

Electrocatalytic oxidation of pyridoxine (vitamin B₆) on aluminum electrode modified by metallic palladium particles/iron (III) hexacyanoferrate (II) film

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Abstract The electrocatalytic activity of a Prussian blue (PB) film on the aluminum electrode by taking advantage of the metallic palladium characteristic as an electron-transfer bridge (PB/Pd–Al) for electrooxidation of 2-methyl-3-hydroxy-4,5-bis (hydroxyl–methyl) pyridine (pyridoxine) is described. The catalytic activity of PB was explored in terms of Fe^{III} [Fe^{III} (CN)₆]/Fe^{III} [Fe^{II} (CN)₆]¹⁻ system. The best mediated oxidation of pyridoxine (PN) on the PB/Pd–Al-modified electrode was achieved in 0.5 M KNO₃+0.2 M potassium acetate of pH 6 at scan rate of 20 mV s⁻¹. The mechanism and kinetics of the catalytic oxidation reaction of PN were monitored by cyclic voltammetry and chronoamperometry. The results were explained using the theory of electrocatalytic reactions at chemically modified electrodes. The charge transfer-rate limiting reaction step is found to be a one-electron abstraction, whereas a two-electron charge transfer reaction is the overall oxidation reaction of PN by forming pyridoxal. The value of α , k , and D are 0.5, $1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, and $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively. Further examination of the modified electrodes shows that the modifying layers (PB) on the Pd–Al substrate have reproducible behavior and a high level of stability after posing it in the electrolyte or Pyridoxine solutions for a long time.

Keywords Modified aluminum electrode · Pyridoxine · Vitamin B₆ · Prussian blue · Palladium-coated aluminum · Electrocatalytic oxidation

Introduction

Vitamins of the B₆ group are compounds (six forms) that contain the pyridine ring in their molecules and are water-soluble vitamins. Pyridoxine (PN) was the first isolated vitamin B₆. It is essential in the diet for the metabolism of amino acids and the maintenance of body cells [1, 2]. The special attention has been paid to PN in clinical and pharmaceutical sciences because of its extensive and essential applications in bio-metabolisms. Recently, it was reported that vitamin B₆ and its derivatives have a major influence in gene modulation, sexual behavior, cancer research, and immune modulation in HIV-1 infection [3, 4]. In a biological system, PN is oxidized to pyridoxal derivative (PL) to act as a coenzyme for the amino group transformation [5, 6]. Thus, it is important to investigate the oxidation kinetics and mechanism of vitamin B₆ in vitro.

Söderhjelm and Lindquist [7] were the first to study the voltammetric behavior of PN using a carbon paste electrode. Other voltammetric studies involving square wave voltammetry [8], differential pulse voltammetry [9, 10], direct current, and differential pulse polarography [11] were reported. To the best of our knowledge, there are a few papers on electrooxidation of PN using chemically modified electrodes [12, 13]. The uses of polynuclear transition metal cyanoferrates as a modifier appear to be especially attractive because a large number of these compounds can be easily prepared from cheap and available inorganic chemicals. In addition, the well-defined zeolite-like structure of these compounds makes the description and understanding of the charge-transfer process easier compared to that of organic polymer films [14].

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The prototype transition metal cyanoferrate is iron (III) hexacyanoferrate (II), often referred to as Prussian Blue (PB), which is the oldest and the most intensively examined coordination compound reported in the scientific literature. PB films are of interest because of their electrochromism [15] and also for photoelectrochemical applications [16]. Moreover, PB films are known as useful electrocatalysts in selected electrochemical process and are suitable as electrode modifiers to make amperometric sensors for the determination of solution components [17–30].

In the search for suitable matrices for PB immobilization, it was found that PB films have been deposited on a variety of surfaces, the most frequent being glassy carbon [23–25, 29–33], graphite [24, 26, 27, 33], platinum [34, 35], and carbon fiber [22]. It has been also incorporated into polypyrrole [36, 37], and very little attention has been given to carbon paste electrodes modified with PB [38–40]. Our group first announced the development of transition metal ferricyanide-modified electrodes on the basis of an Al substrate [41–44]. Recently, we have communicated the electroless preparation route of the PB films-modified Al electrodes using an Al surface, covered by metallic palladium that acts as a conductor allowing electron transfer between the Al and the PB [45]. This protocol may be denoted as “palladium-bridged PB film-modified aluminum electrode” or PB/Pd–Al. To the best of our knowledge, no electrocatalytic and electrochemical studies of the electrooxidation of PN using PB film as mediator even on conventional substrates, such as Pt, Au, and GC, have been reported. The present work concerns the electrocatalytic characterization of the PB/Pd–Al-modified electrode toward the electrooxidation of PN and determination of the kinetics by various electrochemical techniques.

Experimental

Chemicals

Palladium chloride, ammonia solution (25%), potassium hexacyanoferrate (III) trihydrate, ferric nitrate, nitric acid, and potassium hydroxide were of analytical grade from Merck, and pyridoxine hydrochloride was from Fluka. 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%. 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, saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode, were used at room temperature.

Preparation of the PB/Pd–Al-modified electrode

The aluminum disk electrode mounted in a Teflon tube, as described in our previous work [40], was polished with emery paper (320 grit), first, and then with a finer grade (1,500 grit) to obtain a relatively mirror-like surface. After through rinsing, the electrode was cleaned in concentrated nitric acid for 1 min and, finally, rinsed with twice-distilled water before use. The two-step electroless modification of the Al disk electrode involves an initial Al surface palladization and, subsequently, PB film deposition in a nonelectrolytic procedure. The electroless palladization of the Al surface was carried out by dipping the cleaned surface in 50 mM PdCl_2 dissolved in 25% ammonia solution with formation of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ complex (plating solution) for 2 min. However, the thickness of metallic palladium deposited on the electrode surface depends on the immersion time of the electrode in the plating solution. The palladized aluminum electrode was rinsed with twice-distilled water and then subjected to PB film deposition by immersing it in a fresh solution of 2 mM $\text{Fe}(\text{NO}_3)_3$, 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, and 0.5 M KNO_3 of pH 1–3 (adjusted with HNO_3) for 4 min. A blue color due to the formation of PB film on the electrode surface was observed at the beginning of the electroless procedure. To obtain morphological crystal lattice stabilization of the film, the freshly prepared modified electrode was dried in air for 2 h, and then, the electrode potential was cycled between -0.1 and 0.5 V in 0.5 M potassium nitrate solution (pH 3) for about 10 cycles with scan rate of 20 mV/s. For some comparative study, the PB film-modified Al (PB/Al) was prepared by simply dipping the polished surface of aluminum in a fresh solution of 2 mM $\text{Fe}(\text{NO}_3)_3$, 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, and 0.5 M KNO_3 of pH 1–3 (adjusted with HNO_3) for few minutes.

Results and discussion

Cyclic voltammetric study

The cyclic voltammograms of the PB/Pd–Al-modified electrode in the absence and presence of PN at scan rate of 20 mV s^{-1} are shown in Fig. 1. As seen in Fig. 1, the modified electrode in the electrolyte solution (0.5 M KNO_3 +0.2 M, acetate of pH 6) in the absence of PN

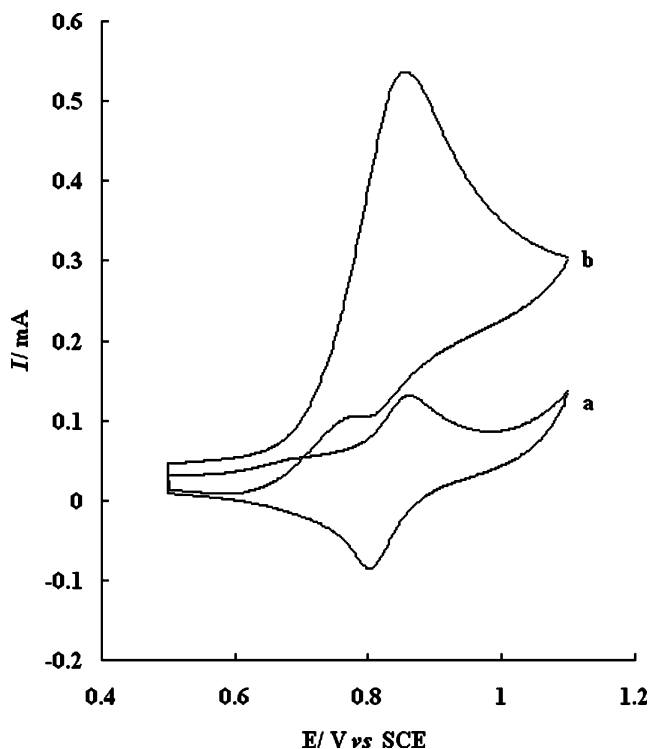
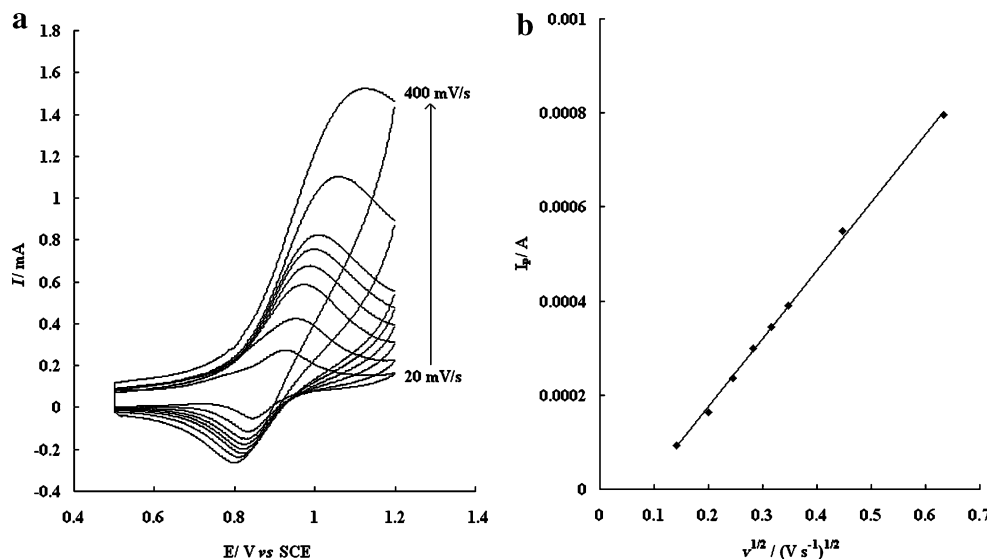


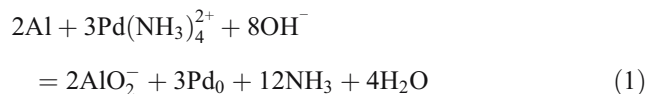
Fig. 1 Cyclic voltammograms of the PB/Pd–Al-modified electrode in the **a** absence and **b** in the presence of 30 mM of PN, supporting electrolyte=0.5 M KNO₃+0.2 M acetate solution of pH 6, scan rate=20 mV s⁻¹

exhibits a response of surface redox couple at $E_{1/2} = (E_p^a + E_p^c)/2 = 0.85\text{V}$, due to Fe^{III} [Fe^{III/II} (CN)₆]^{0/1-} system (curve a). Upon the addition of 30 mM PN, an enhancement in the anodic peak current was observed (curve b), and the corresponding cathodic peak almost disappeared. This behavior is typical of that expected for mediated oxidation. Note that the PB film on the bare Al electrode did not exhibit its characteristic redox peaks, due to the lack of electronic connection between modifier and

Fig. 2 a Cyclic voltammograms of the PB/Pd–Al-modified electrode in the presence of 14 mM of PN at scan rates of 10, 20, 40, 60, 80, 100, 120, 200, and 400 mV s⁻¹, **b** variation of the anodic peak current vs the square root of scan rate $v^{1/2}$. Supporting electrolyte as in Fig. 1

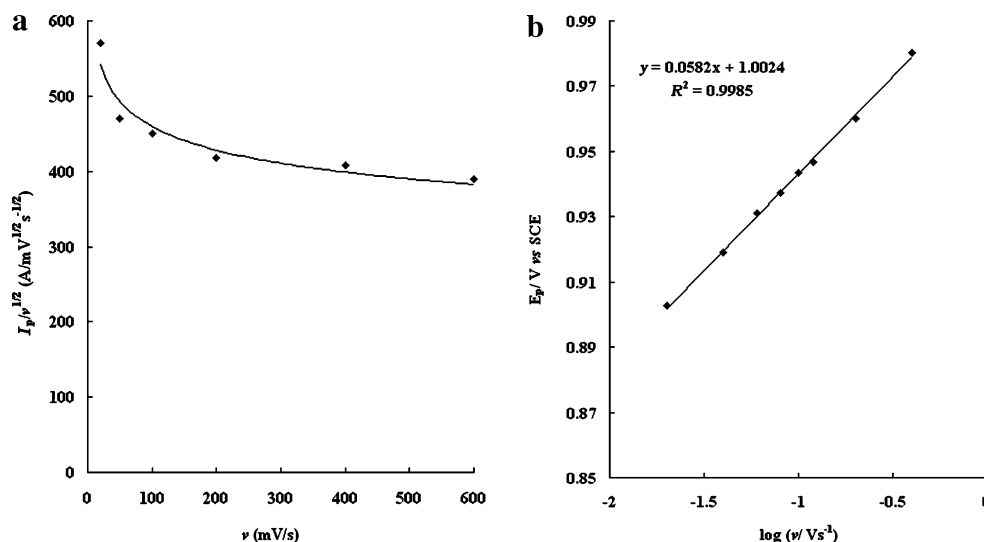


aluminum substrate. Indeed, during deposition of PB on the bare Al surface, an insulating layer of Al₂O₃ is formed, and the electron transfer between Al substrate and PB film is not established. Although, the pretreatment of Al surface in PdCl₂ dissolved in 25% ammonia solution gives rise to the formation of Al–Pd binary metal and prevention of the Al₂O₃ layer deposition on the electrode surface according to following suggested reaction:



The anodic peak current for a PN concentration of 14 mM on the PB/Al–Pd electrode increased with scan rate, whereas the cathodic peak began to appear for scan rates higher than 50 mV s⁻¹ (Fig. 2a). This reveals that the catalytic effect of the PB/Pd–Al electrode appears only at lower scan rates up to 50 mV s⁻¹, due to a relatively slow catalytic reaction rate. The plot of the anodic peak current I_p vs the square root of the scan rate $v^{1/2}$ is linear (Fig. 2b), suggesting that the reaction is mass transfer controlled. Furthermore, the plot of the current function $(I/v^{1/2})$ vs the scan rate (Fig. 3a) exhibits an indicative shape typical of an EC' catalytic process. The peak potential for the catalytic oxidation of PN shifts to more positive potentials with increasing the scan rate suggesting a kinetic limitation in the reaction between the Fe^{III} [Fe^{III/II} (CN)₆]^{0/1-} redox sites of the PB film and PN (Fig. 3b). Note that the cyclic voltammetry of the PB/Pd–Al electrode in the absence of PN at scan rates between 10–200 mV s⁻¹ showed that the peak potential of the modifier did not shift significantly and current function maintained almost constant with scan rate (not shown). These confirm the absence of ohmic drop effect on the cyclic voltammograms.

Fig. 3 Plots of **a** anodic current function $I_p/V^{1/2}$ and **b** peak potential E_p vs scan rate ν for the cyclic voltammograms of Fig. 2a



To obtain information on the number of electrons (n_α) involved in the rate-determining step, a Tafel plot was drawn using background-corrected data from the rising part of the current-voltage curves (where there is not any concentration polarization) at a scan rate of 20 mV s^{-1} (Fig. 4). For 30 mM of PN, a slope of $9.03 \text{ (V decade}^{-1})^{-1}$ was observed, which indicates that a one-electron process is

a rate-limiting step, assuming a transfer coefficient of $\alpha = 0.5$.

The Tafel slope can be obtained by another method according to following equation valid for a totally irreversible diffusion-controlled process [46]:

$$E_p = (b/2) \log \nu + \text{Cons.} \quad (2)$$

On the basis of this equation, the slope of E_p vs $\log \nu$ plot (Fig. 3b) is $b/2 = \partial E_p / \partial \log \nu$, where b indicates the Tafel slope. Therefore, $b = 2 \times 58.2 = 113 \text{ mV/decade}$. This slope also indicates a one-electron transfer to be a rate-limiting step assuming a transfer coefficient of $\alpha = 0.5$.

Similarly, to get information on the final product of the PN oxidation on the modified electrode, we have evaluated the total electrons (n) involved in PN oxidation at a time scale of cyclic voltammetric technique. For the totally irreversible diffusion-controlled electrode processes (EC'), the following equation can be used for evaluation of n [46]:

$$I_p = 2.99 \times 10^5 n [(1 - \alpha)n_\alpha]^{1/2} A C D^{1/2} \nu^{1/2} \quad (3)$$

The plot of I_p of voltammograms of Fig. 5 vs C is linear with slope of 0.0183 and relation coefficient of 0.9993 (inset Fig. 5). Using the slope of this plot and considering $(1 - \alpha)n_\alpha = 0.5$, $D = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $A = 0.07 \text{ cm}^2$, and $\nu = 20 \text{ mV s}^{-1}$, it is found that the total number of electrons involved in the anodic oxidation of PN is about 1.9 , close to 2 , confirming that PL is the unique oxidation product of PN. These findings lead to conclude that the electro-oxidation rate of PN on the PB film-modified Al electrodes might be controlled by the kinetic of one-electron cross-exchange process between PN and Fe^{III} [$\text{Fe}^{\text{III}}(\text{CN})_6$] sites of PB film and its final products are PL. Therefore, in the solution conditions, the electrooxidation process of PN

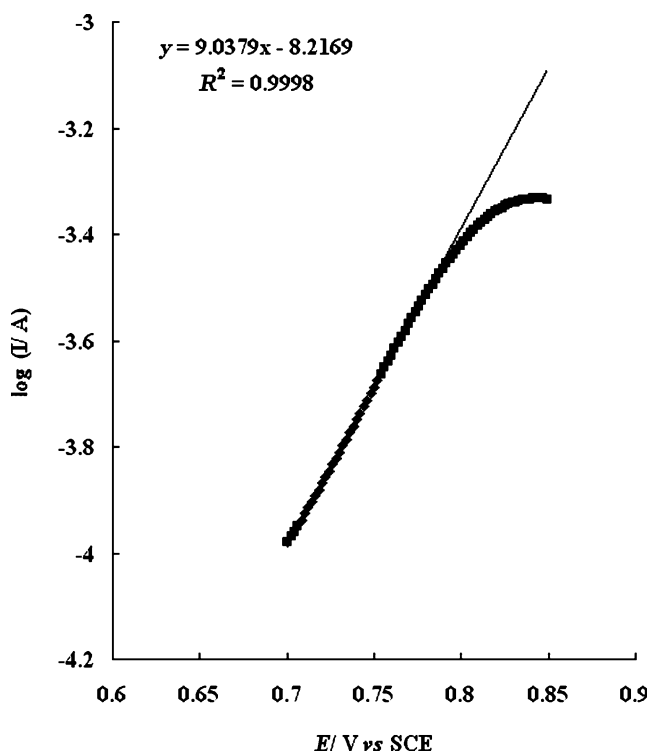


Fig. 4 Tafel plot obtained from current-potential curves recorded at the PB/Pd–Al electrode in the presence of 30 mM PN in supporting electrolyte as in Fig. 1 at a scan rate of 20 mV s^{-1}

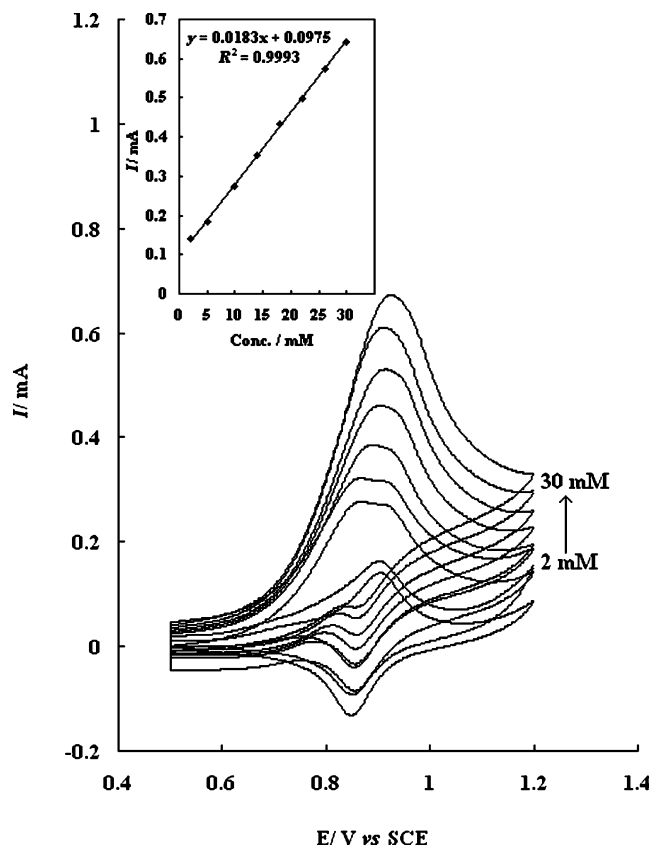
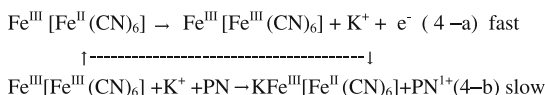
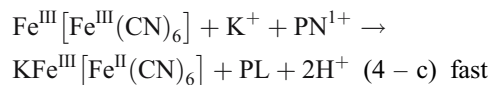


Fig. 5 Cyclic voltammograms of the PB/Pd–Al electrode in the presence of PN with different concentrations 2, 7, 10, 14, 18, 22, 26, and 30 mM, inset calibration graph. Potential scan rate=20 mV/s; supporting electrolyte as in Fig. 1

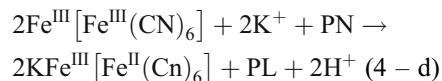
according to an EC catalytic mechanism can be expressed as follows:



Subsequent fast cross reaction:



Total cross reaction:



where PN, PN^{1+} , and $\text{PLC}_8\text{H}_8\text{N}(\text{OH})_3$, $\text{C}_8\text{H}_8\text{N}(\text{OH})_3^+$, $\text{C}_8\text{H}_7\text{NO}(\text{OH})_2$, respectively.

Kinetics of the electrocatalytic oxidation of PN

If the electron-exchange process at the electrode|PB film interface is assumed to be fast, based on the experimental conditions, the rate-determining step must be one of the following processes [46]:

- 1) Diffusion of PN in the solution to the electrode surface
- 2) Diffusion of PN through the PB film
- 3) Diffusion of electron within the film
- 4) Electron exchange between $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ in the PB film and PN

When thin PB films and high substrate (PN) concentrations are used, the contributions of PN and electron diffusion within the film are negligibly small and mass-transport process in the solution and the catalytic reaction become dominant.

The rate-determining step is given by reaction 4-b with a heterogeneous rate constant, k , can be evaluated by two different approaches.

Cyclic voltammetry

As indicated by Figs. 3 and 4, the catalytic oxidation peak potential gradually shifts slightly toward positive potentials with increasing scan rate ν and the oxidation currents increase linearly with $\nu^{1/2}$. These results show that a kinetic limitation exists in the reaction between PN and $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ redox sites of PB film. For the case of slow scan rate and large catalytic rate constant k , Andrieux and Saveant [47] developed a theoretical model for a heterogeneous catalytic reaction:

$$I_{\text{cat}} = 0.496nFAD^{1/2}\nu^{1/2}C_b(nF/RT)^{1/2} \quad (5)$$

where D and C_b are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and bulk concentration (mol cm^{-3}) of PN, respectively, and the other symbols have their usual meaning. Low values of k , result in values of the constant lower than 0.496. For scan rates of 20, 40, 60, 80, and 100 mV s^{-1} , we find the average value of this constant to be 0.465 for PB/Al–Pd electrode with a surface coverage Γ of $2.2 \times 10^{-7} \text{ mol cm}^{-2}$, geometric area A of 0.07 cm^2 , and diffusion coefficient D of $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (see “Chronoamperometry”) in the presence of 14 mM of PN. By using the working curves in [47] and value of 0.465 obtained for this constant, we determine $\log [(k\Gamma)/D^{1/2}(F\nu/RT)^{1/2}] = 0.82$, allowing to calculate a value of $k = 1.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$.

Chronoamperometry

To confirm the results obtained by cyclic voltammetry, the chronoamperometry as another electrochemical technique was used to evaluate the kinetics. Figure 6 represents the current-time profiles obtained by setting the working electrode potential at 1.2 V for the PB film-modified Al electrode with surface coverage Γ of 2.2×10^{-7} mol cm^{-2} in the absence and presence of various PN concentrations of (18–30 mM). As seen in Fig. 6, the behavior is typical of that expected for a mediated oxidation. At long experimental times ($t > 1.5$ s or $t^{-1/2} < 0.5$ s $^{-1/2}$), where the oxidation of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is complete, the rate of electro-catalyzed PN oxidation exceeds that of PN diffusion, and therefore, the current has a diffusional nature. In this region, the plot of I vs $t^{-1/2}$ gives a straight line (see the inset of Fig. 6), and the slope of such a line can be used for the estimation of the diffusion coefficient D of PN. From the slopes of plots of inset Fig. 6, the mean value of D was found to be 1.4×10^{-5} cm^2 s $^{-1}$.

At intermediate times ($t = 0.5$ –4 s in the present work), the catalytic current (I_{cat}) is dominated by the rate of the

electron cross-exchange between the $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ in the film and PN, and the rate constant is determined according to the method described in the literature [48]

$$I_{\text{cat}}/I_L = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (6)$$

where I_{cat} and I_L are the currents of the PB film-modified electrode in the presence and absence of PN, respectively, and $\gamma = kc_o t$ (c_o is the bulk concentration of PN) is the argument of the error function $\text{erf}(\gamma^{1/2})$. In the cases that γ exceeds 2 (it is true in the present case), the error function is almost equal to 1, and the above equation can be reduced to:

$$I_{\text{cat}}/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kc_o t)^{1/2} \quad (7)$$

where k , C_o , and t are the catalytic rate constant (M^{-1} s $^{-1}$), catalyst concentration (M), and time elapsed (s). From the slope of the I_{cat}/I_L vs $t^{1/2}$ plot, we can calculate the value of k for a given concentration of PN. Figure 7 shows one such plot, constructed from the chronoamperograms for the PB/Al-Pt electrode in the absence and presence of 20 mM PN, and value for k was found to be 1.3×10^2 M^{-1} s $^{-1}$, which is in good agreement with that obtained from cyclic voltammetry (1.1×10^2 M^{-1} s $^{-1}$).

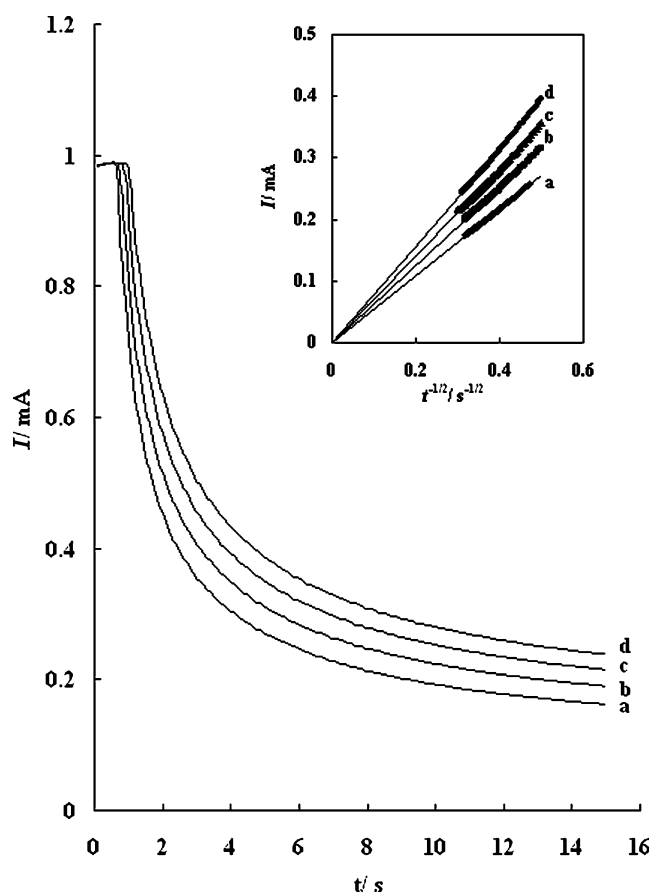


Fig. 6 Chronoamperograms obtained at the PB/Pd–Al electrode in the presence of **a** 18, **b** 22, **c** 26, and **d** 30 mM of PN; potential step=1.2 V, inset plots of current vs $t^{-1/2}$, supporting electrolyte as in Fig. 1, surface coverage= 2.2×10^{-7}

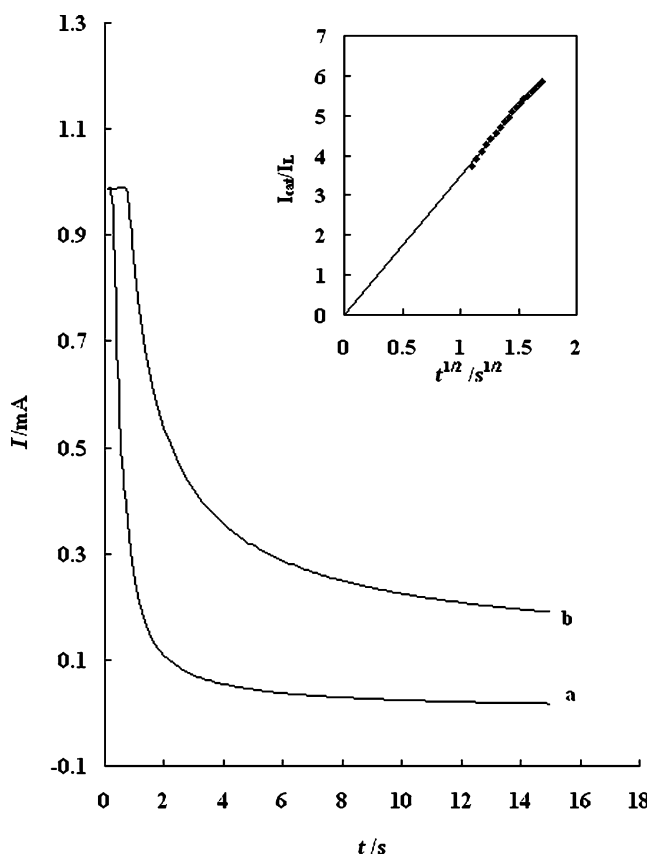


Fig. 7 Chronoamperograms obtained at the PB/Pd–Al electrode in the absence (**a**) and in the presence of 26 mM PN (**b**); potential step=1.2 V, inset plots of I_{cat}/I_L vs $t^{1/2}$, supporting electrolyte as in Fig. 1, surface coverage= 2.2×10^{-7}

Stability of the electrode

The effect of various factors, including the nature of the supporting electrolyte cation, the number and potential range of voltammetric cycles, the exposing time of the electrode in air and in supporting electrolyte on the stability, and the electrochemical behavior of the electrode, were investigated. We concluded that the stability and reproducibility of the electrode response are less affected by the factors mentioned above. The stability of the electrode and reproducibility of its electrocatalytic activity in PN solution were also examined, and we have found that the stability and current response of the electrode in the presence of PN 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 PN concentration and maintained almost constant with the time (about for 40 min.).

Conclusion

The PB film on the naked Al substrate is electro-inactive, while it exhibits the electro-active characteristics on the Al–Pd electrode via metallic palladium bridge and can catalyze the oxidation of PN via surface layer-mediated charge transfer. The charge transfer step of the rate-limiting reaction is found to be a one-electron abstraction step by forming PN^{1+} . The kinetic of the catalytic reaction can be explained using cyclic voltammetry and chronoamperometry. The rate constant of the catalytic reaction k , obtained for PN by two approaches, are in good agreement.

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