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Electrocatalytic Reduction of Nitrite at an $[Os(bipy)_2(PVP)_{10}Cl]Cl$-modified Electrode

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The electrocatalytic reduction of nitrite at an electrode modified with the redox polymer $[Os(bipy)_2(PVP)_{10}Cl]Cl$, where bipy = 2,2′-bipyridyl, PVP = poly(4-vinylpyridine), is described. A possible mechanism for the mediated reaction is proposed. The kinetics of the mediated reaction are examined and compared to a theoretical rate equation describing the proposed mechanism. The reaction most likely proceeds through the species, NO^+. Kinetic analysis reveals that the kinetic situation *Lk* best describes the electrocatalytic reaction, with mediation occurring throughout the polymer film and electrode currents being controlled by the rate constant for the cross-exchange reaction. An equation relating limiting currents to known and easily measurable parameters is also presented which may be used for the internal calibration of sensors constructed from these electrodes.

The preparation, characterisation and charge-transport properties of redox polymer-modified electrodes have received considerable attention recently.[1–4] Theoretical models describing mediated electrocatalysis at these electrodes have also appeared.[5,6] These methods have been applied to electrocatalytic reactions occurring at polythionine[7] polypyrrole[8,9] and metallo-polymers[10,11] and kinetic models have been proposed.

It has recently become evident that current densities predicted from charge-transport measurements using transient techniques can seriously underestimate the charge-carrying capacity of redox polymers[12,13] and consequently the prediction of modified electrode behaviour under operational conditions can be difficult from charge-transport results. Detailed investigation of the electrocatalytic properties of these redox polymer-modified electrodes is therefore important in order to establish the type of electrocatalytic reactions which are feasible and the optimum conditions for operational electrochemical devices.

We have recently described a novel electrochemical sensor for the reductive determination of nitrite based on glassy carbon electrodes modified with the electrocatalyst $[Os(bipy)_2(PVP)_{10}Cl]Cl$,[14] where bipy is 2,2′-bipyridyl and PVP is poly(4-vinylpyridine) (see Fig. 1). In this contribution the electrochemical behaviour of nitrite at such modified electrodes and the kinetics of the mediated process are described.

Experimental

Materials

The electrocatalytic polymer, $[Os(bipy)_2(PVP)_{10}Cl]Cl$, was synthesized as previously described.[3] Modification of the electrode surface was carried by droplet evaporation using a 1% methanolic solution of the polymer.

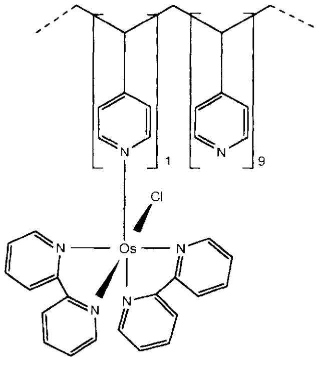

Fig. 1 Structure of the metallopolymer $[Os(bipy)_2(PVP)_{10}Cl]Cl$

All reagents used were analytical grade. All aqueous solutions were prepared from water obtained from a Milli-Q water purification system. The electrolyte used throughout was 0.1 mol dm^{-3} in Na_2SO_4 and 0.05 mol dm^{-3} in H_2SO_4. In situations where the hydrogen ion concentration was varied, this was achieved by dilution of appropriate amounts of the above electrolyte while maintaining the Na_2SO_4 concentration at 0.1 mol dm^{-3}. Stock nitrite solutions were prepared in neutral electrolyte to prevent acidic decomposition. All measurements were carried out using freshly prepared acidic nitrite solutions by dilution of the stock nitrite solution with the electrolyte.

Apparatus

Cyclic voltammetry and rotating-disc electrode (RDE) voltammetry were carried out using a Princeton Applied Research model 362 potentiostat, a Metrohm 628-10 rotating-disc electrode assembly and Linseis LY 17100 X-Y recorder. Electrodes were 3 mm diameter glassy carbon shrouded in PTFE (Metrohm). A saturated calomel electrode (SCE) served as the reference electrode; all potentials are quoted without regard to the liquid-junction potential. A platinum gauze of 1 cm^2 area was used as the counter electrode. All measurements were made at 20 ± 2 °C. UV–VIS spectroscopy was carried out using a Shimadzu UV 240 spectrophotometer.

Results and Discussion

Electrochemical Behaviour of Nitrite at the Modified Electrode

Fig. 2 shows a cyclic voltammogram (CV) of the redox polymer $[Os(bipy)_2(PVP)_{10}Cl]Cl$. The half-wave potential of the redox polymer in sulfuric acid electrolyte was found to be 0.25 V *vs.* SCE. The peak-to-peak separation of the redox waves was close to zero for slow potential sweep rates (< 10 mV s^{-1}) and a plot of peak current *vs.* sweep rate is linear up to 50 mV s^{-1}. These features are indicative of well behaved surface-bound species.[15] The rate of charge transport through the polymer film was estimated using high-sweep-rate CV to be $(1 \pm 0.1) \times 10^{-10}$ cm^2 s^{-1}. This fast rate is important as it allows rapid regeneration of the electrocatalyst within the polymer film.

Fig. 3 shows a CV for the reduction of nitrite at a polymer modified electrode, when this CV is compared to Fig. 1, significant elongation along the current axis is evident. This behaviour is a result of redox cycling of the surface bound

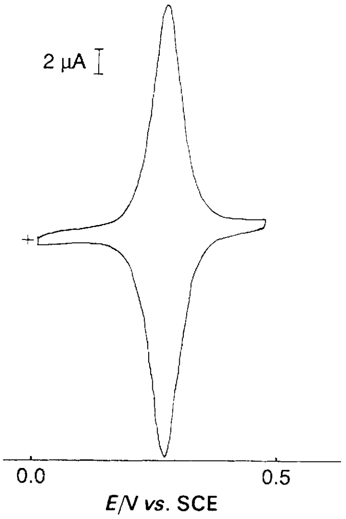

Fig. 2 Cyclic voltammogram of the polymer $[Os(bipy)_2(PVP)_{10}Cl]Cl$ coated on a glassy carbon electrode. Electrolyte, 0.1 mol dm^{-3} Na_2SO_4 containing 0.05 mol dm^{-3} H_2SO_4, potential sweep rate 100 mV s^{-1}, surface coverage 1.0×10^{-8} mol cm^{-2}

osmium sites with electron transfer to a solution species and is indicative of an electrocatalytic process occurring at the electrode surface. Note that the shoulders on both the forward and reverse waves are due to the Os^{II}/Os^{III} redox couple. It can be seen that the electrode is 'switched on' at *ca.* 0.4 V *vs.* SCE in the forward scan (negative sweep) and is 'switched off' in the reverse sweep at about the same potential, showing the start of the mediated reaction occurring at the onset of osmium reduction within the film. This behaviour clearly indicates that the electron-transfer process is mediated by the osmium centres within the polymer film. No cathodic current wave on the reverse scan is evident, indicating that the mediated reaction is irreversible.

In Fig. 4, current *vs.* potential curves for the reduction of nitrite at a bare glassy carbon electrode (*a*) and at a polymer-modified electrode (*b*) are shown. Nitrite reduction occurs only to a small extent at glassy carbon. It is known that this reaction causes severe passivation of the glassy carbon surface.[16] However, at the modified electrode a significant improvement in limiting currents is achieved and passivation is not observed. The magnitude of the limiting current at the modified electrode indicates that the mediated reaction is relatively facile while the steepness of the wave indicates well behaved electrode kinetics. In general, an amplification in response by a factor of 60 to 70 can be obtained depending on polymer film thickness, with greater currents generated at thicker polymer films.

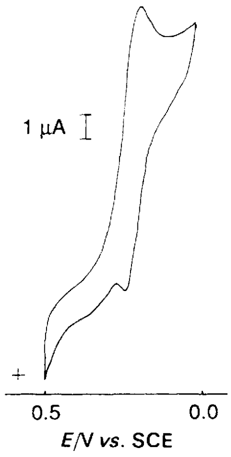

Fig. 3 Cyclic voltammogram for the reduction of 5.0×10^{-3} mol dm^{-3} nitrite at a polymer-modified electrode. Surface coverage 1.0×10^{-9} mol cm^{-2}, sweep rate 10 mV s^{-1}, electrolyte as in Fig. 2

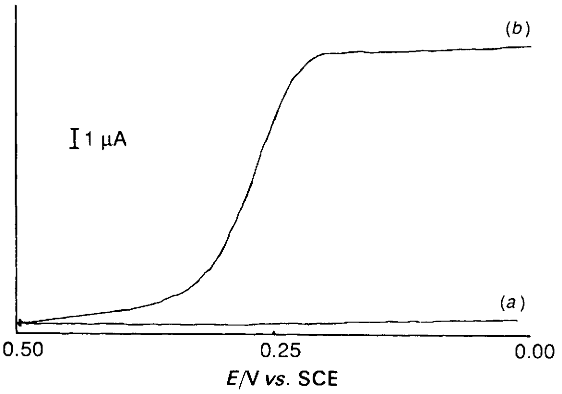

Fig. 4 Rotating-disc electrode voltammogram of 5.0×10^{-3} mol dm^{-3} nitrite at bare glassy carbon electrode (*a*) and at a modified electrode (*b*). Electrolyte as in Fig. 2, sweep rate of 5 mV s^{-1}, rotation speed of 500 r.p.m., the potential sweep direction was negative

Recently the electrochemical reduction of nitrite coordinated to osmium,[17] ruthenium[17] and iron[18] centres has been reported. The reduction process involves adduct formation, inner-sphere electron transfer and appears to proceed through the nitrosonium ion, (NO^+). For the reaction studied here, the mediation reaction is centred at 0.25 V *vs.* SCE, the $E_{1/2}$ of the electrocatalytic centre within the polymer film. The limiting current plateau for the mediated reduction reaction is found to be very flat [Fig. 4(*b*)]. Both of these features are indicative of a purely outer-sphere electron-transfer[19] reaction, which is indeed expected for this type of electrocatalytic material. This has been confirmed by UV–VIS spectroscopy, no change in the UV–VIS spectrum of the polymer complex is observed in the presence of nitrite under acidic conditions over the range 200–900 nm, clearly suggesting that no change is occurring in the coordination sphere round the central osmium ion.

In order to establish a possible mechanism for the reduction process the nature of the species to be reduced must be established. The pK_a of nitrous acid is 3.4,[20] consequently nitrite is protonated in the acidic electrolyte used here. Based on the results obtained and on studies reported in the literature, we propose that mediation involves outer-sphere electron transfer to the nitrosonium ion.[14] In the proposed reaction scheme NO^+ is formed in acidic nitrite solution according to the following acid–base equilibrium[21]:

$$HNO_2 + H^+ \underset{k_{-1'}=k_{-1}[H_2O]}{\overset{k_1}{\rightleftharpoons}} NO^+ + H_2O \qquad (1)$$

We propose that the nitrosonium ion then undergoes a cross-exchange reaction with mediator sites present in the polymer film according to:

$$NO^+ + Os^{II} \xrightarrow{k_2} NO + Os^{III} \qquad (2)$$

To verify this assumption a theoretical kinetic equation has been derived and compared to experimental data.

For a mediating redox polymer which shows a through-layer reaction and with efficient partitioning of substrate into the film (*vide infra*) the flux of the electrochemical reaction j_Σ is given by:[5]

$$j_\Sigma = \Gamma K k_2 [NO^+] \qquad (3)$$

where Γ is the surface coverage of electroactive centres and K is the partition coefficient. The quantity $[NO^+]$ may be evaluated using the steady-state approximation:

$$d[NO]/dt = k_1[HNO_2][H^+] - \{k'_{-1}[NO^+] + \Gamma K k_2[NO^+]\} = 0 \qquad (4)$$

Solving for $[NO^+]$:

$$[NO^+] = k_1[HNO_2][H^+]/k'_{-1} + k_2\Gamma K \qquad (5)$$

Combining with eqn. (4) we obtain:

$$j_\Sigma = \Gamma K k_2\{k_1[HNO_2][H^+]/k'_{-1} + k_2\Gamma K\} \qquad (6)$$

Assuming that $k_2 \ll k'_{-1}$ the second term can be neglected and the total interfacial flux is given by:

$$j_\Sigma = k_2\Gamma K\{k_1([HNO_2][H^+]/k'_{-1}\} \qquad (7)$$

As $k_1/k'_{-1} = K'_{eq}$ then:

$$j_\Sigma = \Gamma K k_2 K'_{eq}[HNO_2][H^+] \qquad (8)$$

So the current at steady state is given by:

$$i_\Sigma = nFAKk_2\Gamma K'_{eq}[HNO_2][H^+] \qquad (9)$$

Consequently the current at steady state should be first order with respect to $[HNO_2]$, $[H^+]$ and Γ.

To check the validity of eqn. (10), the order of the reaction with respect to the above parameters was investigated experimentally. The reaction order for the solution species may be evaluated using the following equation:

$$m_j = d \log i_{lim}/d \log c_j \qquad (10)$$

where m_j and c_j represents the reaction order with respect to species j and the concentration of j, respectively, and i_{lim} is the limiting current. A plot of log i_{lim} *vs.* log c_j should be linear with a slope equal to the reaction order for the species under investigation. Examples of such plots are given in Fig. 5 and 6. From these plots reactions orders of 1.0 and 0.9 are obtained for $[HNO_2]$ and $[H^+]$, respectively. The order with respect to surface coverage was found to be 0.9 (see Table 1, as the limiting current is independent of the rotation rate, the values obtained for k'_{me} are equal to the limiting current).

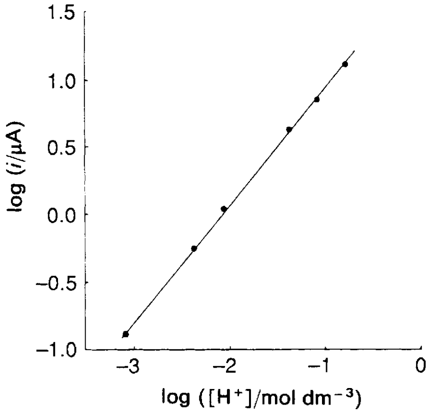

Fig. 6 Reaction order plot for $[H^+]$. Experimental conditions as in Fig. 5

These experimental results are in good agreement with eqn. (9) and support the proposed reaction mechanism.

Tafel analysis is also useful for delineating kinetic aspects of electrochemical reactions.[22] A Tafel plot constructed from data extracted from the rising portion of curves such as Fig. 4(*b*) is shown in Fig. 7. Tafel analysis was carried out with the knowledge that interfacial dynamics control limiting currents rather than mass transfer to the electrode surface (*vide infra*). This plot reveals a Tafel slope of −84 mV. The plot is linear which is indicative of an irriversible process occurring at the electrode.[22] This confirms the observation using CV concerning the reversibility of the electrode reaction. This is not surprising as the product of the reaction is gaseous. The slope

Table 1 Dependence of k'_{me} on polymer layer thickness

k'_{me} /10^{-6} cm s^{-1}	L /nm	k_2 /dm^3 mol^{-1} s^{-1}
1.9 ± 0.2	25	1.10 ± 0.10
3.5 ± 0.2	65	0.76 ± 0.10
6.2 ± 0.2	90	0.98 ± 0.10
11.5 ± 0.2	180	0.91 ± 0.10

$[NO_2^-] = 2.0 \times 10^{-3}$ mol dm^{-3} and $[H^+] = 0.1$ mol dm^{-3}.

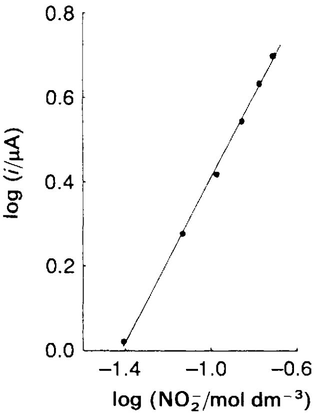

Fig. 5 Reaction order plot for $[NO_2^-]$. Data obtained with a rotation speed of 500 r.p.m. and a sweep rate of 2 mV s^{-1}. Electrolyte as in Fig. 2

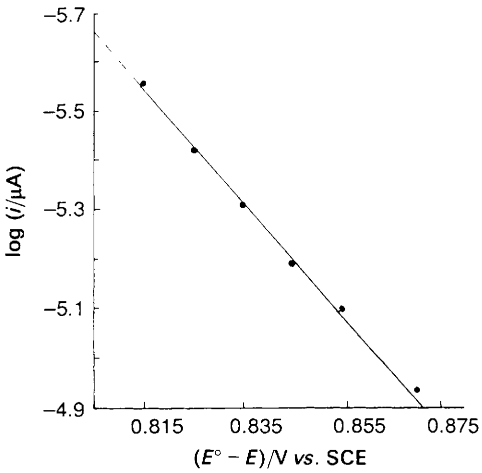

Fig. 7 Tafel plot for the reduction of nitrite at a modified electrode. Experimental conditions as for Fig. 4

Table 2 Experimentally obtained kinetic parameters for the reduction nitrite at a modified electrode

Tafel slope/mV per decade	-84 ± 5
symmetry factor	0.7 ± 0.05
reaction order w.r.t $[H^+]$	0.9 ± 0.03
reaction order w.r.t. $[NO_2^-]$	1.0 ± 0.02
reaction order w.r.t. Γ	0.9 ± 0.05
$k_2/dm^3\ mol^{-1}\ s^{-1}$	$(9.4 \pm 2) \times 10^{-1}$

suggests a symmetry factor of 0.7, which indicates considerable assymetry of the energy barrier for reaction. The experimentally obtained kinetic data concerning the electrochemical behaviour of nitrite at these electrodes are summarised in Table 2.

Modified Electrode Kinetics

Theoretical treatments of the kinetics and transport limitations of electrocatalytic reactions at redox polymer-modified electrodes have been proposed[5,6] to establish the kinetic behaviour of the modified electrode and to optimise operational performance of the electrodes. The kinetic analysis presented here is based on the examination of Koutecky–Levich plots generated from data obtained from rotating-disc electrode voltammetry. In Fig. 8 a typical Koutecky–Levich plot for various surface coverages of redox polymer for the reduction of nitrite is shown. The intercepts of these plots are inversely related to the surface coverage of the polymer film and the slopes are zero. Increasing the surface coverage of the polymer film results in an increase in the number of possible electrocatalytic sites at the electrode surface where cross-reaction may take place. The behaviour observed here corresponds to the kinetic situation *Lk* according to the notation of Albery[5] and the equivalent situation, R, using the Saveant[6] notation. This kinetic situation corresponds to a reaction which is occurring throughout the polymer film and is controlled by the kinetics of the cross-reaction. In order to establish this situation, the rate of charge transport and substrate diffusion within the polymer film must be rapid in comparison to the rate of the cross-reaction.[5]

The reciprocals of the intercepts of the Koutecky–Levich plots yield the apparent rate constant k'_{me} for the mediated reaction at the modified electrode.[5] The analytical expression relating k'_{me} under these conditions to the rate constant, k_2, for the cross-reaction is given by:

$$k'_{me} = k_2 K b_0 L \tag{11}$$

where K is the partition coefficient for the reactant between the electrolyte and the polymer film, b_0 is the concentration of electroactive centres within the film (0.7×10^{-3} mol cm^{-3})[11] and L is the polymer layer thickness. The concentration of the redox centres has been obtained from the density of the material as measured in non-swelling solvents. Swelling of the polymers is not taken into account. This term, k'_{me}, is equivalent to $k_2 K\Gamma$ used in the previous section. In Table 1, values for k'_{me} for several surface coverages are shown.

To obtain an estimate for the penetration of nitrite into the polymer layer, the oxidation of nitrite at an electrode coated with a similar thickness of the osmium polymer was investigated. The currents obtained for the oxidation of nitrite at such an electrode are equal to those obtained for a bare glassy carbon electrode. Since the oxidation of nitrite cannot be mediated by the polymer coating the oxidation occurs solely at the underlying glassy carbon. As a result we can conclude that the partition coefficient K, is likely to be close to unity with rapid penetration and diffusion of the substrate in the film. With this in mind k_2 was estimated to be $(9.4 \pm 2) \times 10^{-1}$ $dm^3\ mol^{-1}\ s^{-1}$ using layer thicknesses calculated from the dry density of the redox polymer. This rate constant may be considered small when compared to the value of 2.8×10^3 $dm^3\ mol^{-1}\ s^{-1}$ obtained for the reduction of $[Fe(H_2O)_6]^{3+}$ with the same electrocatalyst.[11] The relatively small value estimated for k_2 is consistent with the through-film nature of the catalytic reaction.

An unusual feature of the Koutecky–Levich plots is the zero slope, in situations where mass transport of substrate controls limiting currents, the slope is given by the inverse of the Levich constant, Lev^{-1}, where:

$$Lev = 1.554\ D^{2/3} \nu^{-1/6} \tag{12}$$

As the slope is zero the two controlling mass-transfer terms (diffusion coefficient of the substrate in solution, D, and kinematic viscosity of he electrolyte, ν) do not exert control over the limiting currents observed under the hydrodynamic conditions studied here. The absence of mass-transfer control is consistent with the slow rate of the cross-exchange observed. From the magnitude of the current generated for nitrite reduction (*ca.* 1 μA $mmol^{-1}$ cm^{-2}), the flux of substrate reacting at the modified electrode, j, as given by Ficks first law is *ca.* 2×10^{-10} mol cm^{-2} s^{-1}. Therefore, only a small portion of NO^+ arriving at the electrode is consumed and consequenty the surface concentration of NO^+ is essentially equal to that in solution. Effectively, the rate of the cross-reaction is sufficiently slow to prevent concentration polarisation at the electrode surface consequently the diffusion layer thickness tends towards zero. Under these conditions increasing the rate of mass transport to the electrode surface does not result in increased electrode currents. The significance of this is that the modified electrode may be applied for analysis in situations where the reactant flux is difficult to control and also in situations where the diffusion coefficient of the reactant is variable due to changes in sample matrix. It has been pointed out that control of mass transport is of paramount importance for the operation of amperometric sensors,[23] but in the case studied here this requirement is eliminated by ensuring that reaction kinetics control electrode currents.

With the observation that mass transport does not control limiting currents it can be shown that the limiting currents obtained under moderate hydrodynamic conditions are related to known and easily measurable parameters. The pK_a for nitrous acid is 3.4,[21] therefore reaction (3) would lie com-

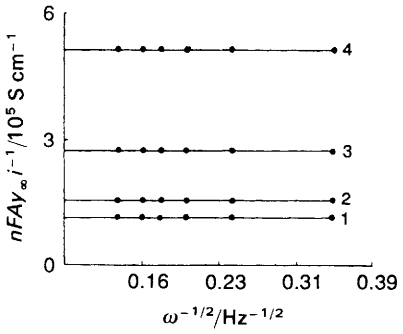

Fig. 8 Koutecky–Levich plot for the reduction of 2.0×10^{-3} mol dm^{-3} nitrite at polymer-modified electrodes with surface coverages of (1) 1.8×10^{-8}, (2) 6.2×10^{-9}, (3) 4.0×10^{-9} and (4) 1.5×10^{-9} mol cm^{-2}. Experimental conditions as in Fig. 2

pletely to the right at pH 1.0. The Koutecky–Levich equation for nitrite reduction at the polymer-modified electrode therefore is of the form:

$$1/i_{\mathrm{lim}} = 1/nFA(K'_{\mathrm{eq}}[\mathrm{HNO_2}][\mathrm{H^+}])k'_{\mathrm{me}} + 1/\mathrm{Lev}\ nFAW^{1/2}(K'_{\mathrm{eq}}[\mathrm{HMO_2}][\mathrm{H^+}]) \quad (13)$$

Since Lev = 0 then the entire right-hand term can be eliminated. With $k'_{\mathrm{me}} = k_2 K\Gamma$ then the limiting current under the experimental conditions used is given by:

$$i_{\mathrm{lim}} = nFAk_2 K\Gamma(K'_{\mathrm{eq}}[\mathrm{HNO_2}][\mathrm{H^+}]) \quad (14)$$

Since the terms n, F, A, k_2, K, Γ, K'_{eq} and $[\mathrm{H^+}]$ are known and constant at constant pH, a measurement of the limiting current can be used directly to estimate the concentration of $\mathrm{NO_2^-}$ in solution without a requirement for additional external sensor calibration.

A difficulty concerning the investigation of polymer-modified electrodes is the swelling of the polymer when immersed in electrolyte. This might lead to stability problems such as the slow stripping of the polymer from the electrode surface. For through-film reactions such as the reaction studied here this results in lowering the sensor response. However, for a nitrite sensor based on the osmium polymer reported in this contribution a measurement of Γ *in situ* can be used to correct internally for such a change on surface coverage.

Concluding Remarks

Good agreement between the experimental results and the theoretically derived rate equation suggests that the reduction of nitrite proceeds through outer-sphere electron transfer from the mediating metallopolymer to the nitrosonium ion with the rate constant for the cross-reaction controlling electrode currents.

The results obtained suggest that the osmium metallopolymer greatly enhances the kinetics of nitrite reduction in acidic electrolyte and although the rate of the cross-exchange reaction, k_2, is relatively slow, easily measurable currents can be obtained. These slow reaction kinetics introduce the possibility of making the measurement independent of the rate of mass transport of the substrate. The absence of mass-transport control on limiting currents also introduces the possibility of using internal calibration. This feature is of particular importance for the development of sensor systems where the use of calibration solutions is difficult or impossible. Finally, while it is generally assumed that fast electrochemical reactions are desirable, it is shown here that also slow reaction kinetics can present important advantages for the development of electrochemical sensors.

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