ORIGINAL PAPER

Electrochemical reduction and kinetics of hydrogen peroxide on the rotating disk palladium-plated aluminum electrode modified by Prussian blue film as an improved electrocatalyst

M. H. Pournaghi-Azar · F. Ahour

Abstract This paper describes the use of an aluminum electrode plated by metallic palladium and modified by Prussian blue (PB/Pd-Al) in the electrocatalytic reduction of hydrogen peroxide (H_2O_2). The effect of pH on the electroreduction of H_2O_2 on the modified electrode is investigated and a simple irreversible reduction pathway is suggested. The electroreduction kinetics including transfer coefficient α, potential-dependent charge transfer rate constants k_f, and diffusion coefficient D are estimated by means of forced hydrodynamic voltammetry using a rotating disk PB/Pd-Al electrode. The mean values obtained for kinetics are 0.38, 10^{-2} cm^{-1}, and 7.6×10^{-6} cm^2 s^{-1}, respectively. The long-term stability of the modifying layers on the Al substrate was studied.

Keywords Modified aluminum electrode · Prussian blue · Hydrogen peroxide · Electrocatalysis · Hydrodynamic voltammetry

Introduction

The monitoring of H_2O_2 with a reliable, rapid, and economic method is of great significance for numerous processes such as clinical and food industrial process, pharmaceutical, environmental analysis, and biosensing [1–7]. Electrochemical methods are preferred over other techniques because of their simplicity and relatively low cost on the basis of direct oxidation or reduction of H_2O_2. Because the oxidation of H_2O_2 is performed at a quite positive potential, severe interference can occur unless selectivity is achieved with attendant separation method or through a chemical step. However, reduction at low over-potential would offer a better approach. In general, bulk noble metals, even deposited noble metals on other matrices, were not suitable for low over-potential or selective reduction of H_2O_2 in the presence of O_2 [8]. An effective approach for low over-potential and selective reduction of H_2O_2 was made using chemically modified electrodes [9–18]. Prussian blue (PB)-modified electrode is probably the most advantageous hydrogen peroxide transducer [19]. The insoluble PB on the electrode can be reduced to Prussian white (PW) at approximately 0.1 V versus saturated calomel electrode (SCE). A Prussian blue basal pyrolytic graphite-modified electrode has been reported for electrocatalytic reduction as well as electro-oxidation of H_2O_2 in 0.1 M KNO_3 + 0.05 M phosphate buffer pH 6.5 [11]. Under certain deposition conditions or certain electrode matrices, the PB film can selectively catalyze the electroreduction of H_2O_2 in the presence of molecular oxygen in 0.1 M KCl, 0.02 M phosphate pH 7.5 [12], and in 0.1 M KCl + phosphate buffer pH 6 [13, 17, 18]. However, these electrodes still face a number of drawbacks with regards to long-term stability, when the potential is scanned towards the negative values during H_2O_2 reduction [19]. To record a current–potential curve of H_2O_2 reduction by the PB-modified electrode, it was necessary to cover the PB-modified electrode surface with

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a Nafion layer [11, 12, 17]. The electrocatalytic reduction of H_2O_2 on the PB-modified GC electrode was exploited for its amperometric measurement at various media, and the reproducible results were obtained at pH 3 [16]. Catalytic reduction of H_2O_2 occurs also at a PB-modified F-doped tin oxide electrode (PB/FTO) at pH 2. Dissolved oxygen affects H_2O_2 detection at the modified electrode and contributes additive current responses [14].

It was interesting from both fundamental and applied point of view to investigate the mechanism and kinetics of H_2O_2 reduction on PB-modified electrodes of improved stability at the operational potential range. To our knowledge, until now, there is no detailed and perfect study on the electrochemical behavior and kinetic characteristic of H_2O_2 reduction, displaying some experimental voltammograms related to its reduction, on the PB-modified electrodes at various pH and determination of its kinetics. Recently, we have reported an electroless preparation path of the PB films on the bare Al surface as well as on the Al surface plated by metallic palladium (Pd-Al), describing that the PB film on the bare Al surface is electroinactive, whereas it is well electroactive on the PB/Pd-Al electrode in which the Pd layer acts as a conducting body, insuring electron transfer between Al and Prussian blue film [20]. The major advantages of PB/Pd-Al electrode are the simplicity, rapidity of preparation (only a few minutes), high stability of the PB film on the Pd-Al surface, and its effective catalytic activity for the electrooxidation of some organic compounds [21–23].

The main purpose of the present work is to study the electrochemical behavior and kinetics characterization of H_2O_2 on the PB/Pd-Al electrode using cyclic voltammetry and forced convection voltammetry.

Experimental

Chemicals

Palladium chloride, ammonia solution (25%), potassium hexacyanoferrate (III) trihydrate, ferric nitrate non-anhydrate, nitric acid, potassium hydroxide, sodium acetate, hydrochloric acid, nitric acid, and H_2O_2 were of analytical grade from Merck. The electrolyte solution was 0.5 M KNO_3 with 0.2 M acetate and the pH adjusted with nitric acid or acetate solutions. All solutions were prepared with twice distilled water.

Instrumentation

All voltammetry experiments were performed using a potentiostat/galvanostat *AUTOLAB*, model *PGSTA30*. The working electrode was a homemade aluminum disk electrode

prepared from an aluminum bar with a purity of 99.9±0.2%. The aluminum bar was mounted in a Teflon tube, exposing a geometrical area of 0.071 cm^2, which was modified as detailed below. A conventional three-electrode cell, consisting of a PB/Pd-Al-modified electrode as the working electrode, SCE as the reference electrode, and a platinum wire as the counter electrode, was used at room temperature.

Electrode preparation

A cylindrical aluminum bar of 12 mm in diameter and 90 mm in length was used for the preparation of the disk aluminum electrode as follows: One end of the Al bar was threaded by means of a suitable screw tap in order to connect it to an available holder and rotating disk system. The other end of the bar (30 mm in length) was ground in order to obtain a diameter of 3 mm, then was fitted into the hole which was previously made in a Teflon rod of 12 mm in diameter and 30 mm in length [24]. The aluminum disk electrode mounted in a Teflon tube was polished with emery paper (320 grit) first and then with a finer grade (1,500 grit) to obtain a relatively mirror-like surface. The electrode was rinsed and then cleaned in concentrated nitric acid for 1 min and finally rinsed with twice distilled water before use. The two-step chemical modification of the Al disk substrate involves an initial Al surface palladization and subsequently, PB film deposition by simple dipping procedure performed as described earlier [20].

Results and discussion

Cyclic voltammetry

Figure 1 shows the cyclic voltammograms of the PB/Pd-Al electrode in the presence and absence of H_2O_2 in 0.5 M KNO_3 + 0.2 M acetate of pH=2. As seen in Fig. 1 (curve a), the characteristic redox peaks of the mediator (I and I') appeared at potentials around E_{pc}=0.15 V and E_{pa}=0.2 V corresponding to the $Fe^{III/II}$ $[Fe^{II}(CN)_6]^{1-/2-}$ redox system. Upon the addition of 10 mM H_2O_2 in the solution, a new cathodic peak (II) appeared at potential about 0.2 V (curve b). In the non-modified Pd-Al electrode, the reduction peak (III) of H_2O_2 appeared at −0.2 V (curve c), about 0.4 V less negative potentials. Note that in a bare Al electrode, a current for the reduction of H_2O_2 is not observed (curve d). This indicates that the PB layer on the Pd/Al electrode provides the electron transfer ability between H_2O_2 and electrode, i.e., H_2O_2 is reduced electrocatalytically. The effect of the solution pH in 0.5 M KNO_3 + 0.2 M acetate, over 2–6 in which the modified electrode is stable [20], was investigated. As seen in Fig. 2, the peak potential shifted to more positive potential as the solution pH decreased. The
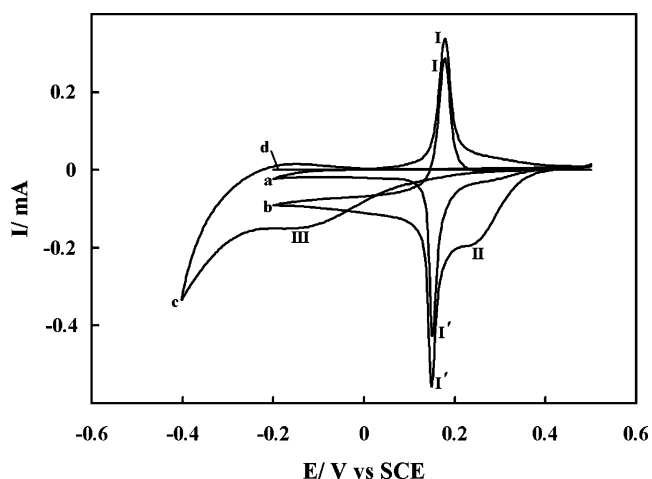
Fig. 1 Cyclic voltammograms of (a) PB/Pd-Al in 0.5 M KNO$_3$ + 0.2 M acetate solution pH 2, (b) a +10 mM H$_2$O$_2$, (c) the same as *b*, at Pd-Al electrode and (d) the same as *b*, on the bare Al electrode. Scan rate 20 mV s^{-1}

reduction peak of H$_2$O$_2$ is nearly confused with PB reduction peak at about pH 6. Therefore, in order to obtain a well-defined and separated voltammogram, further studies were performed at pH 2. Similarly, the effect of anion of some pH-adjusting acids was investigated and the results are shown in Fig. 3. As seen in Fig. 3, the modifier on the
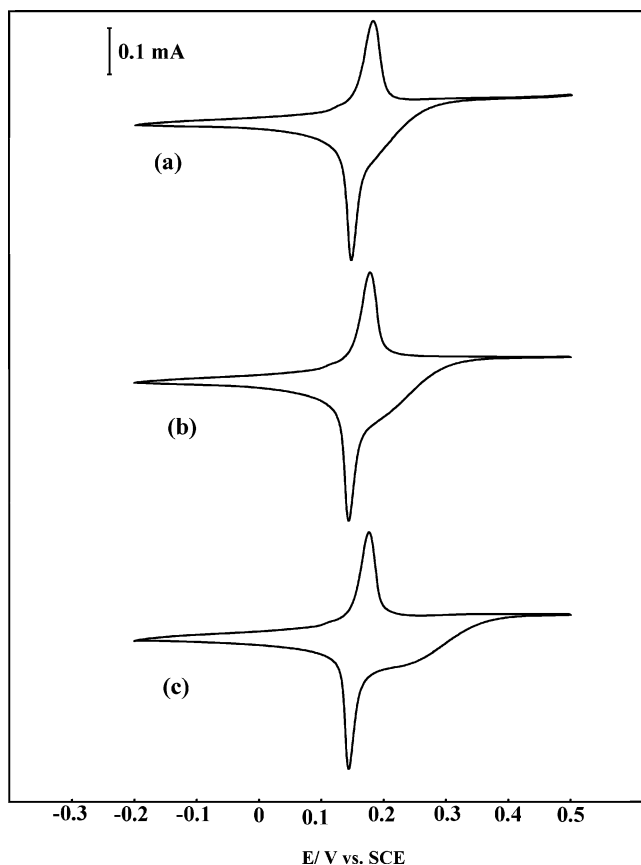
electrode is degraded by the addition of 7 M H$_2$O$_2$ in the 0.5 KNO$_3$ or 0.5 M KNO$_3$ + 0.2 M glycinate, while it is stable in 0.5 M KNO$_3$ + 0.2 M acetate of pH 2.

Figure 4 shows the cyclic voltammograms of the PB/Pd-Al electrode in the presence of 10 mM H$_2$O$_2$ at various scan rates (2–20 mV s^{-1}). The peak potential for the reduction of H$_2$O$_2$ shifts to less positive potentials when increasing the scan rate (inset A) suggesting a kinetic limitation in the electrode reaction. Also, the reduction current for H$_2$O$_2$ increased linearly with the square root of the scan rate (inset B) confirming that the reduction reaction is a mass transfer-controlled process. The cyclic voltammograms for H$_2$O$_2$ reduction of various concentrations (3–40 mM) in 0.5 M KNO$_3$ + 0.2 M acetate of pH 2 are displayed in Fig. 5. The results show that the peak current of H$_2$O$_2$ reduction is linearly dependent on its concentration (inset in Fig. 5).

Considering that the electroreduction of H$_2$O$_2$ occurred at a moderate low potential region, the interference of molecular oxygen by its simultaneous reduction in this region is probable. Figure 6 shows the cyclic voltammo-grams of 10 mM H$_2$O$_2$ solutions at the PB/Pd-Al-modified electrode in the presence (a) and in the absence (b) of dissolved O$_2$ (deaerated solution). As seen in Fig. 6, the response of the modified electrode for molecular oxygen is
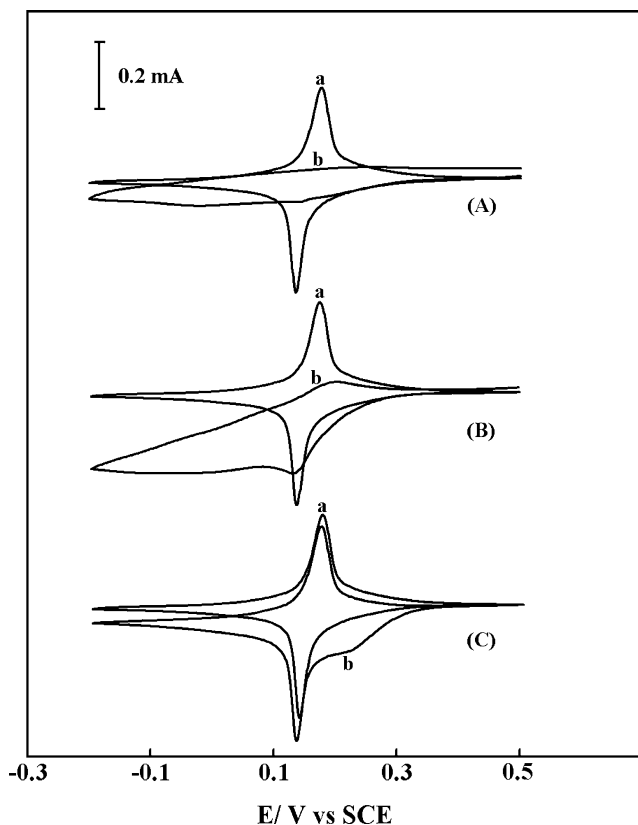

Fig. 2 Effect of pH: *a* pH 2, *b* pH 4, and *c* pH 6. Scan rate 20 mV s^{-1}

Fig. 3 Effect of adjusting pH buffer: *A* 0.5 M KNO$_3$, *B* 0.5 M KNO$_3$ + 0.2 M glycine, and *C* 0.5 M KNO$_3$ + 0.2 M acetate *a* in the absence and *b* in the presence of 7 mM H$_2$O$_2$. Scan rate 20 mV s^{-1}
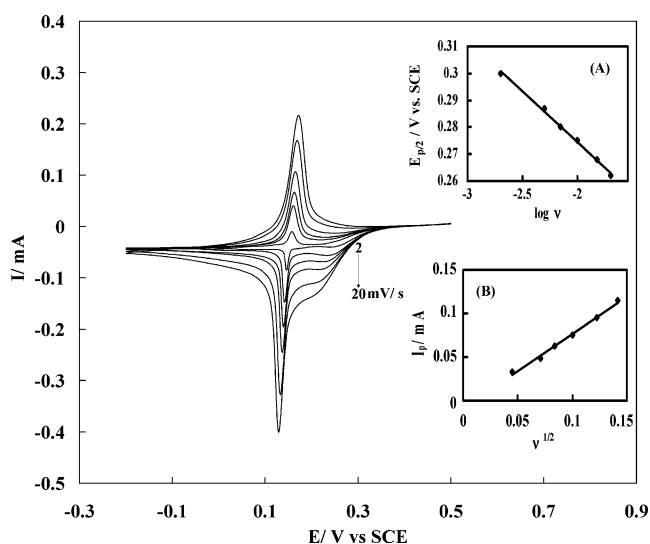
Fig. 4 Cyclic voltammograms of the PB/Pd-Al-modified electrode in the presence of 4.5 mM H_2O_2 at scan rates of 2, 5, 7, 10, 15, and 20 mV s^{-1}, respectively at pH 2. *Insets*: *A*, plot of $E_{p/2}$ versus log *v*; *B*, plot of I_p versus $v^{1/2}$. Supporting electrolyte as in Fig. 1

Fig. 6 Cyclic voltammograms of 10 mM H_2O_2 in PB/Pd-Al-modified electrode in the presence (*a*) and in the absence of dissolved oxygen (*b*). Supporting electrolyte as in Fig. 1

negligible, confirming the selectivity of the modified Pd-Al electrode by PB for the electrocatalytic reduction of H_2O_2 in the presence of dissolved oxygen in the operational conditions.

In order to obtain information on the number of electrons involved in the rate determining step n_α, a Tafel plot is drawn (Fig. 7) using the rising part of the current–voltage curves (where there is no any concentration polarization) at a low scan rate, e.g., 20 mV s^{-1}. Subjecting the cyclic voltammogram recorded for the 7 mM solution of H_2O_2, a slope of $F\alpha n_\alpha/RT=12.9$ (V/decade)$^{-1}$ was obtained for the Tafel plot, presenting that the value of αn_α is equal to 0.764 and the rate limiting is a two-electron process, assuming a

transfer coefficient α of 0.38. The value of αn_α can be obtained by another method, i.e., according to Eq. 1, valid for a totally irreversible diffusion-controlled process [25]:

$$E_p - E_{p/2} = 47.7/\alpha\,n_\alpha \tag{1}$$

On the basis of Eq. 1, a mean value of 62 mV for $E_p-E_{p/2}$ using the cyclic voltammograms recorded with various low scan rates was obtained. This confirms that αn_α equals to 0.764 and the rate limiting is a two-electron process, assuming a transfer coefficient α of 0.39. Similarly, to get information on the final product of H_2O_2, reduction on the modified electrode, we have evaluated the total electrons (*n*) involved in its reduction at a time scale of cyclic voltammetric technique. For the totally irreversible
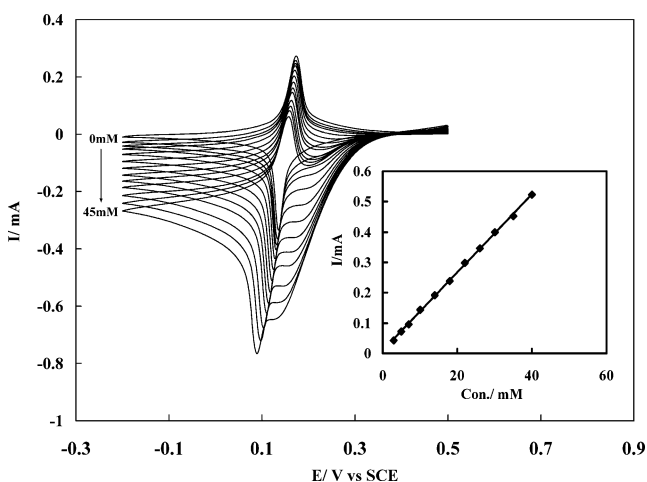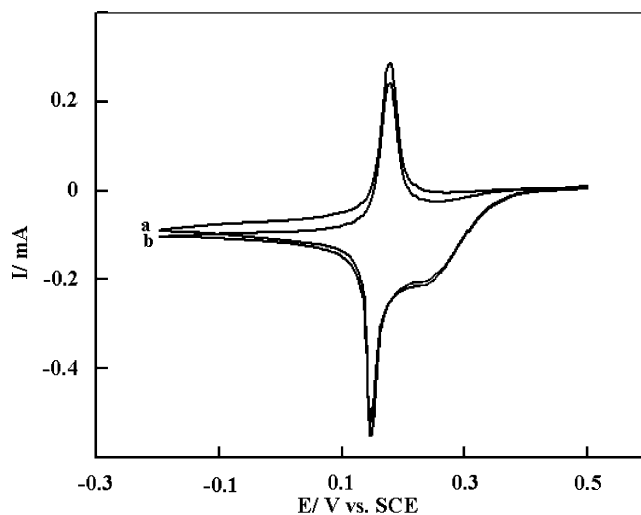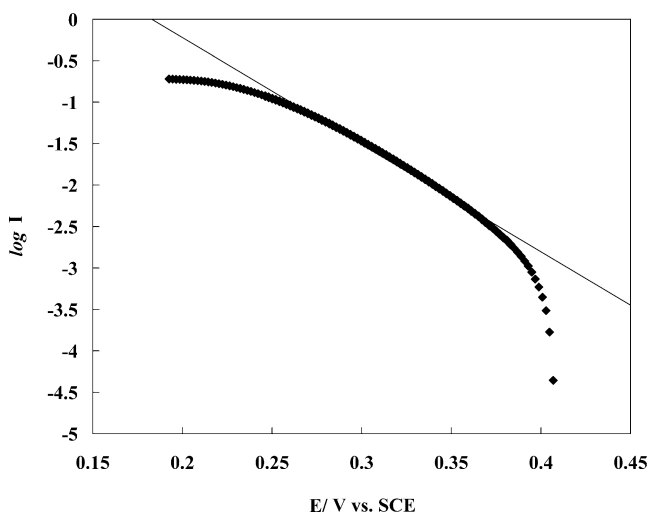

Fig. 5 Cyclic voltammograms for various concentrations of H_2O_2 (0, 3, 5, 7, 10, 14, 18, 22, 26, 30, 35, 40, and 45 mM, respectively). *Inset*: calibration graph, in 0.5 M KNO$_3$ + 0.2 M acetate solution of pH 2. Scan rate 20 mV s^{-1}

Fig. 7 Tafel plot obtained from current–potential curves recorded at the PB/Pd-Al electrode in the presence of 7 mM H_2O_2 at a scan rate of 20 mV s^{-1} at pH 2

diffusion-controlled electrode processes, the following equation can be used for the evaluation of n [25]:

$$I_p = 2.99 \times 10^5 n[(1-\alpha)n_\alpha]^{1/2} A\ C\ D^{1/2}v^{1/2} \qquad (2)$$

The plot of I_p of voltammograms versus C is linear with slopes of 0.0129 (inset in Fig. 5). Using these slopes and considering αn_α equal to 0.764, $D = 7.1 \times 10^{-6}$ cm^2 s^{-1} (determined by voltammetry on the rotating disk PB/Pd-Al electrode as below), $A = 0.07$ cm^2, and $v = 20$ mV s^{-1}, it is found that the total number of electrons involved in the cathodic reduction of H$_2$O$_2$, is about 2. A similar result was obtained using the slope of I_p versus $v^{1/2}$ plot (inset B, Fig. 4) using Eq. 2.

On the basis of the results obtained from the cyclic voltammetry, the reduction pathway of H$_2$O$_2$ can be shown simply as follows:

$$H_2O_2 + 2e + 2H^+ \rightarrow 2H_2O \quad \text{Slow.} \qquad (3)$$
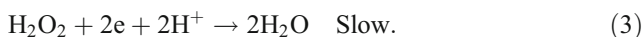
Voltammetry on the rotating disk PB/Pd-Al electrode

Current–potential curves by forced convection for the reduction of H$_2$O$_2$ of various concentrations were recorded by a homemade rotating disk PB/Pd-Al-modified electrode (RDE) and are shown in Fig. 8. Similarly, the RDE voltammograms for the reduction of 5 mM H$_2$O$_2$ were recorded at the modified electrode with different rotating speeds, ω, shown in Fig. 9. As seen in Figs. 8 and 9, the well-defined single cathodic waves, whose limiting current was proportional to the concentration or $\omega^{1/2}$, respectively, were obtained (insets in Figs. 8 and 9). The linearity of the plots I_l versus C or $\omega^{1/2}$ confirms that the reduction wave of H$_2$O$_2$ has a diffusional nature and slopes
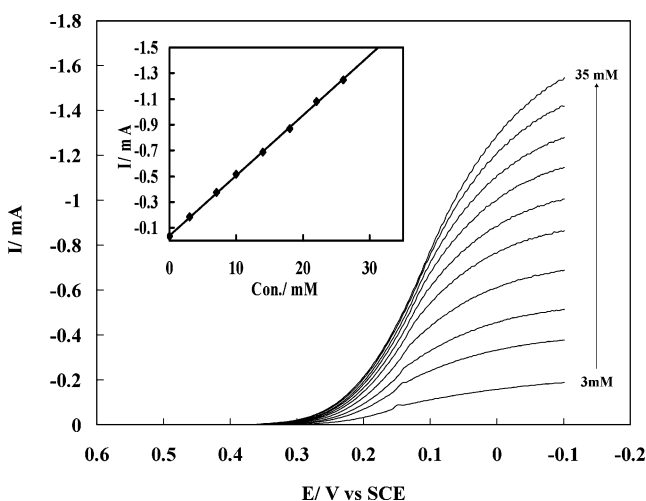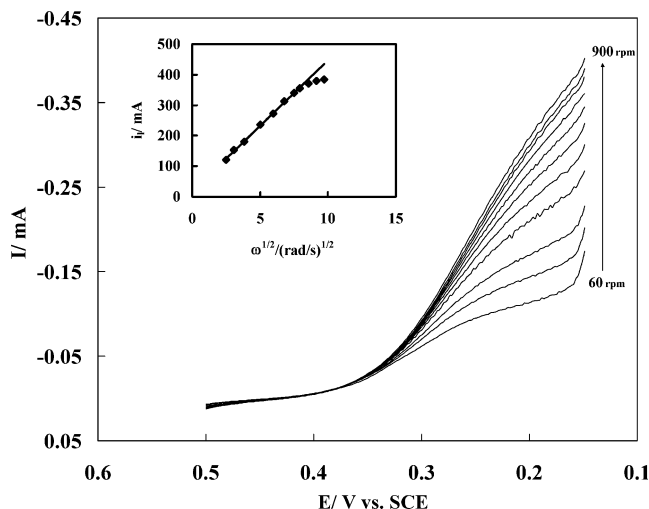

Fig. 9 RDE voltammograms of 5 mM H$_2$O$_2$ recorded by rotation speed (60, 90, 140, 240, 340, 440, 540, 600, 700, 800, and 900 rpm, respectively). *Inset*: plot of I versus $\omega^{1/2}$. Sweep rate 5 mV s^{-1}. Supporting electrolyte as in Fig. 1

(0.62 $nFAv^{-1/6}D^{2/3}\omega^{1/2}$ or 0.62 $nFAv^{-1/6}D^{2/3}C$) allowed to determine diffusion coefficient of H$_2$O$_2$. The average value found from the slopes for D was 7.1×10^{-6} cm^2 s^{-1} assuming that $v = 0.01$ cm^2 s^{-1} and $A = 0.07$ cm^2.

The charge transfer rate constant k_f, the potential-dependent constant, was determined by the mass transport extrapolation method using the Koutecky–Levich relation and subjecting the couple I–E data in both charge transfer and mass transfer limiting region of current–potential curves [25]:

$$\frac{1}{I} = \frac{1}{I_{\omega \to \infty}} + \frac{K}{\omega^{1/2}} \qquad (4)$$

Where $I_{\omega \to \infty} = nFk_fC$ is the current corrected for diffusion and k_f is the potential-dependent constant. The intercept of

Fig. 8 RDE voltammograms of H$_2$O$_2$ recorded for different concentrations of 3, 7, 10, 14, 18, 22, 24, 26, 30 and 35 mM, respectively. *Inset*: plot of I_l versus C. Sweep rate 5 mV s^{-1}. Supporting electrolyte as in Fig. 1
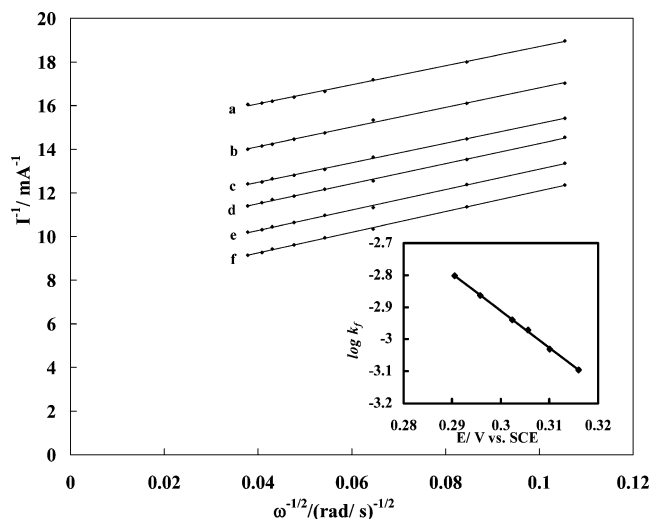

Fig. 10 Plot of Γ^{-1} versus $\omega^{-1/2}$ for electrode potential: *a* 0.317, *b* 0.312, *c* 0.306, *d* 0.302, *e* 0.296, and *f* 0.290 V

$1/I$ versus $\omega^{-1/2}$ plot gives $1/I_{\omega\to\infty}$ that allows to determine the values of k_f. An example of such a series of the extrapolated plots is shown in Fig. 10. The values of k_f calculated for electrode potentials of 0.317, 0.311, 0.305, 0.295, and 0.289 V are 1.58, 1.37, 1.15, 0.93, and 0.8×10^{-2}, respectively. According to Eq. 5, the variation of $\log I_{\omega\to\infty}$ or $\log k_f$ as function of $(E-E_0')$ gives a plot that is linear (not shown) [26]:

$$\log I_{\omega\to\infty} = \log nFAck^0 + \frac{\alpha nF}{2.3 RT}\left(E_0' - E\right) \qquad (5)$$

Where $I_{\omega\to\infty}$ is current corrected for diffusion (ampere), A is electrode area (square centimeter), c is H_2O_2 concentration (mole per cubic centimeter), E_0' is apparent standard potential (volt), and E electrode potential (volt). The value of α obtained from the slope of this plot (8.4 decade/V) was 0.37 which is in good agreement with that obtained by cyclic voltammetry.

Stability of the electrode

The effect of various factors including the number of potential cycling and the exposing time of the electrode in air and in supporting electrolyte on the stability and electrochemical behavior of the electrode were investigated in a previous work. We have concluded that the stability and reproducibility of the electrode response is less affected by the factors mentioned above [20]. In the present work, the stability of the modifier and reproducibility of its electrocatalytic activity in H_2O_2 solutions were examined and showed that the stability and current response of the electrode did not change significantly for several uses (about 20 times). On the other hand, at a constant potential under hydrodynamic conditions (stirred solutions), the oxidation current is proportional to the H_2O_2 concentrations and the amperometric behavior of the electrode maintained almost constant for long times (about 30 min).

Conclusion

The PB film on the Al substrate plated by thin layer of metallic palladium exhibits the good characteristic via improved stability and electrocatalytic ability for the electroreduction of H_2O_2 at a moderate low potential versus SCE, but more positive compared with the other PB film-modified electrodes. The later has an obvious advantage providing a considerable stability of the modifier on the electrode surface during non-mediated electroreduction of H_2O_2 (a lack of PB reduction to nearly soluble PW). The reaction pathway in acidic medium is simple two electron

process. The forced convection voltammetry on the rotating disk PB/Pd-Al electrode can be used as an effective technique for determination of kinetics of the electrocatalytic reduction of hydrogen peroxide.

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