

Electrocatalytic oxidation of nitrite at a terpyridine manganese(II) complex modified carbon past electrode

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Abstract A carbon past electrode modified with $[\text{Mn}(\text{H}_2\text{O})(\text{N}_3)(\text{NO}_3)(\text{pyterpy})]$, (pyterpy = 4' - (4 - pyridyl) - 2, 2' : 6', 2'' - terpyridine) complex have been applied to the electrocatalytic oxidation of nitrite which reduced the overpotential by about 120 mV with obviously increasing the current response. Relative standard deviations for nitrite determination was less than 2.0%, and nitrite can be determined in the ranges of 5.00×10^{-6} to 1.55×10^{-2} mol L⁻¹, with a detection limit of 8×10^{-7} mol L⁻¹. The treatment of the voltammetric data showed that it is a pure diffusion-controlled reaction, which involves one electron in the rate-determining step. The rate constant k' , transfer coefficient α for the catalytic reaction, and diffusion coefficient of nitrite in the solution, D , were found to be 1.4×10^{-2} , 0.56×10^{-6} , and 7.99×10^{-6} cm² s⁻¹, respectively. The mechanism for the interaction of nitrite with the Mn(II) complex modified carbon past electrode is proposed. This work provides a simple and easy approach to detection of nitrite ion. The modified electrode indicated reproducible behavior, anti-fouling properties, and stability during electrochemical experiments, making it particularly suitable for the analytical purposes.

Keywords Nitrite · Electrocatalytic oxidation · Manganese (II) complex · Carbon past electrode · Modified electrodes

Introduction

Nitrite is a very interesting analytical substrate because of its prevalence in industrialized meats as preserving agent

and appearance builder. But, when ingested, it can react with hemoglobin oxidizing it to metahemoglobin and with amines converting them into nitrosamines, which are well-known carcinogenic substances [1, 2]. The environmental impact caused by the buildup of high nitrite and nitrate concentrations, owing to their use as fertilizers, and the problems caused by the contamination of water sources for human consumption are also big concerns [3, 4]. Therefore, many methods for nitrite determination have been developed in recent years, such as spectroscopic analysis [4–6] and chromatography [7–9], and there is an upsurge of interest in the application of electroanalytical techniques to the determination of nitrite in the last two decades [10–16]. Electrochemical sensor is useful since it is faster, cheaper, and safer. However, a fast and reliable sensing method is still a challenge for low-concentration detection [17].

Electrochemical determination of nitrite is either by reduction or oxidation. Oxidation of nitrite ions offers several advantages, namely no interference from nitrate ion and from molecular oxygen, which are usually the major limitations in the cathodic determination of nitrite [18, 19].

The oxidation of nitrite ions requires undesirably high overvoltage [20, 21]. The voltammetric or amperometric determination of nitrite is, therefore, prone to suffer interference from other readily oxidizable compounds. In order to improve the selectivity of the determination of nitrite, the operating potentials should be efficiently lowered. The purpose can be achieved by modifying suitable electrocatalyst on the surface of carbon electrodes.

The aim of this study is to extend the use of pyridinterpyridin-type catalysts to the electrooxidation reaction of nitrite. Thus, we report here the electrocatalytic oxidation of nitrite on carbon past electrodes modified with different amounts of $[\text{Mn}(\text{H}_2\text{O})(\text{N}_3)(\text{NO}_3)(\text{pyterpy})]$, (pyterpy = 4' - (4 - pyridyl) - 2, 2' : 6', 2'' - terpyridine)

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complex to establish the role of the metal complex and its surface coverage.

Experimental

Reagents and solutions

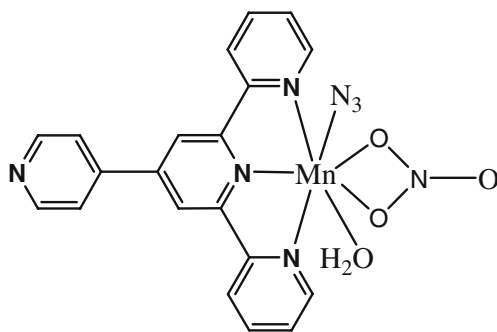
All reagents were of analytical grade from Merck or Fluka and were used as received without further purification. The ligand pyterpy [22] and $[\text{Mn}(\text{H}_2\text{O})(\text{N}_3)(\text{NO}_3)(\text{pyterpy})]$, (pyterpy = 4'-(4-pyridyl)-2,2':6',2''-terpyridine) complex (Scheme 1) were prepared similar to reported methods [23]. Triple distilled water was used to prepare buffer and reagent solutions.

Apparatus

Voltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a bare or chemically modified carbon past electrode (CPE) as working electrode, (Ag/AgCl, KCl, 3 M), reference electrode, and a platinum wire counter electrode. A digital pH/mV meter model 780 Metrohm was applied for the preparation of the buffer solution, which was used as the supporting electrolyte in the voltammetric experiments.

Electrode preparation

The unmodified carbon-past electrode was prepared as our pervious works [24–26], by mixing graphite powder with appropriate amount of paraffin oil (65:35 w/w) and a portion of the composite mixture was packed into a Teflon tube (ca. 2 mm i.d.) that connected to the end of a glassy carbon electrode. The tip of the electrode was polished with a weighing paper. The modified electrode was prepared by mixing unmodified composite with the manganese(II) complex (5.0% w/w) and homogenized by spatula. The modified composite was then used in the same way as the unmodified electrode. The area of these electrodes was



Scheme 1 Structure of the $[\text{Mn}(\text{H}_2\text{O})(\text{N}_3)(\text{NO}_3)(\text{pyterpy})]$

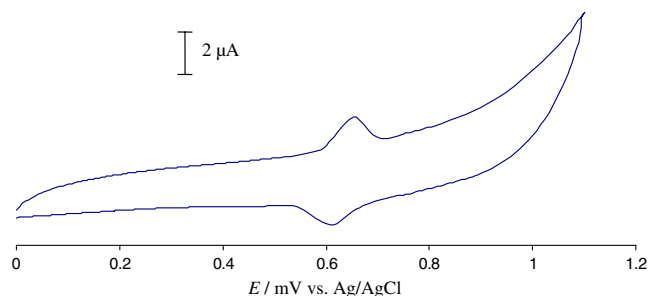


Fig. 1 Cyclic voltammetry of a 1.0-mM solution of the Mn(II) complex in methanol solvent, supporting electrolyte, 0.1 M TBAP; scan rate 100 mV s^{-1} ; electrode: glassy carbon

$0.065 \pm 0.004 \text{ cm}^2$, which was evaluated from cyclic voltammetric experiments.

Results and discussion

Electrochemical behavior of terpyridine manganese(II) complex in methanol

The electrochemical behavior of the complex in methanol containing 0.1 M tetrabutylammonium perchlorate (TBAP) was investigated for definition of the identity of the couple of redox peak and the number of electron transfer (Fig. 1). The cyclic voltammetric experiments were performed in the potential range of 0.0–1.1 V (vs. nonaqueous Ag/AgCl), a couple of redox peaks were observed in the acidic solution (pH 4), the formal potential for the couple of reversible redox peak is 0.63 V vs. nonaqueous Ag/AgCl, and it can be assigned to $\text{Mn}^{\text{III/II}}$ couple.

Electrocatalytic oxidation of nitrite at the modified electrode

Figure 2 shows the cyclic voltammograms (CVs) of nitrite at a bare CPE (curves a, b) and at the modified CPE (curve c, d) in 0.1 M phosphate buffer solution pH 4. Curve c in this figure shows the modified CPE in phosphate buffer pH 4. At a bare electrode, anodic current due to the oxidation of nitrite is observed in b, but no cathodic peak is found, which indicates an irreversible charge transfer in this system. At the surface of the unmodified electrode, the direct oxidation of nitrite produces a small anodic wave at a relatively high positive potential that is not well defined. However, a sharp anodic wave at a lower positive potential is obtained for nitrite at the surface of the Mn(II)-complex-modified carbon past electrode (Fig. 2 curve d). Increasing the anodic peak current in conjunction with the sharpness of the peak, which is related to a decrease of the overpotential of the process at the surface of the modified electrode, revealed that the modified electrode could act as

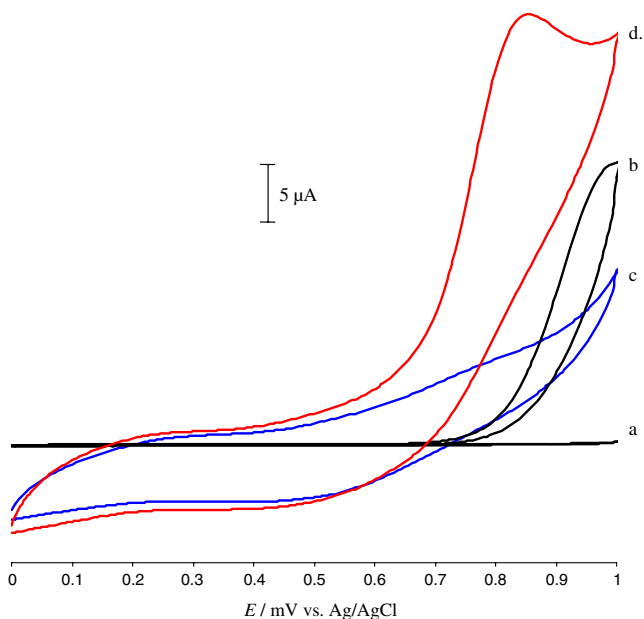


Fig. 2 Cyclic voltammograms: at bare carbon past electrode *a* in the absence and *b* in the presence of 1 mM nitrite; and at the Mn(II)-complex-modified carbon past electrode *c* in the absence and *d* in the presence of 1 mM nitrite; supporting electrolyte, 0.1 M phosphate buffer, pH 4; scan rate 100 mV s^{-1}

an effective promoter to enhance the kinetics of the electrochemical process. By using the Mn(II) complex as an electron mediator in the matrix of the modified electrode, the overpotential for the anodic oxidation of nitrite becomes considerably lower and the rate of the heterogeneous electron transfer is increased.

Influence of the modifier percentage and pH

The effects of the Mn(II) complex percentage ranging from 1% to 10% on the CV of 1.0 mM nitrite in 0.1 M phosphate buffer (pH 4.0) were studied, and this is shown more distinctly in Fig. 3, which is a plot of peak current and peak potential versus the modifier percentage. As this figure illustrates, the nitrite oxidation peak is enhanced between 0% and 5% of the modifier and then decreases when the amount of the modifier is increased further. This occurs, may be, due to a decrease in the graphite content in the past and consequent reduction of the conductive electrode area. The peak potential for the oxidation of nitrite is also affected by a change in the percentage of the modifier, i.e., the peak potential is decreased between 0% and 5% modifier and then increases with increasing amount of the modifier. Therefore, the role of the modifier is to enhance the peak current (sensitivity) and also to decrease the overpotential for the oxidation of nitrite. It was found that the best carbon past composition for an electrode is 5% (w/w) Mn(II) complex, 62% (w/w) graphite, and 33% (w/w) paraffin oil.

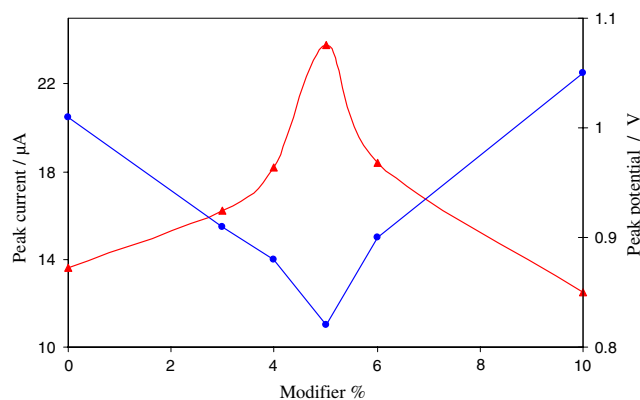


Fig. 3 Effect of modifier percentage on the peak current (*triangles*) and peak potential (*circles*) of cyclic voltammograms for 1 mM of nitrite in 0.1 M phosphate buffer, pH 4

The electrochemical behavior of the nitrite ion is dependent on the pH value of an aqueous solution. To optimize the electrochemical response of the modified electrode for nitrite oxidation, the effects of pH on the electrode response and the oxidation potential were investigated by cyclic voltammetry in the solution containing 1 mM nitrite (Fig. 4). For the oxidation of nitrite, the anodic peak potential shifts to more negative values with increasing pH up to 4. However, as Fig. 4 shows, by further increasing the solution pH, the potential of anodic wave increases, revealing that the Mn(II) complex has a better electrocatalytic activity for the oxidation of nitrite in solution with a pH equal to 4; and also, the sensitivity is enhanced by working at this pH, which the current is maximum. The decreases of current at lower pH (<4) can be due to the protonation of nitrite ions or the conversion of NO_2^- to NO at very low pH [27]. The decrease in current

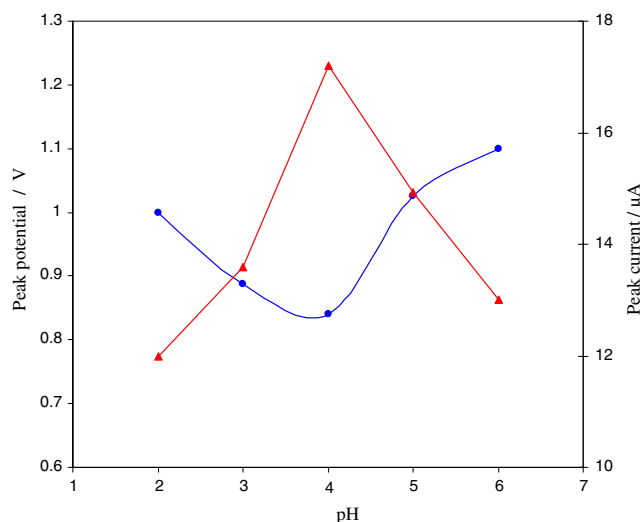


Fig. 4 Dependence of the oxidation peak current (*circles*) and peak potential (*triangles*) of 1.0 mM nitrite on pH values in 0.1 M KCl, at a scan rate of 100 mV s^{-1}

response with increasing pH (>4) is probably due to the decrease in the electrochemical activity of the manganese (II) complex to nitrite ion.

Calibration curve

Figure 5 displays the cyclic voltammograms of various concentrations of nitrite ion ranging from 5.00×10^{-6} to 1.55×10^{-3} M at the modified CPE in 0.1 M phosphate buffer pH 4. As this figure shows, by increasing nitrite concentration; the peak potentials shift to more positive potentials. The similar behavior is also observed at a bare carbon past electrode (not shown). The calibration curves that were obtained from these voltammograms are shown in the Fig. 6. In the ranges 5.00×10^{-6} to 1.86×10^{-3} and 1.86×10^{-3} to 1.55×10^{-2} mol L⁻¹, the oxidation current (I_{pa}) has a good linear relationship with nitrite concentration, as shown in Fig. 6, which could be, respectively, described as:

$$I_p(\mu A) = 7.66C + 1.27(R^2 = 0.999) \quad (1)$$

$$I_p(\mu A) = 0.85C + 17.40(R^2 = 0.960) \quad (2)$$

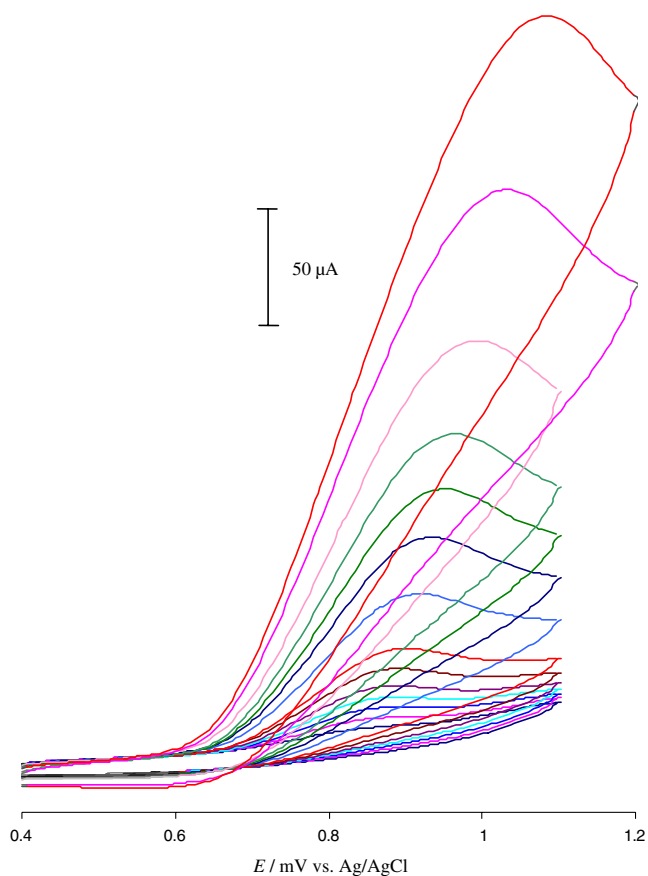


Fig. 5 Cyclic voltammograms of various concentrations of nitrite ion (5.00×10^{-6} to 1.55×10^{-2}). Supporting electrolyte of all experiments was 0.1 M phosphate buffer, pH 4

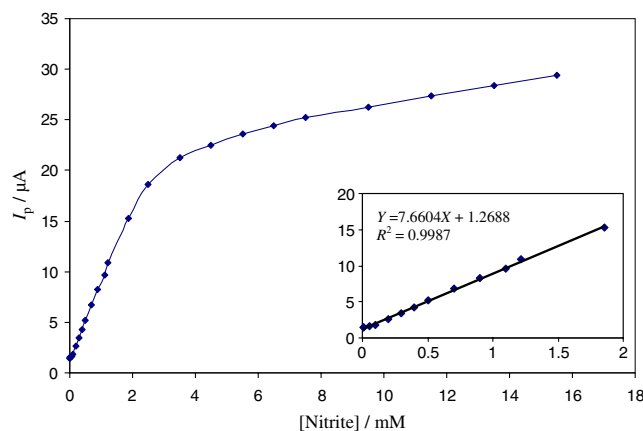


Fig. 6 Calibration curve for nitrite at a 5% modified CPE in 0.1 M phosphate buffer pH 4. The inset shows the calibration curve in the concentration range from 5.00×10^{-6} to 1.86×10^{-3} M. Conditions: 0.1 M phosphate buffer pH 4; scan rate 100 mV s⁻¹

The detection limit of 8×10^{-7} M for nitrite was estimated at these conditions based on $3S_b$ ($n=10$), where S_b is standard deviation of the blank.

Mechanistic studies of the electrocatalytic oxidation of nitrite at the surface of the modified electrode

The effect of the potential scan rate on the electrocatalytic property of the modified CPE towards nitrite was studied. Figure 7a shows the cyclic voltammograms in the phosphate buffer solution (pH 4.0) containing 1.0 mM nitrite at various scan rates. It was found that the electrocatalytic oxidation peak potential shifts to positive potentials on increasing scan rates. The obtained results show that the catalytic effect of the mediator appeared at all testing scan rate. It can also be noted from this figure that with an increasing scan rate, the peak potential for the catalytic oxidation of the nitrite ion shifts to more positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of the modifier and the nitrite ion. The positive shift of the peak potential is quicker at low scan rates, and it becomes smaller with increasing the scan rate. However, the peak current for the anodic oxidation of the nitrite ion is proportional to the square root of scan rate (Fig. 7b), which it can be stated that the oxidation of nitrite at the modified CPE, at sufficient overpotential, is controlled by diffusion.

In order to obtain information on the rate-determining step, Tafel slope (b) was determined using the following equation for a totally irreversible diffusion process [28]

$$1/I_{lim} = 1/I_k + 1/(0.62nFA\nu^{-1/6}D^{2/3}\omega^{1/2}c) \quad (3)$$

Based on the Eq. 3, the slope of E_p vs. $\log \nu$ plot is $(b/2)$, where b indicates the Tafel slope. The slope of E_p vs. $\log \nu$

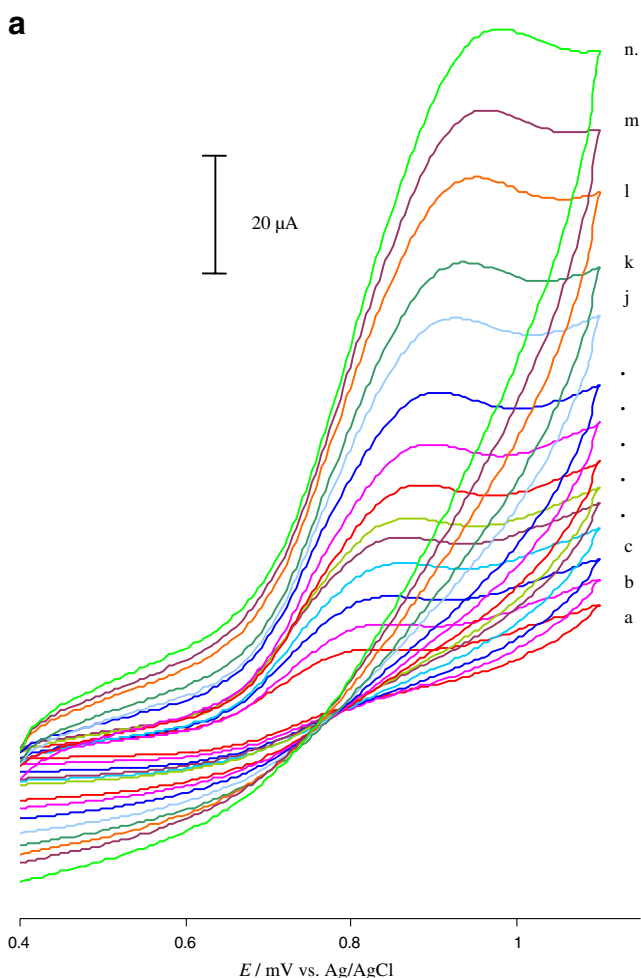
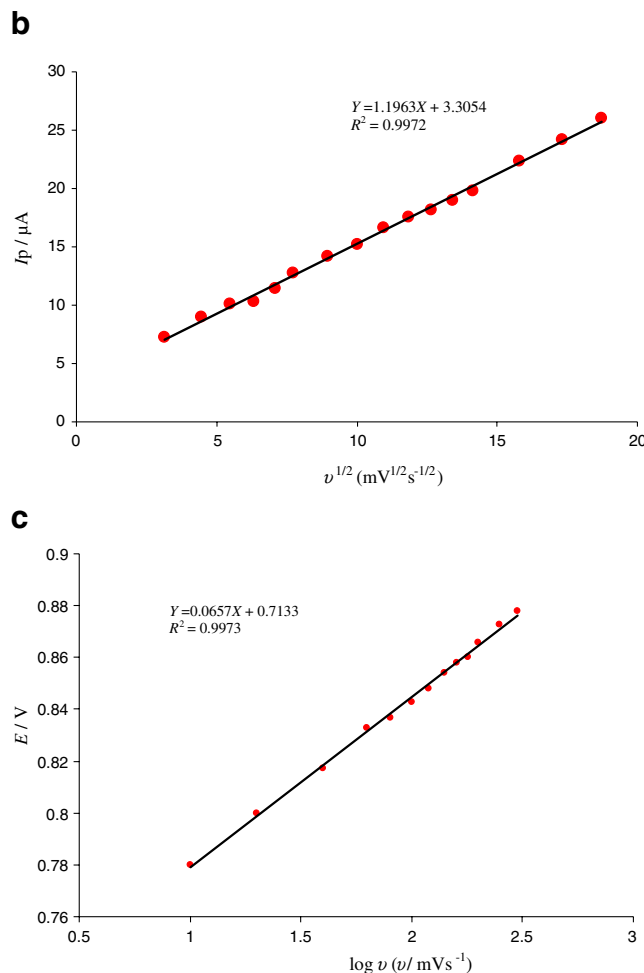


Fig. 7 a Dependence of the cyclic voltammetric response at a modified CPE on sweep rate in 0.1 M acetate buffer (pH 6.0) containing 0.5 mM hydrazine. Scan rate a 10, b 20, c 30, d 40, e 50, f



60, g 70, h 80, i 90, j 100, k 120, l 140, m 160, and n 200 mV s^{-1} ; **b** variation of the catalytic current with the square root of sweep rate; **c** plot of anodic peak potential versus logarithm of scan rate

plot is $\partial E_p / \partial \log v$, which was found to be 65.7 mV in this work (Fig. 7c). Assuming the number of electrons transferred in the rate-limiting step is equal to 1, a transfer coefficient, α , was estimated as 0.55. If we assume $n=2$, α would then be equal to 0.77 which is not a common value, because for most electrode processes, it is in a ranges between 0.75 and 0.25 [29].

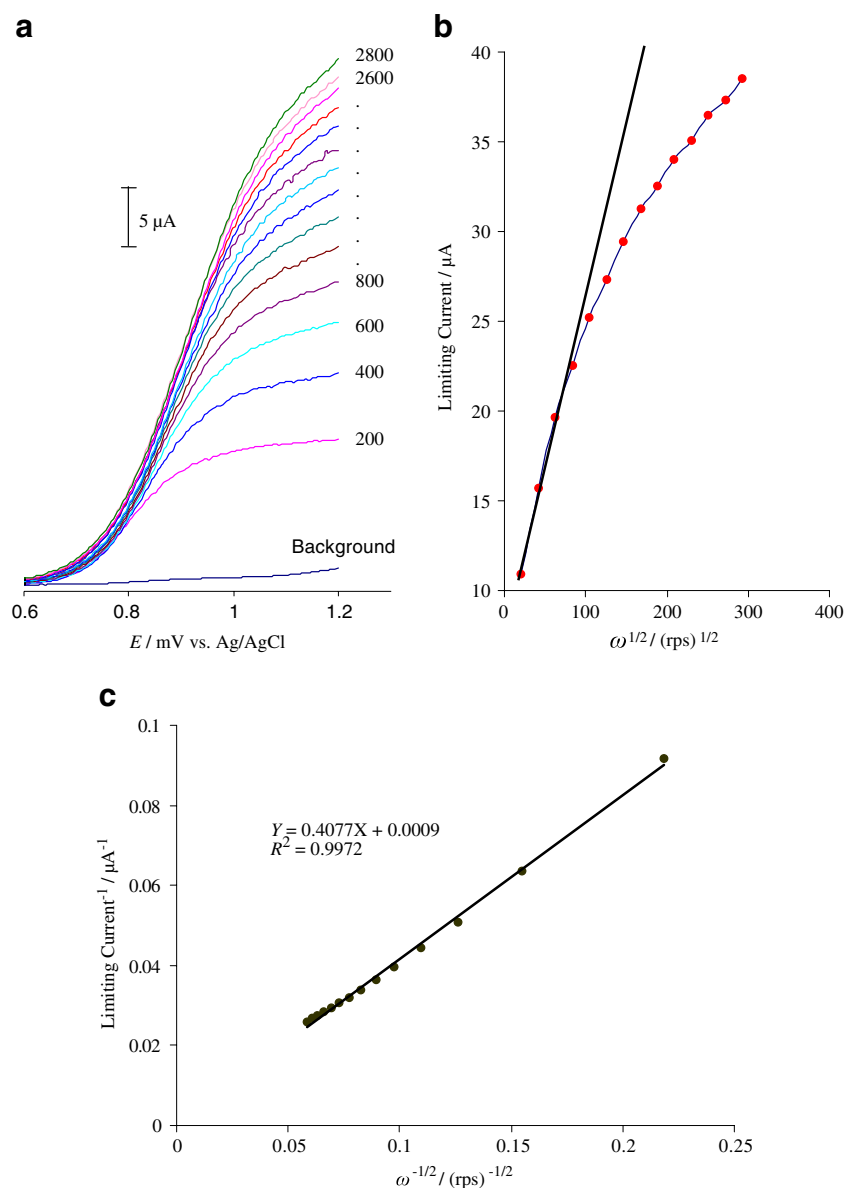
The hydrodynamic voltammograms of 1 mM nitrite solution in 0.1 M phosphate buffer (pH 4.0) on the surface of the chemically modified CPE were recorded at different rotation rates over a range of 200–2,800 rpm (Fig. 8a). Using these hydrodynamic voltammograms, the limiting currents, I_{lim} , at different rotating rates versus square root of rotation rate were plotted as shown in Fig. 8b (Levich plot). It would be expected from the Levich equation that this plot should be linear, but as is seen in Fig. 8b, the plot is not linear and tends to level off at higher rotation rates, as expected for a catalyzed oxidation in which a current limiting chemical step precedes electron transfer. Hence, it

can be concluded that the rate-determining step in this process is related to the oxidation of nitrite at the modified CPE. The corresponding Koutecky–Levich plot, I^{-1} vs. $\omega^{-1/2}$, which is shown in Fig. 8c, is linear with a positive intercept. This behavior is consistent with the fact that the rate of electron transfer is sufficiently slow to act as a limiting factor [29]. The total current corresponding to both mass and charge transfer can be described by the following equation:

$$1/I_{lim} = 1/I_k + 1/(0.62nFAv^{-1/6}D^{2/3}\omega^{1/2}c) \quad (4)$$

where I_k represents the current in the absence of any mass transfer for a totally irreversible reaction, c is the bulk concentration of nitrite (mol cm^{-3}), ω is the angular frequency of rotation (rad s^{-1}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), v is the kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$), and all other parameters have their conventional meanings. The rate constant, k' can be calculated from the intercept of the Koutecky–Levich plot.

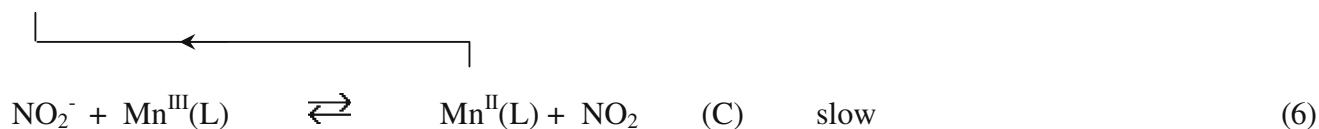
Fig. 8 **a** Voltammograms of a modified carbon past rotating disk electrode in a 1 mM solution of nitrite in 0.1 M phosphate buffer (pH 4.0) at rotation rates from 200 to 2,800 rpm, **b** Levich plot derived from RDE voltammograms of a modified CPE in 1 mM nitrite in 0.1 M phosphate buffer (pH 4.0), **c** Koutecky–Levich plot corresponding to the Levich plot shown in (b)



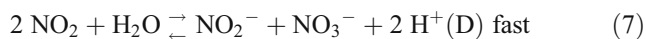
From the value of the intercept, the k' was found to be $1.4 \times 10^{-2} \text{ cm s}^{-1}$. The diffusion coefficient of nitrite in buffered aqueous 1 mM nitrite of pH 4.0 was determined as $7.99 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, from the slope of Koutecky–Levich equation at various rotation speeds of the modified carbon past electrode.

These values are comparable with those reported previously for the electrocatalytic oxidation of nitrite at the electrodes modified with other mediators [18, 30].

Finally, a catalytic mechanism that is compatible with the behavior observed is given in the following reactions:



The formation of NO_2 will be followed by its disproportionation to give the nitrite and nitrate ions [31].



The overall chemical reaction is shown as follows:



Conclusions

In the present article, the electrocatalytic activity of an Mn(II)-complex-modified carbon past electrode toward the oxidation of nitrite in 0.1 M phosphate buffer (pH 4) medium was demonstrated. The Mn(II) complex forms a reversible oxidation to Mn(III) complex at potential about 0.62 V. The electrocatalytic determination of nitrite involves the $\text{Mn}^{\text{(III)}/\text{Mn}^{\text{(II)}}$ redox process. The optimum conditions of experimental variables for the electrocatalytic oxidations of nitrite have been evaluated. Voltammetric results indicate that the catalytic process is controlled by the substrate diffusion. On the basis of the Tafel plot, the charge transfer step of the rate-limiting reaction is suggested to be a one-electron reaction and the transfer coefficient of ca. 0.56. The heterogeneous rate constant, k' , for the oxidation of nitrite at the surface of the modified electrode and also the diffusion coefficient of nitrite in buffered aqueous 1 mM nitrite of pH 4.0 were determined by rotating disk electrode voltammetry using the Koutecky–Levich plot. Finally, a catalytic mechanism that is compatible with the behavior observed is proposed. This modified electrode provides a sensitive method for the detection of nitrite and can avoid interference from the nitrate ion and the molecular oxygen. Also, this modified electrode exhibits good catalytic activity for the oxidation of nitrite with good sensitivity over a wide range 5.00×10^{-6} to $1.55 \times 10^{-2} \text{ mol L}^{-1}$, with a detection limit of $8 \times 10^{-7} \text{ mol L}^{-1}$ ($S/N=3$).

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