

Electrocatalytic reduction of hydrogen peroxide at Prussian blue modified electrodes: a RDE study

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Abstract Electrocatalytic reduction of hydrogen peroxide at Prussian blue modified electrode has been studied with rotating disk electrode in pH5.5 and 7.3 solutions. It has been shown that the electrocatalytic cathodic reduction obeys Koutecky–Levich relationship at electrode potentials ranging from 0.1 to -0.4 V vs. Ag/AgCl for low concentrations of peroxide not exceeding 0.3 mM. Within this potential window, the calculated kinetic cathodic current ranges within the limits of 2.15–6.09 and 1.00–3.60 $\text{mA cm}^{-2} \text{mM}^{-1}$ for pH5.5 and 7.3, respectively. For pH5.5 and 7.3 solutions, a linear slope of the dependence of kinetic current on electrode potential of -10.8 and $-2.89 \text{ mA cm}^{-2} \text{mM}^{-1} \text{V}^{-1}$, respectively, has been obtained. At a higher concentration of peroxide, exceeding 0.6 mM, deviations from Koutecky–Levich relationship have been observed. These deviations appear more expressed at higher potentials and higher solution pH. The results obtained have been interpreted within the frame of two-step reaction mechanism, including (1) dissociative adsorption of hydrogen peroxide with the formation of OH radicals and (2) one-electron reduction of these radicals to OH^- anions. At a higher concentration of peroxide, and especially at a higher pH, the second process becomes rate limiting.

Keywords Electrocatalysis · Hydrogen peroxide · Prussian blue · Rotating disk electrode · Modified electrode

Introduction

During the past decade, electrocatalytic reduction of hydrogen peroxide at Prussian blue (PB) modified electrodes has attracted a great deal of attention due to its possible application in bioanalysis and biosensors. Some three decades ago, Neff reported deposition of a thin layer of PB at electrodes and electrochemical properties of the resulting modified electrode [1]. Sometime later, the electrochemistry of PB modified electrodes has been extensively studied [2–7], mostly due to their interesting spectral properties, potentially useful for applications in electrochromic systems. Itaya et al. demonstrated the ability of PB modified electrode to electrocatalyze cathodic reduction of oxygen and hydrogen peroxide within the electrode potential range corresponding to the reduced form of PB (Prussian white) and anodic oxidation of hydrogen peroxide at electrode potentials corresponding to oxidized form of PB [8]. This valuable property has been adopted first by Karyakin et al. for amperometric peroxide detection and biosensor applications [9, 10].

The main advantage of PB modified electrodes over traditional platinum electrodes used for peroxide detection and for biosensor applications is a low operation potential (around 0 V vs. Ag/AgCl in nearly pH-neutral solution vs. 0.6–0.7 V necessary for platinum electrodes) because, in contrast to platinum working electrodes, PB modified ones are operated in cathodic manner. As a result, nearly all common interferences usually present in biological probes, like ascorbate, urate, or paracetamol, causes no effect on operation of PB based sensor, resulting in its high selectivity. Since these first publications [9, 10], a huge number of papers have appeared dealing with the use of PB modified electrodes in biosensing. PB modified electrodes have been combined with different oxidase class enzymes

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like glucose, lactate, glutamate, choline, alcohol, lysine, and other oxidases, yielding numerous biosensors for the corresponding metabolites. Also, different electrode configurations have been proposed, including enzyme immobilization over PB layer or in a combination with additional modifier layers like Nafion, polyaniline, polypyrrole, poly(*o*-phenylenediamine), or with the use of paste electrodes. The state of the art in this field has been reviewed in details by different authors [11–13]. Recently, electrochemistry of PB and other polycyano-metalate complexes has been reviewed [14], and new electrode configurations for electroanalytic applications have been proposed [15–18].

Extensive studies on the use of PB modified electrodes as hydrogen peroxide sensors disclosed also some disadvantages of this electrocatalyst. The main drawback of PB as electrocatalyst for peroxide cathodic reduction in nearly pH-neutral solutions is its gradual degradation. PB is unstable in alkaline solutions; thus, hydroxyl ions formed in the course of peroxide reduction cause its degradation and, as a result, loss of its electrocatalytic ability. This instability has been stressed by many researchers. Earlier, we studied the kinetics of PB degradation during electroreduction of peroxide and found the rate of this unfavorable process to be dependent on peroxide concentration and solution pH [19, 20]. The next obstacle is a catalytic reduction of hydrogen peroxide by ascorbate at the surface of PB modified electrode, leading to diminished cathodic current and its dependence on ascorbate concentration in solution [21]. Obviously, a deeper insight into the mechanism of electrocatalytic reduction of hydrogen peroxide at PB modified electrodes is needed to circumvent these and probably other obstacles of this very important and promising process. The present study has been aimed to rotating disk electrode study of electrocatalytic hydrogen peroxide reduction at PB modified electrode.

Experimental

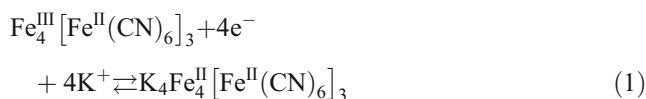
A BASi-Epsilon model potentiostat and BASi RDE-2 rotating disk electrode system (both of Bioanalytical Systems, USA) were used throughout the work. The rotating electrode presented a glassy carbon flat circular electrode, 3 mm in diameter, press-fitted into a plastic holder. As a reference electrode, BASi RE-5B Ag/AgCl electrode, filled with 3 M NaCl solution, has been used. All potential values reported below refer to this reference electrode.

Before use, the surface of the working electrode has been polished with 1.0 and 0.3 μm alumina slurry (Kemet, UK). Electrodeposition of Prussian Blue layer at the working electrode has been performed in a freshly prepared solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$,

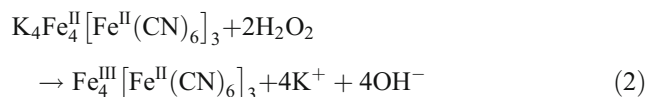
and 2.5 mM FeCl_3 by applying a controlled potential of 0.4 V for 1 min. After that, the electrode has been rinsed with water. Electrochemical experiments have been performed in 0.05 M phosphate buffer solution at pH 5.5 or 7.3, containing additionally 0.1 M of KCl. Hydrogen peroxide has been added to test solution to obtain its final concentration ranging from 0.1 to 0.8 mM. The rotating disk electrode has been rotated at a controlled velocity ranging from 0 to 2,000 rpm.

Results and discussion

In pH 5.5 solution, PB modified glassy carbon electrode shows under cyclic potentiodynamic conditions a pair of well-developed cathodic and anodic peaks, characterized by the midpoint potential of 0.19 V and peak separation of 0.06 V. These peaks correspond to the well-known reversible redox process of interconversion of PB (oxidized form) and Prussian White (reduced form) and could be summarized by reaction scheme:



In the presence of hydrogen peroxide, again, a cathodic peak located at 0.16 V is observed at a cathodic potential scan, along with a cathodic current plateau within the potential limits of 0.05 to -0.25 V (Fig. 1). This plateau corresponds to electrocatalytic reduction of hydrogen peroxide with the participation of PB as electrocatalyst, as it could be described by Eqs. 5 and 4:



As a result, a net reaction of a cathodic peroxide reduction proceeds [22]:



Rotation of PB modified electrode in peroxide containing solution causes a slight shift of cathodic peak potential by 7–10 mV to higher values and an increase of peroxide reduction current in an entire potential range below the peak potential (Fig. 1). At a relatively slow rotation, not exceeding 100 rpm, again, a plateau of cathodic current is observed below 0.1 V, whereas an increase of cathodic current at negative potential shift is observed at a higher rotation speed (Fig. 1).

In pH 7.3 solution, a flat cathodic peak for PB reduction is observed, located at 0.09 V for non-rotated PB modified electrode. The rotation of electrode results in an increase of

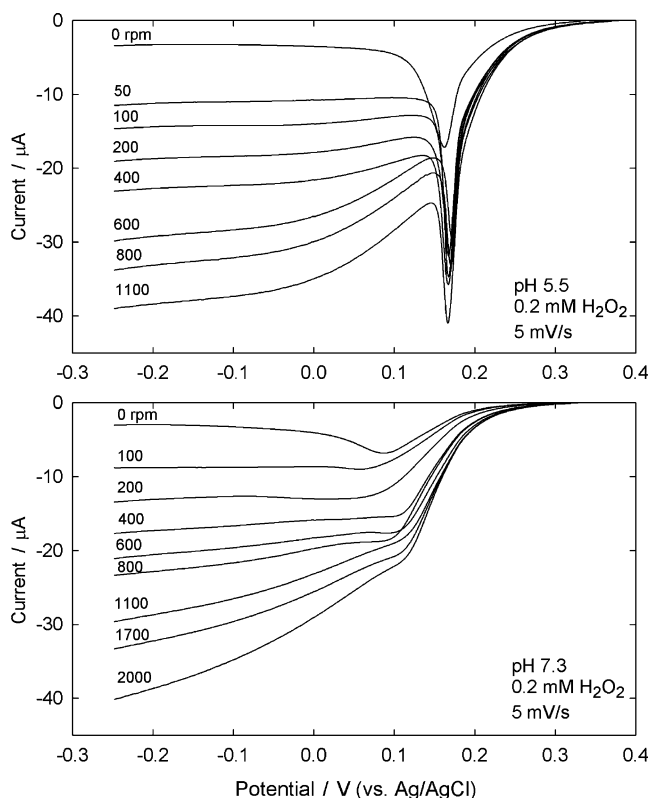


Fig. 1 Voltammograms of PB modified rotating disk electrode, obtained within scan limits of 0.4 to −0.25 V at a scan rate of 5 mV s^{−1} in pH5.5 (top) or pH7.3 (bottom) phosphate buffer solution containing 0.1 M of KCl and 0.2 mM of hydrogen peroxide at different rotation speed (as indicated)

cathodic current at potentials more negative than the peak potential (Fig. 1). In the present case, the cathodic current appears to be somewhat lower, as compared to pH5.5 solution.

Figure 2 presents the dependence of cathodic current on square root of electrode rotation angular velocity, as obtained at a constant peroxide concentration of 0.1 mM within a wide rotation velocity range of 40 to 2,000 rpm at solution pH of 5.5. It is well seen that the limiting cathodic current increases by the shift of electrode potential towards negative values. At any given rotation velocity, nearly a twofold increase of a limiting current is observed by shifting the potential from 0.1 to −0.4 V. The limiting current for rotating disk electrode is described by the Koutecky–Levich equation [23]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{l,c}} = \frac{1}{i_k} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c} \quad (4)$$

where i is a total current, i_k is the kinetic current (in absence of any mass transfer effects), $i_{l,c}$ is the mass transfer limited cathodic current, n is the the number of transfered electrons, F is the Faraday constant, A is the rotating electrode area, D is the diffusion coefficient for hydrogen peroxide, ω is the

rotation angular velocity, ν is the kinematic viscosity of solution, and c is the hydrogen peroxide concentration.

Figure 2 (bottom) presents treatment of the data obtained in inverse coordinates according the Koutecky–Levich equation. Except for the data obtained at the highest electrode potential of 0.1 V, straight lines have been obtained with a good correlation. Extrapolation of these data to indefinite high rotation velocity ($1/\omega^{0.5} \rightarrow 0$) yields intercepts at the inverse current axis, from which kinetic current (i_k) could be calculated. For particular conditions used in obtaining the data presented in Fig. 2 (pH5.5, 0.1 mM of hydrogen peroxide), i_k values ranging from 0.49 to 0.63 mA cm^{−2} can be obtained for electrode potential of 0.1 and −0.4 V, respectively. Thus, the kinetic current density, normalized for 1 mM of hydrogen peroxide and ranging from 4.9 to 6.3 mA cm^{−2} mM^{−1}, has been obtained for pH5.5 solution at electrode potential ranging from 0.1 to −0.4 V, respectively, assuming a linear current-concentration dependence.

Most sensor applications of a PB modified electrode relate to pH-neutral solutions corresponding to an optimum

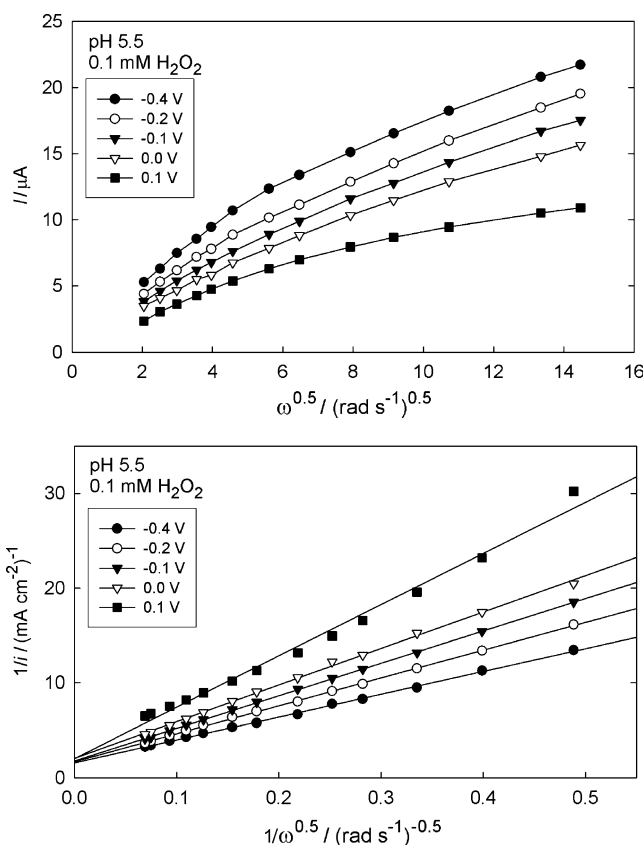


Fig. 2 Dependence of cathodic current on square root of rotation speed, as obtained for PB modified electrode in pH5.5 solution containing 0.1 mM of hydrogen peroxide, at different electrode potentials (top), and transformation of the data in inverse coordinates according to Koutecky–Levich equation (bottom)

pH of oxidase enzymes like glucose oxidase. Thus, Fig. 3 presents an example of the corresponding data obtained in pH7.3 buffer solution. In this case, again, nearly twofold increase of electrocatalytic current has been observed by shifting of electrode potential from 0.1 to -0.4 V. The data, obtained within a broad rotation velocity range of 40–2,000 rpm, does well linearize in inverse coordinates. From linearized data, i_k values ranging from 0.61 to 1.30 mA cm^{-2} have been obtained for electrode potential ranging from 0.1 to -0.4 V, respectively, in pH7.3 solution containing 0.3 mM of hydrogen peroxide. As normalized for 1 mM of peroxide, kinetic current density ranging from 2.03 to $4.33 \text{ mA cm}^{-2} \text{ mM}^{-1}$ can be obtained in this solution for potentials ranging from 0.1 to -0.4 V. As compared to pH5.5 solution, the kinetic current densities appear to be approx. 1.5- to twofold lower for pH7.3 solution. This indicates somewhat lower efficiency of electrocatalytic reduction of hydrogen peroxide in nearly pH-neutral solution as compared to a slightly acidic one.

The data of rotating disk electrode study can be satisfactory linearized in Koutecky–Levich coordinates both in pH5.5 and pH7.3 solutions for relatively low concentration of hydrogen peroxide, not exceeding approx. 0.3 or 0.4 mM. At a higher concentration, exceeding

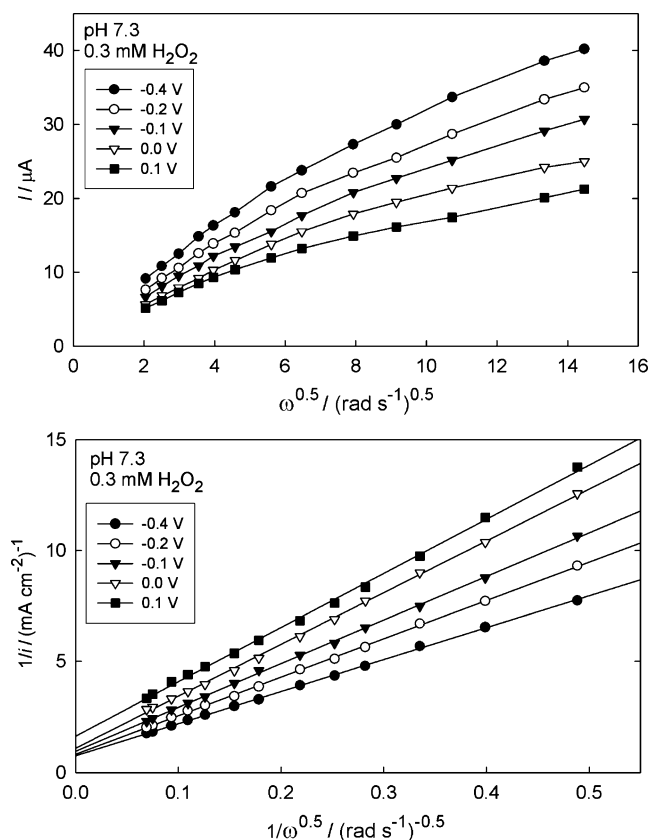


Fig. 3 Same as in Fig. 2, obtained in pH7.3 solution containing 0.3 mM of hydrogen peroxide

approx. 0.6 mM, remarkable deviations from linearity are observed. Figure 4 presents the corresponding linearized data for 0.8 mM of hydrogen peroxide, as obtained in both solutions studied. It is seen that serious deviations are observed for higher electrode potentials and higher rotation velocities. Also, much more expressed deviations have been obtained for pH7.3 solution, compared to pH5.5 one. From the linear parts of these dependencies, again, kinetic current densities could be estimated. For pH5.5 solution, normalized according to peroxide concentration i_k values ranges between 2.15 and $6.09 \text{ mA cm}^{-2} \text{ mM}^{-1}$ for potentials ranging between 0.1 and -0.4 V. For pH7.3 solution, normalized i_k values ranging between 1.00 and $3.60 \text{ mA cm}^{-2} \text{ mM}^{-1}$ have been obtained for the same potential window. Although being somewhat lower, the data obtained correlate with the corresponding data for lower concentrations of hydrogen peroxide.

In a physical sense, the deviations from linearity obtained at a high peroxide concentration correspond to a decrease of cathodic current at increasing rotation velocity. This effect could be probably related to the mechanism of cathodic reduction of hydrogen peroxide at a PB modified electrode. A net reaction of cathodic reduction of hydrogen peroxide (Eq. 3) implies the transfer of two electrons per one peroxide molecule. It is well known that the mixed potential for hydrogen peroxide at a platinum or gold electrode does not depend on peroxide concentration, but depends on solution pH according to known equation [24]:

$$E = 0.84 - 0.059 \text{ pH}, \quad (5)$$

whereas potential-determining reactions are as follows:

1. Cathodic:



2. Anodic:



All these reactions involve one-electron transfer processes with the participation of transient species like OH radicals. It is also known [24] that electrochemical reduction of

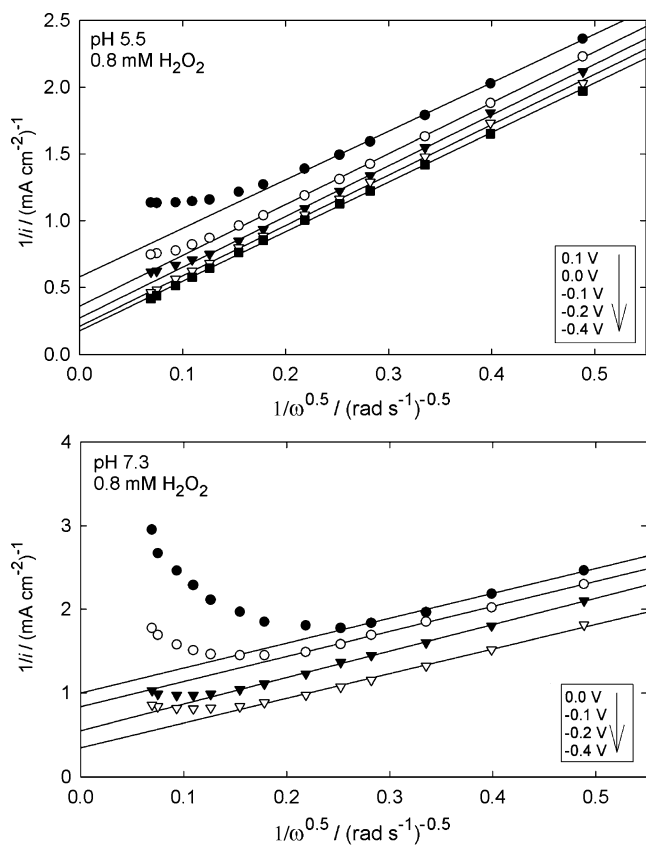
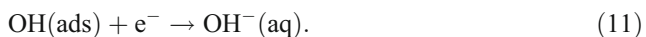


Fig. 4 Transformation of the data obtained at different electrode potentials (as indicated) according to Koutecky–Levich equation for cathodic reduction of 0.8 mM hydrogen peroxide at PB modified electrode in pH5.5 (top) or pH7.3 (bottom) solution

hydrogen peroxide involves an adsorption step, followed by the split of peroxide molecule to OH radicals:



and the next following one-electron reduction of OH radicals to hydroxyl anions:



It is clear that in case if the reduction of OH radicals proceeds much faster than the dissociative adsorption of hydrogen peroxide, the linearity between an inverse cathodic current and $1/\omega^{-0.5}$ should be retained even at the highest rotation velocity. In an opposite case, viz., at a slow electron transfer to OH radicals, it is probable that at a high rotation velocity, the OH radicals are removed from electrode surface by the centrifugal force without being electrochemically reduced to hydroxyl anions. In this case, a decrease of cathodic current at elevated rotation should be observed. Thus, taking into account the present model, consisting of dissociative adsorption 10 and electron transfer 11 steps, it could be concluded that an overall

reduction process is probably limited by the rate of electron transfer to OH radicals. Alternatively, supposing a one-by-one electron transfer mechanism as described by Eqs. 6 and 7 to be valid, it also could be concluded that the transfer of the second electron (viz., cathodic reduction of OH radicals to hydroxide anions) becomes rate limiting. Obviously, the rate of this limiting step depends on electrode potential (being remarkably higher for lower electrode potentials) and on solution pH (being lower for higher pH value) as it follows from the data presented in Fig. 4.

The values of kinetic current density obtained depend on electrode potential. For pH5.5 solution, nearly linear dependence of i_k on electrode potential is observed, as presented in Fig. 5 (top). Extrapolation of these dependences, obtained at higher peroxide concentrations (0.3–0.8 mM), to zero kinetic current ($i_k \rightarrow 0$) yields a mean value for electrode potential of 0.34 V. This potential presents an upper potential limit for cathodic reduction of peroxide to proceed. In accordance with Eq. 5, the mixed potential for hydrogen peroxide at pH5.5 should be 0.52 V, i.e., approx. 0.32 V vs. Ag/AgCl reference. Thus, the value

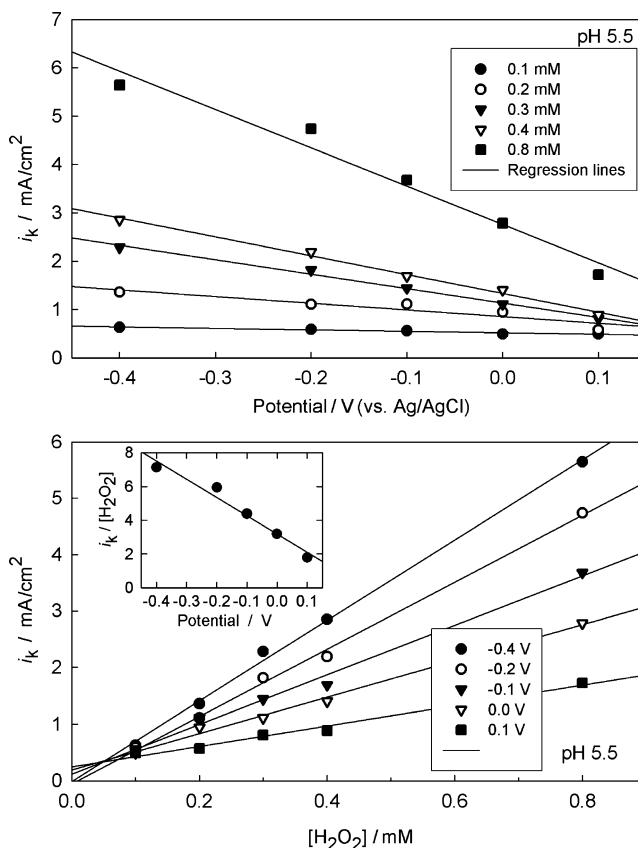


Fig. 5 Dependence of calculated i_k values on electrode potential as obtained in pH5.5 solution at different hydrogen peroxide concentrations (top) and on hydrogen peroxide concentration as obtained at different electrode potentials (bottom). Inset shows dependence of the ratio of i_k to peroxide concentration on electrode potential

of an upper potential limit for peroxide reduction, obtained from extrapolation of the data to $i_k \rightarrow 0$, coincides within error limits with the mixed potential known [24]. Also, nearly linear dependence of kinetic current on peroxide concentration has been obtained within an entire potential window studied, as presented in Fig. 5 (bottom). From these dependencies, a linear dependence of normalized kinetic current (the ratio of $i_k/[H_2O_2]$) on electrode potential has been obtained, as presented in an inset of Fig. 5. The latter dependence could be described by the correlation as follows:

$$\frac{i_k}{c} = \left(\frac{i_k}{c} \right)_0 + aE \quad (12)$$

where i_k/c presents normalized kinetic current (in $\text{mA cm}^{-2} \text{mM}^{-1}$), $(i_k/c)_0$ is its value at a zero potential, $(i_k/c)_0 = (3.19 \pm 0.25) \text{ mA cm}^{-2} \text{mM}^{-1}$, E is the electrode potential (in V vs. Ag/AgCl reference), and a is an empiric coefficient, presenting the slope of linear dependence, $a = (-10.8 \pm 1.17) \text{ mA cm}^{-2} \text{mM}^{-1} \text{V}^{-1}$.

Again, extrapolation of the latter dependence to the zero normalized kinetic current intercepts the potential axis at approx. 0.29 V, which does not differ markedly from the potential of zero kinetic current as calculated above and from the known mixed peroxide potential as well.

For pH7.3 solution, however, no linear dependence of kinetic current on electrode potential has been obtained (Fig. 6, top). A probable reason for this is a deviation of experimental data from linearity in Koutecky–Levich coordinates, as discussed above. For pH7.3 solution, this deviation appears more evident than for pH5.5 one, as shown in Fig. 4. In this case, again, a linear dependence of normalized kinetic current on electrode potential has been obtained, characterized by lower values of $(i_k/c)_0 = (2.21 \pm 0.07) \text{ mA cm}^{-2} \text{mM}^{-1}$ and $a = (-2.89 \pm 0.33) \text{ mA cm}^{-2} \text{mM}^{-1} \text{V}^{-1}$ (Fig. 6, bottom).

Conclusions

Efficient electrocatalytic reduction of hydrogen peroxide takes place at Prussian blue modified electrode at potentials where the oxidized form of this modifier exists. At a low peroxide concentration, not exceeding 0.3 mM, electrooxidation obeys Koutecky–Levich relationship, from which kinetic electrocatalytic reduction current could be calculated. Depending on reaction conditions, kinetic current densities calculated range within the limits of ca. 1–6 $\text{mA cm}^{-2} \text{mM}^{-1}$. Shifting the operating potential from 0.1 to -0.4 V vs. Ag/AgCl results in ca. threefold increase of kinetic current. At any given potential, kinetic current appears to be ca. twofold higher in pH5.5 solution, as compared to pH7.3 one. At higher

peroxide concentrations, exceeding 0.6 mM, deviations from Koutecky–Levich behavior were observed, resulting in decreased cathodic current at higher rotation velocity. These deviations are more expressed in pH7.3 solution and at higher electrode potentials. The results obtained have been interpreted within the frame of two-step reaction mechanism, including (1) dissociative adsorption of hydrogen peroxide with the formation of OH radicals and (2) one-electron reduction of these radicals to OH^- anions. At a higher concentration of peroxide and especially at a higher pH, the second process becomes rate limiting. From the results obtained, some recommendations for electroanalytical applications of PB modified electrodes could be derived: (1) higher kinetic currents and thus a better sensitivity to hydrogen peroxide is obtained in slightly acidic solutions compared to pH-neutral ones. In a combination with higher operational stability described earlier [19–21], this makes PB modified electrodes especially useful for peroxide assay in slightly acidic solutions; (2) because of deviation from Koutecky–Levich relationship at higher peroxide concentrations, observed in nearly pH-neutral solutions, the linear dependence of cathodic current on peroxide concentration should be observed within a narrower concentration range for neutral solutions, compared to slightly acidic ones.

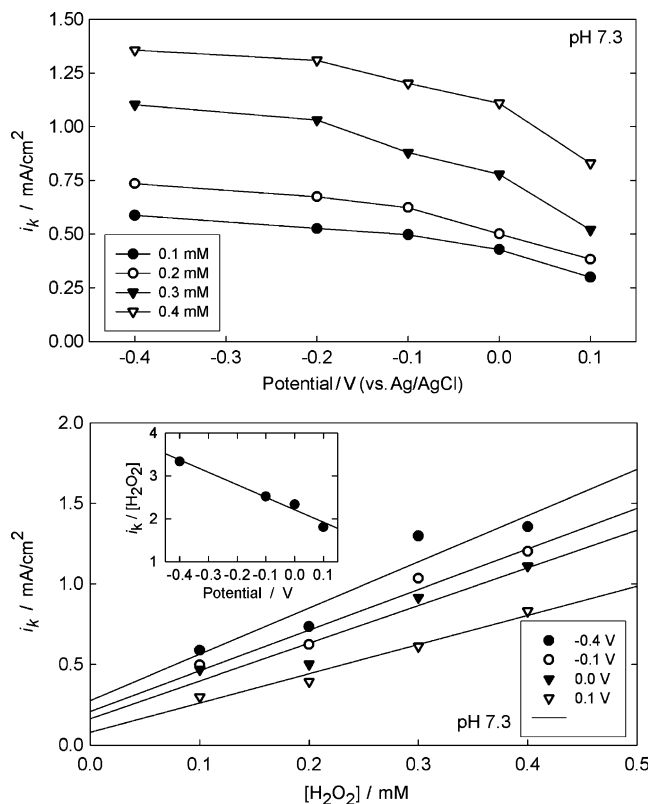


Fig. 6 Same as in Fig. 5, as obtained in pH7.3 solution

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