Electro-oxidation of ascorbic acid catalyzed on cobalt hydroxide-modified glassy carbon electrode

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Abstract: The electrochemical behavior of ascorbic acid on a cobalt hydroxide modified glassy carbon (CHM–GC) electrode in alkaline solution was investigated. The process of the involved oxidation and its kinetics were established using the cyclic voltammetry, chronoamperometry techniques, as well as by steady state polarization measurements. The results revealed that cobalt hydroxide promotes the rate of oxidation by increasing the peak current; hence ascorbic acid is oxidized at lower potentials, which is thermodynamically more favorable. The cyclic voltammograms and chronoamperometry indicate a catalytic EC mechanism is operative with the electrogeneration of Co(IV) as the electrochemical process. Also, the process is diffusion-controlled and the current–time responses follow Cottrellian behavior. This result was confirmed by steady state measurements. The rate constants of the catalytic oxidation of ascorbic acid and the electron-transfer coefficient are reported.

Keywords: ascorbic acid; electrocatalysis; modified electrode; alkaline media; cyclic voltammetry; chronoamperometry.

INTRODUCTION

The electrochemical modification of electrodes with a suitable reagent has been widely used for analytical applications. The resulting electrodes were designed to provide the desired selective sites towards the analytes. Electrochemically modified electrodes have played an important role in the studies of electrocatalysis,[1–4] electron transfer kinetics,[5,6] membrane barriers.[7,8] electro-organic synthesis,[9] *etc*. One of the most important electrode modification techniques involves the formation of an electrocatalytic system on to the electrode sur-

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face in which redox species are capable of undergoing a rapid and reversible electrode reaction are incorporated. These electrodes reduce the overpotential required for either oxidation or reduction of compounds. Many mixed valent compounds, such as oxides, complexes, or alloys of copper,[10–12] cobalt [13–15] and ruthenium[16–18] exhibit electrocatalytic properties.

Ascorbic acid (AA) is a powerful antioxidant naturally present in many foods, especially fruits and vegetables, and plays an important role in the prevention of infectious diseases. Apart from its vitamin activity, ascorbic acid is frequently used in the food industry as an antioxidant to prevent undesirable changes in color, taste and odor. Due to its biological and technological importance, it is of great interest in the food field to have rapid and sensitive methods for its routine and reliable determination.

The direct electrochemical oxidation of ascorbic acid is possible but requires high overpotentials, the equilibrium potential of the couple is −0.185 V *vs*. SCE[19] but its oxidation at bare glassy carbon or platinum electrodes requires potentials of 0.40 and 0.60 V *vs*. SCE, respectively. These high overpotentials result in electrode fouling, poor reproducibility, low selectivity and poor sensitivity and thus this technique is rarely employed analytically. The poor reproducibility of direct electrochemical oxidation of ascorbic acid has led to interest in the use of mediators and modified electrodes to catalyze the electrochemical oxidation of ascorbic acid.

Recently, a cobalt hydroxide modified glassy carbon (CHM–GC) electrode was used for the electrocatalytic oxidation of carbohydrates[20] and hydrazine.[21] The present study is an attempt aimed at inspecting the kinetics and mechanisms of electrochemical processes on application of modified electrodes. The findings of this study show the results of the anodic oxidation of ascorbic acid on a glassy carbon surface on which catalytically active cobalt hydroxide had been deposited. The studies were performed in 100 mM sodium hydroxide solution.

EXPERIMENTAL

All employed chemicals were of analytical grade from Merck (Darmstadt, Germany) and used without further purification. All solutions were prepared with doubly distilled water. The electrochemical measurements were performed in a conventional three-electrode cell powered by an electrochemical system comprising an Autolab system with PGSTAT12 boards (Eco Chemie, Utrecht, The Netherlands). The system was run on a PC using GPES 4.9 software. A saturated calomel electrode (SCE) was the reference electrode. All potentials were measured with respect to the SCE, which was positioned as close to the working electrode as possible by means of a luggin capillary. Films of cobalt hydroxide were formed on the GC electrode with surface area 0.125 cm^2 by the method previously reported by Casella.[22] The modified electrodes were prepared by cycling the potential of the working electrode in the range of –250 to 750 mV *vs*. SCE at a scan rate of 100 mV s^{-1} for 70 cycles. The surface concentration of cobalt hydroxide which was controlled by the number of cycles applied to the deposition process was electrochemically evaluated in 100 mM NaOH solution. Prior to the modification,

the GC electrode was polished with a 0.05 µm alumina suspension on a polishing micro-cloth and rinsed thoroughly with doubly distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard solution in an appropriate volume of 100 mM sodium hydroxide solution (which was also used as the supporting electrolyte), and then stored in the dark at 4 °C. All experiments were performed at ambient temperature 22±3 °C.

RESULTS AND DISCUSSION

Cyclic voltammetry

Seventy-five consecutive cyclic voltammograms (CV) of a GC electrode in the presence of 100 mM Na_2CO_3 + 40 mM NaK tartrate + 4.0 mM $CoCl_2$ at pH 11.6, recorded at a potential sweep rate of 100 mV s^{-1}, are presented in Fig. 1A. The voltammograms are similar to those reported in literature.[22,23] A cyclic voltammogram of the CHM–GC electrode in 100 mM NaOH solution in the range of −200 to 690 mV, recorded at a potential sweep rate of 100 mV s^{-1}, is shown in Fig. 1B. It consists of anodic peaks located at 225 and 550 mV *vs.* SCE, which were attributed to Co(II)/Co(III) and Co(III)/Co(IV) redox transitions associated with different cobalt oxide species on the electrode surface[24,25]. The cathodic
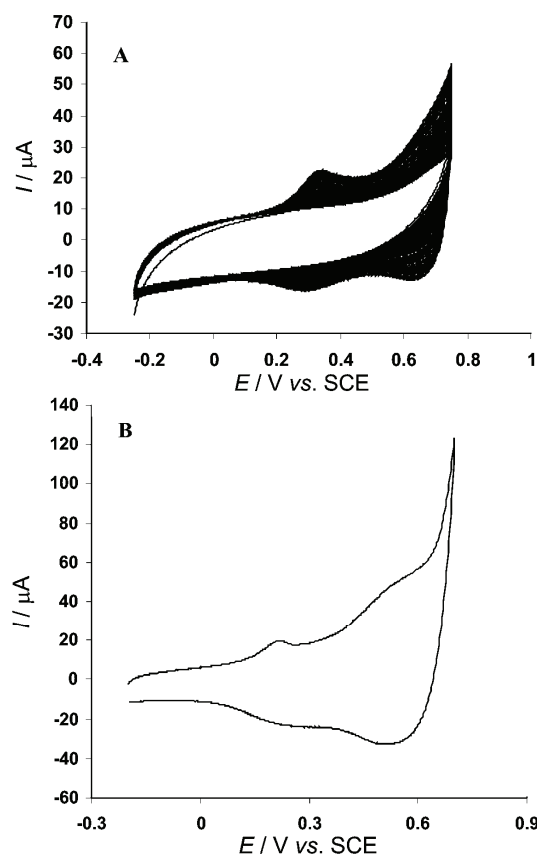

Fig. 1. Cyclic voltammograms for 4.0 mM $CoCl_2$ + 40 mM NaK tartrate + 100 mM Na_2CO_3 using a GC electrode. The potential was scanned continuously at 100 mV s^{-1} between –250 and 750 mV (A); cyclic voltamogram of CHM–GC in 100 mM NaOH solution in the range of –200 to 690 mV at a sweep rate 100 mV s^{-1} (B).

peaks at 186 and 522 mV correspond to the reduction of various cobalt oxide species formed during the positive sweep.

Typical CVs of a CHM–GC electrode in 100 mM NaOH solution at various potential sweep rates from 2.0–150 mV s^{-1}are presented in Fig. 2A. The peak currents were proportional to the sweep rates in the range 2.0–75 mV s^{-1}, as
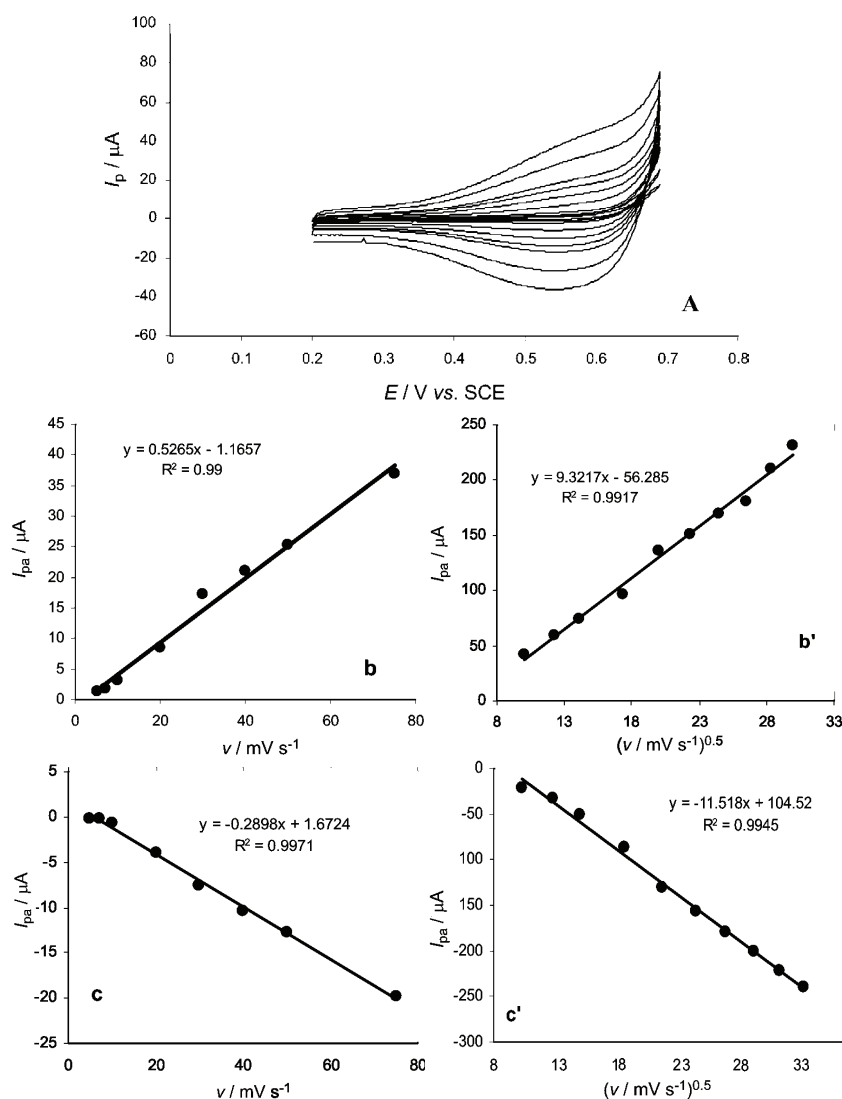

Fig. 2. Typical cyclic voltammograms of a CHM–GC electrode in 100 mM NaOH at potential sweep rates of 2, 5, 7, 10, 20, 30, 40, 50, 75, 100, 150 mV s^{-1} (A); the dependence of the anodic (b) and cathodic (c) peak currents on the sweep rate at lower values (2.0–75 mV s^{-1}) and the proportionality between the anodic (b') and cathodic (c') peak currents and the square root of sweep rate at higher values (100–900 mV s^{-1}).

shown in Figs. 2b and 2c, indicating the electrochemical activity of the surface redox couple. From the slope of both lines and using:

$$I_\mathrm{p} = \left(\frac{n^2 F^2}{4RT}\right) v A \Gamma^*$$ (1)

where Γ^* is the surface coverage of the redox species and v the potential sweep rate[26], and taking the average of both the cathodic and anodic results, Γ^* values of around 1.98×10^9 mol cm^{-2} were derived. In all the range of sweep rates, this dependency is of square root form, as shown in Figs. 2b' and 2c', signifying the dominance of diffusion controlled processes.

The CVs of a freshly prepared CHM–GC in 100 mM NaOH solution in the presence of ascorbic acid at various potential sweep rates in the range 2–300 mV s^{-1} are shown in Fig. 3A. As the scan rate increases, the anodic peak potentials shift to positive and the cathodic peak potentials are converted to a slightly negative
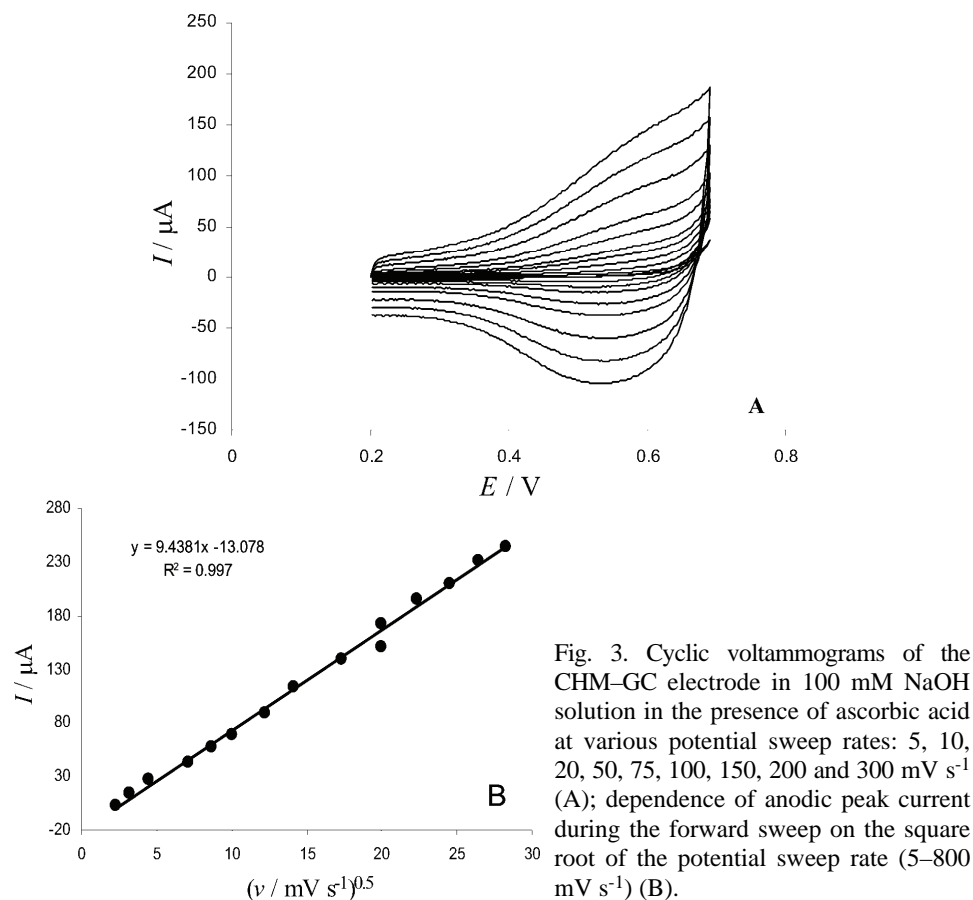

Fig. 3. Cyclic voltammograms of the CHM–GC electrode in 100 mM NaOH solution in the presence of ascorbic acid at various potential sweep rates: 5, 10, 20, 50, 75, 100, 150, 200 and 300 mV s^{-1} (A); dependence of anodic peak current during the forward sweep on the square root of the potential sweep rate (5–800 mV s^{-1}) (B).

direction. Figure 3B indicates the plot of the anodic peak current against the square root of the scan rate. As can be seen, the anodic peak current is linearly proportional to $v^{1/2}$, showing the dominance of a diffusion-controlled process.

Upon increasing the ascorbic acid concentration, its irreversible oxidation developed in the region of the electrochemical formation of Co(IV), as can be seen from Fig. 4. Thus, it is likely that electro-generated Co(IV) species is the active moiety, which efficiently accelerate the oxidation of ascorbic acid. Any increase in the concentration of ascorbic acids causes a proportional and almost linear enhancement of the anodic wave. It is worth emphasizing that the anodic formation of Co(IV) seems to be an irreversible process. Also, plotting the current function (peak current divided by the square root of the potential sweep rate) against the square root of the potential sweep rate (Fig. 5) revealed a negative slope, confirming the electrocatalytic nature of the process.

Based on the reported results, the following mechanism can be proposed for the mediated oxidation of ascorbic acid on the modified surface. The correspond-
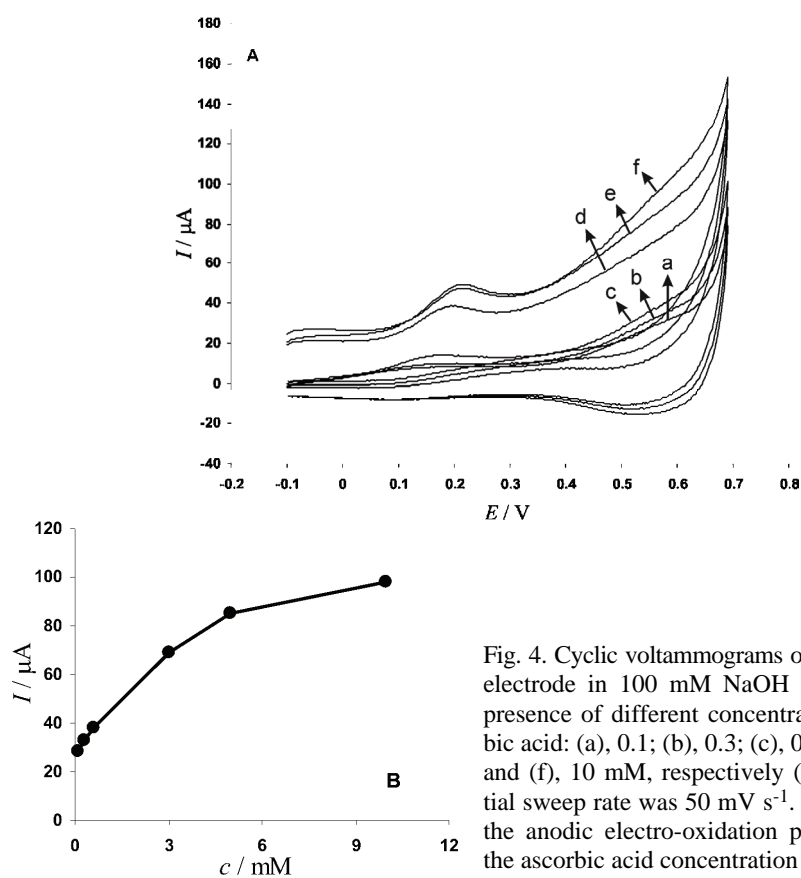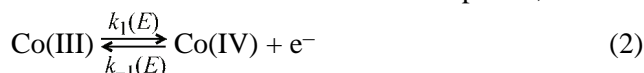

Fig. 4. Cyclic voltammograms of the CHM–GC electrode in 100 mM NaOH solution in the presence of different concentrations of ascorbic acid: (a), 0.1; (b), 0.3; (c), 0.6; (d), 3; (e), 5 and (f), 10 mM, respectively (A). The potential sweep rate was 50 mV s^{-1}. Dependency of the anodic electro-oxidation peak current on the ascorbic acid concentration (B).

ing kinetics is also formulated. The redox transition of the cobalt species,

$$\text{Co(III)} \underset{k_{-1}(E)}{\overset{k_1(E)}{\rightleftarrows}} \text{Co(IV)} + \text{e}^- \tag{2}$$

$$\text{Co(IV)} + \text{Ascorbic acid} \xrightarrow{k_2(E)} \text{Intermediate} + \text{Co(III)} \tag{3}$$

where the intermediate is further oxidized to the product through a similar electro-oxidation process:

$$\text{Co(IV)} + \text{Intermediate} \xrightarrow{k_3(E)} \text{Product} + \text{Co(III)} \tag{4}$$
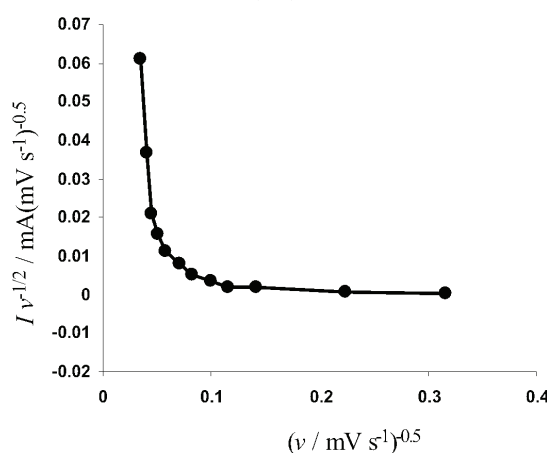

Fig. 5. $Iv^{-1/2}$ vs. $v^{-0.5}$ for 100 mM NaOH solution in the presence of 0.20 mM ascorbic acid.

Chronoamperometry

Chronoamperograms were recorded by setting the working electrode potential to the desired values and measuring the catalytic rate constant on the CHM–GC electrode surface. The chronoamperograms for the CHM–GC electrode in the absence (curve a) and presence (curves b–f) of ascorbic acid over the concentration range of 0.20–10 mM are shown in Fig. 6A. The applied potential step was 586 mV. Plotting the net current *vs*. the minus square root of time gives a straight line (Fig. 6B). This indicates that a diffusion-controlled process is dominant for electro-oxidation of ascorbic acid, as was demonstrated previously using cyclic voltammetry (Fig. 3).

The rate constants of the reactions of ascorbic acid and the ensuing intermediates with the redox sites of the CHM–GC electrode can be derived from the chronoamperograms according to:[27]

$$\frac{I_{\text{catal}}}{I_{\text{d}}} = \lambda^{1/2}\left[\pi^{1/2}erf(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}}\right] \tag{5}$$

where I_{catal} is the catalytic current in the presence of ascorbic acid, I_{d} the limiting current in the absence of ascorbic acid and $\lambda = kct$ (where k, c and t are the catalytic rate constant, the bulk concentration of ascorbic acid and the elapsed

time, respectively) is the argument of the error function. For $\lambda > 1.5$, *erf* ($\lambda^{1/2}$) almost equals unity and Eq. (5) reduces to:[25]

$$\frac{I_{cata1}}{I_d} = \lambda^{1/2}\pi^{1/2} = \pi^{1/2}(kct)^{1/2} \tag{6}$$

From the slope of the I_{cata1}/I_d *vs.* $t^{1/2}$ plot, as shown in Fig. 6C, the value of k was estimated as 2.36×10^6 cm^3 mol^{-1} s^{-1}. It should be pointed out that k is either k_2 or k_3 (see reactions (3) and (4)), whichever is smaller.
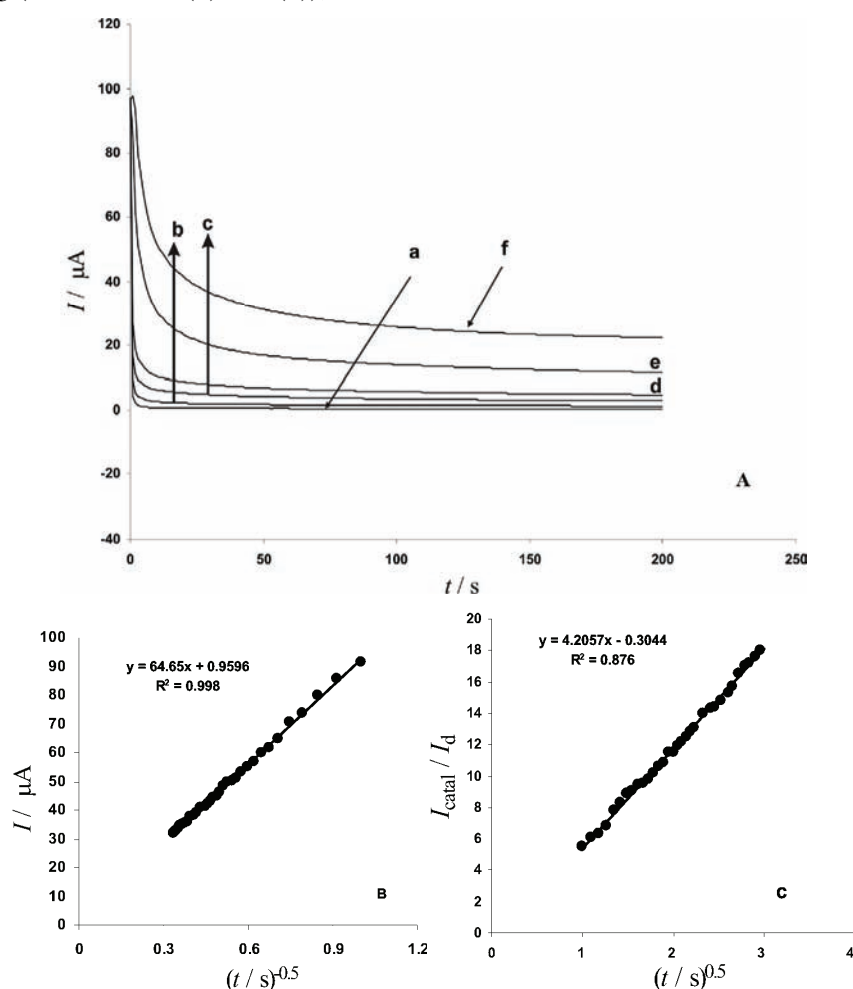

Fig. 6. Chronoamperograms of the CHM–GC electrode in the absence (a) and the presence of (b), 0.20; (c), 0.60; (d), 1.0; (e), 5.0 and (f), 10 mM ascorbic acid in 100 mM NaOH solution (A). The potential step was 586 mV; dependency of the transient current on $t^{-0.5}$ (B). Dependence of I_{catal}/I_d on $t^{0.5}$ derived from the data of the chronoamperograms of (a) and (e) in the main panel (C).

Steady state polarization[28]

The rate laws for the reactions (2) and (3) have the forms:

$$v_1 = k_1 \Gamma \theta_{\text{III}} - k_{-1} \Gamma \theta_{\text{IV}} \tag{7}$$

$$v_2 = k_2 \Gamma \theta_{\text{IV}} c \tag{8}$$

where Γ is the total number of adsorption sites per unit area of the electrode surface, the θ represents the fractional surface coverage of different cobalt valence states and c is the bulk concentration of ascorbic acid. With only the 3 and 4 valence states of cobalt prevailing, then:

$$\theta_{\text{III}} + \theta_{\text{IV}} = 1 \tag{9}$$

and the rates of changes of their surface coverage, as well as that of the intermediate compounds are:

$$\frac{d\theta_{III}}{dt} = -\frac{d\theta_{IV}}{dt} = -k_1\theta_{\text{III}} + k_{-1}\theta_{\text{IV}} + k_2\theta_{\text{IV}}c + k_3\theta_{\text{IV}}c_i \tag{10}$$

$$\frac{dc_i}{dt} = k_2\theta_{\text{IV}}c - k_3\theta_{\text{IV}}c_i \tag{11}$$

where c_i is the concentration of the intermediate.

Assuming that the steady state dominates:

$$\frac{d\theta_{III}}{dt} = -\frac{d\theta_{IV}}{dt} = 0 \tag{12}$$

$$\frac{dc_i}{dt} = 0 \tag{13}$$

the values of the coverage are given by:

$$\theta_{\text{III}} = \left(\frac{k_{-1} + 2k_2c}{k_1 + k_{-1} + 2k_2c} \right) \tag{14}$$

$$\theta_{\text{IV}} = \left(\frac{k_1}{k_1 + k_{-1} + 2k_2c} \right) \tag{15}$$

and subsequently:

$$v_1 = \left(\frac{2k_1\Gamma k_2 c}{k_1 + k_{-1} + 2k_2c} \right) \tag{16}$$

Based on this rate equation, the Faradic current will be:

$$i_{\text{f}} = \left(\frac{2FAk_1\Gamma k_2 c}{k_1 + k_{-1} + 2k_2c} \right) \tag{17}$$

where A is the surface area of the electrode and the rate constants k_1 and k_{-1} are obviously potential-dependent and are of the forms:

$$k_1(E) = k_1^0 \exp\left[\frac{\alpha n F E}{RT}\right]$$ (18)

$$k_{-1}(E) = k_{-1}^0 \exp\left[\frac{(\alpha-1) n F E}{RT}\right]$$ (19)

where k_1^0 and k_{-1}^0 are the chemical rate constants measured at E *vs.* SCE = 0, α is the anodic transfer coefficient and the other parameters have their usual meaning. Equation (17) is well suited for the calculation of rate constants and is the validity test of the kinetics and mechanism of the oxidation process.

The pseudo-steady state polarization curves of the electro-oxidation of ascorbic acid on the CHM–GC electrode at a number of ascorbic acid concentrations are presented in Fig. 7. The oxidation process was found to begin at nearly 520 mV *vs.* SCE and reach a plateau at 590 mV *vs.* SCE, while oxygen evolution commenced at still higher potentials. In the course of reaction, the coverage of Co(IV) increases and reaches a saturation (steady state) level and the oxidation current follows accordingly. According to Eq. (17), plots of the inverse of current against the inverse ascorbic acid concentration should be linear:

$$i_f^{-1} = (FAk_1\Gamma)^{-1} + \left[\frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma}\right]c^{-1}$$ (20)
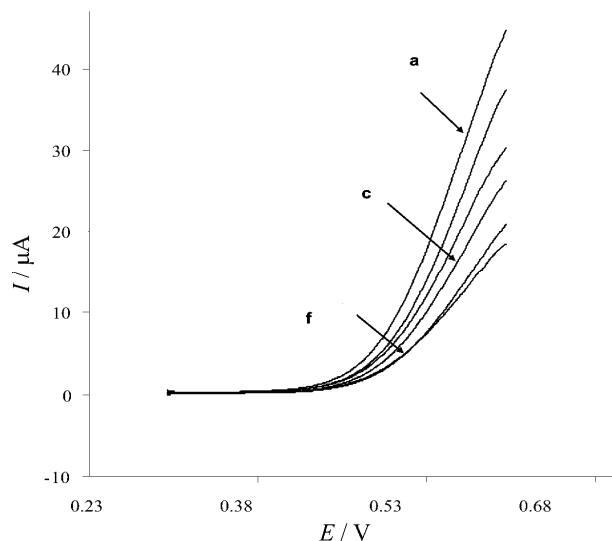

Fig. 7. Typical pseudo-steady state polarization curves of the CHM–GC electrode obtained in (a), 10; (b), 5.0; (c), 3.0; (d), 1.0; (e), 0.40 and 0.10 (f) mM ascorbic acid.

The i_f^{-1} *vs.* c_m^{-1} dependencies are presented in Fig. 8A, from which it can be seen that straight lines at various potentials were obtained. Both the intercepts

and slopes of the straight lines appearing in this figure were potential dependent. The slopes were plotted against exp $(-nFE/RT)$ with $n = 1$ and the obtained graph is presented in Fig. 8B. Using this graph together with Eq. (20), it was found that the rate constant of reaction 3, $k_2\Gamma$, and the ratio of k_{-1}^0/k_1^0 are 4.13×10^{-11} and 2.01×10^{10} cm s^{-1}, respectively. The variation of the intercepts of the lines in Fig. 8A with the applied potential on a semi-log scale is presented in Fig. 8C. Using this graph and Eq. (20), the magnitudes of $k_1^0\Gamma$, 2.26×10^{-16} mol s^{-1} cm^{-2}, and the anodic transfer coefficient, 0.64, were obtained. From the above findings, the value of $k_{-1}^0\Gamma$ was calculated to be 4.54×10^{-6} mol s^{-1} cm^{-2}.
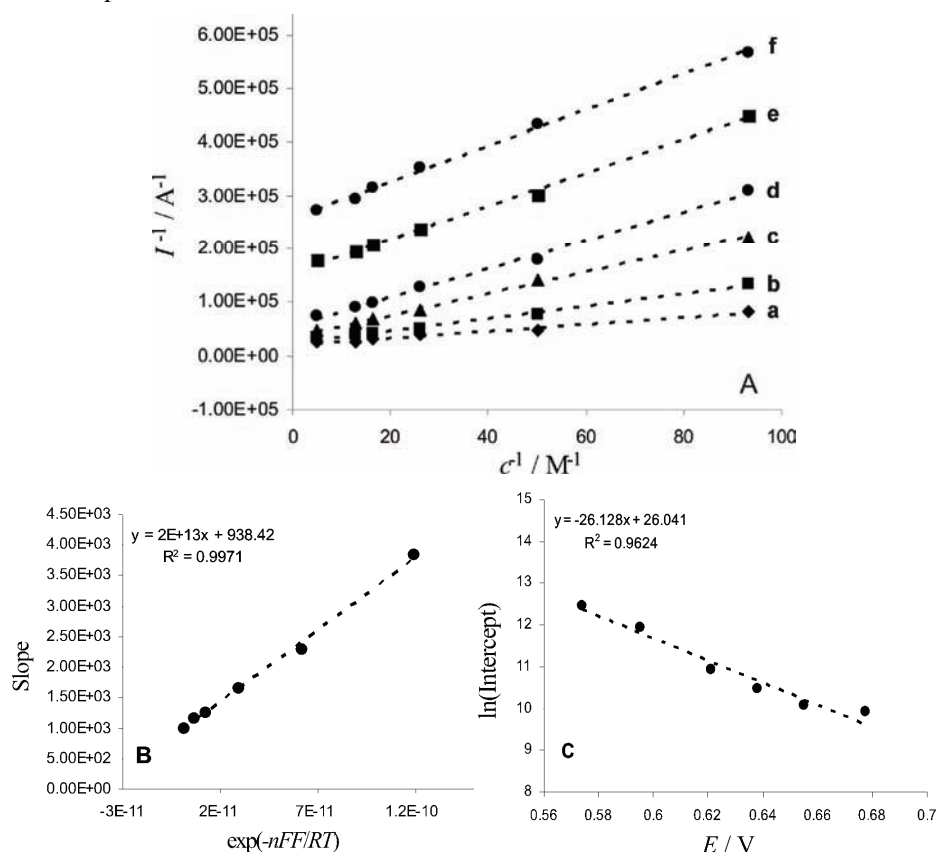

Fig. 8. Plot of i^{-1} (from the polarization curves in Fig. 6) against C_m^{-1} at various potentials: 574, 559, 616, 638, 659 and 680 mV *vs.* SCE, curves a–f, respectively (A); plot of the slopes of the curves in (a) *vs.* exp $(-nFE/RT)$ (B); plot of the ln (intercepts) of the curves in (a) *vs.* the applied potential (C).

The results obtained for ascorbic acid on a cobalt hydroxide modified glassy carbon electrode are compared in Table I with those previously reported for

cyclohexanol on a copper electrode.[28] It can be seen that the catalytic properties are comparable.

TABLE I. Comparison of the catalytic properties of Co(IV) on the cobalt hydroxide-modified electrode with the catalytic properties of Cu(III) species on a copper electrode

Property	Electrode	
	Copper	Cobalt hydroxide modified glassy carbon electrode
Mediator	Cu(III)	Co(IV)
Compound	Cyclohexanol	Ascorbic acid
$k_2\Gamma$ / cm s^{-1}	8.74×10^{-12}	4.13×10^{-11}
k^0_{-1}/k^0_1	2.10×10^7	2.01×10^{10}
$k^0_1\Gamma$ / mol s^{-1} cm^{-2}	1.91×10^{-13}	2.26×10^{-16}
$k^0_{-1}\Gamma$ / mol s^{-1} cm^{-2}	4.01×10^{-5}	4.54×10^{-6}

CONCLUSIONS

A cobalt hydroxide film was formed electrochemically in a regime of cyclic voltammetry on a glassy carbon electrode and checked for the electro-oxidation of ascorbic acid in alkaline media. The modified electrode showed electrocatalytic activity for the oxidation of ascorbic acid at around 565 mV *vs*. SCE. Using the cyclic voltammetry and chronoamperometry techniques and also steady-state polarization measurements, the kinetic parameters, such as charge transfer coefficient (α) and the catalytic reaction rate constant (k) for oxidation of ascorbic acid were determined. Moreover, the cobalt hydroxide glassy carbon electrode can be used for the determination of real samples. The kinetics of the reaction based on the reported mechanism was developed and the magnitudes of the rate constants and anodic transfer coefficient of the electro-oxidation reaction were obtained.

ИЗВОД

КАТАЛИЗА ЕЛЕКТРОХЕМИЈСКЕ ОКСИДАЦИЈЕ АСКОРБИНСКЕ КИСЕЛИНЕ НА СТАКЛАСТОМ УГЉЕНИКУ МОДИФИКОВАНОМ КОБАЛТ-ХИДРОКСИДОМ

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Испитивано је електрохемијско понашање аскорбинске киселине у алкалној средини на електроди од стакластог угљеника модификованој кобалт-хидроксидом. Кинетика реакције је одређена коришћењем цикличне волтаметрије, хроноамперометрије и стационарних поларизационих мерења. Резултати показују да кобалт-хидроксид убрзава реакцију оксидације тако да се она одиграва на нижим потенцијалима. Циклична волтаметрија и хроноамперометрија су показале да се реакција одиграва по ЕС механизму са генерисањем Co(IV) врсте као електрохемијским ступњем. Процес је дифузионо контролисан и зависност струје од времена прати Котрелову једначину. Овај резултат је такође потврђен стационарним поляриза-

ционим мерењем. Одређене су вредности константе брзине каталитичке оксидације аскор-бинске киселине и коефицијента прелаза.

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