Amperometric Detection of Nitrite on Glassy Carbon Electrode Modified with Cobalt Nitroprusside

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Abstract

The glassy carbon electrode (GCE) modified with cobalt nitroprusside (CoNP) was prepared by electrochemical method. The CoNP modified electrode (ME) prepared electrochemically on a GCE in two-step. The electrochemical behavior of the modified electrode was studied by cyclic voltammetric technique. The cyclic voltammogram of CoNP showed a redox couple with formal potential $[E^0 = (E_{pa} + E_{pc})/2]$ of 500 mV vs. SCE. The electrocatalytic oxidation of nitrite was studied on the CoNP modified glassy carbon electrode. The CoNP films on the glassy carbon electrode show an excellent electrocatalytic activity toward the oxidation of nitrite in 0.5 mol L^{-1} KNO_3. Hydrodynamic amperometry was used to the detection of nitrite with CoNP. The linear detection limit of the CoNP elctrode for NO_2^- was from 20×10^{-6} to 220×10^{-4} mol L^{-1} and the detection limit was 10×10^{-6} mol L^{-1} (S/N=3).

Keywords: amperometric detection, cobalt nitroprusside, nitrite oxidation, modified electrode, modified glassy carbon electrode.

Introduction

The chemical behavior and structure of metal nitroprusside (MNP) (where M = Cd^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}) as inorganic salts have been studied [1-4]. In aqueous solution the electrochemical reduction of NP on the mercury electrode occurs at three-reduction steps. The electrophilic character of NP and, consequently, its reducibility as well as its non-oxidizability via the Fe^{II} centers are ascribed to the NO^+ ligand [5]. In the first one-electron reduction step, the NO^+ ligand has been reduced to NO. The obtained NP ion loss the axial cyanide ligand; the remaining NP ion is further reduced in a three-electron three-proton step [6].

For fabrication of ME's several organic and inorganic compounds have been used. Among these, MNP salts as a modifier have attracted considerable interest

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in recent years, where M= Co [7-11], Cu [12-14], Fe [15], Ni [16-21], Pd [22-23], Zn [24].

Nitrite, one of the pollutants widely found in natural waters, is an essential precursor in the formation of nitrosamines, many of which have been shown to be potent carcinogens [25,26]. Therefore, the detection of nitrite has been done by different techniques such as spectrophotometry [27-28], electrochemical methods [23, 29-30], which offer useful alternatives since they allow a faster and precise analysis. Electrochemical determination based on oxidation of nitrite offers several advantages, namely no interference from nitrate ion and from molecular oxygen, which are usually the major limitations in cathodic determination of nitrite [23,30].

The present work describes the electrocatalytic properties of CoNP on the GC electrode toward the electrocatalytic oxidation of the nitrite using cyclic voltammetry and hydrodynamic amperometric techniques.

Experimental

$CoCl_2$, $Na_2[Fe(CN)_5NO]$, KNO_2, and KNO_3 were of analytical grade from Merck and used without further purification. All solutions were prepared with distilled water.

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP-2063 electrochemical analysis system, Behpajooh, Iran). A conventional three-electrode cell was used at room temperature. A saturated calomel electrode and platinum wire were used as reference and auxiliary, respectively.

Fabrication of CoNP Me

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 2.0×10^{-2} mol L^{-1} $CoCl_2$ + 0.1 mol L^{-1} KNO_3 (plating solution) onto the glassy carbon electrode by applying a constant cathodic current of 0.1 mA for 10 - 40 s. The glassy carbon electrode covered by metallic cobalt was immersed in a 2.5×10^{-4} mol L^{-1} KNO_3 + 5.0×10^{-2} mol L^{-1} $Na_2[Fe^{II}(CN)_5NO]$ 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 mVs^{-1}) .

Results and discussion

Electrochemical behavior of CoNP

The CoNP ME has been fabricated in two steps. First metallic cobalt deposited on GCE and then this electrode derivatized to CoNP ME. Fig. 1 shows typical cyclic voltammograms of 5.0×10^{-4} mol L^{-1} NP, recorded in 0.25 mol L^{-1} KNO_3. By scanning the potential the CoNP film growth on GCE, until a steady state voltammogram obtained. After preparation of ME, the electrode rinsed with

distillated water and then immersed in 0.5 mol L^{-1} KNO$_3$ solution as supporting electrolyte.

Scanning potential between 0 and 1 V vs. SCE, shows a pair of peaks with formal potential 500 mV vs. SCE (scan rate 100 mVs^{-1}). Fig. 2 shows a typical voltammogram of CoNP GCE. The redox observed peaks could be attributed to the following reaction:

$$Co^{II}[FeIII(CN)_5NO] + K^+ + e^- \rightleftharpoons KCo^{II}[Fe^{II}(CN)_5NO] \quad E° = 0.500 \text{ V}$$
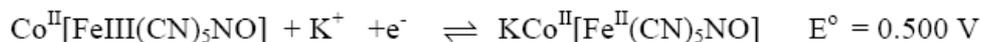
For high scan rates or thick films linear diffusion behavior predominates and peak currents are proportional to $v^{1/2}$, usually associated with a diffusional process for solution species. The limit of these different scan rate dependent zones can be varied from one electrode to another, depending on the film thickness on the electrode. The ratio I$_{pa}$/I$_{pc}$ remains almost unity as expected for surface-type behavior and a peak separation, $\Delta E_p = /E_{pa\text{-}}/E_{pc}$, of 60 mV at a scan rate of 50 mV s^{-1} was found; at higher scan rates, a wider splitting appears, indicating the limitation arising from charge-transfer kinetics. The peak currents of the voltammograms are linearly proportional to the scan rate up to 200 mVs^{-1} (Fig. 3). At scan rates higher than 300 mVs^{-1}, the anodic and cathodic peak currents are linearly proportional to the square root of the scan rate, which is expected for a diffusion-controlled electrode process.
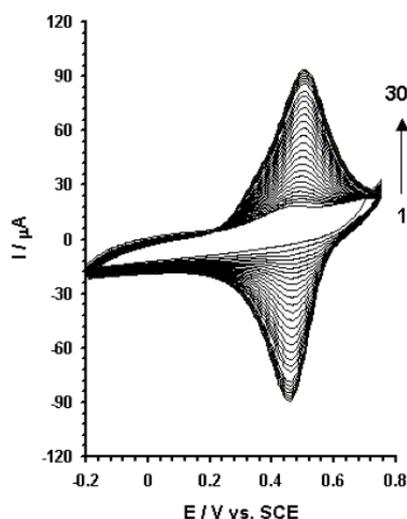
Figure 1. Cyclic voltammograms of CoNP ME synthesized from 5.0×10^{-5} mol L^{-1} of NP in 0.25 mol L^{-1} KNO$_3$ on the glassy carbon electrode in the potential range -0.2 to 0.75 V with a scan rate of 50 mV s^{-1}.

Electrocatalytic oxidation of nitrite
Fig. 4 shows the cyclic voltammograms obtained at the CoNP GCE in 0.5 mol L^{-1} KNO$_3$ solution, which contains 1.0×10^{-4} mol L^{-1} concentrations of nitrite. The cyclic voltammograms are obtained at the CoNP GC ME in 0.5 mol L^{-1} KNO$_3$ solution which contains nitrite with different concentrations (data not shown); a significant increase of anodic wave appears with the addition of nitrite, while the

cathodic wave becomes smaller and smaller until it disappears completely. With increasing nitrite concentration and subsequent scanning over the same potential range, the height of this anodic peak current increases step by step. This phenomenon suggests that the CoNP GC ME has an efficient catalytic activity toward nitrite oxidation. The anodic peak current is found to be linear with the square root of the scan rate, which suggests that the catalytic oxidation of nitrite is a diffusion-controlled reaction.
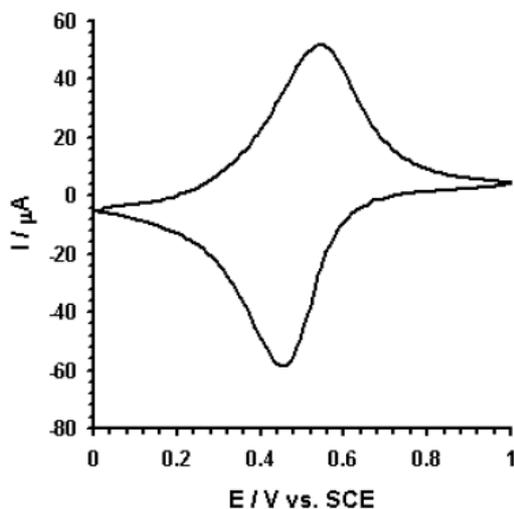
Figure 2. Cyclic voltammograms of CoNP in 0.5 mol L^{-1} KNO$_3$ on the GC electrode. Scan rate: 100 mV s^{-1}.
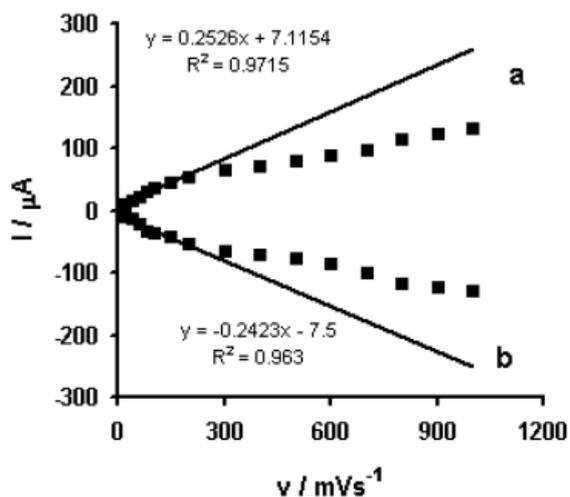
Figure 3. Plot of anodic (a) and cathodic peak currents vs. scan rate of the CoNP GC modified electrode in 0.5 mol L^{-1} KNO$_3$ solution as supporting electrolyte.

In order to obtain information on the rate determining step, a Tafel slope, b, was determined using the following equation valid for a totally irreversible diffusion controlled process [31]:

$$E_p = (b/2) \log v + \text{constant} \tag{1}$$
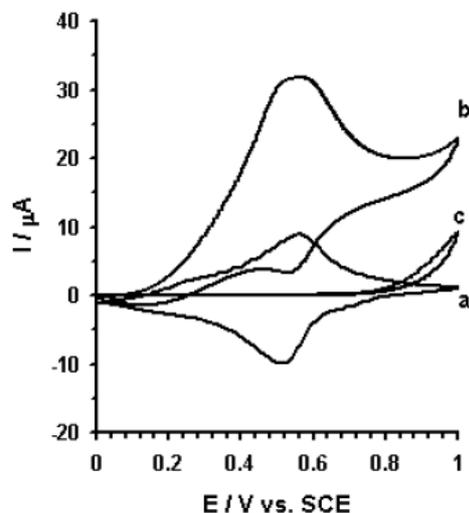
Figure 4. Cyclic voltammograms of the CoNP GC electrode (a) in the absence and in the (b) presence of 10×10^{-3} mol L^{-1} nitrite (c) as (b) for bare GC electrode (scan rate 20 mV s^{-1}).

On the basis of Eq. (1), the slope of E_p versus log v plot is b/2, where b indicates the Tafel slope. The slope of E_p versus log v was found to be 0.12 V; in this work b=2×0.12 = 0.24 V. This slope indicates that a one electron transfer process is the rate limiting step assuming transfer coefficient of $\alpha = 0.75$ (Fig. 5).
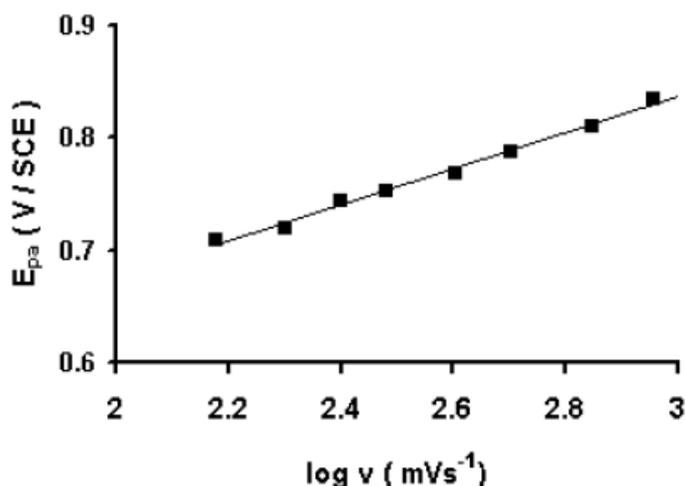
Figure 5. Dependence of the peak potential, E_p on log(v) for the oxidation of nitrite at the CoNP GC electrode obtained from data of cyclic voltammograms in presence of 10 mM of nitrite with different scan rates.

The electrocatalytic oxidation of nitrite probably proceeds through the stepwise, one-electron transfer processes since $Co^{II}[Fe^{III}(CN)_5NO]$ can easily take one electron from nitrite in the one–electron transfer processes proposed as below. The overall process according to an EC′ catalytic mechanism can be expressed as:

$$KCo^{II}[Fe^{II}(CN)_5NO] \longrightarrow Co^{II}[Fe^{III}(CN)^5NO] + K^+ + e^- \; (E) \; Fast$$

$$Co^{II}[Fe^{III}(CN)^5NO] + K^+ + NO_2^- \longrightarrow KCo^{II}[Fe^{II}(CN)_5NO] + NO_2 \; (C') \; Slow$$
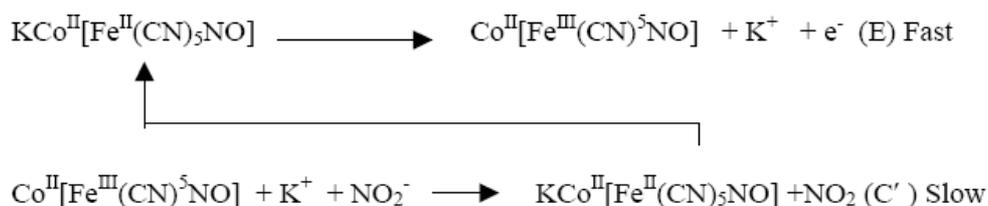
Formation of NO_2 will be followed by its fast disproportionation to give nitrite and nitrate ions. The overall chemical reaction is shown as follows:

$$2\,KCo^{II}[Fe^{III}(CN)_5NO] + 2K^+ + NO_2^- + H_2O \longrightarrow 2\,KCo^{II}[Fe^{II}(CN)_5NO] + NO_3^- + 2H^+$$
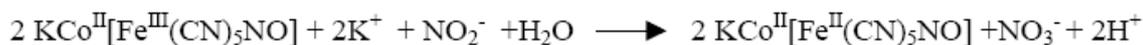
Hydrodynamic amperometry

The nitrite oxidation at the CoNP modified GCE shifts negatively about 300 mV compared with that at the unmodified GCE, and the oxidation peak current is enhanced several times, which suggests that nitrite was electrocatalytically oxidized by CoNP (Fig. 4). On the basis of the voltammetric results, it appears that amperometric detection of nitrite by the CoNP modified GCE is possible. A typical hydrodynamic amperometry (Fig. 6) was obtained by successively adding a series of standards of nitrite to continuously stirred 0.5 mol L^{-1} KCl solution. Quantitative determination of nitrite was carried out amperometrically in a stirred solution. The potential of the electrode was kept constant at 0.60 V vs. SCE. The response was recorded by adding a series of standards of the analyte to a stirred solution. The linear plot with a slope of 3.5 µA /µM and correlation coefficient r, of 0.9968 were obtained. Limit of detection (LOD for S/ND = 3) is 1.0×10^{-5} mol L^{-1}, and the relative standard deviation for the linear range is $(20–220\pm 5) \times 10^{-6}$ mol L^{-1}, which gives the measure of reproducibility of the data. The electrode response time was less than 3 s.
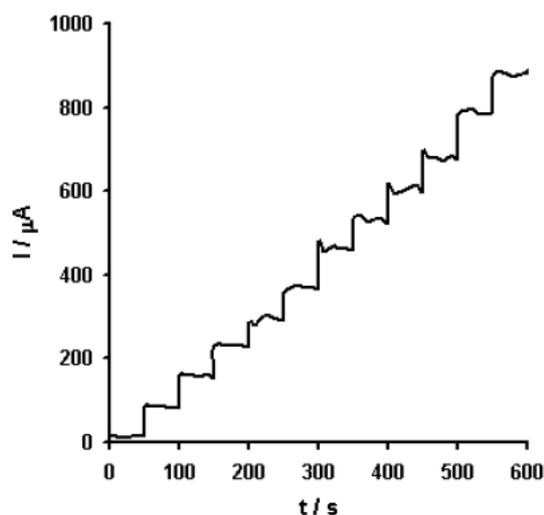
Figure 6. Typical amperograms showing the current response for different concentration of nitrite to 10 mL supporting electrolyte, the linear concentration range was $(20-220) \times 10$ mol L^{-1}. supporting electrolyte: 0.5 mol L^{-1} KNO$_3$. Applied potential: 0.60 V.

The responses of the CoHCF CME are stable and reproducible. The electrode was stable during a week period of operation with no evidence of chemical and mechanical deterioration.

Conclusion

The CoNP modified GCE has been fabricated by electrochemical deposition method. The chemically modified electrode can electrocatalyze the oxidation of nitrite, and exhibits a distinct advantage of simple preparation, good chemical and mechanical stability. The linear range $(20-220)\times10^{-6}$ mol L^{-1} was obtained for CoNP ME. The ME shows good stability during the period of operation.

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