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ORIGINAL PAPER

# Rhodium stabilized Prussian Blue-modified graphite electrodes for $H_2O_2$ amperometric detection

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**Abstract** Graphite electrodes chemically modified with Prussian Blue (G/PB) were obtained by spreading, on the electrode surface, appropriate volumes of 100 mM $K_3[Fe(CN)_6]$ and 100 mM $FeCl_3$ solutions, both containing 10 mM HCl. In order to improve the electrochemical response stability, the potential of G/PB electrodes was cycled (in the domain where PB exhibits electrochemical activity) in 0.1 M KCl solution (G/PB-K), as well as in 2 mM $RhCl_3$ solution, containing 0.05 M KCl (G/PB-Rh). Compared with G/PB-K, the G/PB-Rh modified electrodes showed: (i) higher relative stability of the PB electrochemical response; (ii) better analytical parameters for $H_2O_2$ amperometric detection; (iii) slightly lower rate constant corresponding to the second order electrocatalytic reaction for $H_2O_2$ amperometric detection; (iv) an electrocatalytic activity not affected by the $H_2O_2$ concentration.

**Keywords** $H_2O_2$ amperometric detection · Modified electrodes · Prussian Blue · Rh(III) stabilizing effect

## 1 Introduction

Prussian Blue (PB; ferric hexacyanoferrate) has been known from the beginning of the 18th century, but its electrochemical behavior was investigated for the first time only in 1978 [1]. A few years later, PB electrochemistry began to be investigated systematically, and its electrocatalytic activity towards molecular oxygen and hydrogen peroxide reduction, dissolved in aqueous solutions, was demonstrated [2–4].

It was established that, due to its favorable properties, Prussian Blue is a very suitable redox mediator which can be included in different electroanalytical systems, for: (i) nonelectroactive cation detection [5]; (ii) easily oxidizable compound determination, such as $H_2O_2$ [6, 7], hydrazine [8] or thiols [9]; (iii) $H_2O_2$ mediated electroreduction which was exploited as a key step in various biodetection schemes incorporating various oxidases, such as glucose oxidase [10–16], choline oxidase [17], glutamate oxidase [18], lactate oxidase [19, 20], alcohol oxidase [21].

When used as mediator for $H_2O_2$ electroreduction, PB has important advantages, such as ease of preparation and deposition, low cost and suitability to a variety of electrode materials, good chemical stability, and, especially, a redox potential well placed in the optimal potential range for amperometric detection [22].

The main disadvantages of PB are related to a significant decrease in electrochemical activity and a reduced operational stability, especially in neutral and basic pH [23]. Therefore, the major concern regarding the use of PB for sensor and biosensor design is the enhancement of its stability. Ricci and coworkers have reported an improvement in PB stability, even in alkaline media, when PB was chemically deposited on the electrode surface in the presence of KCl [23, 24]. However, it was shown that the stability of PB-modified electrodes still depends strongly on the storage conditions, pH and the composition of the test solutions.

Based on recently published results, which describe the beneficial effect of $Ru^{3+}$ [25–27] and $Rh^{3+}$ [28] on the stability of PB and its analogues (Ni(II)-, In(III)-, and Co(II)- hexacyanoferrates), the present work aims, firstly, to investigate the influence of $Rh^{3+}$ on the electrochemical

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behavior of PB. Secondly, PB-modified graphite electrodes (G/PB), obtained using the Ricci method [23] coupled with potential cycling in the presence of $K^+$ or $Rh^{3+}$, were compared as amperometric sensors for $H_2O_2$ detection. Finally, rotating disc electrode measurements, performed for both kinds of modified electrodes (G/PB-K and G/PB-Rh) at different $H_2O_2$ concentrations, allow comparison at the $K^+$ and $Rh^{3+}$ effect on the process of $H_2O_2$ mediated electroreduction.

## 2 Experimental

### 2.1 Reagents and solutions

The $H_2O_2$, HCl, KCl and $K_3[Fe(CN)_6]$ were supplied by Merck (Germany), and the $RhCl_3$ and $FeCl_3$ by Fluka (Germany). The phosphate buffer salts, $KH_2PO_4$ and $K_2HPO_4$, were purchased from Sigma (USA). All chemicals were of analytical grade and were used as received.

About 0.1 M KCl solution (pH 3) or 2 mM $RhCl_3$ solution (pH 3) containing 0.05 M KCl were used for activation of the PB-modified graphite electrodes (G/PB).

The 0.05 M phosphate buffer solution, used as supporting electrolyte, was prepared by mixing the appropriate volumes of $KH_2PO_4$ and $K_2HPO_4$ solutions. The final ionic strength was fixed at 0.15 M using KCl. The pH was adjusted to 3 with concentrated $H_3PO_4$.

The $H_2O_2$ standard solutions were prepared in 0.05 M phosphate buffer, containing 0.1 M KCl, by diluting a stock solution of 1 M $H_2O_2$.

All solutions were prepared with purified water from a Milli-Q system (Millipore, Milford, USA) and the optimal pH was adjusted using a MV-870 Digital pH-meter (Pracitronic, Germany).

### 2.2 Electrochemical measurements

Electrochemical measurements were performed in a conventional single-compartment three-electrode cell using a computer controlled voltammetric analyzer AutoLab-PGSTAT 10 (Echochemie, Utrecht, Netherlands). The G/PB modified electrodes were used as working electrodes, the reference electrode was a saturated calomel electrode (SCE) (Radiometer, Denmark), and the counter electrode was a platinum plate.

The amperometric batch measurements, used for $H_2O_2$ calibration of G/PB electrodes, were performed under controlled stirring at an applied potential of −50 mV vs. SCE. The rotating disc electrode (RDE) measurements were carried out using a Radiometer set-up (France). The chosen applied potential was in the diffusion controlled region for the redox process corresponding to PB.

### 2.3 G/PB modified electrodes preparation

Prior to the modification, the graphite electrode surface (Ringsdorff-Werke Gmbh, Bonn-Bad, Godesberg, Germany; 3 mm diameter) was mechanically polished with $\gamma$-$Al_2O_3$ and ultrasonicated for 5–15 min in distilled water. Before electrode modification the graphite was electrochemically pretreated for 180 s, by mild oxidation at +1.7 V vs. SCE in contact with 0.05 M phosphate buffer containing 0.1 M KCl (pH = 3).

The chemical deposition of Prussian Blue on graphite was accomplished by spreading 5 μl of 100 mM $K_3[Fe(CN)_6]$ and 5 μl of 100 mM $FeCl_3$ solution, both freshly prepared in 10 mM HCl [23]. The two solutions were mixed directly on the electrode surface and the mixture was kept at rest for 10 min. Then, the modified electrodes were washed with 10 mM HCl solution and, finally, heated at 100 °C for 90 min in order to ensure the removal of the coordination water and to facilitate the structure rearrangement [23].

## 3 Results and discussions

### 3.1 $Rh^{3+}$ influence on the electrochemical behavior of G/PB modified electrodes

The voltammetric response of G/PB modified electrodes was recorded during repetitive potential cycling performed in contact with 0.1 M KCl solution (Fig. 1A) or 2 mM $RhCl_3$ containing 0.05 M KCl solution (Fig. 1B). As expected, the two pairs of peaks (A1/C1 and A2/C2), which are characteristic for PB electrochemical behavior [29], were noticed. The presence of $K^+$ ions at a concentration level higher than 0.01 M was found to be essential to obtain well-shaped and reversible voltammetric waves for the PB film [20].

The two peak pairs, occuring at around +0.2 V vs. Ag/AgCl (resulting from the reduction/oxidation of a high-spin system $Fe^{3+/2+}$) and +1.0 V vs. Ag/AgCl (resulting from the redox reaction of a low-spin system $Fe(CN)_6^{3-/4-}$), were attributed to the following two sets of redox reactions:

"*Soluble*" form of PB [2]

$$KFe^{III}\left[Fe^{II}(CN)_6\right] + e^- + K^+ \rightleftarrows \underset{\text{Prussian White}}{K_2Fe^{II}\left[Fe^{II}(CN)_6\right]} \qquad (A1/C1)$$

$$KFe^{III}\left[Fe^{II}(CN)_6\right] \rightleftarrows \underset{\text{Berlin Green}}{K_{1/3}\left[Fe^{III}(CN)_6\right]_{2/3}\left[Fe^{II}(CN)_6\right]_{1/3} + 2/3\ e^- + 2/3K^+} \qquad (A2/C2)$$

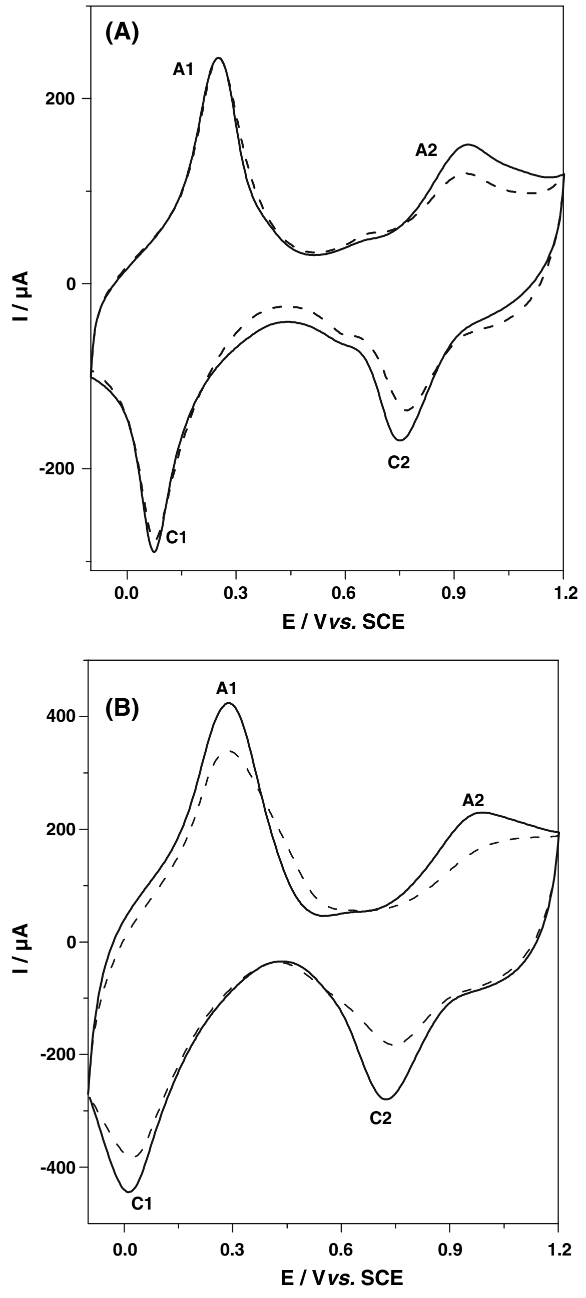

**Fig. 1** Repetitive cyclic voltamograms recorded for G/PB-K electrodes in 0.1 M KCl solution (**A**) and G/PB-Rh electrodes in 2 mM $RhCl_3$ solution containing 0.05 M KCl (**B**). Experimental conditions: starting potential, −0.1 V vs. SCE; scan rate, 50 mV $s^{-1}$; pH 3; surface coverage, $3.8 \times 10^{-8}$ mol $cm^{-2}$ (G/PB-K) and $1.5 \times 10^{-7}$ mol $cm^{-2}$ (G/PB-Rh); 2nd scan (– – – –), 50th scan (——)

"*Insoluble*" form of PB [3]

$$\mathrm{Fe_4^{III}\left[Fe^{II}(CN)_6\right]_3 * 6H_2O + 4e^- + 4K^+ \rightleftarrows K_4Fe_4^{II}\left[Fe^{II}(CN)_6\right]_3 * 6H_2O} \qquad (\mathrm{A1/C1})$$

Prussian White

$$\mathrm{Fe_4^{III}\left[Fe^{II}(CN)_6\right]_3 * 6H_2O + 3X^- \rightleftarrows Fe_4^{III}\left[Fe^{III}(CN)_6X\right]_3 * 6H_2O + 3e^-} \qquad (\mathrm{A2/C2})$$

Berlin Green

A comparison between the voltammetric response observed for G/PB in contact with 0.1 M KCl solution (G/PB-K from Fig. 1A) and the voltammetric response obtained for G/PB in contact with 2 mM $RhCl_3$ solution containing 0.05 M KCl (G/PB-Rh from Fig. 1B), shows that, in both cases, the last voltammogram (the 50th cycle) is better shaped than the second one. Irrespective of the electrode type, all recorded voltammetric waves point to a quasi-irreversible redox process ($\Delta E_p \neq 0$). Moreover, the electrode relative stability (defined as specified in Table 1) corresponds to an increase of the electrode response of ~6% in the case of G/PB-K electrode, while for G/PB-Rh electrode a higher increase (~17%) was observed (Table 1A). This beneficial effect of $Rh^{3+}$ ion in the adjacent solution is similar to the stabilizing effect reported for $Ru^{3+}$ ion on Co(II)-, Ni(II)-, In(III))-hexacyanoferrates, and Fe(II/III)-hexacyanorutenate [25, 30, 31]. It is worth noting that, in our case, the stabilizing effect attributed to $Rh^{3+}$ (whose characteristics are very similar to that of $Ru^{3+}$) is accompanied by an activation effect attributable to the presence of $K^+$ ions.

The presence of $Rh^{3+}$ influences the electrochemical parameters corresponding to the A1/C1, A2/C2 voltammetric waves as follows: (i) $\Delta E^{0'}_{II-I} = E^{0'}_{A2/C2} - E^{0'}_{A1/C1}$, is not affected; (ii) the peak potential split, corresponding to the A1/C1 peaks pair, increases significantly (G/PB-K: $\Delta E_p = 170\,\mathrm{mV}$, G/PB-Rh: $\Delta E_p = 260\,\mathrm{mV}$); (iii) the width at half maximum ($E_{FWHM}$) evaluated for A1/C1 peaks pair for G/PB-Rh electrode ($E^{A1}_{FWHM} = 210\,\mathrm{mV}$, $E^{C1}_{FWHM} = 148\,\mathrm{mV}$) is bigger than that corresponding to G/PB-K electrode ($E^{A1}_{FWHM} = 136\,\mathrm{mV}$, $E^{C1}_{FWHM} = 111\,\mathrm{mV}$); (iv) the ratio between the anodic peak current and cathodic peak current for the A1/C1 peak is higher in the case of G/PB-Rh electrode (1.95) than in the case of G/PB-K electrode (1.06).

Summarizing, the potential cycling of G/PB electrode in the presence of $Rh^{3+}$ induces an increase in the voltammetric stability (Fig. 1), simultaneously with a slight decrease in reversibility for the heterogeneous charge transfer process (resulting from variations of the electrochemical parameters). As was found in the case of the stabilizing effect of $Ru^{3+}$ on Co(II)-, Ni(II)-, In(III))-hexacyanoferrates, and Fe(II/III)-hexacyanorutenate [25–27, 30, 31], the stabilizing effect of $Rh^{3+}$ [28] should be due to its ability to establish an extensive cross linking between hydrate microparticles through dinuclear oxo and cyanide bridges [25, 30]. Moreover, it was shown that the presence

**Table 1** Influence of electrode pretreatment (A) and repetitive potential cycling (B) on the stability of G/PB voltammetric response

| Type of experiment | | Relative stability* |
|---|---|---|
| A | 0.1 M KCl | 0.06 ± 0.02 |
| | 2 mM $RhCl_3$ | 0.17 ± 0.08 |
| B | G/PB-K | 0.18 ± 0.05 |
| | G/PB-Rh | 0.09 ± 0.02 |

*$(I_{pf} - I_{p2})/I_{p2}$; $I_{pf}$ and $I_{p2}$ stand for the anodic peak currents corresponding to the final and second potential cycle, respectively

Experimental conditions: starting potential, −0.1 V vs. SCE; scan rate, 50 mV $s^{-1}$; number of potential cycles, 50 (A), 80 (B); contacting solution, 0.1 M KCl or 2 mM $RhCl_3$, pH 3 (A), 0.05 M phosphate buffer (pH 3) containing 0.15 M KCl (B). All given values are reported as the mean for 3 different electrodes

of $K^+$ ion during the potential cycling of the G/PB electrodes induces a stabilization effect, attributable to a gradual transformation of the "insoluble" PB into its "soluble" form [32–34]. Consequently, the simultaneous presence of $K^+$ and $Rh^{3+}$ ions is expected to exert a stronger effect on the G/PB voltammetric response than the effect induced by whatever ion, alone. Indeed, potential cycling in the presence of only one of the above-mentioned ions was found to have a positive effect only when the G/PB electrode was cycled firstly in the presence of $K^+$ ion (results not shown).

Additionally, the "activation" effect specific to the $K^+$ ion and the stabilizing effect characteristic of the $Rh^{3+}$ ion are proved by the electrode stability measurements performed in phosphate buffer. Thus, as expected based on the results presented above, when the G/PB-K and G/PB-Rh electrodes were cycled in 0.05 M phosphate buffer solution containing 0.15 M KCl, a higher increase in electrode activity was noticed in the case of G/PB-K electrodes (Table 1B).

The importance of the electrode pretreatment procedure used to obtain stable G/PB-modified electrodes, is again underlined by comparing the relative stability of G/PB-K electrodes evaluated when they were successively cycled for 80 cycles in 0.05 M phosphate buffer solution containing 0.15 M KCl [+(18 ± 5)%], and for 100 cycles in 2 mM $RhCl_3$ solution containing 0.05 M KCl, [−(7 ± 3)%].

It has been reported that the PB stability is strongly affected by solution pH [4, 23, 35, 36], and the optimal pH range was found as 2–3 [35]. For this reason, all measurements performed in order to investigate G/PB electrode stability were done at pH 3. The crucial role of solution pH used for G/PB electrode pretreatment was proved by evaluating the relative stability for G/PB electrodes in contact with 0.1 M KCl solution at pH 5.8: [−(30 ± 5)%]. In spite of the high concentration of $K^+$ this value was significantly lower than the reference value found at pH 3 (Table 1A).

## 3.2 $Rh^{3+}$ influence on electrocatalytic behavior of G/PB electrodes

Earlier work on the electrocatalytic properties of PB films for hydrogen peroxide reduction [4] showed that this process involved the high-spin redox system $Fe^{3+/2+}$ (~0.2 V vs. SCE) [29]. For this reason, all further results will concern only the A1/C1 peak.

The G/PB-K and G/PB-Rh modified electrodes were investigated as amperometric sensors for $H_2O_2$ electrocatalytic detection, described by the following reaction:

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad (1)$$

The analytical parameters, corresponding to the $H_2O_2$ calibration for both investigated electrodes, are presented in Table 2. Better sensitivities and slightly lower detection limits were found for G/PB-Rh electrodes.

In order to investigate the $Rh^{3+}$ effect on $H_2O_2$ electrocatalytic detection, the apparent electrocatalytic rate constant for $H_2O_2$ reduction at G/PB-K and G/PB-Rh electrodes were estimated using rotating disk electrode (RDE) measurements.

For a given $H_2O_2$ concentration, the dependences of the electrocatalytic current (I) vs. $\omega^{1/2}$ indicate that, in the explored range of the rotation speeds (0–1,000 rpm) the process is under kinetic-diffusion mixed control (results not shown). Consequently, the dependence between 1/I and $\omega^{-1/2}$ was assumed to obey the simple Koutecky-Levich equation:

$$\frac{1}{I_{max}} = \frac{1}{nFAk_{obs}\Gamma C_{H_2O_2}} + \frac{1}{0.62nFA\nu^{-1/6}D^{2/3}\Omega^{1/2}C_{H_2O_2}} \qquad (2)$$

**Table 2** Analytical parameters for $H_2O_2$ amperometric detection at G/PB-K and G/PB-Rh modified electrodes. Experimental conditions: applied potential, −0.05 V vs. SCE; supporting electrolyte, 0.05 M phosphate buffer solution containing 0.1 M KCl (pH 3); rotating speed, 400 rpm

| Electrode | Average sensitivity/ mA $M^{-1}$ | *Linear range/ mM* R/N | Detection limit[a]/μM |
|---|---|---|---|
| G/PB-K | 43.4 ± 2.5* | *0.01–5*<br>0.9972/13 | 29 ± 8* |
| | 50.2 ± 2.2* | *0.01–10*<br>0.9979/12 | 26 ± 10* |
| G/PB-Rh | 62.2 ± 1.8* | *0.01–5*<br>0.9998/13 | 20 ± 10* |
| | 56.9 ± 0.1* | *0.01–10*<br>0.9979/10 | 27 ± 1* |

[a] Estimated for signal/noise ratio equal to 3

*Standard deviation for 2 measurements

where n is the number of electrons involved in the electrode process; F = 96,487 (C $mol^{-1}$) is the Faraday constant; A ($cm^2$) is the electrode surface; $k_{obs}$ ($M^{-1}$ $s^{-1}$) is the apparent rate constant for the electrocatalytic reaction between $H_2O_2$ and PB; $\Gamma$ (mol $cm^{-2}$) represents the surface coverage with PB and was calculated as $\Gamma = Q/nFA$, where Q (C) is the charge estimated from the underpeak area for A1 peak; $C_{H_2O_2}$ (mol $cm^{-3}$) is the $H_2O_2$ bulk concentration, $\nu$ ($cm^2$ $s^{-1}$) is the kinematic viscosity; D ($cm^2$ $s^{-1}$) is the diffusion coefficient of $H_2O_2$ in solution; $\omega$ (rad $s^{-1}$) is the rotation speed.

The results obtained for both investigated modified electrodes are presented in Fig. 2, at three different $H_2O_2$ concentrations. The corresponding $k_{obs}$ values are summarized in Table 3.

As seen from Table 3, the $k_{obs}$ values for the G/PB-K electrode are strongly affected by the $H_2O_2$ concentration, in agreement with results reported for glassy carbon electrodes modified with PB [37]. Assuming that the electrocatalytic process follows a Michaelis-Menten formalism:

$$\frac{1}{k_{obs}} = \frac{K_M}{k_2} + \frac{C_{H_2O_2}}{k_2} \tag{3}$$

the parameters of the linear dependence ($1/k_{obs}$ vs. $C_{H_2O_2}$) allow calculation of the values of the Michaelis-Menten constant ($K_M$ = 3.05 mM) and the rate constant for the second order electrocatalytic reaction ($k_2$ = 2.1 $s^{-1}$).

Surprisingly, in the case of G/PB-Rh electrodes, within experimental error, the $k_{obs}$ values were found to be almost independent of $H_2O_2$ concentration. Thus, an average $k_{obs}$ value of 326.5 $M^{-1}$ $s^{-1}$ was estimated for G/PB-Rh electrode, with a relative standard deviation of 11%. This behavior agreed with results reported earlier for PB-modified glassy carbon electrodes by Itaya [4], but at this time we have no explanation for the difference noticed between G/PB-K and G/PB-Rh modified electrodes.

Concluding, G/PB-Rh electrodes exhibit a slightly lower electrocatalytic activity for $H_2O_2$ reduction than that corresponding to G/PB-K electrodes, as seen if $k_{obs}$ values are compared at the same $H_2O_2$ concentrations (Table 3). Therefore, the electrochemical stability observed for G/PB-Rh electrodes, was gained at the expense of their electrocatalytic efficiency.

Based on Eq. 2, the $H_2O_2$ diffusion coefficient was estimated at 3.2 × $10^{-6}$ $cm^2$ $s^{-1}$ for G/PB-K electrodes, and 5.8 × $10^{-6}$ $cm^2$ $s^{-1}$ for G/PB-Rh electrodes. These values are well placed in the range from 2.3 × $10^{-6}$ to 1.6 × $10^{-5}$ $cm^2$ $s^{-1}$ corresponding to those reported elsewhere [38–41].

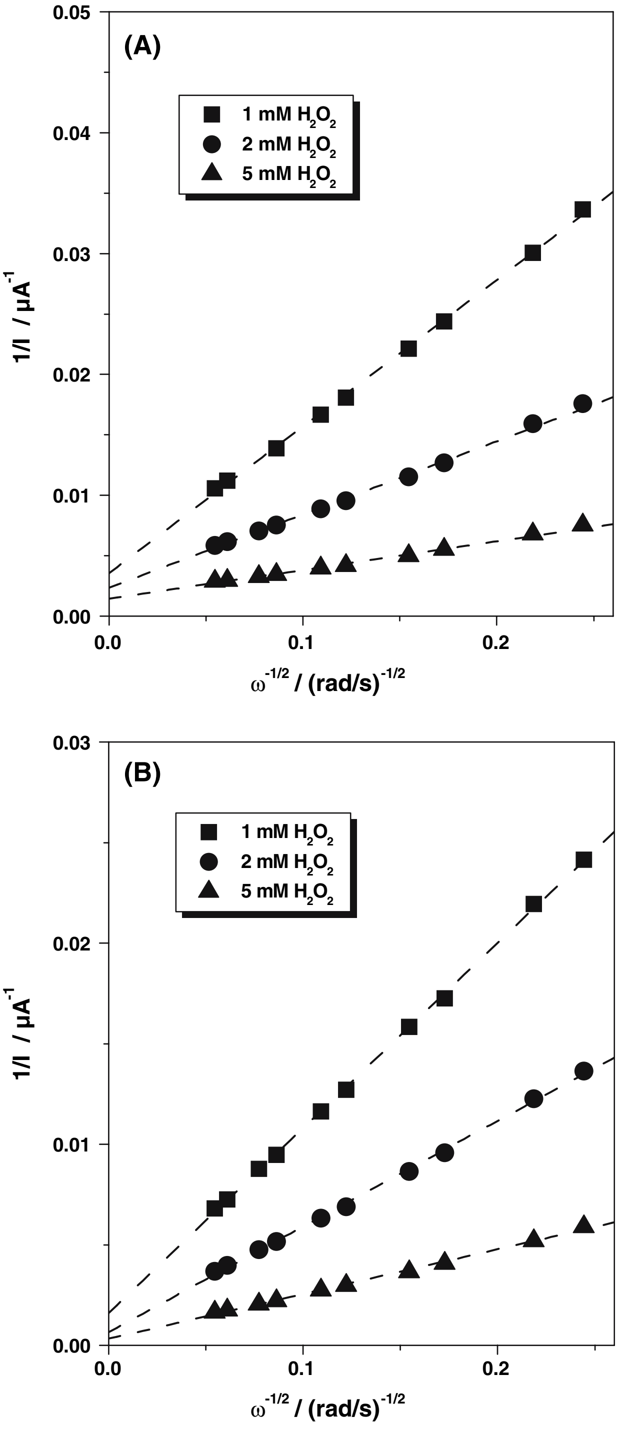

**Fig. 2** Koutecky-Levich plots for electrocatalytic reduction of $H_2O_2$ at G/PB-K (**A**) and G/PB-Rh (**B**) modified electrodes. Experimental conditions: applied potential, −0.1 V vs. SCE; supporting electrolyte, 0.05 M phosphate buffer solution containing 0.1 M KCl (pH 3); rotating speed, 0–1,000 rpm; [$H_2O_2$], $10^{-3}$–5 × $10^{-3}$ M

The short term stability of the modified electrodes was estimated as the electrode relative stability over different periods of time. Between experiments, the electrodes were kept in dry atmosphere, at room temperature and away from light. For example, it was found that, after one day, the G/PB-K modified electrodes tested in $H_2O_2$ showed a

**Table 3** Kinetic parameters for $H_2O_2$ electrocatalytic reduction at G/PB-K and G/PB-Rh modified electrodes

| Electrode | $[H_2O_2]$/mM | Slope × $10^4$/$A^{-1}$ $rad^{1/2}$ $s^{-1/2}$ | Intercept × $10^3$/$A^{-1}$ | R/N | $k_{obs}$/$M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|---|
| G/PB-K | 1 | 12.1 ± 0.2 | 3.6 ± 0.2 | 0.9995/9 | 541.3 |
| | 2 | 6.1 ± 0.1 | 2.4 ± 0.2 | 0.9986/9 | 411.4 |
| | 5 | 2.4 ± 0.1 | 1.5 ± 0.1 | 0.9967/9 | 266.2 |
| G/PB-Rh | 1 | 9.2 ± 0.1 | 1.6 ± 0.1 | 0.9997/10 | 306.2 |
| | 2 | 5.3 ± 0.1 | 0.7 ± 0.1 | 0.9993/10 | 376.2 |
| | 5 | 2.20 ± 0.04 | 0.3 ± 0.1 | 0.9985/10 | 297.1 |

Experimental conditions: see Fig. 2

sudden loss of response of ~62%. In contrast, for G/PB-Rh modified electrodes, the response to $H_2O_2$ gradually diminished, so that at the end of two weeks their activity decreased by ~32%.

## 4 Conclusions

In order to obtain stable G/PB modified electrodes, Prussian Blue was chemically deposited on graphite by spreading appropriate volumes of 100 mM $K_3[Fe(CN)_6]$ and 100 mM $FeCl_3$ solutions, both containing 10 mM HCl. Potential cycling (in the domain of PB electrochemical activity) of the G/PB electrodes immersed in acidic ($pH < 3$) KCl solutions, enhanced their electrochemical activity. The relative stability of the G/PB-modified electrodes was: (i) considerably improved by potential cycling in a 2 mM $RhCl_3$ solution, containing 0.05 M KCl; (ii) strongly affected by the pH value of the surrounding solution (pH values lower than 3 are optimal).

Compared with G/PB-K electrodes, the G/PB-Rh electrodes exhibit a higher relative stability, but a slightly lower electrocatalytic activity towards $H_2O_2$ reduction (estimated quantitatively by the rate constant of the second order electrocatalytic reaction, obtained from RDE measurements). However, the analytical parameters for $H_2O_2$ amperometric detection at G/PB-Rh electrodes are significantly better than those observed for G/PB-K electrodes. Moreover, unlike the G/PB-K electrodes, the electrocatalytic response of G/PB-Rh electrodes does not obey the Michaelis-Menten mechanism for $H_2O_2$ mediated electroreduction.

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