Electrocatalytic Determination of Ascorbic Acid on a Glassy Carbon Electrode Chemically Modified with Cobalt Pentacyanonitrosylferrate

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An electrochemically prepared thin film of cobalt pentacyanonitrosylferrate (GC/CoPCNF) was used as a surface modifier for glassy carbon electrodes. The oxidation of ascorbic acid on a glassy carbon electrode modified with GC/CoPCNF as a working electrode was studied using cyclic voltammetry, rotating disk electrode (RDE) voltammetry and chronoamperometry in a 0.25 M KNO₃ + 0.25 M phosphate buffer (pH 7) solution. The glassy carbon modified with CoPCNF showed good electrocatalytic activity toward ascorbic acid oxidation. The kinetics of the catalytic reaction was investigated, and the average value of the rate constant (*k*) for the catalytic reaction and the diffusion coefficient (*D*) were evaluated by different approaches for ascorbic acid, and were found to be $3.3 \pm 0.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $3.2 \pm 0.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

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Introduction

L-Ascorbic acid (AH₂) is a water-soluble vitamin, and is a compound that takes part in many important life processes. It is one of the most important vitamins, due to its antioxidant and pH regulator properties often being added to various food products and pharmaceuticals.¹ It is very easily oxidized chemically and electrochemically to dehydro-L-ascorbic acid (DHA).² Its analytical determination from different and complex matrices is frequently requested. The most basic of these methods is generally based on its reducing properties. Several methods for the determination of (AH₂) have been reported, such as fluorometric and electrochemical methods.³ The voltammetric,^{4–6} potentiometric^{7,8} or amperometric^{9–11} methods for the determination of ascorbic acid are based on its electrochemical behavior. The electrooxidation of ascorbic acid has already been examined in detail by many researchers using mercury,^{12–14} gold^{15,16} and carbon^{17–19} electrodes. Ruitz *et al.* have proposed an electrooxidation mechanism of AA on a mercury electrode.^{13,14} It is well known that cyclic voltammograms of AA dramatically change at glassy carbon electrodes, depending on the pretreatment of the electrodes.^{20–22} A similar change in voltammograms has also been confirmed at gold electrodes.^{23–25} Because of a large overpotential of AA at conventional electrodes, it is not suited for oxidation *via* these electrodes. One promising approach for minimizing over-voltage effects is by using an electrocatalytic process at chemically modified electrodes. The catalytic oxidation of ascorbic acid has also been studied on many mediator-modified electrodes.^{26–30} However, most of them still suffer from the pollution of ascorbic acid due to its adsorption on the electrode surface.

Chemically modified electrodes (CMEs) have attracted considerable interest over the past two decades as researchers attempted to exert more control over the chemical nature of an electrode. During the past years, inorganic film-modified electrodes have received increased attention due to their potential in technical applications. One important group of inorganic compounds utilized for electrode modifications, and used for electrocatalytic purposes, is the transition-metal hexacyanoferrates. Pentacyanonitrosylferrate, commonly known as nitroprusside, is a member of the polycyanide metal complexes. This family of complexes, mainly hexacyanides, has been widely studied.³¹ Bocarsly and coworkers have reported that complexes such as [Fe^{II}(CN)₅L]^{n−} (L = CN, H₂O, NO and histidine) have successfully bound to a Ni electrode.³²

We recently reported on the preparation of a cobalt pentacyanonitrosylferrate film modified glassy carbon electrode (CoPCNF/GC), and in the present work we plan to examine the electrocatalytic properties of the CoPCNF/GC electrode toward the electrooxidation of ascorbic acid using various electroanalytical procedures.³³ A CoPCNF-modified electrode was prepared as a new ME and examined for its electrocatalytic properties. This electrode has been prepared in a short time and it has shown a good response to the electrooxidation of ascorbic acid. Further, its response is fast. The prepared electrode exhibited a high stability, and no loss of electroactivity of a modified electrode was found for a continuous sweep of the potential for 300 cycles. The detection limit of the modified electrode was less than that of other modified electrodes that were previously reported.^{1,30,34} It is also intended to determine the kinetic parameters.

Experimental

Reagents

CoCl₂, Na₂[Fe(CN)₅NO] (nitroprusside), KNO₃ and ascorbic

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Fig. 1 Cyclic voltammograms of a CoPCNF/GC electrode with a scan rate of 20 mV s^{-1} in $0.25 \text{ M KNO}_3 + 0.25 \text{ M}$ phosphate buffer (pH 7) (a), in the absence (b), in the presence of 20 mM ascorbic acid (c), as b for a bare glassy carbon electrode.

acid were of analytical grade from Merck, and used without further purification. All solutions were prepared with doubly distilled water. A solution of $0.25 \text{ M KNO}_3 + 0.25 \text{ M}$ phosphate buffer (pH 7) was used as a supporting electrolyte.

Apparatus

Electrochemical experiments were carried out using an AUTOLAB PGSTAT-30 potentiostat/galvanostat. A conventional three-electrode cell was used at room temperature. A saturated calomel electrode, platinum wire, and a glassy carbon disk modified electrode of 0.0314 cm^2 surface area were used as reference, auxiliary, and working electrodes, respectively. A rotating electrode system (Model 682 from Metrohm) was employed.

Electrode preparation

A glassy carbon electrode surface was polished with 0.05 μm alumina powder on a wet polishing cloth. The polished electrode was rinsed with distilled water several times. To prepare the modified electrode, first metallic cobalt was deposited from $20 \text{ mM CoCl}_2 + 0.1 \text{ M KNO}_3$ (plating solution) onto the glassy carbon electrode by applying a constant cathodic current of 0.1 mA for $10\text{--}40 \text{ s}$. The glassy carbon electrode covered by metallic cobalt was immersed in a $0.25 \text{ M KNO}_3 + 50 \text{ mM Na}_2[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]$ solution (derivatization solution) and derivatized by cycling the electrode potential between -0.2 and 0.75 V until a stable voltammogram was observed (about 30 cycles with a scan rate of 50 mV s^{-1}). The total surface area of the electrode (Γ^0) was determined from the area under anodic cyclic voltammograms for the GC-CoPCNF electrode.

Results and Discussion

Cyclic voltammetric studies

Cyclic voltammograms of a CoPCNF-modified glassy carbon electrode between 0 and 1 V exhibited a pair of peaks with a formal potential, $E^{\circ'} = (E_{\text{pa}} + E_{\text{pc}})/2$, of 520 mV versus SCE (scan rate 100 mV s^{-1}). We observed that this peak was not affected by stirring of the electrolyte, offering proof that the material is well associated with the electrode surface under the solution conditions. Figure 1 shows cyclic voltammograms of the CoPCNF/GC electrode in both the absence (curve a) and presence of 20 mM ascorbic (curve b) in $0.25 \text{ M KNO}_3 + 0.25 \text{ M}$ phosphate buffer (pH 7). As can be seen in Fig. 1, after the addition of 20 mM ascorbic acid, an increase in the anodic peak

Fig. 2 CoPCNF film modified GC electrode with a surface coverage of $5 \times 10^{-8} \text{ mol cm}^{-2}$ in the absence (a) and presence of ascorbic acid over a concentration range of $0.1\text{--}12 \text{ mM}$ (b–i) at applied potential steps of 0.7 and 0.0 V for forward and backward chronoamperometry, respectively.

current is observed, whereas the cathodic peak is depressed. This behavior is typical of that expected for mediated oxidation; but, under the same conditions at a bare GC electrode, no peak is observed (curve c). The height of the anodic peak increases with increasing the ascorbic acid concentration, and the plot of I_p versus ascorbic acid concentration between $0.1\text{--}14 \text{ mM}$ is linear. The oxidation current for ascorbic acid increases linearly with the square root of the scan rate, indicating that the reaction is mass-transfer controlled. A plot of the scan rate-normalized current ($I/v^{1/2}$) versus the scan rate exhibits a shape typical of an electrochemical-chemical (EC) catalytic process. In order to obtain information on the rate-determination step, a Tafel slope (b) was determined using the following equation, valid for a totally irreversible diffusion controlled process:³⁵

$$E_p = (b/2) \log v + \text{constant} \quad (1)$$

On the basis of Eq. (1) the slope of E_p versus $\log v$ plot is $b/2$, where b indicates the Tafel slope. Because the slope was found to be 0.121 , $b = 2 \times 0.118 = 0.236 \text{ V}$. This slope indicates that a one-electron transfer process is the rate-limiting step, assuming a transfer coefficient of $\alpha = 0.75$. The number of electrons involved in the rate-determination step can be obtained using another method. Tafel plots ($\log I = f(E)$) have been used. These plots were drawn using data from the rising part of the current-voltage curve at a scan rate of 20 mV s^{-1} for three different concentrations of ascorbic acid. The mean slope, $0.238 \text{ V decade}^{-1}$ or $4.2 \text{ V decade}^{-1}$, was obtained, presenting a one-electron process that was rate limiting, assuming a transfer coefficient of $\alpha = 0.75$ (not illustrated).

Chronoamperometric studies

Chronoamperometry as well as other electrochemical methods may be used to investigate the electrode processes at a chemically modified electrode.³⁶ Figure 2 shows well-defined chronoamperograms for a CoPCNF film modified GC electrode with a surface coverage of $5 \times 10^{-8} \text{ mol cm}^{-2}$ in the absence (a) and presence of ascorbic acid over a concentration range of $0.1\text{--}12 \text{ mM}$ (b–i) at applied potential steps of 0.7 and 0.0 V for forward and backward chronoamperometry, respectively. As can be seen from Fig. 2, the forward and backward potential step chronoamperometry of the modified electrode in the absence of ascorbic acid shows very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of surface-confined CoPCNF sites.

Fig. 3 Plot of I_{cat}/I_L vs. $t^{1/2}$, derived from the chronoamperogram data in both the absence and the presence of 10 mM ascorbic acid.

However, in the presence of ascorbic acid, the charge value associated with the forward chronoamperometry (Q_f) is significantly greater than that observed for backward chronoamperometry (Q_b). This behavior is typical of that expected for mediated oxidation.

Chronoamperometry is also used to estimate the diffusion coefficient of ascorbic acid in the solution. For an electroactive material with diffusion coefficient D , the current corresponding to the electrochemical reaction (under diffusional control) is described by Cottrell's law,³⁷

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

where D and C are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and bulk concentration (mol cm^{-3}), respectively. The plot of I vs. $t^{-1/2}$ will be linear, and from the slope the value of D can be obtained. In the presence of ascorbic acid at long experimental times (*e.g.* $t > 4$ s) the $\text{KCo[Fe}^{\text{II}}(\text{CN})_5\text{NO]}$ oxidation is complete and the rate of electrocatalyzed ascorbic acid oxidation exceeds that of ascorbic acid diffusion from the bulk to the film/solution interface, and therefore the current has a diffusional nature. The mean value of D was found to be $3.2 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, which is in good agreement with values reported in the literature.³⁸ Chronoamperometry can also be used to evaluate the kinetics (K). At intermediate times ($t = 0.2 - 4$ s in the present work) the catalytic current (I_{cat}) is dominated by the rate of the electron cross-exchange between the CoPCNF redox sites and ascorbic acid, and the rate constant is determined according to a method described in the literature, using Eq. (3).³⁹

$$I_{\text{cat}}/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0 t)^{1/2} \quad (3)$$

Here k , C_0 , t , I_{cat} and I_L are the catalytic rate constant ($\text{M}^{-1} \text{s}^{-1}$), catalyst concentration (M), elapsed time (s), currents of CoPCNF/GC modified electrode in the presence and the absence of ascorbic acid, respectively. 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 ascorbic acid. Figure 3 shows one such plot, constructed from the chronoamperograms for the CoPCNF/GC electrode in both the absence and presence of 10 mM ascorbic acid. The value for k was found to be $3.3 \times 10^2 \text{ M}^{-1} \text{s}^{-1}$, which is in good agreement with those obtained from the other two techniques.

RDE voltammetric studies

The electrocatalytic activity of the CoPCNF/GC electrode toward the oxidation of ascorbic acid was investigated by the RDE voltammetry technique. The steady state I-E curves for

Fig. 4 A) I_L from Levich equation vs. $\omega^{1/2}$ for ascorbic acid oxidation at a CoPCNF/GC and B) Koutecky-Levich plot.

the oxidation of ascorbic acid at a CoPCNF film modified rotating GC disk electrode under various experimental conditions were recorded. In the case that solely the mass-transfer process in the solution controls the oxidation of ascorbic acid at the surface-modified GC electrode, the relationship between the limiting current and the rotation speed should obey the Levich equation,⁴⁰

$$I_L = I_{\text{Lev}} = 0.620nFAD^{2/3} \nu^{-1/6} \omega^{1/2} C_0 \quad (4)$$

where D , ν , ω and C_0 are the diffusion coefficient, the kinematic viscosity, the rotation speed and the bulk concentration of the reactant in the solution, respectively. All other parameters have their conventional meanings. On the basis of Eq. (4) a plot of the limiting current (I_L) versus $\omega^{1/2}$ should be a straight line. Under extreme conditions, the plot of I_L versus $\omega^{1/2}$ becomes nonlinear; indeed, a cross-exchange process between the substrate and the redox sites of the film solution interface is also an important factor in the rate-limiting process. The value of the D from the slope of the Levich equation was found to be $3.5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ (Fig. 4A).

When the mass-transfer process in the solution and the catalytic reaction become dominant, the following Koutecky-Levich equation can be used for kinetics analysis:⁴⁰

$$\frac{1}{I_L} = \frac{1}{nFAC_0 k \Gamma} + \frac{1}{0.62nFAD^{2/3} \nu^{-1/6} C_0 \omega^{1/2}} \quad (5)$$

where A , C_0 , k and Γ are the electrode area (cm^2), substrate concentration (mol cm^{-3}), catalytic rate constant ($\text{M}^{-1} \text{s}^{-1}$) and surface coverage (mol cm^{-2}). According to Eq. (5) the plot of I^{-1} versus $\omega^{-1/2}$ gives a straight line (as shown in Fig. 4B). The value of the rate constant (k) for the catalytic reaction can be obtained from the intercept of the Koutecky-Levich plot. The value of k was found to be $2.9 \times 10^2 \text{ M}^{-1} \text{s}^{-1}$ using $\Gamma = 6 \times 10^{-8} \text{ mol cm}^{-2}$. The slope of the Koutecky-Levich equation is dependent on the reactant concentration (C_0). The reverse relationship between the slope of the Koutecky-Levich plot and the ascorbic acid concentration confirms that the catalytic reaction is first order with respect to the concentration of ascorbic acid.

Hydrodynamic amperometry

Hydrodynamic amperometry investigations were carried out by successively adding 10 μM of AA to a continuously stirred 0.25 M KNO_3 + 0.25 M phosphate buffer (pH 7) solution. The applied potential was 0.65 V vs. SCE. The linear response range reached from 10 to 120 μM . The relative standard

deviation for 5 runs at 10 μM was only 5%. The experimental investigation showed that the slope of the calibration plot increased with increasing the electrode surface coverage. The detection limit was 8 μM . The linear-response range with this technique was extended to lower concentrations of ascorbic acid (10 – 120 μM), as expected.

Conclusion

The experimental results reported above demonstrate that the CoPCNF film modified GC electrode can catalyze the electrooxidation of ascorbic acid *via* a surface layer-mediated charge transfer. The kinetic process of the catalytic reaction can be explained using cyclic voltammetry, chronoamperometry and RDE voltammetry. The results obtained for the rate constant (k) and the diffusion coefficient of ascorbic acid (D) in the solution by different approaches are in good agreement.

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