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Research Article

A novel Sensor for Determination of Ascorbic Acid Based on Modified Carbon Paste Electrode

Sakineh Bahmani

Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

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✉: S. Bahmani
sakineh.bahmani@yahoo.com

ABSTRACT

In this study a new method for electrocatalytic oxidation and determination of ascorbic acid (AA) was developed. The proposed electrode was a zeolite-modified carbon paste electrode, which was doped with Ni (II) ions ($Ni^{2+}Y$/ZMCPE). Ni (II) ions were doped in Y-zeolite framework by ion-exchange mechanism and actd as catalyst to oxidize ascorbic acid. Then, electrocatalytic oxidation of ascorbic acid, using cyclic voltammetry and chronoamperometry techniques was investigated. The diffusion coefficient and current density of ascorbic acid were calculated as 1.491×10^{-4} cm^2 s^{-1} and 5.17×10^3 respectively. A linear dynamic range for determination of ascorbic acid and detection limit using proposed modified electrode were 0.02– 4.10 $mmolL^{-1}$ and $2.8\times10^{-6}$$mol\ L^{-1}$ respectively.

Keywords: Voltammetry; Ascorbic acid; Electrooxidation; Zeolite; Modified electrode

1. Introduction

Vitamin C or L-ascorbic acid (AA) is distributed usually in both plant and animal kingdoms. Among animal organs, the liver, leukocytes and anterior pituitary lobe show the highest concentration levels of ascorbic acid [1]. AA is an essential vitamin for humans, and has been used for the prevention and treatment of the mental illness, infertility, common cold, AIDS and cancer [2,3]. Vitamin C, a water-soluble vitamin, which is essential to metabolism and is consumed on a large scale, is electroactive and, then, a variety of methods have been developed for its analysis [1]. Spectrophotometric and chromatographic methods have been applied for the analyses of vitamin C in fruit juices and pharmaceutical preparations [4,5]. But electrochemical methods are more famous because of their higher sensitivity, lower cost and faster response than other methods. Enzyme based electrodes, polymer based electrodes, dye based electrodes, etc. have been also proposed for the electrochemical detection and determination of ascorbic acid [6-9]. The simplicity and speed of preparation and obtaining a new reproducible surface, low residual current, porous surface and low cost are advantages of carbon paste electrodes (CPEs) over all other solid electrodes [10] and zeolite due to the advantages like stability, catalytic and molecular sieving properties are good candidate for modifying carbon paste electrodes. Zeolites are hydrated microporous crystalline materials which composed mostly of aluminum, silicon and oxygen. The normal microporous structure of the zeolite guarantees an improvement of the chemical and physical stabilities of the immobilized agent, whereas the porosity of the zeolite keeps open the access of the guest molecules or ions to the ambient [11] . also, zeolites are able to exchange ions with some other ions or compounds. An important characteristic of zeolites is the Si/Al ratio and with increase of the Si/Al ratio results in hydrophobicity and higher thermal stability like silicalite. All aluminosilicate zeolites offer a number of chemical, physical, and structural characteristics of high interest in the design of electroanalytical systems: shape, size, and charge selectivities; physical and chemical stabilities; high ion-exchange capacity; and hydrophilic character [12]. Recently zeolite-modified electrodes (ZMEs) have been used in determination of wide range of materials such as organic, inorganic and pharmaceutical compounds. The ZMEs, compared to other chemically-modified electrodes have the unique shape, size and charge selectivity, due to molecular sieve property of zeolites, with a high cation-exchange capacity . The cation exchange capacity of zeolites let to load various transition metals with catalytic property into the zeolite for using them in electrocatalytical purpose [13-15]. In the present work, we have attempted to improve the response characteristics of the Ni-zeolite as modifier by incorporating it in carbon-paste matrix. A simple electrode was designed with a reservoir for holding the carbon paste. The electrochemical response characteristics of the zeolite modified electrode were investigated. The modified electrodes were used for the electrocatalytic oxidation and determination of ascorbic acid using cyclic voltammetry and chronoamperometry techniques.

2. Experimental

2.1. Apparatus and chemicals

The NaY zeolite was purchased from SPAG Company (Iran). Graphite powder, nickel chloride, ascorbic acid, oxalic acid and sodium hydroxide used in this work were also purchased from Merck Co. All solutions were prepared by double-distilled water. Oxalate buffer solutions in the pH range of 3.0 – 9.0 were prepared using oxalic acid and NaOH solutions. All reagents were of analytical grade and used without further purification. Electrochemical experiments were carried out using a potentiostat/galvanostat (Auto Lab PG302N). An Ag|AgCl|KCl (3M) electrode as a reference electrode, a platinum wire as a auxiliary electrode and Ni^{+2}Y/ZMCPE as a working electrode were used. Scanning electron microscopy image (SEM) was taken for selected sample to determine the zeolite crystal size and morphology using a LEO 1455 VP SEM.

2.2. The Scanning Electron Microscopy of used NaY zeolite

The SEM image is a useful approach that one can illustrate morphology and determine the size of obtained crystals. SEM micrograph of the NaY zeolite is shows in Fig. 1, which the formation of cubical crystallites with average particle size of 1.0 µm can be seen.

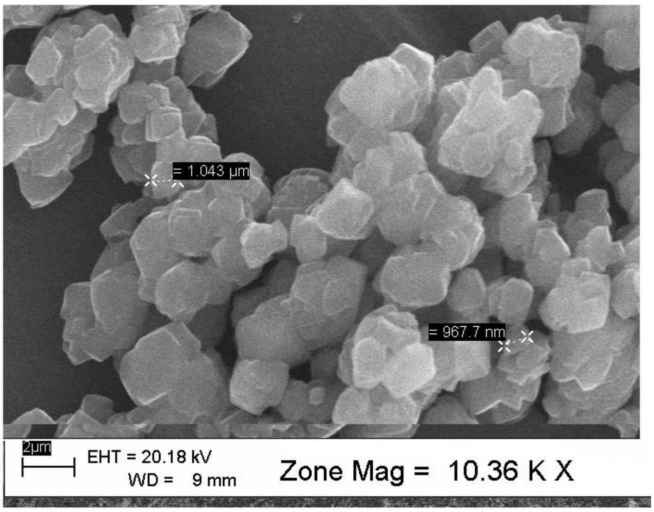

Fig. 1. Scanning electron micrograf of NaY zeolite

2.3. Preparation of working electrode

Appropriate of NaY zeolite was lightly ground and immersed to 10 ml of 1.0 M $NiCl_2$ solution for 5 h. Then the solide was dried in oven at 373 k for 10 h. The ion exchanged zeolite (NiY) was washed with deionized water to remove surface-adsorbed species. The working electrode with 20% (W/W) Ni^{2+}-zeolite and graphite powder was made by mixing appropriate amount of Ni^{2+}zeolite and graphite in diethyl ether and hand mixing to obtain a homogeny powder and evaporation of diethyl ether. Then the paraffin oil was blended by hand mixing and the resulting paste was inserted in the bottom of a glass tube and the electrical connection was implemented with a copper wire lead fitted in to the glass tube (with internal radius 1.5 mm). The carbon paste electrode used for comparison, was prepared in the same way but omitting the zeolite addition step.

3. Result and discussion

3.1. Electrochemical oxidation of ascorbic acid using cyclic voltametry method

The cyclic voltammograms (CV) of AA at the surface of CPE, ZMCPE and Ni^{+2}Y/ZMCPE electrodes are shown in Fig. 2. As can be seen a very small oxidation peak current was observed for AA using CPE (Fig 2(a)). The ZMCPE showed a slight enhancement of the oxidation peak current for AA when compared with CPE (Fig 2(b)). It resulted that the presence of zeolite in the carbon paste framwork can improve the oxidation of AA related to carbon paste electrode. The CV of AA at the surface of Ni^{+2}Y/ZMCPE showed excellent improvement in oxidation peak current (Fig 2 (c)). The modified electrode in the form of Ni^{+2}Y/ZMCPE is the best electrode for oxidation and determination AA. Obtained results show that the Ni ions act as a catalyst for oxidation of AA at the surface of proposed electrode.

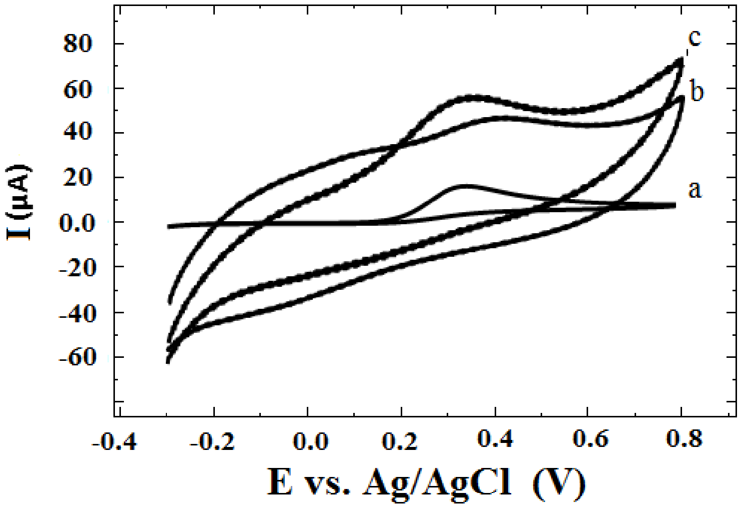

Fig. 2. Cyclic voltammograms of AA at the surface of (a) CPE, (b) ZMCPE and (c) Ni^{+2}Y/ZMCP

3.2. Electrocatalytic determination of ascorbic acid at the Ni^{+2}Y/ZMCPE

The cyclic voltamograms of AA in different concentration at the surface of proposed electrode were investigated. Fig.3A, show the cyclic voltamograms of AA oxidation at the surface of zeolite modified electrode. The obtained results show that the oxidation peak currents of AA at the surface of Ni^{+2}Y/ZMCPE were proportional to the concentration of AA within the range of $2.0*10^{-5}$- $4.1*10^{-3}$M with correlation coefficient of 0.9939, with the further increase of ascorbic acid concentration, the oxidation current of the cyclic voltamograms curve retained towards a constant value. The detection limit was calculated 2.8×10^{-6}mol L^{-1} (Fig 3B).

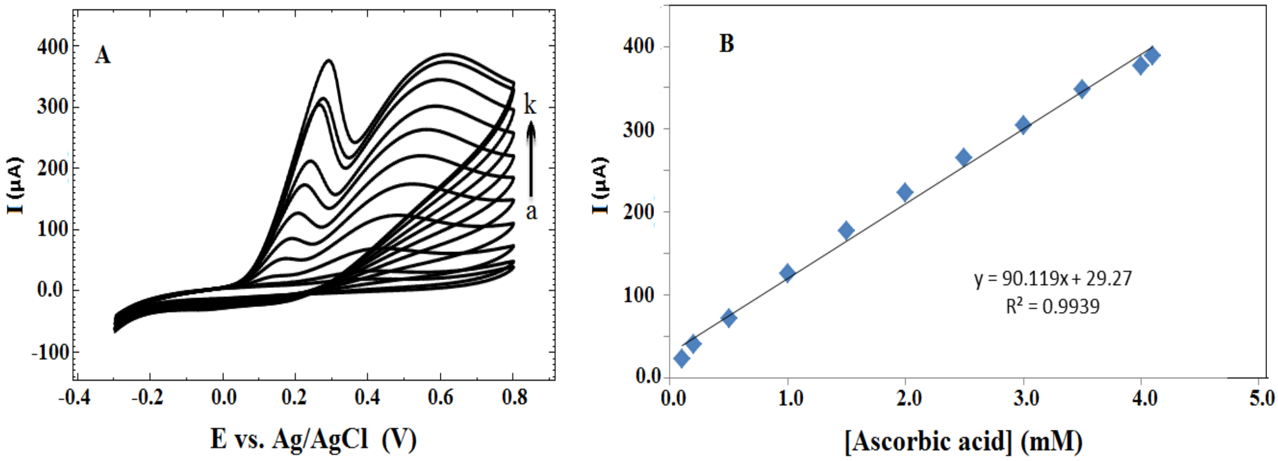

Fig. 3. Cyclic voltammograms of Ni^{+2}Y/ZMCPE of (a) 0.1,(b) 0.2,…,(k) 4.1 mM ascorbic acid

3.3. Chronoamperometric study

The chronoamperometry as well as the other electrochemical methods was employed for the investigation of electrode processes at chemically modified electrodes. Fig. 4a shows the obtained chronoamperograms of different concentrations of ascorbic acid at the surface of Ni^{2+}Y/ZMCPE. The oxidation current for the electrochemical reaction (under mass transfer control) of an electroactive material with a diffusion coefficient, *D* is described through the Cottrell equation:

$$I = nFAD^{1/2}C^*/\pi^{1/2}t^{1/2}$$

where D and C* are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration ($mol\ cm^{-3}$) respectively. The surface area of the working electrode was 0.076 cm^2. The plot of I vs. $t^{-1/2}$ for a modified electrode in the presence of ascorbic acid gives a straight line. The plot of I vs. $t^{-1/2}$ will be linear, and from the slope of such plot, the value of D can be obtained (fig (4B)). Diffusion coefficient of ascorbic acid was found to be 4.74×10^{-5} $cm^2\ s^{-1}$. Also current density for the maximum concentration of AA was obtained 5.08 mA/cm^2.

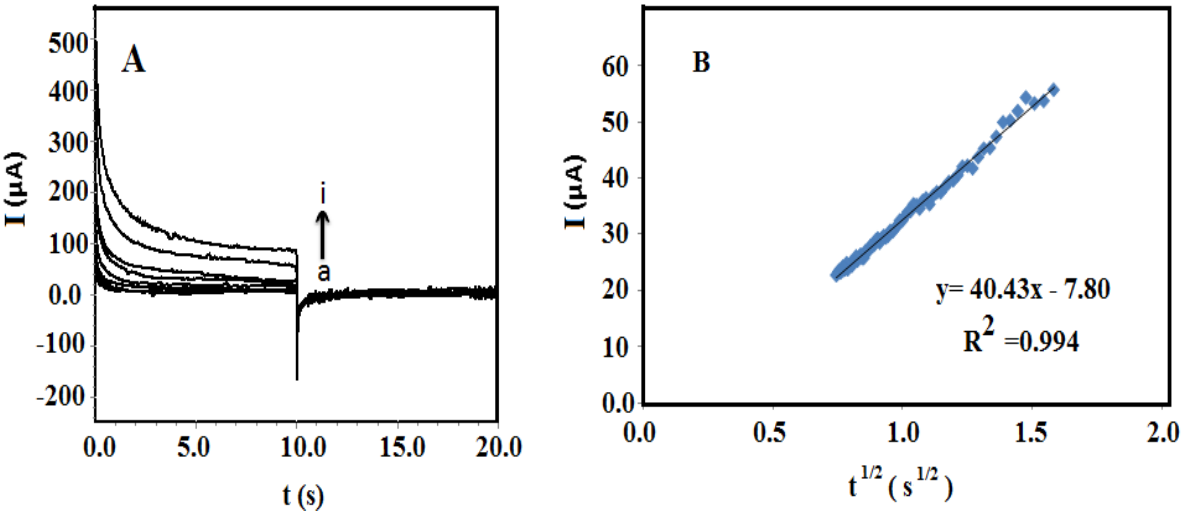

Fig. 4. (A)CHAs obtained at Ni^{+2}Y/ZMCPE in the (a) absent and presence of (b) 0.02Mm,…, (i) 5mM of ascorbic acid, and (B) oxidation current of ascorbic acid vs. $t^{-1/2}$

4. Conclusion

In the present work, we introduced a new electrode based on Nickel (II) doped zeolite modified carbon paste. Nickel (II) loaded in zeolite matrix acted as catalyst and can increase the anodic peak currents of ascorbic acid. The results indicated that Ni^{+2}Y/ZMCPE facilitate the determination of AA with good sensitivity and selectivity. The simple fabrication procedure, reproducibility, high stability, wide linear dynamic range, low detection limit, high sensitivity and a distinct advantage of polishing in the event of surface fouling, suggest that this electrode is an attractive candidate as a sensor for practical applications.

References:

[1] T. Rohani, M.A. Taher, *Talanta*, 78, (2009) 743-752

[2] M. Rohani Moghadam, Sh. Dadfarnia, A. M. Haji Shabani, P. Shahbazikhah, *Anal. Biochem.*, 410 (2011) 289-301.

[3] J. Arguello, V.L. Leidens, H.A. Magosso, R.R. Ramos, Y. Gushikem, *Electrochimica Acta* 54 (2008) 560-574.

[4] M. Salkic, A. Selimovic, *Croat. Chem. Acta*, 88 (2015) 73-87.

[5] D. A. Santos , K. P. Lima , P. H. Março, P. Valderrama, *J. Braz. Chem. Soc*. 27 (2016) 651-662.

[6] S. Skrovankova, J. Mlcek, J. Sochor, M. Baron, J. Kynicky, T. Jurikova, *Int. J. Electrochem. Sci.,* 10 (2015) 2421-2429.

[7] S. Chairam, W. Sriraksa , M. Amatatongchai, E. Somsook, *Sensors*, 11 (2011) 10166.

[8] M. Badea, M. Florescu, V. Veregut, L. Chelmea, O. Corcan, L. Floroian, P. Restani, J. L. Marty, M. Moga, *Adv. Analytical Chem.*, 5 (2015) 69-78.

[9] N.M. Lugonja, D.M. Stankovic, S.D. Spasic, G.M. Roglic, D.D. Manoilovic, M.M. Vrvic, *Food Anal. Method*, 7 (2014) 337-347.

[10] Z. Nasri, E. Shams, *Electrochimica Acta*, 54 (2009) 7416-7434.

[11] H. Hashemi, A. Nezamzadeh–Ejhieh, M. Karimi–Shamsabadi, *Mater. Sci. Eng. C,* 58 (2016) 286-297.

[12] L. M. Muresan, *Pure Appl. Chem.,* 83 (2011) 325-339.

[13] M. Abrishamkar, F. Kiani, *Int. J. hydrogen energy*, 42 (2017) 23826-23831.

[14] L. Ahmadpour-Mobarakeh, A. Nezamzadeh-Ejhieh, *Mater. Sci. Eng. C,* 49 (2015) 493-502.

[15] M. Abrishamkar, M. Barootkoob, *Int. J. hydrogen energy*, 42 (2017) 23821-23825.