Anal. Bioanal. Electrochem., Vol. 6, No. 5, 2014, 595-605

Analytical & Bioanalytical Electrochemistry

Full Paper

Electrocatalytic Oxidation of Ascorbic Acid on a Modified Carbon Ceramic Electrode with Carbon Nanotube and Rh(III)terpyridine Complex

Sohrab Ershad*, Hamzeh Akhoundi-Yamchi

Department of Chemistry, Faculty of Science, Analytical Research Laboratory, Payame Noor University, PO BOX 19395-3697, Tehran, Iran

* Corresponding Author, Tel.: +984142236611; Fax: +984142236978

E-Mail: sohrabsd@yahoo.com

Received: 30 June 2014 / Accepted with minor revision: 12 October 2014 / Published online: 31 October 2014

Abstract- A novel chemically modified electrode containing Rh(III)terpyridine complex was achieved on the surface of glass carbon electrode by sol-gel technique. The electrochemical behavior of modified electrode was characterized by cyclic voltammetry in detail. The film electrode obtained was very stable and exhibited electrocatalytic response for oxidation of ascorbic acid. Results showed at bare GC electrode, a small oxidation peak current was observed at about 0.42 V and a well-formed sharp catalytic oxidation peak at about -0.08 V was observed at Rh(III)terpyridine complex modified electrode. The transfer coefficient (α) for electrocatalytic oxidation of ascorbic acid and the diffusion coefficient of this substance under the experimental conditions were also investigated.

Keywords- Rh(III)terpyridine Complex, Cyclic Voltammetry, Ascorbic Acid, Electrocatalytic Oxidation

1. INTRODUCTION

Research in the field of chemically modified electrodes (CMEs) is still an active area, since there exist several compounds that their oxidation or reductions at commonly used electrodes are accompanied with a considerable overvoltage. The application of chemically

modified electrodes in electroanalysis offers several advantages. They can lower the overpotential, increase the reaction rate and sensitivity and improve selectivity [1-5]. Ascorbic -acid (AA) is present in many biological systems [6] and multivitamin preparations, which are commonly used to supplement inadequate dietary intake. Nevertheless it is widely used in foods as antioxidant for the stabilization of color and aroma with subsequent extension of the storage time of the products. Thus, the determination of ascorbic acid content is particularly important in the pharmaceutical and food industry. It is generally accepted that direct oxidation of AA at conventional electrodes are totally irreversible [7,8] and therefore requires a high overpotential which is much higher than its standard redox potential. Moreover, the direct redox reactions of these compounds at bare conventional electrodes often suffer from pronounced fouling effect, which results in rather poor reproducibility [9,10]. One promising approach for minimizing this effect is the use of chemically modified electrodes (CMEs). Many different strategies have been employed for the electrode modification, such as electrochemical polymerization [11,12], covalent bonding [13,14] and mixing with carbon paste [15,16].

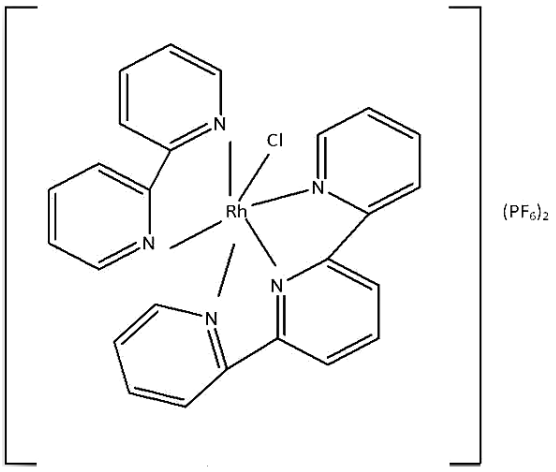
One promising approach is the use of chemically modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode surface. The sol-gel process is very well adopted for coating of thin films on complex shapes. The porosity and pore size of these films can be controlled to maximize the specific surface area and to ensure that permeability of the film remain high. Furthermore, the sol-gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is suitable inclusion of organic moieties that cannot withstand high temperatures [17].

But up to now, the CMEs containing Rh(III)terpyridine complex that were fabricated by sol-gel technique have not been reported. In this paper, we used an electrode for electrocatalytic oxidation of ascorbic acid that was developed via an easy and effective sol-gel immobilization method. This electrode comprises silicon dioxide gel films doped with Rh(III)terpyridine complex, which retains its structure, electrochemical activity and electrocatalytic properties to a large extent.

2. EXPERIMENTAL

2.1. Reagents and Solutions

Ascorbic acid, Methyl trimethoxy silane (MTMOS), methanol and HCl were of analytical grade supplied by Merck. Deionized water was used for the preparation of all solutions. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 7 with phosphate buffer. The ligand of Rh(III)terpyridine complex (Scheme. 1) was synthesized, purified and characterized as reported [18].



Scheme 1. Molecular structure of Rh(III)terpyridine complex

2.2. Instrumentation

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. A GC electrode was used as working electrode. A platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it (all electrode obtained from Azar Electrode Co., Urmia, Iran).

2.3. Preparation of Modified Electrode

The method of immobilizing Rh(III)terpyridine on GC electrode is described briefly as follows. The carbon ceramic electrode was polished with emery paper (p 2000) and then by 0.05 µm alumina powder. Then electrode was rinsed by distilled water and sonicated in water and absolute ethanol, respectively (each for 5 min), and then allowed to dry at room temperature. At the first 5 mg Rh(III)terpyridine was dissolved in 1ml methanol and homogenized thoroughly by sonication for 5 min until a clear solution was obtained. Then, 0.9 ml of this solution was mixed with 0.6 ml (MTMOS), and 0.1 ml hydrochloric acid (0.1 M) and stirred for 5 min until a homogeneous gel solution resulted. The resulting clear solution was aged for 30 min, and then 10 µl of the freshly prepared mixed solution was pipetted onto the surface of GC electrode. The gel films were dried in an air for 24 h and were ready for use. A few I-E runs were needed at the beginning to stabilize the electrode and obtain reproducible results.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Rh-complex/MWCNTs-modified Carbon Ceramic Electrode

The Rh(III)-complex/MWCNT modified carbon ceramic electrode was first characterized by SEM. Scanning electron microscopy (SEM) has been an essential tool for characterizing the surface morphology and fundamental physical properties of the absorbent. A typical scanning electron micrograph image of the carbon ceramic electrode, MWCNT modified CCE and Rh(III)-complex/MWCNT modified CCE surface, are shown in Fig. 1.

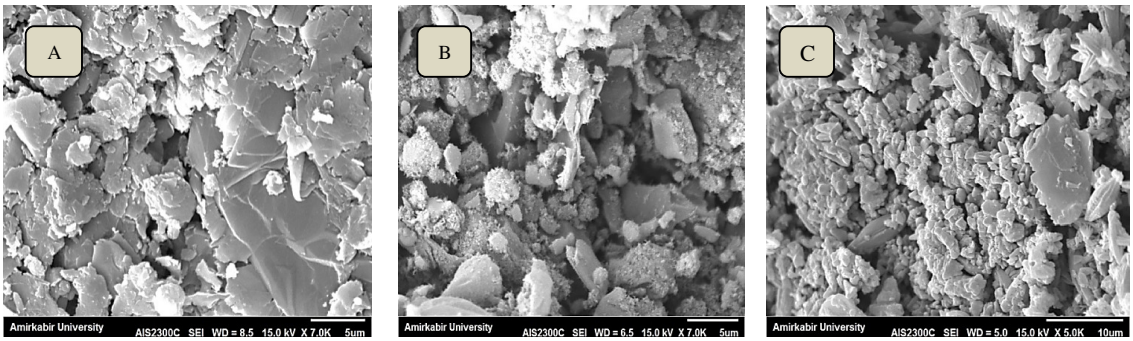


Fig. 1. SEM image of (A) bare carbon ceramic electrode (B) MWCNT modified CCE (C) Rh(III)-complex/MWCNT modified CCE

3.2. Electrocatalytic Oxidation of Ascorbic Acid at the Rh(III)-complex Modified Carbon Ceramic Electrode

The electrochemical properties of the Rh(III)terpyridine modified carbon ceramic electrode with sol-gel technique were studied, using cyclic voltammetry. Fig .2 shows typical cyclic voltammograms of the bare GC electrode and Rh(III)terpyridine modified carbon ceramic electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 50 mV s^{-1} It shows that the oxidation peak areas of Rh(III)terpyridine modified carbon ceramic electrodes are much larger than the bare carbon ceramic electrode.

The nature of the oxidation process was found to be diffusion controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) versus square root of the scan rate ($v^{1/2}$) for ascorbic acid. Fig.4A shows the cyclic voltammograms of Rh(III)terpyridine modified GC electrode in 0.1 M phosphate buffer (pH 7.0) containing 1 mM ascorbic acid at scan rates: 10, 20, 30, 50 and 70 mVs^{-1}.

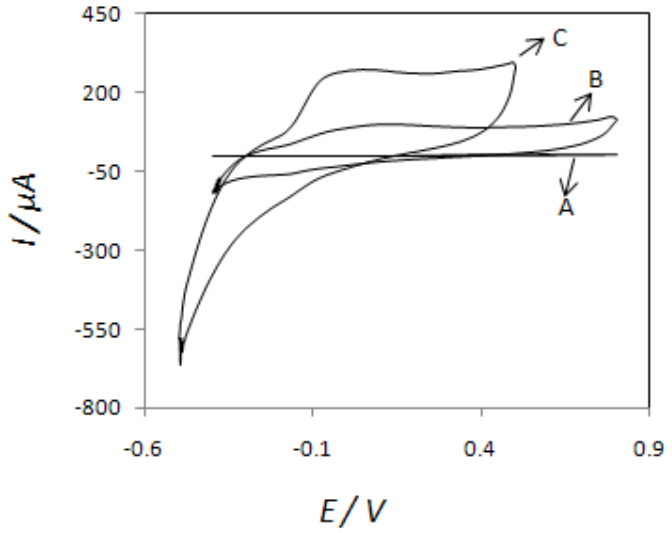


Fig. 2. Cyclic voltammograms for 1.0 mM AA at (A) bare GC electrode (B) modified carbon ceramic electrodes by carbon nanotube (C) carbon nanotube and Rh(III)terpyridine modified carbon ceramic electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 50 mV s^{-1}

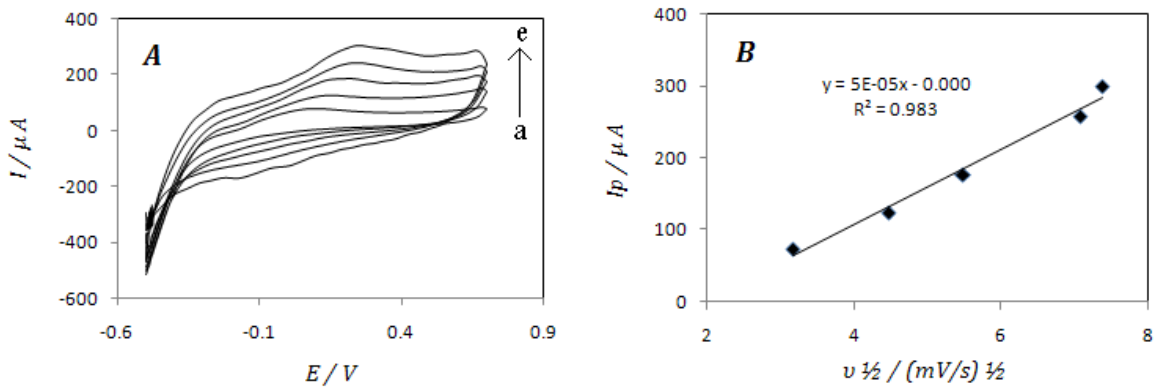


Fig. 3. (A) Cyclic voltammograms of Rh(III)terpyridine modified carbon ceramic electrodes in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) containing 1 mM ascorbic acid at scan rates of (a) 10, (b) 20, (c) 30, (d)50 and (e) 70 mV s^{-1} (B) dependence of the peak current with square root of the scan rate

It can be noted from Fig.4B that the anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$ (Fig.3B), the following linear relationship was obtained:

$I_p=5\times10^{-5}\ v^{1/2}$ (mV / s)$^{1/2}$, $R^2=0.983$ (1)

This behavior suggests that the oxidation process is controlled by diffusion.
Thus, according to the following equation for a totally irreversible diffusive process:

$$I_p=3.01\times10^5 n\,[(1-\alpha)\,n_\alpha]^{1/2} ACD^{1/2}\nu^{1/2} \quad (2)$$

And considering $(1-\alpha)n_\alpha$=0.492 (see below), D=9.77×10^{-7} cm^{2}s^{-1}(see chronoamperometric studies), A=0.125 cm^2, it is estimated that the total number of electrons involved in the anodic oxidation of ascorbic acid is n=1.94 ≈ 2.

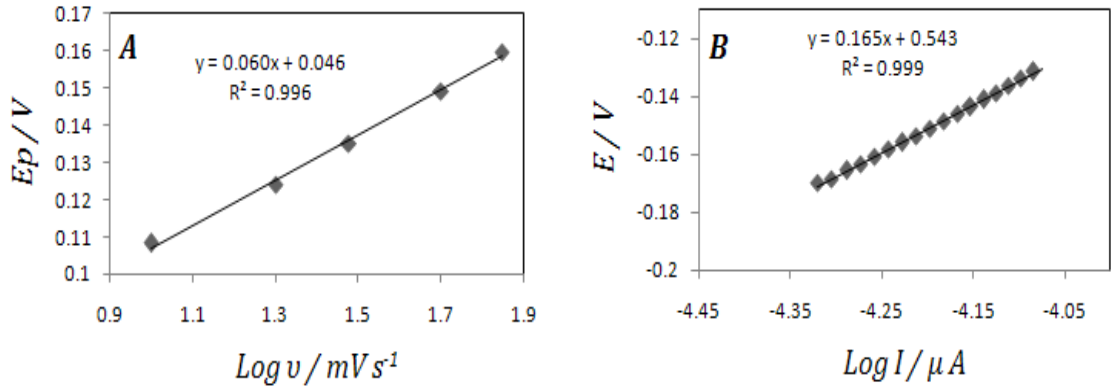


Fig. 4. (A) Plot of Ep *vs.* log ν. (B) Tafel plot derived from data of the rising part of the E *vs.* log *I* curve at a scan rate of 20 mV s^{-1}

In order to get information on the rate determining step, The peak potential, E_p is proportional to log υ as can be seen in Fig.4A. The slope of E_p *vs.* log υ is 0.06 mV. The Tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process:

$$E_{pa}=b/2(\log \upsilon)+\text{constant} \quad (3)$$

So, b=0.120 V. this result is close to that obtained from polarization measurement [19]. This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of α = 0.502.

The Tafel slope, b, can be obtained by another method. A Tafel plot was drawn (Fig.4B). Derived from data of the rising part of the current-voltage curve at a scan rate of 20 mV s^{-1}, A slope of 0.165 V^{-1} is obtained which indicates that the rate limiting step is one electron transfer (assuming a transfer coefficient of α = 0.499) using the following equation:

$$E/\log I=\text{Slope}=0.059/(1-\alpha)n_\alpha \quad (4)$$

Accordingly, the following mechanism can be proposed for the oxidation of ascorbic acid on a Rh(III)terpyridine modified carbon ceramic electrode in neutral solution [20]:

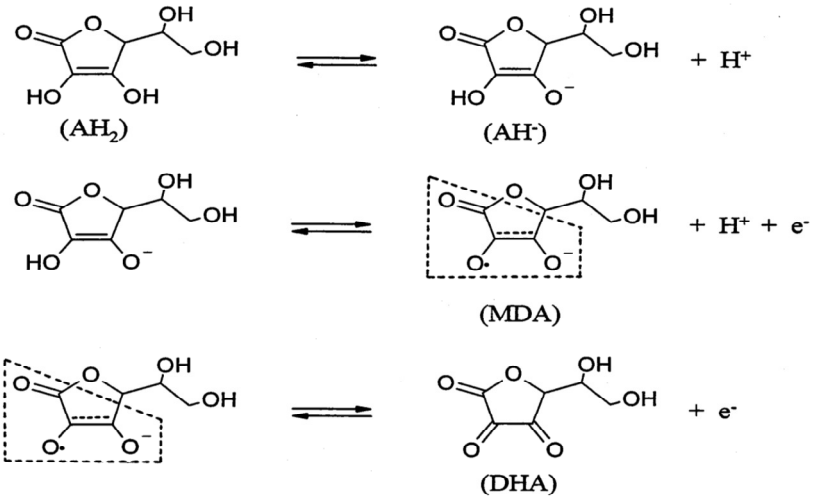


Fig. 5. The oxidation mechanism of ascorbic acid (AA) in an acidic medium [20]; AH_2, fully protonated AA; AH^-, monoprotonated AA; MDA, monodehydroascorbic acid radical anion; DHA, dehydroascorbic acid

Table 1. Comparison of linear range for determination of AA at various Electrodes and Modifiers

Electrodes and Modifiers	Electrochemical methods	Linear range of detection	Ref
GC - Cadmium Pentacyanonitrosylferrate	RDE - CV	12.4×10^{-3} to 31.4×10^{-3} M	[21]
GC - Microparticles Bi_2O_3/MWCNT	CV	20×10^{-6} to 5×10^{-3} M	[22]
GC - Bi_2O_3 Microparticles	RDE - CV	0.5×10^{-3} to 5×10^{-3} M	[23]
GC - SDS-MWCNTs	CV - DPV	0.4×10^{-3} to 3.5×10^{-3} M	[24]
GC - Poly(Caffeic acid)	CV – SWV	0.2×10^{-6} to 1.0×10^{-6} M	[25]
GC - SWCNT/Tungsten Oxide Nanoparticles	CV	0.2×10^{-3} to 10×10^{-3} M	[26]
GC – SWCNT	CV-DPV	0.2 to 150×10^{-6} M	[27]
GC – MWCNT	CV-DPV	15 to 800×10^{-6} M	[28]
Graphene/size-selected Pt nanocamposite	CV-DPV-Chronoamprometry	0.05 to 11.85×10^{-6} M	[29]
GC-Gold nanoparticles	CV-DPV	8×10^{-6} to 5.5×10^{-3} M	[30]
GC – CNT/Rh (III) Terpyridine Complex	CV-Chronoamprometry	0.5×10^{-3} to 6×10^{-3} M	This work

The electrocatalytic oxidation of ascorbic acid at the Rh(III)terpyridine modified electrode was studied by chronoamperometry. The chronoamperograms obtained for a series of ascorbic acid solutions with various concentrations as illustrated in Fig. 6.

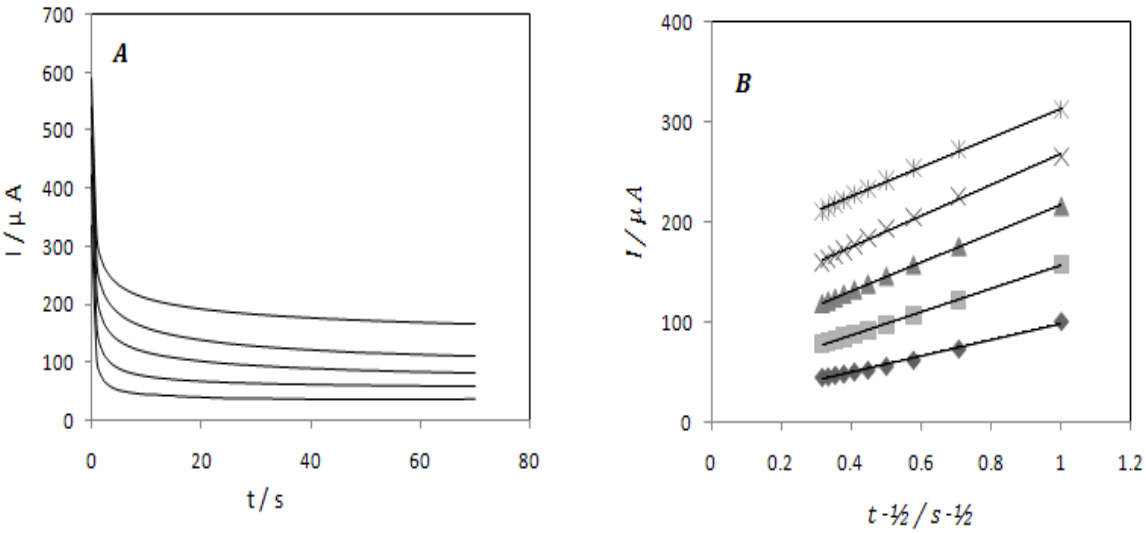


Fig. 6. (A) Chronoamprometric response of a Rh(III)terpyridine modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of ascorbic acid for a potential step of 100 mV vs. SCE In the range of 1, 2, 3, 4 and 5 mM (B) Plot of plot of *I* versus $t^{-1/2}$ obtained from chronoamprometric experiments. Inset shows the relationship between the slope of the linear segments and the ascorbic acid concentration

An increase in concentration of ascorbic acid was accompanied by an increase in anodic currents obtained for a potential step of 100 mV versus SCE. In addition, the level of the Cottrell current, which was measured for 70 s, increase with increasing concentration of ascorbic acid in the range of 1-5 mM. In chronoamperometric studies, the diffusion coefficient of ascorbic acid at the modified electrode can be determined. The relationship between current and time can be described by the Cottrell equation [31]:

$$I = nFAD^{1/2}C/\pi^{1/2}t^{1/2} \quad (5)$$

Where *D* is the diffusion coefficient ($cm^2\ s^{-1}$) and *C* is the bulk concentration ($mol\ cm^{-3}$). The plot of *I* versus $t^{-1/2}$ will be linear, and from the slope, the value of *D* can be obtained. Fig.7A shows the experimental plots of the resulting straight line were then plotted versus the concentration of ascorbic acid (Fig.7B, inset), from which we calculated a diffusion coefficient of $9.77\times10^{-7}\ cm^2\ s^{-1}$ for ascorbic acid.

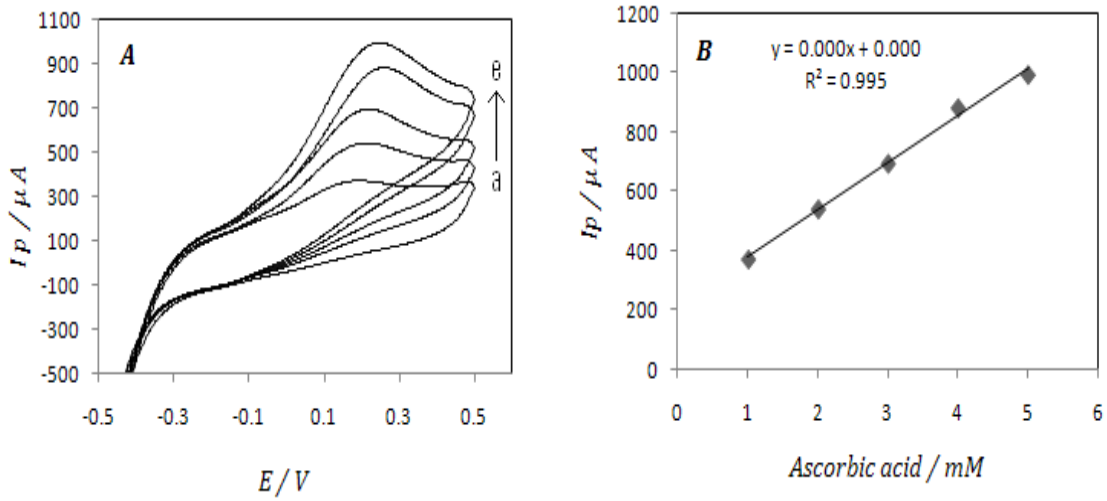


Fig. 7. (A) Cyclic voltammograms for increasing concentrations of ascorbic acid from 1 to 5 (a to e) mM (1-5) in buffer solution (pH 7.0) containing 0.1 M KCl solutions on Rh(III)-terpyridine modified electrode. Scan rate was 50 mVs^{-1}. (B) Calibration plot for concentrations of ascorbic acid from cyclic voltammograms

The cyclic voltammograms at different concentrations of ascorbic acid are shown in Fig.7A. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 1-5 mM ascorbic acid.

The cyclic voltammograms at different concentrations of AA are shown in Fig. 7A. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 1-5 mM AA. A comparison of linear range of AA determination at various electrodes and modifiers from previous reports is given in Table 1.

4. CONCLUSION

GC electrode coated with a thin film of sol-gel doped with Rh(III)terpyridine, act as an electrocatalyst for oxidation of ascorbic acid. This film exhibits excellent electrocatalytic behavior toward ascorbic acid oxidation in aqueous phosphate buffer solution containing K^+ ion. The overall number of electrons involved in the oxidation of ascorbic acid, the number of electrons involved in the rate-determining step and the diffusion coefficient of ascorbic acid were calculated. Thus, the results obtained for ascorbic acid shows that terpyridine complex can be used for determination of other compounds.

ACKNOWLEDGMENT

We gratefully acknowledge the support of this work by the Payame Noor University (PNU) council.

REFERENCES

[1] R. W. Murray, in: A. J. Bard (Ed.), Chemically Modified Electrodesin Electroanalytical Chemistry, vol. 13, Marcel Dekker, New York (1984) pp. 191.
[2] S. M. Golabi, H. R. Zare, and M. Hamzehloo, Electroanalysis 14 (2002) 611.
[3] H. R. Zare, and S. M. Golabi, J. Electroanal. Chem. 464 (1999) 14.
[4] S. M. Golabi, and H. R. Zare, J. Electroanal. Chem. 465 (1999) 168.
[5] J. M. Zen, A. S. Kumar, and D. M. Tsai, Electroanalysis 15 (2003) 1073.
[6] B. A. Fox, and A. G. Cameron, Food Science, Nutrition and Health, 5thed. , Edward Arnold, London (1989) pp. 261.
[7] K. J. Stutts, and R. M. Wightman, Anal. Chem. 55 (1983) 1576.
[8] Z. Gao, A. Ivaska, T. Zha, G. Wang, P. Li, and Z. Zhao, Talanta 40 (1993) 399.
[9] M. A. Kutnik, W. C. Hawkes, E. E. Schaus, and S. T. Omage, Anal. Biochem. 66 (1982) 424.
[10] L. A. Pachla, D. L. Reynolds, and P. T. Kissinger, J. Assoc. Off. Anal. Chem. 68 (1985) 1.
[11] I. G. Casello, and M. R. Guascito, Electroanalysis 9 (1997) 1381.
[12] P. R. Roy, T. Okajima, and T. Ohsaka, J. Electroanal. Chem. 561 (2004) 75.
[13] G. Moreno, F. Pariente, and E. Lorenzo, Anal. Chim. Acta 420 (2000) 29.
[14] H. R. Zare, and S. M. Golabi, J. Solid State Electrochem. 4 (2000) 87.
[15] B. Nalini, and S. S. Narayanan, Anal. Chim. Acta 405 (2000) 93.
[16] E. Miland, A. J. Miranda Ordieres, P. Tunon Blanco, M. R. Smyth, and C. O. Fagain, Talanta 43 (1996) 785.
[17] O. Dvorak, and M. Keith De Armond, J. Phys. Chem. 97 (1993) 2646.
[18] S. Ershad, L. A. Saghatfroush, J. Khodmarz, and S. G. Telfer, Int. J. Electrochem. Sci. 6 (2011) 3997.
[19] M. R. Majidi, A. Jouyban, and K. Asadpoure-Zeynali, Electrochem. Acta 52 (2007) 6248.
[20] J. J. Ruiz, A. Aldaz, and M. Domınguez, Can. J. Chem. 55 (1977) 2799.
[21] H. Razmi, and M. Harasi, Int. J. Electrochem. Sci. 3 (2008) 82.
[22] M. Zidan, T. Wee Tee, Z. Zainal, A. H. Abdullah, and J. K. Goh, Int. J. Electrochem. Sci. 5 (2010) 501.
[23] M. Zidan, T. Wee Tee, A. H. Abdullah, Z. Zainal, and G. J. Kheng, Int. J. Electrochem. Sci. 6 (2011) 289.
[24] J. Zhang, Z. Zhu, J. Zhu, Kechang Li1, and S. Hua, Int. J. Electrochem. Sci. 9 (2014) 1264.
[25] H. Filik, A. A. Avan, S. Aydar, and G. Çetintaş, Int. J. Electrochem. Sci. 9 (2014) 148.
[26] K. S. Ngai, T. Wee Tee, Z. Zaina, R. M. Zawawi, and M. Zidan, Int. J. Electrochem. Sci. 7 (2012) 4210.

[27] B. Habibi, M. Jahanbakhshi, and M. H. Pornaghi-Azar, Anal. Biochem. 411 (2011) 167.
[28] B. Habibi, M. Jahanbakhshi, and M. H. Pornaghi-Azar, Electrochim. Acta 55 (2010) 5492.
[29] C. L. Sun, H. H. Lee, J. M. Yang, and C. C. Wu, Biosens. Bioelectron. 26 (2011) 3450.
[30] G. Hu, Y. Ma, Y. Guo, Sh. Sho, Electrochim. Acta 53 (2008) 6610.
[31] A. J. Bard, and L. R. Faulkner, Electrochemical methods, Fundamentals and Applications, Wiley, New York (1980).