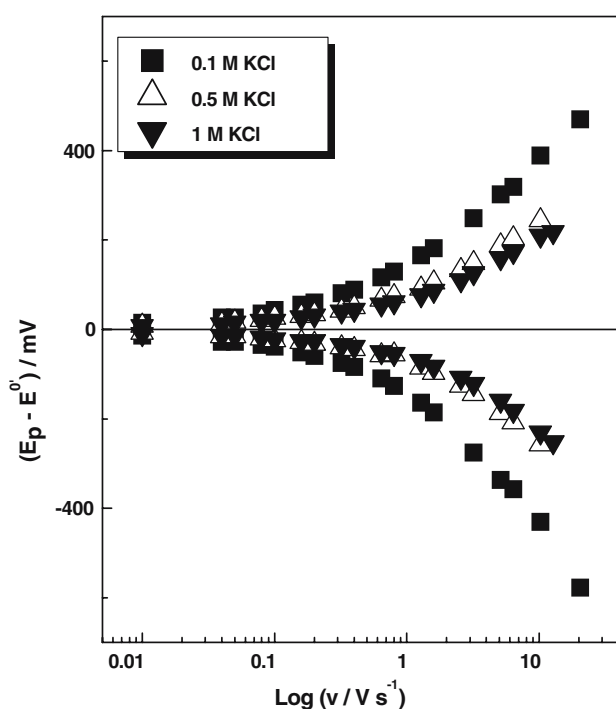


Fig. 1. Dependence of  $(E_p - E^0)$  vs. the logarithm of the potential scan rate for G/PB modified electrodes, in KCl solutions of different concentrations. Experimental conditions: surface coverage, see Table 2.

[15], the heterogeneous electron transfer rate constant ( $k_s, \text{s}^{-1}$ ) and the transfer coefficient  $\alpha$  were estimated for G/PB modified electrodes at different KCl concentrations (Table 2). The  $k_s$  values increase with increase in  $\text{K}^+$  ion concentration, proving the crucial role of  $\text{K}^+$  ions in the enhancement of the electron transfer process rate.

In order to examine the influence of the anion on the electrochemical behavior of G/PB modified electrodes, voltammetric measurements were performed in solutions containing different  $\text{K}^+$  salts, (KCl,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ) (Figure 2), at different concentrations. In all

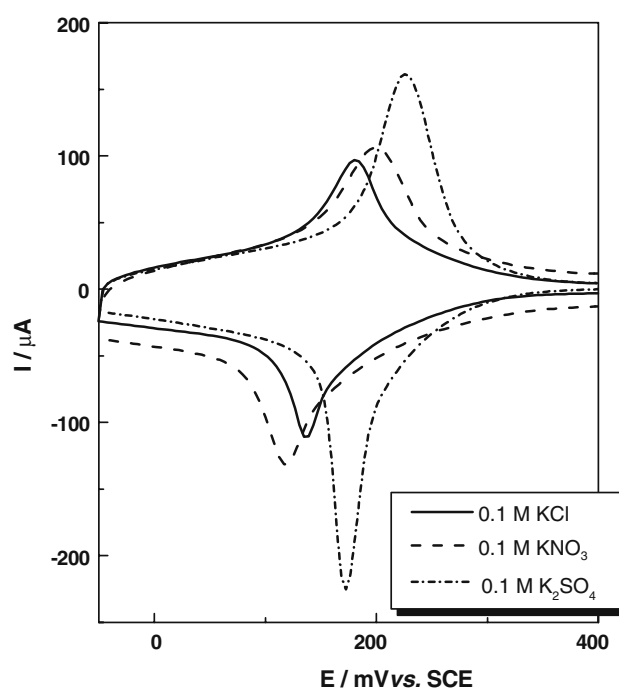


Fig. 2. Cyclic voltammograms recorded at G/PB modified electrodes, in the presence of different anions. Experimental conditions: starting potential, –50 mV vs. SCE; potential scan rate, 50 mV s<sup>-1</sup>, surface coverage, see Table 3.

cases, the electrochemical parameters of the voltammetric response (Table 3) point out to a monoelectronic, quasi-reversible process ( $\Delta E_p < 59 \text{ mV}$  and  $I_{p,a}/I_{p,c} \approx 1$ ), corresponding to a surface-adsorbed redox couple. The peak width at half maximum  $W_{1/2}$  is lower than the theoretical value of 90.6 mV for a monoelectronic process. The discrepancies can be attributed to the attractive interactions between the adsorbed redox centers [14]. Moreover, as expected in the case of lateral interactions [16], the peak parameters were slightly affected by the surface coverage.

The formal potential dependence on the  $\text{K}^+$  ion concentration (Figure 3) showed, in all cases, a positive

Table 2. Kinetic parameters for the heterogeneous electron transfer at G/PB modified electrodes. Experimental conditions: starting potential –50 mV vs. SCE; supporting electrolyte, KCl solution

KCl conc./M	$k_s/\text{s}^{-1}$	$\alpha$	R/no. of experimental points		Surface coverage, $\Gamma/10^8 \text{ mol cm}^{-2}$
			oxidation	reduction	
0.1	7.2	0.40	0.996/7	0.991/7	5
0.5	8.1	0.41	0.997/7	0.993/7	3
1	10.7	0.40	0.998/7	0.992/7	2

Table 3. Electrochemical parameters corresponding to G/PB modified electrodes cycled in KCl, KNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> solutions of different concentrations. Experimental conditions: scan rate, 50 mV s<sup>-1</sup>; starting potential, -50 mV vs. SCE

Solution	Conc./M	$I_{p,a}/\mu\text{A}$	$I_{p,c}/\mu\text{A}$	$\Delta E_p/\text{mV}$	$E^0/\text{mV vs. SCE}$	$W_{1/2,a}/\text{mV vs. SCE}$	$W_{1/2,c}/\text{mV vs. SCE}$	$\Gamma / 10^8 \text{ mol cm}^{-2}$
KCl	0.05	0.82	-0.82	62	239	78	62	2.5
	0.1	0.90	-0.94	45	247.5	70	54	2.7
	0.5	0.93	-0.10	29	293	70	49	2.8
	1	0.71	-0.76	50	315.5	74	62	2.3
KNO <sub>3</sub>	0.05	0.25	-0.24	57	238.5	99	87	1.1
	0.1	0.37	-0.41	57	250.5	87	66	1.2
	0.5	0.51	-0.60	45	294	78	62	1.7
	1	0.54	-0.64	58	313	78	62	1.8
K <sub>2</sub> SO <sub>4</sub>	0.05	0.81	-0.01	70	154	70	41	2.1
	0.1	0.89	-0.12	54	166	62	33	1.2
	0.5	0.12	-0.18	33	197.5	54	25	2.9

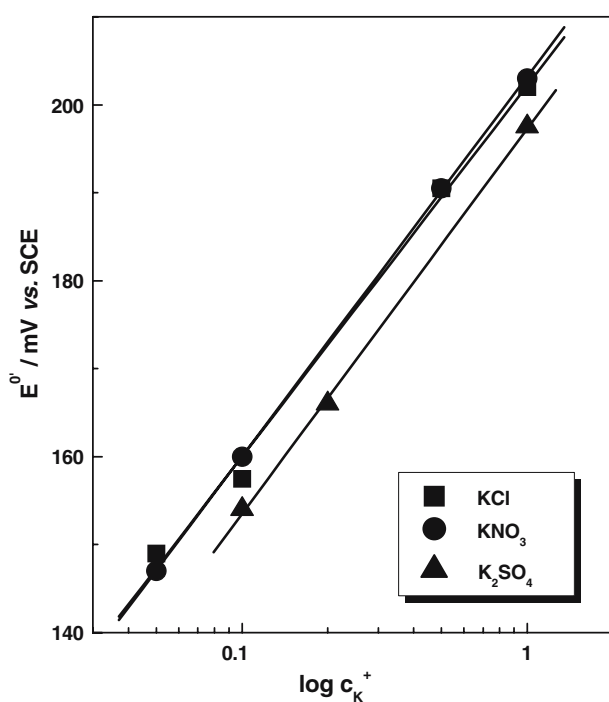


Fig. 3.  $E^0$  vs.  $\log [K^+]$  dependence for G/PB modified electrodes, obtained from cyclic voltammograms recorded in solutions containing different anions. Experimental conditions: see Figure 2.

potential shift with the increase in electrolyte concentration. This is in agreement with the involvement of  $K^+$  ions in the corresponding redox process. However, the slopes of  $\sim 40 \text{ mV}/\Delta \log [K^+]$  are significantly lower than the theoretical value for a monovalent cation, (Nernstian behavior), which would be expected for the only cation involvement in the redox process. This behavior cannot be attributed to junction potentials [17] and suggests the participation of anions from the electrolyte to the partial charge compensation during oxidation according to reaction (2b). This reaction is characteristic only for the “insoluble” form of PB, so it could be assumed that the tested film is a mixture of “soluble” and “insoluble” forms and that the conversion of “insoluble” into “soluble” during cycling was only partial. This assumption is in agreement with other observations which claim that electrochemically grown

and voltammetrically cycled PB films have an intermediate composition between the “soluble” and “insoluble” formulae [18].

Stability tests were carried out for G/PB modified electrodes under potentiodynamic conditions. The electrode potential was continuously cycled at  $50 \text{ mV s}^{-1}$ , within the potential range covering the mediator redox activity ( $\pm 120 \text{ mV}$  relative to its standard formal potential), in  $0.1 \text{ M KCl}$  solution. A progressive decrease surface coverage was observed (Figure 4), while the voltammogram shape remained invariant (results not shown). The electrode deactivation process obeys zero-order kinetics, as confirmed by the  $\Gamma$  vs.  $t$  dependence observed in the time range 0–1 600 s. This behavior suggests that all active centers on the electrode surface

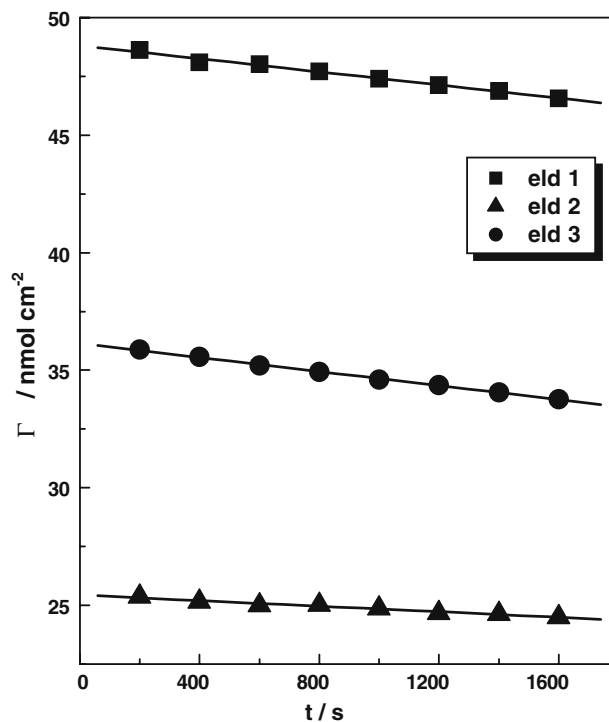


Fig. 4. Time dependence of the surface coverage for G/PB modified electrodes, obtained from repetitive cyclic voltammograms. Experimental conditions: potential scan rate,  $50 \text{ mV s}^{-1}$ ; supporting electrolyte,  $0.1 \text{ M KCl}$ ; potential range,  $130 \div 370 \text{ mV vs. SCE}$ .

Table 4. Deactivation rate constants for G/PB modified electrodes 0.1 M KCl solution

Eld. no.	$\Gamma_{t=0}/10^8 \text{ mol cm}^{-2}$		$k_{\text{deact}}/10^{12} \text{ mol cm}^{-2} \text{ s}^{-1}$		R/no. of experimental points	
	anodic	cathodic	anodic	cathodic	anodic	cathodic
1	$5.9 \pm 0.01$	$3.9 \pm 0.005$	2.0	0.8	0.9868/8	0.9863/8
2	$2.8 \pm 0.008$	$2.2 \pm 0.005$	0.8	0.3	0.9762/8	0.9289/8
3	$4.2 \pm 0.008$	$3.0 \pm 0.003$	1.2	1.1	0.9952/8	0.9970/8

are occupied by adsorbed PB. The low values of the deactivation rate constants (Table 4) proved that in the investigated potential range the G/PB modified electrode has a good chemical stability.

### 3.2. Electrocatalytic activity of G/PB electrodes for $\text{H}_2\text{O}_2$ electroreduction

In order to check the electrocatalytic activity of G/PB modified electrodes towards  $\text{H}_2\text{O}_2$  reduction, their voltammetric responses were recorded in the absence and presence of different concentration of  $\text{H}_2\text{O}_2$ . The results are depicted in Figure 5. In the presence of  $\text{H}_2\text{O}_2$  the cathodic current increased several times, whereas the anodic current decreased continuously. The electrocatalytic efficiency, estimated as the ratio  $(I_{\text{cat}})_{\text{H}_2\text{O}_2}/(I_{\text{cat}})$ , was found to be 3.6 (at an applied potential of 0 mV vs. SCE;  $\Gamma = 5 \times 10^{-8} \text{ mol cm}^{-2}$ ) for a  $\text{H}_2\text{O}_2$  concentration of 5 mM. This behavior indicates that the G/PB modified electrodes have a good electrocatalytic effect for  $\text{H}_2\text{O}_2$  electro-reduction. The electrocatalytic effect is due to the high spin Fe(III) and, as expected, is favored by low pH values.

The calibration curve obtained from voltammetric data (results not shown) revealed a sensitivity of  $29.5 \text{ mA M}^{-1}$  ( $R/N = 0.9972/11$ ). The partial reaction order, relative to  $\text{H}_2\text{O}_2$ , was close to 1 (the slope of  $\log I$  vs.  $\log [\text{H}_2\text{O}_2]$  plots is 1.13,  $R/N = 0.9978/10$ ), suggesting that the G/PB modified electrode works under kinetic control due to the reaction between PB and  $\text{H}_2\text{O}_2$ .

The amperometric calibration, performed in "batch" conditions at an applied potential of  $-50 \text{ mV vs. SCE}$ , allowed estimation of the analytical parameters for  $\text{H}_2\text{O}_2$  detection at a G/PB modified electrode (Table 5): sensitivity,  $\sim 31.6 \text{ mA M}^{-1}$  ( $R/N = 0.9998/6$ ); detection limit,  $0.4 \text{ }\mu\text{M}$ , in  $0.1 \text{ M KCl} + 0.1 \text{ M HCl}$ ,  $\text{pH} = 3$ . The response time to reach 95% ( $t_{95\%}$ ) of the steady state signal was almost independent at the substrate concentration and its average value was less than 50 s.

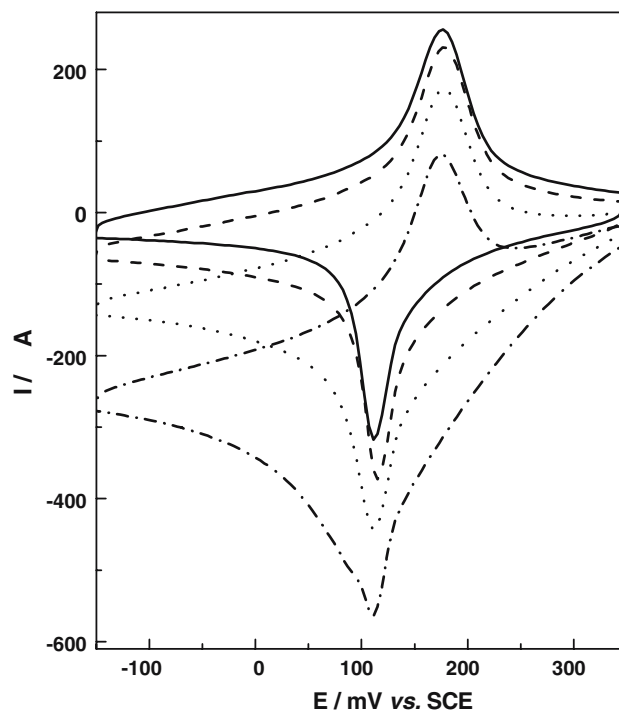


Fig. 5. Electrocatalytic reduction of  $\text{H}_2\text{O}_2$  at G/PB modified electrodes:  $0.1 \text{ M KCl} + 0.1 \text{ M HCl}$  (—);  $2 \text{ mM H}_2\text{O}_2$  (- -);  $5 \text{ mM H}_2\text{O}_2$  (.....);  $10 \text{ mM H}_2\text{O}_2$  (-.-.-). Experimental conditions: starting potential,  $+350 \text{ mV vs. SCE}$ ; potential scan rate,  $50 \text{ mV s}^{-1}$ ; supporting electrolyte,  $0.1 \text{ M KCl} + 0.1 \text{ M HCl}$  ( $\text{pH} 1.3$ ).

## 4. Conclusions

A kinetic characterization of the electrochemical behavior of PB-modified graphite electrodes was performed. Thus, for the first time, the heterogeneous rate constant for the electron transfer between PB and a graphite electrode was estimated for different KCl concentrations. The highest  $k_s$  value ( $10.7 \text{ s}^{-1}$ ) was obtained for the highest investigated KCl concentration ( $1 \text{ M}$ ).

The G/PB modified electrodes were tested for the electrochemical reduction of  $\text{H}_2\text{O}_2$ . Their high electrochemical stability ( $k_{\text{deact}} = 2 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$ ) and

Table 5. The parameters of calibration in  $\text{H}_2\text{O}_2$  for G/PB modified electrodes obtained from amperometric measurements

Experimental conditions	Sensitivity/ $\text{mA}/\mu\text{M}$	Detection limit/ $\mu\text{M}$	R/no. of experimental points
$0.1 \text{ M KCl} + 0.1 \text{ M HCl}$ , $\text{pH} = 3$	31.55	39.7	0.9998 / 6
$0.05 \text{ M phosphate buffer} + 0.1 \text{ M KCl}$ , $\text{pH} = 3$	40.625	52.5	0.9986 / 6

good electrocatalytic efficiency (3.66 at 0 V vs. SCE, in 5 mM H<sub>2</sub>O<sub>2</sub>) were exploited to obtain H<sub>2</sub>O<sub>2</sub> amperometric sensors.

### Acknowledgment

Financial support from CNCSIS (Grants Nr. 51/349 / 2005 and TD 6/89-2005) is gratefully acknowledged.

### References

1. A.A. Karyakin, E.E. Karyakina and L. Gorton, *Electrochem. Commun.* **1** (1999) 78.
2. R. Koncki, *Anal. Chem.* **32** (2002) 79.
3. A.A. Karyakin, E.E. Karyakina and L. Gorton, *J. Electroanal. Chem.* **456** (1998) 97.
4. B.J. Feldman and O.R. Melroy, *J. Electroanal. Chem.* **234** (1987) 213.
5. J.F. Keggin and F.D. Miles, *Nature* **137** (1936) 577.
6. D. Ellis, M. Eckhoff and V.D. Neff, *J. Phys. Chem.* **85** (1981) 1225.
7. K. Itaya, T. Ataka and S. Toshima, *J. Am. Chem. Soc.* **104** (1982) 4767.
8. J.J. Garcia Jareno, J. Navarro-Laboulais and F. Vicente, *Electrochim. Acta* **41** (1996) 835.
9. A. Karyakin, *Electroanalysis* **13** (2001) 813.
10. H. Huck, *Phys. Chem. Chem. Phys.* **1** (1999) 855.
11. R.W. Murray. in A.J. Bard (ed.), *Electroanalytical Chemistry*, (Marcel Dekker, New York, 1984), pp. 191.
12. L. Gorton, *Electroanalysis* **7** (1995) 23.
13. H. Kellawi and D.R. Rosseinsky, *J. Electrochem. Soc.* **131** (1982) 373.
14. R.W. Murray. in R.W. Murray (ed.), *Molecular Design of Electrode Surfaces*, (J. Wiley, New York, 1992), pp. 1.
15. E. Laviron, *J. Electroanal. Chem.* **101** (1979) 19.
16. M.J. Honeychurch and G.A. Rechnitz, *Electroanalysis* **5** (1998) 285.
17. M.A. Malik, G. Horanyi, P.J. Kulesza, G. Inzelt, V. Kertesz R. Schmidt and E. Czirok, *J. Electroanal. Chem.* **452** (1998) 57.
18. B.J. Feldman and R.W. Murray, *Inorg. Chem.* **26** (1987) 1702.