CROATICA CHEMICA ACTA
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X
Croat. Chem. Acta **82** (3) (2009) 599–606.
CCA-3351

Original Scientific Paper

Electrocatalytic Response of Dopamine at a Carbon Paste Electrode Modified with Ferrocene

Mohammad Ali Kamyabi,* and Firoozeh Aghajanloo

Department of Chemistry, Faculty of Sciences, Zanjan University, Zanjan 45195-313, Iran

RECEIVED NOVEMBER 24, 2007; REVISED JUNE 5, 2008; ACCEPTED JUNE 16, 2008

Abstract. Carbon paste electrodes modified by ferrocene (Fc) were used for electrocatalytic oxidation and determination of dopamine. The modified carbon paste electrode shows excellent electrocatalytic activity toward the oxidation of dopamine (DA) in a phosphate buffer solution (pH=6.0). A anodic oxidation of DA (in pH=6.0) at the Fc-modified carbon paste electrode occurred at low overpotential (0.18 V *vs.* Ag|AgCl), and treatment of the voltammetric data showed that it was a purely diffusion-controlled reaction with the involvement of one electron in the rate-determining step. The mechanism for the interaction of DA at the Fc modified CPE is proposed. The rate constant k', transfer coefficient α for the catalytic reaction and the diffusion coefficient of DA in the solution, D, were found to be 6.92×10^{-2} cm s^{-1}, 0.71 and 1.41×10^{-5} cm^2 s^{-1}, respectively. The interference of ascorbic acid was investigated and greatly reduced using sodium tetraphenylborate incorporated modified carbon paste electrodes.

Keywords: dopamine, ferrocene, electrocatalytic oxidation, carbon paste electrode

INTRODUCTION

Dopamine (DA) is a chemical naturally produced in the body. In the brain, DA functions as a neurotransmitter, activating dopamine receptors. Dopamine is also a neurohormone released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary.[1] Its deficiency will lead to brain disorder such as Parkinson's disease and schizophrenia.[2–4] Although it can be detected through electrochemical methods due to DA's electroactive property,[5–7] the irreversibility of its electrochemistry as well as the fouling of electrode surface by the oxidation product results in poor performance at the conventional electrodes. Furthermore, the coexisted ascorbic acid (AA) and uric acid (UA)[8–10] in the body fluids in high levels can be easily oxidized at a potential rather close to that of DA and always interfere with the determination of DA at the conventional electrodes. Therefore, improvement of the sensitivity and selectivity of the working electrode towards DA has been becoming a long-standing of researchers.

Several methods have been applied to overcome the above problems.[11–30] Electrochemical pretreatment and chemically modified electrodes have been investigated to resolve the voltametric peaks of DA and AA[11–13] or those of DA, AA, and UA.[10,14–22] Nafion-modified electrodes were especially interesting for the determination of DA in the presence of AA.[23–25] Nafion film can repel successfully ascorbic acid and other negatively charged species but attract positively charged DA. However, this kind of modified electrode suffers from slow response due to low diffusion coefficients of analytes in the films. To determine DA in the presence of a large excess of AA or to perform their simultaneous determination, some electroanalytical techniques such as differential pulse voltammetry,[20–23] square wave voltammetry,[16,26–27] and fast scan voltammetry[5,28–30] have been reported in the literature.

Ferrocene (Fc) and its derivatives are widely used in electrochemistry because of their good stability in solution and rapid response to many electroactive substances.[31] Fc may show sublimation and ferricinium ion (Fc^+) is soluble in aqueous solution, which may result in a poor reproducibility and a short lifetime. To improve the attachment to electrode surface, a few methods have been developed.[32–50] Cass *et al.*[32] adopted substituted Fc as a mediator to make a ferrocene-mediate enzyme electrode for amperometric determination of glucose. Gorton *et al.*[33] studied ferrocene-containing siloxane polymer modified electrode surface with a poly(ester-sulfuric acid) cation-exchanger to improve the stability

* Author to whom correspondence should be addressed. (E-mail: makamyabi@gmail.com)

of the mediator. Another alternative method is to synthesize a few Fc derivatives with specific functional groups.[34–35] Wang's research group[36] reported the mixed Fc–glucose oxidase-carbon paste electrode with three kinds of Fc derivatives. The method of immobilizing an Fc with no substitutions on to a GC electrode surface by Nafion coating was used as an electron transfer mediator between the electrode and glucose oxidase was by Dong's research group.[37] Bu's research group[38] reported a novel neutral Fc-containing polyacrylamide based redox gel that could be used in biosensor. The other alternative method to increase the stability of Fc and its derivatives is the formation of inclusion complex with cyclodextrin (CD), a class of torpidly shaped cycloamyloses with a hydrophilic outer surface and a hydrophobic inner cavity, which makes the dissolubility of Fc decrease.[39–43] The organic thiols that chemisorbed on gold are the other methods to increase the stability of Fc.[44–50]

In this study, a sensitive and selective electrochemical method for the determination of dopamine was developed using carbon paste electrode modified with Fc. Although, ferricinium ion (Fc^+) is soluble in aqueous solution but cyclic voltammetry experiments shows that Fc-modified carbon paste is stable enough in aqueous solution and it can be used as an electrochemical sensor for determination of DA. The interference of ascorbic acid greatly reduced by using sodium tetraphenylborate incorporated carbon paste modified electrodes. To our knowledge, there are no reports presenting the use of sodium tetraphenylborate as an additive for reducing the anion interference in voltammetry experiments.

EXPERIMENTAL

Chemicals and Solutions

Ferrocene and dopamine were from Merck and were used as received. All the other chemicals were of analytical-reagent grade from Merck or Fluka and were used directly without further purification. High purity nitrogen was used for deaeration. Triply distilled water was used to prepare buffer and reagent solutions. The supporting electrolyte used in all the experiments was 0.1 M KCl or 0.1 M phosphate buffer solutions.

Chemicals and Solutions

Voltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a bare or chemically modified carbon paste electrode as working electrode, Ag|AgCl reference electrode and a platinum wire counter electrode. A digital pH meter model 780 Metrohm was applied for the preparation of the buffer solution, which was used as supporting electrolyte in the voltammetric experiments.

Fabrication of Modified Electrode

The unmodified carbon-paste electrode was prepared as previous works[51–54] by mixing graphite powder with an appropriate amount of paraffin oil (mass ratio, 65 : 35) and a portion of the composite mixture was packed into a teflon tube (*ca*. 2 mm i.d.) that connected to the end of a glass carbon electrode. The tip of the electrode was polished with a weighing paper. The modified electrode was prepared by mixing unmodified composite with Fc (modifier mass fraction, $w(\mathrm{Fc}) = 0.8\,\%$) and then homogenized by spatula. The modified composite was then used in the same way as the unmodified electrode. The area of these electrodes was 0.065 ± 0.004 cm^2, which was evaluated from chronoculometric experiments.

RESULTS AND DISCUSSION

Figure 1 shows the typical cyclic voltamograms of DA in a pH = 6.0 phosphate buffer solution at a bare CPE and a ferrocen ($w(\mathrm{Fc}) = 0.8\,\%$) modified CPE between −0.2 to 1.0 V at scan rate 100 mV s^{-1} in 1.2×10^{-3} mol L^{-1} DA solution. This figure illustrates the cyclic voltammetric responses of a bare carbon paste electrode (curves a, b) and Fc-modified CPE (curves c, d) without and with

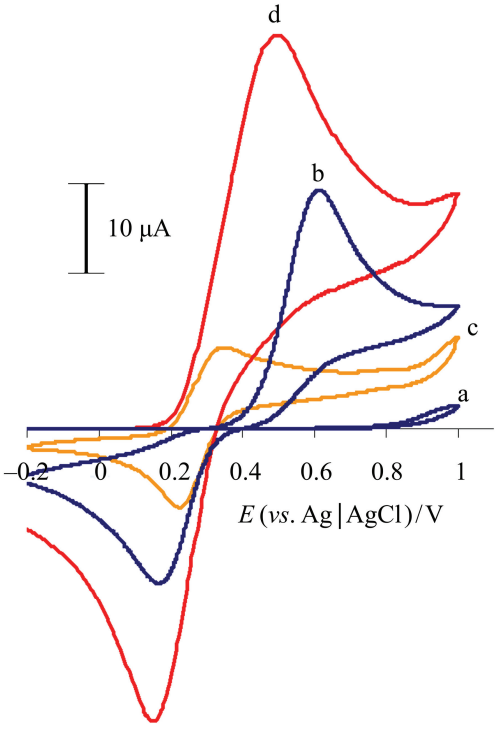

Figure 1. Cyclic voltamograms: at bare carbon paste electrode (a) in the absence, (b) in the presence of 1.2 mmol L^{-1} dopamine; and at 0.8 % Fc-modified carbon paste electrode (c) in the absence, (d) in the presence of 1.2 mmol L^{-1} dopamine; supporting electrolyte, 0.1 M phosphate buffer (pH = 6.0); scan rate 100 mVs^{-1}.

DA solution (1.2×10^{-3} mol L^{-1}) respectively. At the surface of the unmodified electrode, the direct oxidation of DA produces a pair of redox peaks were observed for 1.2×10^{-3} mol L^{-1} DA. The oxidation and reduction peak potentials occurred at 0.61 and 0.18 V, respectively. Under the identical conditions, the ferrocen modified CPE gives increased peak currents to DA. A well defined redox wave of DA was observed with the anodic peak potential at 0.43 V and the corresponding cathodic peak potential at 0.15 V. So, the peak separation was smaller than that at the bare CPE, and further, substantial increases in peak current were also observed due to the improvements in the reversibility of the electron transfer processes. This suggests an efficient oxidation reaction of DA at the Fc modified CPE. By using Fc as an electron mediator in the matrix of the modified electrode, the overpotential for the anodic oxidation of dopamine becomes considerably lower and the rate of the heterogeneous electron transfer is increased.

Since ascorbic acid is the major interference in the electrochemical measurement of DA, its voltammetric behavior at the Fc modified electrode was also studied.

Optimization of Experimental Variables for Electrocatalytic Oxidations

The amount of ferrocene in the carbon paste has a significant influence on the voltammetric response of the modified electrode. This is shown more distinctly in Figure 2, which is a plot of peak current and peak potential *vs*. the modifier mass fraction, w(Fc). As this figure illustrates, the oxidation current for 1.2×10^{-3} mol L^{-1} dopamine increases gradually with modifier, and at w(Fc) = 0.8 % the oxidation current achieves a maximum and then decreases with a further increase of the modifier mass fraction. This occurs may be, due to a decrease in the graphite content in the paste and, consequent reduction of the conductive electrode area. The same behavior was observed in an earlier work.[26] The peak potential for oxidation of dopamine is also affected by a change in the w(Fc), *i.e.* the peak potential is decreased between w(Fc) = 0 and w(Fc) = 0.8 % and then increases with increasing w(Fc). Therefore, the role of modifier is to enhance the peak current and also to decrease the overpotential for oxidation of DA. It was found that the best carbon paste composition for an electrode is with w(Fc) = 0.8 %, w(graphite) = 66.1 % and w(paraffin oil) = 33.1 %.

The influence of the solution pH on the electrochemical response of DA at the ferrocen modified CPE was investigated by cyclic voltammetry using a 0.1 M phosphate buffer at various pH values ranging from 3.0 to 9.0. According to Figure 3, curve a, the electrocatalytic oxidation potential (E_{pa}) of DA shifted to less positive potential with a slope of –58.5 mV/pH, which is close to that expected for a monoelec-

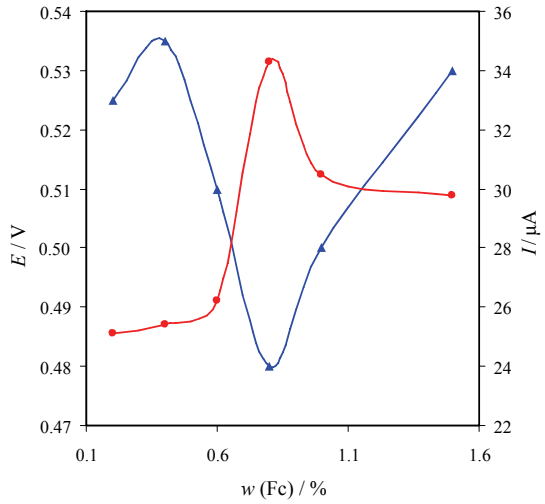

Figure 2. Effect of modifier fraction, w/%, on the peak current (●) and peak potential (▲) of cyclic voltamograms for 1.2 mmol L^{-1} of dopamine in 0.1 M phosphate buffer (pH = 6.0); scan rate of 100 mV s^{-1}.

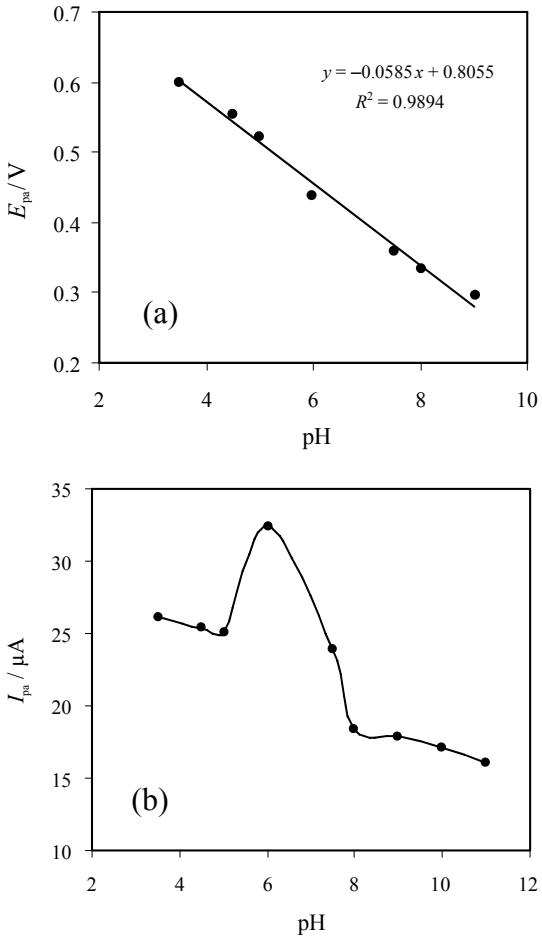

Figure 3. Dependence of the oxidation peak potential (a) and peak current (b) of 1.2 mmol L^{-1} dopamine on different pH values at scan rate of 100 mV s^{-1}.

tronic/monoprotonic electrode reaction which is –59.2 mV/pH at 25 °C. On the other hand, the number of protons involved in this process should be two.

The oxidation peak current I_{pa}, enhances as increasing pH, and decreases after attaining a maximum. Such a behavior for the oxidation of DA has been reported in the literature.[27–30] According to the Figure 3b, the electrocatalytic process drastically occurred at pH = 6.

Cyclic voltamograms (not shown) recorded at a ferrocene modified electrode in the presence of a different concentration of DA show that the anodic peak current increases with DA concentration in the solution. A typical calibration curve (Figure 4) based on the anodic peak current shows a linear range with a correlation coefficient over 0.999, localized in the concentration range 1.2×10^{-4} to 1.1×10^{-2} mol L^{-1}. The lower detection limit,[55] C_m, was obtained by using the equation $C_m = 3S_b/m$, where S_b is the standard deviation of the blank response (expressed in μA) and *m,* sensitivity, is the slope of the calibration plot (11.98 μA mmol L^{-1}). In this study, from the analysis of the data, we estimate that the limit of detection of DA is 9.4×10^{-6} mol L^{-1}.

The stability of electrocatalytic activity of Fc modified CPE toward oxidation of DA was checked by repetitive scanning at scan rate of 100 mV s^{-1}. Although, ferricinium ion (Fc^+) is soluble in aqueous solution which may result in a poor reproducibility and a short lifetime but the results show that the modified electrode has a good stability in aqueous solutions. The results show that the modified electrode has a good stability in aqueous solutions. Figure 5 shows the repeated twenty cyclic voltamograms of an Fc modified CPE in a pH = 6.0 phosphate buffer solution between –0.2 to 0.8 V at scan rate 100 mV s^{-1}. The peak current of

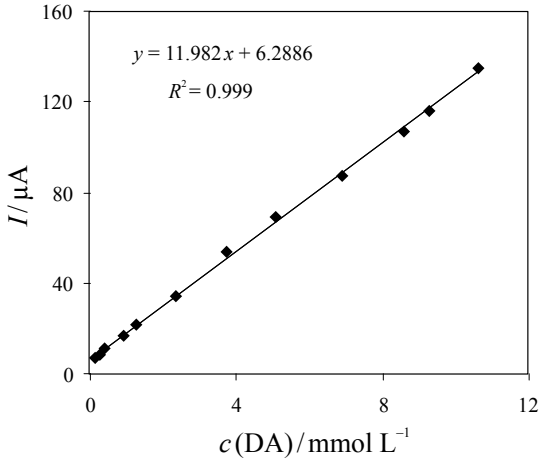

Figure 4. Calibration curve for dopamine at a 0.8 % Fc-modified CPE in 0.1 M phosphate buffer pH = 6; scan rate100 mV s^{-1}.

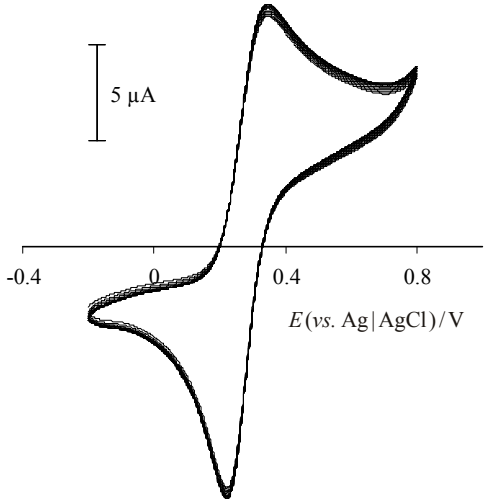

Figure 5. Repeated twenty cyclic voltamograms of an Fc-modified CPE in a pH = 6 phosphate buffer solution between −0.2 to 0.8 V, at scan rate of 100 mV s^{-1}.

the mediator was considered as a factor indicating the stability of modified electrode at various conditions of operation. As this figure shows the anodic peak current has a small decrease (about 5 %) after twenty cyclic voltamograms in the supporting electrolyte. And these phenomena show that the modified electrode is stable in aqueous solution.

Kinetic Aspects and Mechanistic Studies of Electrocatalytic Oxidation of Dopamine at the Surface of a Modified Electrode

Scan Rate Effect Studies

Scan rate can influence the current responses of DA and corresponding electrochemical parameters could be deduced from the relationship between scan rate of potential sweep and current responses of DA. The dependence of oxidation peak current of 1.2 mmol L^{-1} DA on scan rate at the Fc-modified CPE in 0,1 M phosphate buffer (pH = 6), was illustrated in Figure 6. As the scan rate increased; the oxidation peak current (I_{pa}) increased. The I_{pa} was directly proportional to the square root of potential scan rate, $v^{1/2}$, over the range of 10–300 mV s^{-1}. This result indicates that the overall electrochemical reaction of DA at the modified electrode might be controlled by the diffusion of DA as well as by a kinetic process.

In addition, with increasing scan rate, the catalytic oxidation peak potential (E_p) shifts to more positive values and there is a linear correlation between the peak potential and the logarithm of scan rate, log (v/mV s^{-1}), as is illustrated in Figure 6. The Tafel slope *b* can be obtained from the linear relationship of E_p *vs.* log (v/mV s^{-1}) by using the following equation:[56]

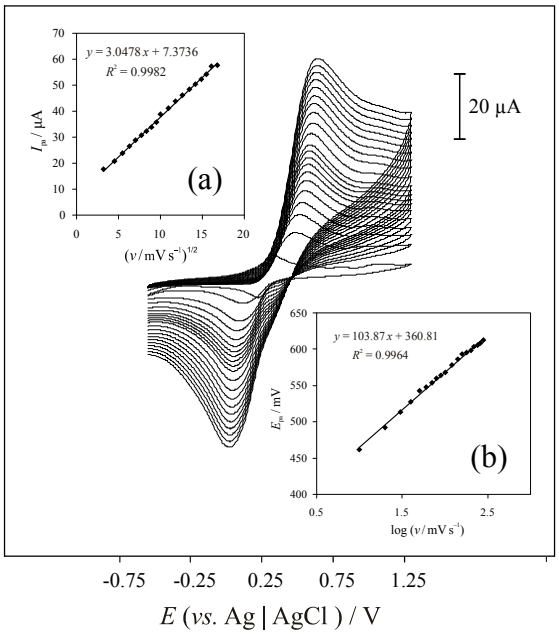

Figure 6. Dependence of the cyclic voltametric response at a modified carbon paste electrode on sweep rate in 0.1 M phosphate buffer (pH = 6.0) containing 1.2 mmol L^{-1} dopamine. Scan rate: over the range of 10 – 300 mV s^{-1}. (a) Variation of the anodic peak current with the square root of sweep rate. (b) Plot of anodic peak potential *vs.* logarithm of scan rate.

$$E_p = (b/2)\log(v/\mathrm{mV\,s^{-1}}) + \text{constant} \qquad (1)$$

On the basis of Eq. (1), the slope of E_p *vs.* log (v) plot is $b/2$, where b indicates the Tafel slope. The plot of E_p versus log (v) indicates a linear variation for scan rates ranging 10–300 mV s^{-1} (inset b of Figure 6). The slope is $\partial E_p/\partial \log(v)$, which was found to be 0.104 V in this work. So, $b = 2 \times 0.104\ \mathrm{V} = 0.208\ \mathrm{V}$. Assuming the number of electrons transferred in the rate-limiting step, n is equal to 1, a transfer coefficient, α, was estimated as 0.71. If we assumed $n = 2$, α would then be equal to 0.86 which is not a common value, because for most electrode processes α ranges between 0.75 and 0.25.[57]

Rotating Disk Electrode Voltammetric Studies

Figure 7 represents the typical voltamograms of DA oxidation at a Fc-modified carbon paste rotating disk electrode as a function of the electrode rotation rates. The limiting current, I_{lim}, increases linearly with an increase of $\omega^{1/2}$ (ω is the rotating rate of the rotation disk electrode) at low rotational rates. However, conspicuous deviations from the theoretical line are observed at high rotational rates, suggesting that I_{lim} is controlled by the kinetics not by the diffusion of DA. When the rotation rate is low, the diffusion of DA through the rather thick

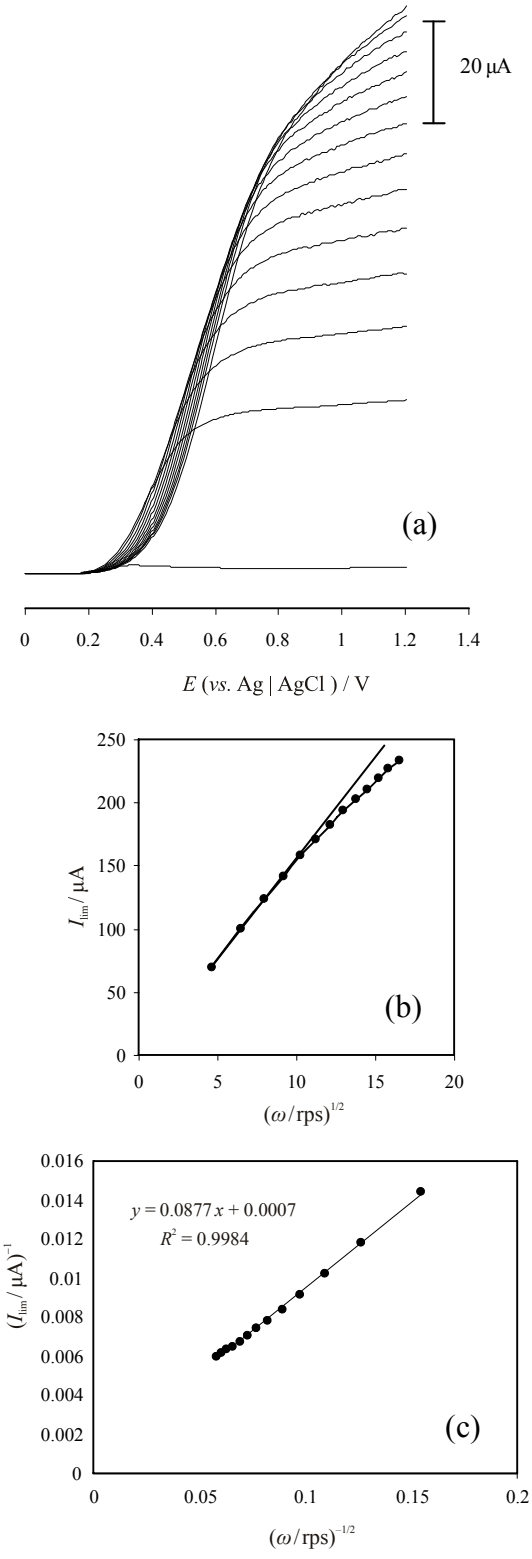

Figure 7. (a) Voltamograms of a Fc-modified carbon paste rotating disk electrode in a 1.2 mmol L^{-1} solution of dopamie in 0.1 M phosphate buffer (pH = 6.0) at various rotation rates from 200 to 3000 rpm, (b) Levich plot derived from RDE voltamograms of a Fc-modified carbon paste electrode in 1.2 mmol L^{-1} dopamine in 0.1 M phosphate buffer (pH = 6.0). (c) Koutecky-Levich plot corresponding to the Levich plot shown in 7.(b).

Levich layer controls the current so that linear I_{lim} *vs.* $\omega^{1/2}$ behavior is obtained. When the rotation rate is high, the thickness of the Levich layer decreases and the magnitude of the current are controlled by the kinetics. In this situation, the currents are conveniently analyzed by plots of $1/I_{lim}$ *vs.* $\omega^{-1/2}$. [31] Figure 7c shows such plots. The linearity of the plots in this figure indicates that the system follows the equation:

$$1/I_{lim} = 1/(nFAk'c) + 1/(0.62nFAv^{-1/6}D^{2/3}\omega^{1/2}c) \quad (2)$$

where c is the bulk concentration of DA (expressed in mol cm^{-3}), ω is the angular frequency of rotation (expressed in rad s^{-1}), D is the diffusion coefficient (expressed in cm^2 s^{-1}), v is the kinematic viscosity (expressed in cm^2 s^{-1}), k' is the reaction rate constant (expressed in cm s^{-1}) and all other parameters have their conventional meanings. The rate constant, k' can be calculated from the intercept of the Koutecky-Levich plot. From the value of the intercept, the k' was found to be 6.92×10^{-2} cm s^{-1}. The diffusion coefficient of DA in buffered aqueous 1.2×10^{-3} M dopamine of pH = 6.0 was determined as 1.41×10^{-5} cm^2 s^{-1}, from the slope of Koutecky-Levich equation at various rotation speeds of the modified carbon paste electrode. These values are comparable with those reported previously for the electrocatalytic oxidation of DA at the electrodes modified with other mediators. Finally, a catalytic mechanism that is compatible with the observed behavior is given in reactions (3) to (5):

$$Fc \rightleftharpoons Fc^+ + e \quad (3)$$

$$Fc^+ + DA \rightleftharpoons Fc + DA(quinone)^o + H^+ \quad \text{slow} \quad (4)$$

$$Fc^+ + DA(quinone)^o \rightleftharpoons Fc + DA_{ox} + H^+ \quad \text{fast} \quad (5)$$

The overall chemical reaction is as follows:

$$2\,Fc \rightleftharpoons 2\,Fc^+ + 2\,e \quad (6)$$

$$2\,Fc^+ + DA \rightleftharpoons 2\,Fc + DA_{ox} \quad (7)$$

In other words, the rate-determining step is a one-electron transfer step followed by a fast one electron process to give DA_{ox} as a final product.

Elimination of the Interference of AA

Usually AA is a major interferent for determination of DA. The interference of ascorbic acid greatly reduced by using sodium tetraphenylborate incorporated carbon paste modified electrodes. Tetraphenylborate is a bulky anion and repels ascorbic acid (AA) and other negatively charged species at optimized conditions. Figure 8 shows the cyclic voltamograms recorded at a carbon paste electrode modified with Fc (A) and modified with Fc and sodium tetraphenylborate (B) in the absence of AA and DA (curves a in all figures), and in presence of 2×10^{-3} mol L^{-1} AA (curves b in all figures), and 2×10^{-3} mol L^{-1} DA (curves c in all figures), at scan rate 100 mV s^{-1}. As can be seen the electrocatalytic activity of the Fc-modified electrode toward oxidation of DA remains almost unchanged in the presence of sodium tetraphenylborate. *Vice versa*, the oxidation response of the ascorbic acid at sodium tetraphenylborate incorporated carbon paste modified electrodes was completely disappeared. Therefore, a sodium tetraphenylborate incorporated Fc-modified carbon paste electrodes may be used for the selective determination of DA in the presence of AA. In order to determine DA in complex

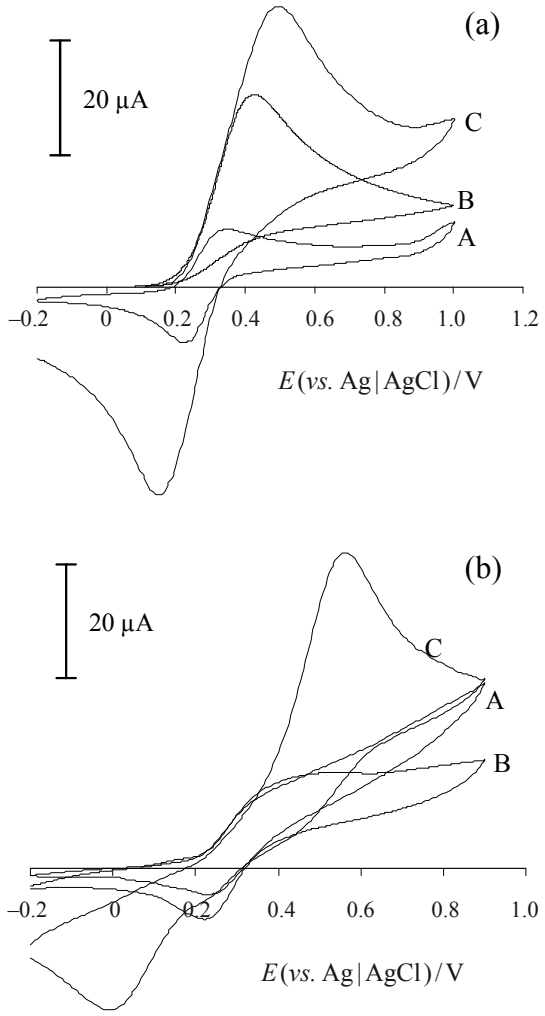

Figure 8. Cyclic voltamograms recorded at a carbon paste electrode modified with Fc (a) and carbon paste electrode modified with Fc and sodium tetraphenylborate (b) in 0.1 M phosphate buffer (pH = 6.0), (A) in the absence of AA and DA, (B) in the 2 mmol L^{-1} AA, (C) in the 2 mmol L^{-1} DA, scan rate 100 mV s^{-1}.

matrices containing different interfering species, the chromatographic methods must be used. The chromatographic separation and electrochemical detection is a powerful technique for separate analytical response of substrates which are oxidized at the same potential.

Determination of DA in human blood serum at the carbon paste modified electrode

The modified electrode was applied to the determination of DA in human blood serum. Although there are AA and some other interfering substances, such as proteins and glucose, they do not interfere with the determination of DA. Using the proposed methods described above, the results were shown in Table 1. The recovery and R.S.D. were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in human blood serum.

Table 1. Experimental results for the determination of DA in human blood serum ($n = 6$)

$10^4\, c$ (DA)/mol L^{-1}			R.S.D.[(b)]	Recovery
S. ph. m.[(a)]	Spiking	Found	%	%
1	3.0	3.03	99.8	101
2	3.0	2.98	100.3	99.3
3	3.0	3.04	100.2	101.3

[(a)] S. ph. m., Sample pharmacopoeia method.

[(b)] R. S. D., relative standard deviation.

Acknowledgments. The authors wish to express their gratitude to the Zanjan University Research Council for financial support of this work.

REFERENCES

1. P. Damier, E. C. Hirsch, Y. Agid, and A. M. Graybiel, *Brain* **122** (1999) 1437.
2. C. Martin, *Chem. Br.* **34** (1998) 40.
3. A. Heinz, H. Przuntek, G. Winterer, and A. Pietzcker, *Nervenarzt* **66** (1995) 662.
4. R. M. Wightman, L. J. May, and A. C. Michael, *Anal. Chem.* **60** (1988) 769A.
5. B. J. Venton and R. M. Wightman, *Anal. Chem.* **75** (2003) 414A.
6. Z. Xun, C. Cai, W. Xing, and T. Lu, *J. Electroanal. Chem*. **545** (2003) 19.
7. J. A. Stamfold, and J. B. Justice Jr., *Anal. Chem*. **68** (1996) 359A.
8. F. Gonon, M. Buda, R. Cespuglio, M. Jouvet, and J. F. Pujol, *Nature* **286** (1980) 902.
9. R. D. O'Neill, *Analyst* **119** (1994) 767.
10. A. Salimi, H. Mam-Khezri, and R. Hallaj, *Talanta* **70** (2006) 823.
11. D. R. Shankaran, K. Iimura, T. Kato, *Sensors Actuat. B* **94** (2003) 73.
12. J. Chen and C. S. Cha, *J. Electroanal. Chem*. **463** (1999) 93.
13. P. Zhang, F. H. Wu, G. C. Zhao, and X. W. Wei, *Bioelectrochem.* **67** (2005) 109.
14. J. M. Zen, C. T. Hsu, Y. L. Hsu, J. W. Sue, and E. D. Conte, *Anal. Chem*. **76** (2004) 4251.
15. H. R. Zare, N. Rajabzadeh, N. Nasirizadeh, and M. Mazloum Ardakani, *J. Electroanal. Chem.* **589** (2006) 60.
16. H. R. Zare, N. Nasirizadeh, and M. Mazloum Ardakani, *J. Electroanal. Chem.* **577** (2005) 25.
17. P. S. Siew, K. P. Loh, W. C. Poh, and H. Zhang, *Diamond Relat. Mater.* **14** (2005) 426.
18. R. Aguilar, M. M. Dávila, M. P. Elizalde, J. Mattusch, and R. Wennrich, *Electrochim. Acta* **49** (2004) 851.
19. W. C. Poh, K. P. Loh, W. D. Zhang, S. Triparthy, J. S. Ye, and F. S. Sheu, *Langmuir* **20** (2004) 5484.
20. Y. Li and X. Lin, *Sensors Actuat. B* **115** (2006) 134.
21. Y. Zhao, Y. Gao, D. Zhan, H. Liu, Q. Zhao, Y. Kou, Y. Shao, M. Li, Q. Zhuang, and Z. Zhu, *Talanta* **66** (2005) 51.
22. H. S. Wang, T. H. Li, W. L. Jia, and H. Y. Xu, *Biosens. Bioelectron.* **22** (2006) 664.
23. G. Nagy, G. A. Gerhardt, A. F. Oke, M. E. Rice, and R. N. Adams, *J. Electroanal. Chem.* **189** (1985) 85.
24. Y. Chen and T. C. Tan, *Talanta* **42** (1995) 1181.
25. J. Wang, P. Tuzhi, and T. Golden, *Anal. Chim. Acta* **194** (1987) 129.
26. C. R. Raj, K. Tokuda, and T. Ohsaka, *Bioelectrochemistry* **53** (2001) 183.
27. M. Zhang, K. Gong, H. Zhang, and L. Mao, *Biosens. Bioelectron*. **20** (2005) 1270.
28. M. L. A. V. Heien, M. A. Johnson, and R. M. Wightman, *Anal. Chem*. **76** (2004) 5697.
29. K. Pihel, Q. D. Walker, and R. M. Wightman, *Anal. Chem*. **68** (1996) 2084.
30. J. E. Baur, E. W. Kristensen, L. J. May, D. J. Wiedemann, and R. M. Wightman, *Anal. Chem.* **60** (1988) 1268.
31. S. L. Brooks, R. E. Ashby, and A. P. F. Turner, *Biosensors* **3** (1987) 45.
32. A. E. G. Cass, G. Davis, G. D. Francis, and H. A. O. Hill, *Anal. Chem*. **56** (1984) 667.
33. L. Gorton, H. I. Karan, P. D. Hale, T. Inagaki, Y. Okamoto, and T. A. Skotheim, *Anal. Chim. Acta* **228** (1990) 23.
34. G. Jönsson, L. Gorton, and L. Pettersson, *Electroanalysis* **1** (1989) 49.
35. N. C. Foulds and C. R. Lowe, *Anal. Chem*. **60** (1988) 2473.
36. J. Wang, L. H. Wu, Z. Lu, R. Li, and J. Sanchez, *Anal. Chim. Acta* **228** (1990) 251.
37. S. J. Dong, B. X. Wang, and B. F. Liu, *Biosens. Bioelectron*. **6** (1991) 215.
38. H. Z. Bu, S. R. Mikkelsen, and A. M. English, *Anal. Chem*. **67** (1995) 4071.
39. X. L. Wang, G. R. Zhang, X. W. Shi, and T. L. Sun, *Chem. J. Chin. Univ*. **21** (2000) 1383.
40. S. H. Liu, W. M. Mo, and F. Chen, *J. Instrum. Anal. (Chin.)* **18** (1999) 42.
41. G. R. Zhang, X. L. Wang, X. W. Shi, and T. L. Sun, *Talanta* **51** (2000) 1019.
42. P. M. Bersier, J. Bersier, and B. Klingert, *Electroanalysis* **3** (1991) 443.
43. C. A. Groom and J. H. T. Luong, *Biosensors* **9** (1994) 305.
44. C. A. Widrig, C. A. Alves, and M. D. Porter, *J. Am. Chem. Soc*. **113** (1991) 2805.
45. C. A. Widrig, C. Chung, and M. D. Porter, *J. Electroanal. Chem*. **310** (1991) 335.
46. M. G. Samant, C. A. Brown, and J. G. Gordon II, *Langmuir* **7** (1991) 437.
47. M. D. Porter, T. B. Bright, D. L. Allara, and C. E. D. Chidsey, *J. Am. Chem. Soc*. **109** (1987) 3559.
48. L. Strong and G. M. Whiteside, *Langmuir* **4** (1988) 546.
49. A. Ulman, J. E. Eilers, and N. Tillman, *Langmuir* **5** (1989) 1147.
50. Sh. Wang, and D. Du, *Sensors and Actuators B* **97** (2004) 373.

51. A. Abbaspour and M. A. Kamyabi, *J. Electroanal. Chem*. **576** (2005) 73.
52. A. Abbaspour, and M. A. Kamyabi, *J. Electroanal. Chem.* **584** (2005) 117.
53. M. A. Kamyabi, and F. Aghajanloo, *J. Electroanalytical Chem.* **614** (2008) 157.
54. M. A. Kamyabi, Sh. Shahabi, H. Hosseini-Monfared, *J. Electrochemical Soc.* **155** (2008) F8-F12.
55. D. A. Skoog, F. J. Holler and T. A. Nieman, *Principles of Instrumental Analysis*, 5th ed., Saunders College Publishing, 1998.
56. J. A. Harrison, and Z. A. Khan, *J. Electroanal. Chem*. **28** (1970) 153.
57. A. J. Bard, and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980, Chapter 3, p. 96.

SAŽETAK

Elektrokatalitički odziv dopamina na elektrodi od ugljikove paste modificiranoj ferocenom

Mohammad Ali Kamyabi i Firoozeh Aghajanloo

Department of Chemistry, Faculty of Sciences, Zanjan University, Zanjan 45195-313, Iran

Elektrode od ugljikove paste modificirane ferocenom korištene su za elektrokatalitičku oksidaciju i određivanje dopamina. Modificirana elektroda pokazuje odličnu elektrokatalitičku aktivnost za oksidaciju dopamina u fosfatnoj puferskoj otopini pH = 6,0. Anodna oksidacija dopamina pod navedenim uvjetima dešava se uz mali prenapon (0,18 V prema Ag|AgCl), a obrada voltametrijskih mjerenja pokazala je da je elektrodna reakcija kontrolirana difuzijom i da uključuje jedan elektron u najsporijem stupnju. Predložen je mehanizam istraživane elektrodne reakcije. Određena je konstanta brzine elektrodne reakcije ($k = 6{,}92 \times 10^{-2}$ cm s^{-1}), koeficijent prijenosa elektrona (α = 0,71) i difuzijski koeficijent dopamina ($D = 1{,}41 \times 10^{-5}$ cm^2 s^{-1}). Utjecaj askorbinske kiseline je istražen i uvelike smanjen dodatkom natrijeva tetrafenilborata u ugljikovu pastu.