

Oxidation pathways and kinetics of morphine in acidic and neutral media on the aluminum electrode covered by metallic palladium and modified by Prussian blue

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Abstract This paper describes the use of an aluminum electrode covered by metallic palladium and modified by Prussian blue prepared by a simple and rapid electroless method for the electro-oxidation of morphine. Two different pathways for electro-oxidation of morphine at various pH ranges were suggested. Also, some thermodynamic and kinetic parameters such as the number of electrons involved in the rate determining step, n_{α} , transfer coefficient α , and the total electrons (n) involved in morphine oxidation at the time scale of the cyclic voltammetric technique, the catalytic rate constant of the electrochemical process k , and diffusion coefficient of morphine D were determined. The mean values obtained are 0.5, 0.5, 1, $26.8 \text{ M}^{-1} \text{ s}^{-1}$ and $3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Keywords Modified aluminum · Prussian blue film · Morphine · Electrocatalysis

Introduction

Morphine (MO), a phenolic compound and an alkaloid which can cause disruption in the central nervous system, is frequently used to relieve severe pain in patients, especially those undergoing a surgical procedure. To prevent overdose-induced toxicity, monitoring MO concentrations in blood or urine is a critical issue in clinical medicine. Therefore, it is very important and highly valuable to develop a sensitive and simple analysis method for MO

determination [1]. To date, various analytical methods have been developed for the determination of MO. Among these, chromatographic methods [2–11] are most commonly used exploiting various sensors in the detector systems, while nonchromatographic direct methods are rare.

Compared to other options, electro-analysis has the advantages of simplicity and high sensitivity. The uses of bare electrodes for electrochemical measurements have a number of limitations, such as slow electron transfer reaction and electrode-fouling problems. The chemical modification of inert substrate electrodes with redox-active thin films offers significant advantages in the design and development of electrocatalyst. In operation, the redox-active sites shuttle electrons between the solution analyte and the substrate electrodes often with significant decreasing in activation overpotential. A further advantage of the chemically modified electrodes is that they are less susceptible to surface fouling and oxide formation compared to inert substrate electrodes.

A few papers concerning the electro-oxidation of MO have been reported. Brett et al. showed that the process of electro-oxidation of MO on bare electrodes is a complex one [12]. Xu et al. reported the mediated electro-oxidation of MO on the cobalt hexacyanoferrate-modified carbon paste electrode [13]. Prussian blue (PB) film is known as a useful electro-catalyst in selected electrochemical process and is suitable as an electrode modifier to make an amperometric device for the determination of solution components [14–26]. It was found that PB films have been deposited on glassy carbon [19–21, 25–27], graphite [20, 22, 23, 27], platinum [28, 29], and carbon fiber [18] and also incorporated into polypyrrole [30, 31] and carbon paste [32, 33]. The electro-catalytic oxidation of MO at an optically transparent indium tin oxide electrode modified by an electrodeposited PB thin film was first briefly demon-

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strated, and the amperometric detection of MO was then investigated on the modified electrode by Ho et al. [14]. To our knowledge, there is no report on the electro-catalytic oxidation of MO involving characterization of the reaction pathways and kinetics at various pH values on the PB film-modified electrode in detail. Recently, we have reported the nonelectrolysis preparation path of the PB films on naked Al surface as well as on an Al surface covered by metallic palladium particles, describing that the PB film on the naked Al surface is electro-inactive. Whereas, it is electro-active on the Al surface covered by metallic Pd layer which acts as a conducting body, insuring electron transfer between Al and the PB film [34]. This modified electrode is denoted as PB/Pd–Al electrode. The major advantages of PB/Pd–Al electrode are the simplicity, rapidity (in few minutes), and miniaturization in preparation and high stability of the PB film on the Pd–Al surface and its effective catalytic activity for the electro-oxidation of some organic [35–37] and inorganic [34] compounds.

The present work deals with the electro-catalytic characterization of the PB/Pd–Al electrode toward the electro-oxidation of MO and determination of the kinetics.

Experimental

Chemicals

Palladium chloride, ammonia solution (25%), potassium hexacyanoferrate (III) trihydrate, ferric nitrate nonahydrate, nitric acid, potassium hydroxide, acetate, hydrochloric acid, and MO hydrochloride were of analytical grade from Merck. The electrolyte solutions were made up from 0.2 M acetate solution with 0.5 M KNO₃, and the pH adjusted with an acid solution. All solutions were prepared with double-distilled water.

Instrumentation

All voltammetry experiments were performed using a potentiostat/galvanostat *AUTOLAB*, model *PGSTA30*. Amperometry experiments were performed using a *Polar-record Metrohm*, model 626. The working electrode was a homemade aluminum disk electrode prepared from an aluminum bar with a purity of 99.9±0.2% [38]. The aluminum bar was mounted in a Teflon tube, exposing a geometrical area of 0.071 cm², 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 counterelectrode, was used at room temperature. All potentials given in this article are referred to the SCE.

Electrode preparation

A cylindrical aluminum bar of 12 mm in diameter and 90 mm in length was used for 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. From the other end of the bar, one part (30 mm in length) was ground until its diameter reaches to 3 mm and then was fitted into the hole which was previously made in a Teflon rod of 12 mm in diameter and 30 mm in length [38]. 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. After thorough rinsing, the electrode was cleaned in concentrated nitric acid for 1 min and finally rinsed with double-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 a nonelectrolytic procedure performed as described earlier [35].

Result and discussion

Primary investigation

Figure 1 shows the cyclic voltammograms of Pd–Al and PB/Pd–Al electrodes in the presence and absence of MO in 0.5 M KNO₃+0.2 M acetate of pH 6. As seen in Fig. 1 (curve a), the characteristic redox peaks of the mediator (I,I') appeared at potentials around $E_{pa}=0.865$ V, $E_{pc}=-$

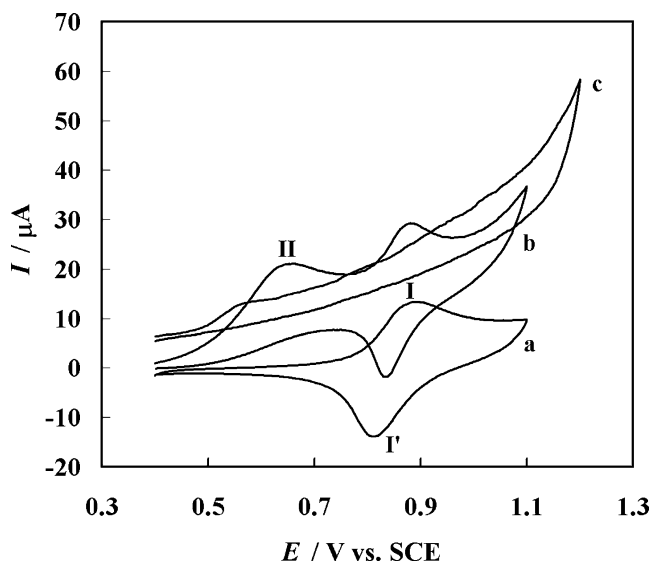


Fig. 1 Cyclic voltammograms of **a** PB/Pd–Al in 0.5 M KNO₃+0.2 M acetate solution, **b** a+4.5 mM morphine, **c** Pd–Al electrode in the presence of 4.5 mM morphine in 0.5 M KNO₃+0.2 M acetate solution

0.839 V corresponding to the $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III/II}}(\text{CN})_6]^{2-/3-}$ redox system [34]. Upon the addition of 4.5 mM MO in the solution, any oxidation peak relevant to MO oxidation did not appear on the unmodified Pd–Al electrode (curve c). Whereas a new separate well-defined and sharp anodic peak (II) appeared at potential about 0.65 V on the PB/Pd–Al electrode at the selected solution conditions (curve b), this indicates that the PB layer on the Pd/Al electrode provides the electron transfer ability between MO and electrode; that is, MO is oxidized electro-catalytically.

The anodic peak current for the MO solution of 4.5 mM on the PB/Pd–Al electrode increased with scan rate. The plot of I_p versus square root of the scan rate $v^{1/2}$ is linear suggesting that the reaction is mass transfer-controlled. The peak potential for the catalytic oxidation of MO shifts to more positive potentials with increasing the scan rate as expected for a totally irreversible diffusion-controlled redox process. Note that the cyclic voltammetry of the PB/Pd–Al electrode in the absence of MO at scan rates between 10 and 150 mV s^{-1} showed that the peak potential did not shift significantly. These confirm the absence of an ohmic drop effect on the cyclic voltammograms of the PB/Pd–Al electrode.

In order to obtain information on the number of electrons involving in the rate-determining step n_α , a Tafel plot is drawn using the rising part of the current–voltage curves (where there is no concentration polarization) at a low scan rate, e.g., 20 mVs^{-1} (Fig. 2). For 4.5 mM of MO, a slope of 5 (V per decade) $^{-1}$ was obtained for the Tafel plot, presenting that rate limiting is a one-electron or an about half-electron process, assuming a transfer coefficient α of 0.7 or 0.5, respectively. These processes may be demonstrated as follows:

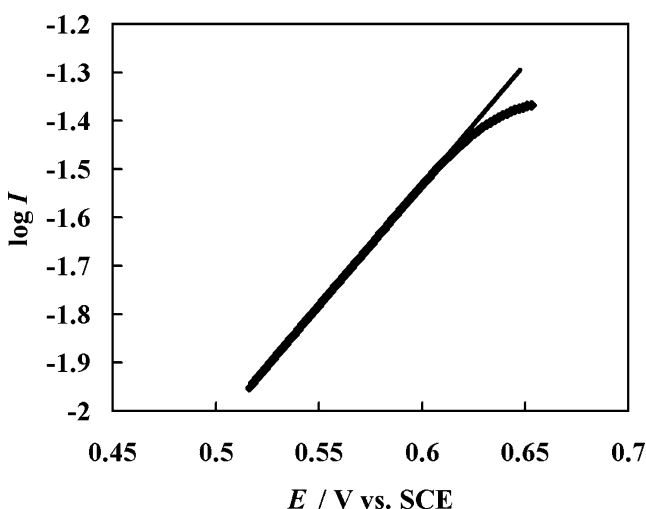


Fig. 2 Tafel plot obtained from current–potential curves recorded at the PB/Pd–Al electrode in the presence of 4.5 mM MO at a scan rate of 20 mV s^{-1} at pH 6

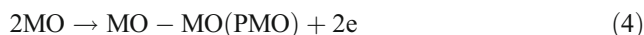
or formation a coupled species as:



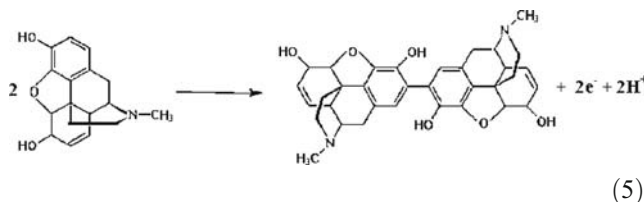
Similarly, in order to get information on the final product of the MO oxidation on the modified electrode, we have evaluated the total electrons (n) involved in MO oxidation at the time scale of cyclic voltammetric technique. For the totally irreversible diffusion-controlled electrode processes (EC *), the following equation can be used for the evaluation of n [39]:

$$I_p = 2.99 \times 10^5 n [(1 - \alpha)n_\alpha]^{1/2} ACD^{1/2} v^{1/2} \tag{3}$$

The plot of I_p of voltammograms versus $v^{1/2}$ is linear with a slope of 312.4 and a relation coefficient of 0.999. Using the slope obtained and considering $(1 - \alpha)n_\alpha = 0.3$, $D = 3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $A = 0.071 \text{ cm}^2$, $C = 4.5 \times 10^{-6} \text{ mol/cm}^3$, it is found that the total number of electrons involved in the anodic oxidation of 2 mol MO is about 1.92, close to 2, confirming that pseudo-MO (PMO) is a unique oxidation product.



These findings lead to conclude that under solution conditions (pH 6), the MO electro-oxidation rate on the modified Al electrodes might be controlled by the kinetics of the electrode processes as shown in Eqs. 1 or 2, and its final oxidation product is PMO displayed as follows:



As mentioned above, any oxidation peak relevant to MO oxidation did not appear on the unmodified Pd/Al electrode. Whereas, the results obtained from our previous studies confirmed that some organic and inorganic compounds can be oxidized on the Pd/Al electrode. These findings reveal the key role of the metallic Pd layer as a conductive bridge for charge transfer between the PB monolayer and Pd/Al electrode and capability of PB as a nonmediated catalyst affecting the kinetics of electron transfer [39–41] in the electro-oxidation of substrates (i.e., MO).

Effect of pH

On the basis of Eq. 5, the oxidation of MO is pH dependent. The effect of solution pH over 2–6 in which the modified electrode is stable was investigated. Typical cyclic voltammograms related to electrolyte solution containing 4.5 mM MO at pH 2, 4, and 6 are shown in Fig. 3. As seen in Fig. 3, the peak potential shifted to a more positive potential as the solution pH decreased, and the

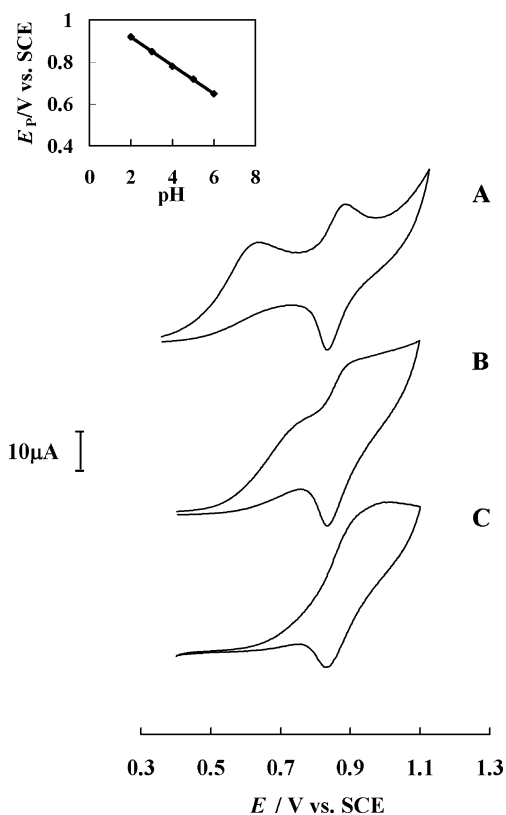
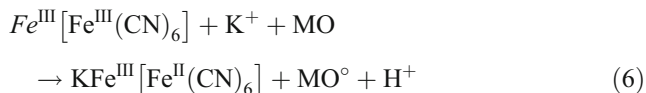


Fig. 3 Effect of pH. **a** pH 6, **b** pH 4, **c** pH 2, *inset*: plot of E_p versus pH

slope is about 0.065 V (inset Fig. 3) until the oxidation of MO is matched catalytically with PB oxidation at pH 2, and the anodic current enhanced, while the corresponding cathodic current is decreased. It is worth mentioning that in the presences of more concentrated solutions of MO, the cathodic peak disappeared completely (not shown). This behavior is typical of a mediated electrode process (EC') and attributed to the influence of H^+ on the thermodynamics and kinetics of cross-reaction [40, 41] between MO and $Fe^{III}[Fe^{III}(CN)_6]$ sites formed by PB oxidation on the electrode surface (Eq. 6):



Indeed, the rate of mediated oxidation of MO on the PB-modified electrode depends on the rate of cross-reaction 6. The occurrence of the cross-reaction necessitates the electro-oxidation of PB to precede the MO oxidation on the electrode. Relevant conditions can be provided by decreasing the substrate solution pH. Thus, the oxidation potentials of MO should shift toward the more positive values (i.e., PB oxidation potential). This can be achieved at relatively strong acidic media, and therefore, a solution pH of 2 is selected for further studies.

Mediated electro-oxidation pathway of MO at pH 2

The anodic peak current for MO solution of 4.5 mM on the PB/Pd–Al electrode at pH 2 increased with scan rate (Fig. 4). The plot of I_p versus square root of the scan rate $v^{1/2}$ is linear (inset, Fig. 4) suggesting that the reaction is mass transfer-controlled.

For obtaining information on the value of $(1-\alpha)n_\alpha$ involved in the rate-determining step, a Tafel plot was drawn using background-corrected data from the rising part of the current–voltage curve at a scan rate of 20 mV s^{-1} (Fig. 5a). For 4.5 mM of MO, the slope of $4.98 (\text{V per decade})^{-1}$ was observed, which yields a value of about 0.3. The value of $(1-\alpha)n_\alpha$ can be obtained by another method according to following equation valid for a totally irreversible diffusion-controlled process:

$$E_p = a + (b/2) \log v. \quad (7)$$

where b indicates the Tafel slope.

Subjecting the cyclic voltammograms shown in Fig. 4, a value of 89 mV per decade was obtained for b (Fig. 5b) and consequently a value 0.3 for $(1-\alpha)n_\alpha$.

To get information on the final product of the MO-mediated oxidation on the modified electrode, we have evaluated the total electrons (n) involved in the MO oxidation at a time scale of the cyclic voltammetric technique. For the totally irreversible diffusion-controlled electrode processes, Eq. 3 can be used for evaluation of n [39]: The plot of I_p of voltammograms shown in Fig. 4 versus $v^{1/2}$ is linear with a slope of 0.338 (inset, Fig. 4). Using the slope of this plot and considering $(1-\alpha)n_\alpha$ equal

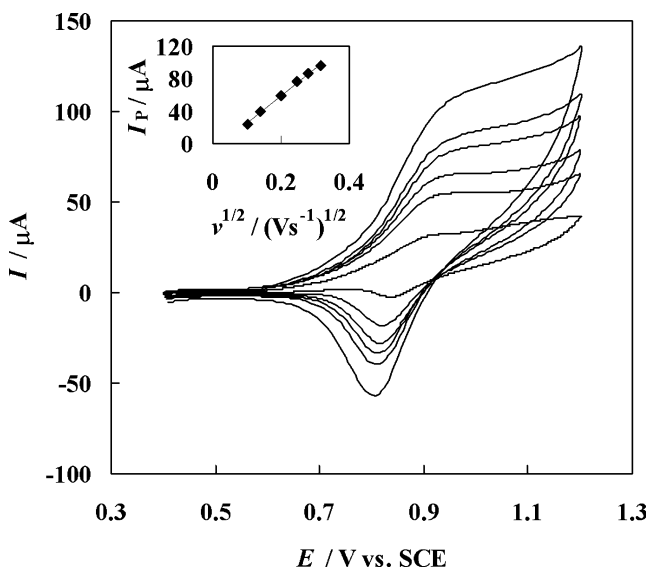


Fig. 4 Cyclic voltammograms of the PB/Pd–Al-modified electrode in the presence of 4.5 mM MO at scan rates of 10, 20, 40, 60, 80, and 100 mV s^{-1} , respectively, at pH 2. *Inset*: plot of I_p versus $v^{1/2}$. Supporting electrolyte as Fig. 1

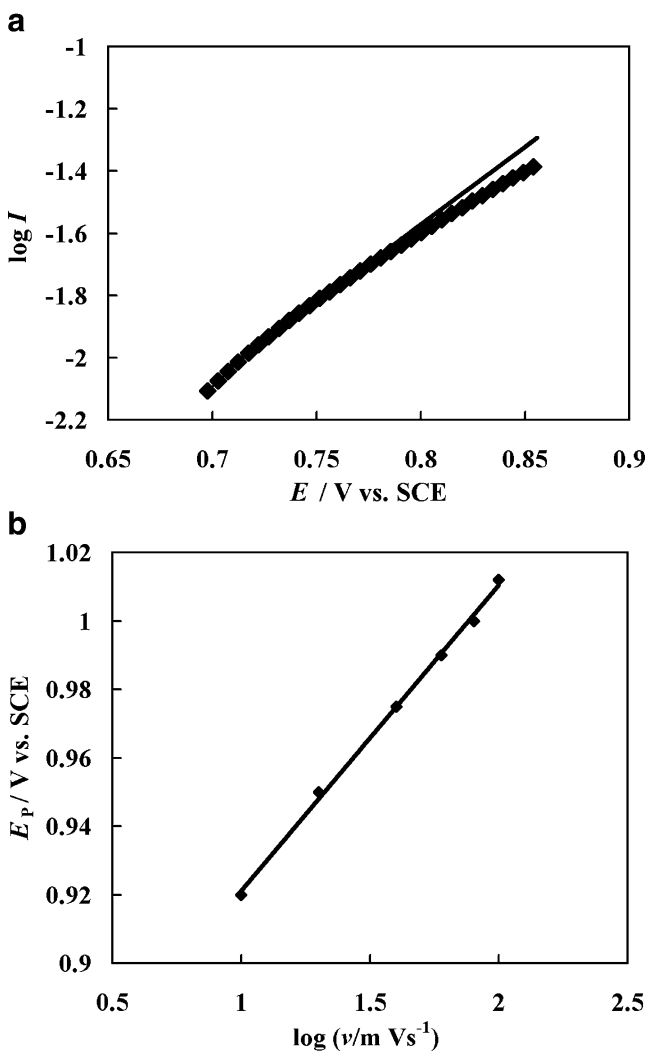
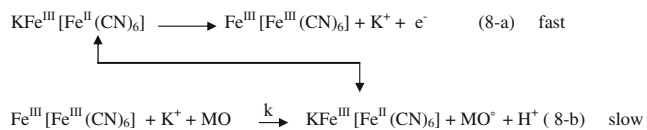


Fig. 5 **a** Tafel plot obtained from current–potential curves recorded at the PB/Pd–Al electrode in the presence of 4.5 mM MO at a scan rate of 20 mV s⁻¹ at pH 2. **b** Plot of *E_p* versus log *v*

to 0.3, $D=3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $A=0.09 \text{ cm}^2$, $C=4.5 \text{ mM}$, it is found that the total number of electrons involved in the anodic oxidation of 2 mol MO is about 2. These findings lead to conclude that the mediated electro-oxidation rate of MO on the PB/Pd–Al electrodes might be controlled by the kinetics of the cross-reaction between MO and Fe^{III}[Fe^{III}(CN)₆] sites of oxidized PB, and its final product is PMO. Therefore, under the solution conditions, the electro-oxidation process of MO according to an EC' catalytic mechanism can be expressed as follows:

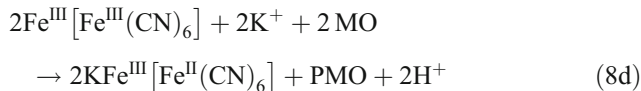
– By assuming $\alpha \sim 0.7$ and $n_\alpha \sim 1$



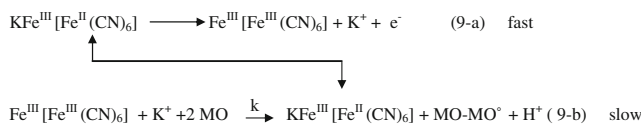
Subsequent fast dimerization of MO[°]



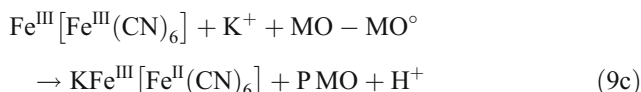
with total cross reaction:



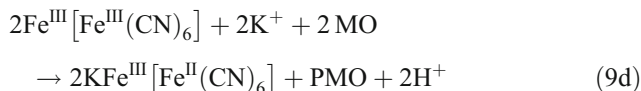
– By assuming $\alpha \sim 0.5$ and $n_\alpha \sim 0.5$



Subsequent fast cross-reaction:



with total cross reaction:



It is worth mentioning that these findings lead to conclude that the kinetics of both catalytic and mediated oxidation of MO on the PB/Pd/Al electrode at neutral and acidic media, respectively, controlled by MO[°] or (MO–MO[°]) cation radicals formation, and the final oxidation product is, however, PMO.

Kinetics of the mediated oxidation of MO at pH 2

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 [39]:

1. Diffusion of the MO in the solution to the electrode surface
2. Diffusion of MO through the PB film
3. Diffusion of the electron in the film
4. Electron exchange between Fe^{III}[Fe^{III}(CN)₆] in the modifier monolayer and MO

When thin PB films and high MO concentrations are used, the contributions of MO and electron diffusion within the film to rate limiting are negligibly small, the mass transport process in the solution and the electron cross-exchange between the Fe^{III}[Fe^{III}(CN)₆] in the film and MO becomes dominant. The rate-determining step of MO electro-oxidation is given by reactions 8b or 9b with a catalytic rate constant *k* that can be evaluated by chronoamperometry.

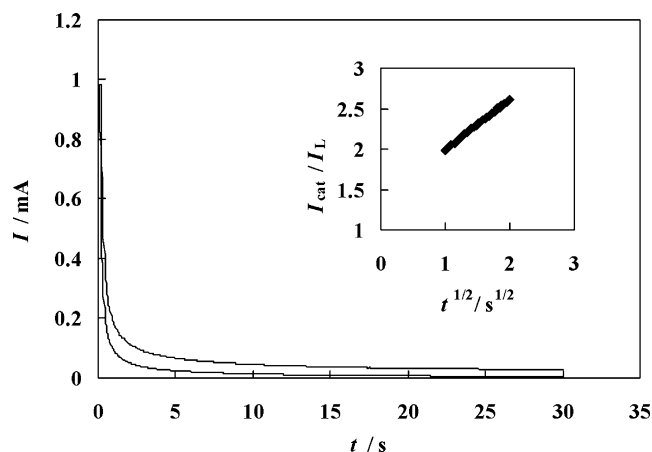


Fig. 6 Chronoamperograms obtained at the PB/Pd–Al electrode **a** in the absence and **b** in the presence of 4.5 mM MO at pH 2; potential step=1 V. *Inset*: plot of variation of I_{cat}/I_L versus $t^{1/2}$. Supporting electrolyte as Fig. 1

Chronoamperometry

Chronoamperometry as an effective electrochemical technique was used to evaluate the kinetics of MO-mediated oxidation. Figure 6 represents the current–time profiles obtained by setting the working electrode potential at 1 V for PB/Pd–Al electrode in the absence (curve a) and in the presence of 4.5 mM MO at pH 2 (curve b). As seen in Fig. 6, the behavior is typical of that expected for a mediated oxidation.

At intermediate times, where the oxidation of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is almost complete, 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 MO (electrocatalytic rate), and the rate constant can be determined according to the method described in the literature [42]:

$$I_{\text{cat}}/I_L = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (10)$$

where I_{cat} and I_L are the currents of the PB/Pd–Al electrode in the presence and absence of substrate, respectively, and $\gamma = kct$ (c is the bulk concentration of MO) is the argument of the error function $\text{erf}(\gamma^{1/2})$. In the case that γ exceeds 2 (it is true in the present case), the error function is almost equal to 1, and Eq. 10 can be reduced to:

$$I_{\text{cat}}/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kct)^{1/2} \quad (11)$$

where k and t are the catalytic rate constant ($\text{M}^{-1} \text{s}^{-1}$) 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 MO. The inset of Fig. 6 shows such plot, constructed from the chronoamperograms for the PB/Al–Pt electrode in the absence and presence of 4.5 mM MO, and the value for k was found to be $26.8 \text{ M}^{-1} \text{ s}^{-1}$.

At long experimental times ($t > 1.5 \text{ s}$ or $t^{-1/2} < 0.5$), where the oxidation of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is complete, the rate of electro-catalyzed MO oxidation exceeds that of MO diffusion, and therefore, the current has a diffusional nature. In this region, the plot of I versus $t^{-1/2}$ gives a straight line (not shown), and the slope of such a line can be used for the estimation of the diffusion coefficient D of the substrate. From the slopes of these plots, the mean value of D was found to be $3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for MO.

Conclusion

The PB film on the Al substrate covered by a thin layer of metallic palladium exhibits the electro-active characteristics via a metallic palladium bridge. The modified PB/Pd/Al electrode can catalyze the electro-oxidation of MO through surface-layer charge transfer processes. The reaction pathway at two different pH ranges can be explained by cyclic voltammetry. In both cases, the rate-limiting step is a cation radical formation and subsequent fast transformation of cation radical to PMO products. The chronoamperometry can be used as an effective technique for determination of kinetics of the mediated oxidation of MO.

References

- Bosch ME, Sanchez AR, Rojas FS, Ojeda CB (2007) J Pharm Biomed Anal 43:799, doi:10.1016/j.jpba.2006.12.005
- Liu Y, Bilfinger TV, Stefano GB (1997) Life Sci 60:237, doi:10.1016/S0024-3205(97)89478-7
- Tyrefors N, Hyllbrant B, Ekman L, Johansson M, Långström B (1996) J Chromatogr A 729:279, doi:10.1016/0021-9673(95)01090-4
- Schänzle G, Li S, Mikus G, Hofmann U (1999) J Chromatogr B Biomed Appl 721:55, doi:10.1016/S0378-4347(98)00438-1
- Zuccaro P, Ricciarello R, Pichini S, Pacifici R, Pellegrini M, Ascenzo GD (1997) J Anal Toxicol 21:268
- Hara S, Mochinaga S, Fukuzawa M, Ono N, Kuroda T (1999) Anal Chim Acta 387:121, doi:10.1016/S0003-2670(99)00108-7
- Theodoridis G, Papadoyannis I, Papadopoulou HT, Vasilikiotis G (1995) J Chromatogr A 18:1973
- Aderjan R, Hofmann S, Schitt G, Skopp G (1995) J Anal Toxicol 19:163
- Marigo M, Tagliaro F, Poesi C (1986) J Anal Toxicol 10:158
- Venn RF, Michalkiewicz A (1990) J Chromatogr B Biomed Appl 525:379, doi:10.1016/S0378-4347(00)83414-3
- Papadoyannis I, Zotou A, Samanidou V, Theodoridis G, Zougrou F (1993) J Liq Chromatogr 16:3017, doi:10.1080/10826079308019630
- Garrido JMPJ, Delerue-Matos C, Borges F, Macedo TRA, Oliveira-Brett AM (2004) Electroanalysis 16:1419, doi:10.1002/elan.200302966
- Xu F, Gao M, Wang L, Zhou T, Jin L, Jin J (2002) Talanta 58:427, doi:10.1016/S0039-9140(02)00312-0
- Ho KC, Chen CY, Hsu HC, Chen LC, Shiesh SC, Lin XZ (2004) Biosens Bioelectron 20:3, doi:10.1016/j.bios.2003.11.027

15. Itaya K, Shoji N, Uchida I (1984) *J Am Chem Soc* 106:3423, doi:10.1021/ja00324a007
16. Lin MS, Jan BI (1997) *Electroanalysis* 9:340, doi:10.1002/elan.1140090416
17. Gatjonyte R, Mlinauskas A (1998) *Sens Actuators B Chem* 46:236, doi:10.1016/S0925-4005(98)00123-3
18. Karyakin AA, Karyakina EE, Gorton L (1998) *J Electroanal Chem* 456:97, doi:10.1016/S0022-0728(98)00202-2
19. Karyakin AA, Gitelmacher OV, Karyakina EE (1995) *Anal Chem* 67:2419, doi:10.1021/ac00110a016
20. Karyakin AA, Gitelmacher OV, Karyakina EE (1994) *Anal Lett* 27:2861
21. Chi Q, Dong S (1995) *Anal Chim Acta* 310:429, doi:10.1016/0003-2670(95)00152-P
22. Karyakin AA, Karyakina EE, Gorton L (1996) *Talanta* 43:1597, doi:10.1016/0039-9140(96)01909-1
23. Jaffari SA, Turner APF (1997) *Biosens Bioelectron* 12:1, doi:10.1016/0956-5663(96)89084-1
24. Deng Q, Li B, Dong S (1998) *Analyst (Lond)* 123:1995, doi:10.1039/a803309i
25. Zhang X, Wang J, Ogorevc B, Spichiger US (1999) *Electroanalysis* 11:945, doi:10.1002/(SICI)1521-4109(199909)11:13<945::AID-ELAN945>3.0.CO;2-7
26. Karyakin AA, Karyakina EE (1999) *Sens Actuators B Chem* 57:268, doi:10.1016/S0925-4005(99)00154-9
27. Karyakin AA, Karyakina EE, Gorton L (2000) *Anal Chem* 72:1720, doi:10.1021/ac990801o
28. Narayanan SS, Sholz F (1999) *Electroanalysis* 11:465, doi:10.1002/(SICI)1521-4109(199906)11:7<465::AID-ELAN465>3.0.CO;2-#
29. Itaya K, Akahoshi H, Toshima S (1982) *J Electrochem Soc* 129:1498, doi:10.1149/1.2124191
30. Garjonyte R, Mlinauskas A (1999) *Sens Actuators B Chem* 56:93, doi:10.1016/S0925-4005(99)00161-6
31. Koncki R, Wolfbeis OS (1999) *Biosens Bioelectron* 14:87, doi:10.1016/S0956-5663(98)00095-5
32. Karyakin AA, Chaplin MF (1994) *J Electroanal Chem* 370:301, doi:10.1016/0022-0728(93)03163-J
33. Boyer A, Kalcher K, Pietsch R (1990) *Electroanalysis* 2:155, doi:10.1002/elan.1140020212
34. Zakharchuck NF, Meyer B, Hennig H, Scholz F, Jaworski A, Stojek Z (1995) *J Electroanal Chem* 398:23, doi:10.1016/0022-0728(95)04225-2
35. Pournaghi-Azar MH, Dastangoo H (2004) *J Electroanal Chem* 573:355, doi:10.1016/j.jelechem.2004.07.023
36. Pournaghi-Azar MH, Dastangoo H, Ziaei M (2007) *J Solid State Electrochem* 11:1221, doi:10.1007/s10008-007-0273-9
37. Pournaghi-Azar MH, Ahoor F (2008) *J Electroanal Chem* (in press)
38. Pournaghi-Azar MH, Razmi-Nerbin H (1998) *J Electroanal Chem* 456:83, doi:10.1016/S0022-0728(98)00284-8
39. Bard AJ, Faulkner IR (2001) *Electrochemical methods, fundamentals and applications*. Wiley, New York
40. Marcus RA (1965) *J Chem Phys* 43:679, doi:10.1063/1.1696792
41. Anson FC (1980) *J Phys Chem* 84:3336, doi:10.1021/j100462a002
42. Galus Z (1994) *Fundamentals of electrochemical analysis*, 2nd edn. Ellis Horwood, New York