

Selective NO reduction using blue ferrocenyl cation

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Abstract

In this work, a new analytical protocol for the selective recognition of NO is described. The mediated reduction of NO by ferrocene forms the basis of analysis. The formation of blue ferrocenyl cation formed as the intermediate during the mediated reduction of NO is confirmed by spectral method and by generating the blue ferrocenyl cation by the chemical oxidation of dichromate in sulphuric acid. The formation of paramagnetic ferrocenyl cation is an interesting feature of this work. Four different methodologies have been followed to incorporate the ferrocene molecules onto the gold electrode surface. The four modified configurations have been evaluated for the selective sensing of NO.

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1. Introduction

Biologically NO was first characterized as an endothelial derived relaxing factor (EDRF) [1], which is being synthesized within endothelial cells of the blood vessels. Direct specific detection of NO in vivo is now a necessity for studying the role in the physiological processes. Methods actually used for measuring NO in biological systems are very difficult because of its low stability and high fugacity. In fact NO is easily oxidized by O_2 to nitrite (NO_2^-) and most of the measurement techniques of NO release have involved indirect chemical detection of the oxidation products removed from biological media. Now amperometric microelectrode probes have been developed to detect NO and the use of electrochemistry is very promising. Basically two approaches are normally used. The first approach is the direct oxidation of NO on electrode surfaces like Pt with a membrane coating like Nafion [2] or cellulose acetate or chloroprene by dipping procedure to prevent interference of anions [3]. The second approach is the electrocatalytic oxidation of NO by metalloporphyrin [4] and other catalysts [5].

Electrocatalytic reduction of NO by metal complexes is another alternative interesting approach which is already done with metal complexes like metal porphyrin (Mn, Co and Fe) [6], Fe-phenanthroline [7] or pyridine and EDTA complexes,

transition metal substituted heteropolyanions [8,9] or bipyridyl. Electrochemical reduction can be considered more advantageous in the sense that the interferences of biological origin like ascorbic acid, uric acid will not interfere on the cathodic side. Selective reduction over NO_2^- is possible since NO_2^- undergoes reduction only at high negative potentials.

In this work, we use a new electrocatalyst, ferrocene (Fc) for the electrochemical detection of NO (Fig. 1). Ferrocene is oxidized to ferrocenyl cation (Fc^+) and NO is reduced to NO^- , which regenerates ferrocene. The formation of blue ferrocenyl cation formed as the intermediate is confirmed by chemical oxidation of ferrocene by dichromate. Ferrocene is introduced on to the electrode surface by four different methodologies and each configuration is evaluated for the detection of NO.

Electrochemical recognition of NO is based on the mediated reduction of NO by ferrocene, which forms the basis of detection. Ferrocene is the molecular recognition unit. The four different configurations are as described below:

1. Au/ferrocene + Nafion (A);
2. Au/ferrocene + hydroxy propyl- β -cyclodextrin (CD) + Nafion (B);
3. Au/mercaptopundecanoic acid (MUA)/ferrocene carboxylic acid (FCA)/Nafion (C);
4. Au/MUA/ferrocene + CD/Nafion (D).

All the four configurations have been evaluated for the analysis of NO.

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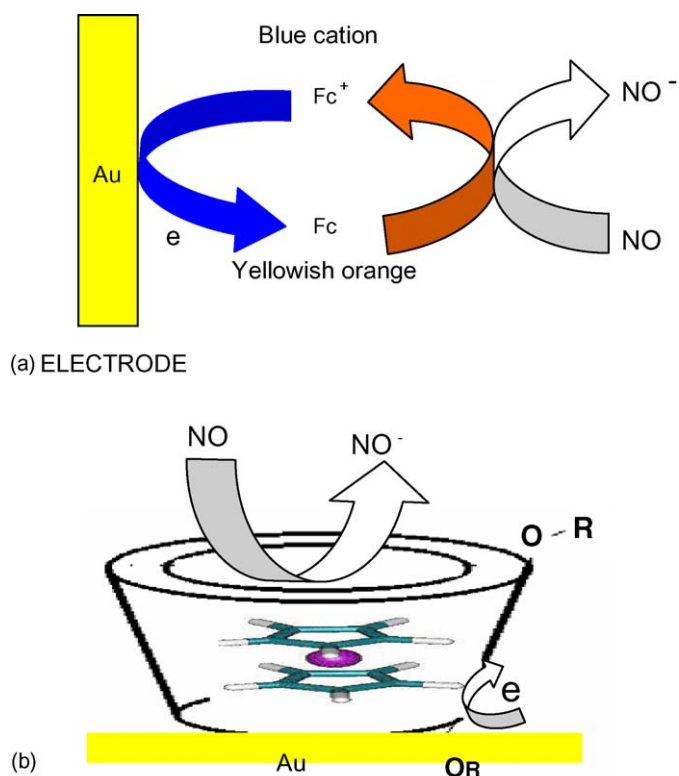


Fig. 1. Scheme showing the electrocatalytic reduction of NO with ferrocene: (a) directly incorporated on the electrode surface and (b) ferrocene complexed with hydroxy propyl- β -cyclodextrin incorporated on the electrode surface.

2. Experimental

2.1. Chemicals and reagents used

Sodium nitrite (AR, Merck), sulphuric acid (AR, Merck), ferrocene, Fc (Aldrich), hydroxy propyl- β -cyclodextrin, CD (Cerestar, USA), ethanol were used as received.

The gold electrode was cleaned and standardized as described earlier [10]. The surface of gold electrodes needs proper pre-treatment to get a smooth and reproducible surface. The surface cleanliness is checked by recording cyclic voltammograms in 0.5 M H_2SO_4 which exhibits peaks corresponding to gold oxide formation and reduction. Further the electrode is checked by recording cyclic voltammogram for the standard redox species ferrocyanide anion. The appearance of reversible voltammogram with a peak separation of 59 mV is considered as another criterion for the surface cleanliness. The electrodes thus checked are used for further investigations and the electrodes are said to be standardized for further use.

The four configurations of the electrode were prepared by following the modification procedures given below.

2.1.1. Au/ferrocene + Nafion-modified electrode (A)

The standardized electrode was coated with a drop of 2 mM ferrocene in ethanol + 1% Nafion mixture and allowed for curing for 1 h. The modified electrode surface was used for further experiments.

2.1.2. Au/ferrocene + CD + Nafion-modified electrode (B)

The standardized electrode was coated with a drop of a mixture of 2 mM ferrocene + 5 mM CD + 1% Nafion mixture. The electrode was allowed to dry for 1 h and then used for further experiments.

2.1.3. Au/MUA/ferrocene carboxylic acid/Nafion mixture-modified electrode (C)

The standardized gold electrode was dipped in ethanolic solution of 1 mM MUA for overnight then rinsed with ethanol and dipped in a mixture of 200 μM methyl morpholine + 200 μM ethyl chloroformate in 2 ml DMF for 20 min for covalent bonding. The electrode was then rinsed with ethyl acetate and dipped in 3 ml of ethanolic mixture of 2 mM ferrocene carboxylic acid for 45 min. The electrode was then taken out after the dip time rinsed with ethanol and coated with a drop of 1% Nafion and allowed for drying. The electrode thus modified was used for further experiments.

2.1.4. Au/MUA/ferrocene + CD/Nafion mixture-modified electrode (D)

The standardized gold electrode was dipped in ethanolic solution of 1 mM MUA for overnight then rinsed with ethanol and dipped in a mixture of 200 μM methyl morpholine + 200 μM ethyl chloroformate in 2 ml DMF for 20 min for covalent bonding. The electrode was then rinsed with ethyl acetate and dipped in 3 ml of ethanolic mixture of 2 mM Fc + 5 mM CD mixture for 45 min. The electrode was then taken out after the dip time, rinsed with ethanol and coated with a drop of 1% Nafion and allowed for drying. The electrode thus modified was used for further experiments.

The principle of surface modification is based on two different approaches: a monolayer and a multilayer approach. In the first two cases the mediator ferrocene is mixed with Nafion solution and a thin film is cast on the surface by allowing a drop of the solution to evaporate on the surface. The essential difference between these two methods is that in the first method ferrocene solution in ethanol (Fc) is directly mixed with Nafion solution and in the second method ferrocene is complexed with hydroxypropyl- β -cyclodextrin (Fc + CD) and then it is mixed with Nafion solution. Third and fourth methods involve covalent linking of ferrocene carboxylic acid and a solution of Fc + CD to a self-assembled monolayer of mercaptoundecanoic acid (MUA). The carboxylic acid groups of MUA were activated by adding methyl morpholine and ethyl chloroformate. Methyl morpholine is added to generate the carboxylate anion which then reacts with ethyl chloroformate to give mixed anhydride which subsequently reacts with carboxyl groups of FCA or hydroxyl groups of β -cyclodextrin complexed with Fc to give an anhydride and ester linkage, respectively [11–14].

2.2. Preparation of standard solution of NO

Saturated NO solution is prepared [15] in a closed system which is rigorously excluded from the presence of any oxygen. By means of a dropping funnel concentrated H_2SO_4 is slowly dropped into a solution of NaNO_2 . The generated gaseous NO

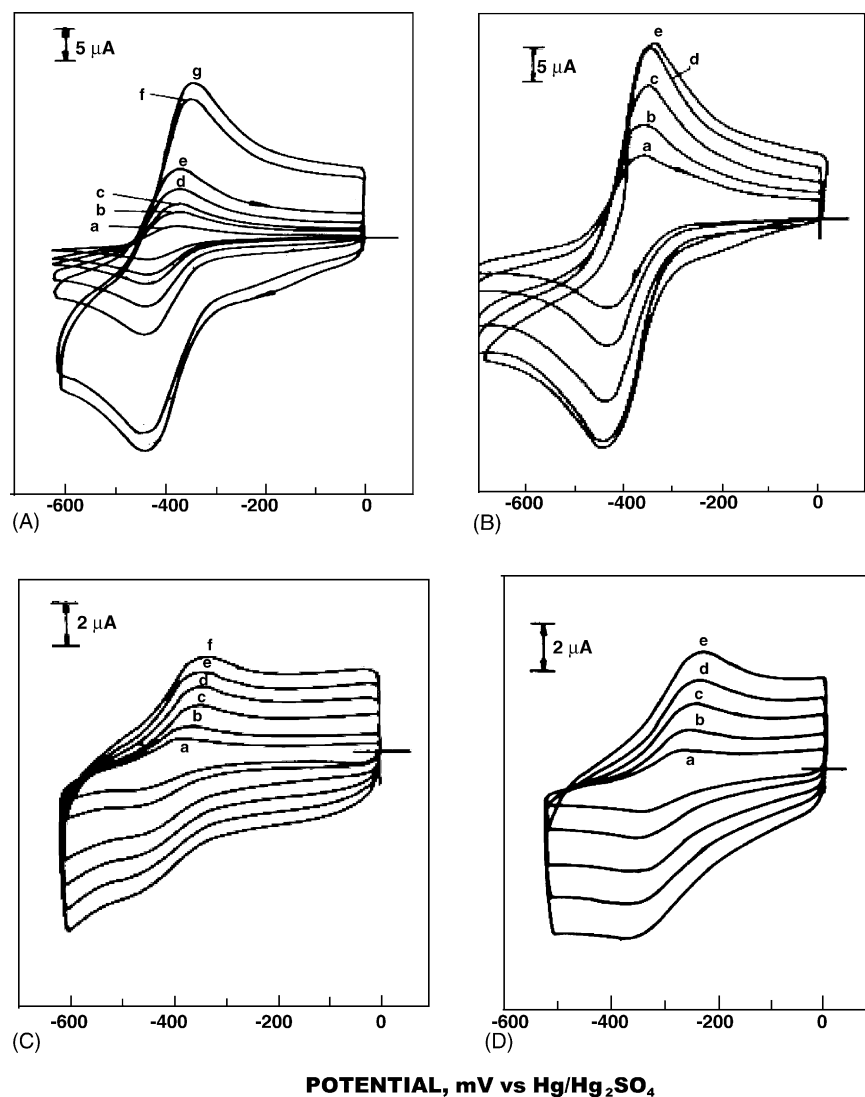


Fig. 2. Cyclic voltammograms representing the response of ferrocene-modified electrodes for the four modified configurations (A–D) at different scan rates in mV/s at ambient temperature in 0.5 M sulphuric acid (pH 2). (A) (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 400 and (g) 500; (B) (a) 50, (b) 100, (c) 200, (d) 300 and (e) 400; (C) (a) 50, (b) 100, (c) 200, (d) 300, (e) 400 and (f) 500; (D) (a) 50, (b) 100, (c) 200, (d) 300 and (e) 400.

is bubbled through 5 ml triply distilled water in a glass cell equipped with an inlet to obtain a saturated and oxygen free NO solution with a final concentration of 2 mM. The bubbling was continued till the generation of NO gas is complete.

The cyclic voltammograms were recorded using Wenking LB 75L potentiostat, Wenking VSG 72 voltage scan generator and Rikadenki X-Y recorder.

3. Results and discussion

Fig. 2A–D show the cyclic voltammetric response of modified electrode for the configurations A–D. It shows the features of electrochemical response for surface-modified ferrocene at different scan rates. With scan rate variation ΔE_p values also vary. In all the cases $E_{FWHM} > 90.6$ mV. Hence, the situation corresponds to that of destabilizing/repulsive interactions. Non-zero ΔE_p corresponds to relative lowering of electron transfer kinetics.

Fig. 3A–D represents the peak current versus scan rate variation for the different electrode configurations used in this work. From the figures it is seen that the peak current varies linearly with scan rate in the case of C and D configurations. In the case of A and B the current is proportional to the square root of scan rate. Though all the cases represent surface processes, i.e., ferrocene electron transfer immobilized on the surfaces, the difference arises due to thickness factor arising due to different modifications. In the case of A and B, the thickness will be greater than a monolayer. In the case of C and D ferrocene molecules are covalently linked to the electrode surface through a monolayer. Hence, diffusion limitations in the film make the process diffusion-dependent.

Fig. 4A–D shows the electrocatalytic reduction of NO (g) for various concentrations on the modified electrode A–D. NO is electrocatalytically reduced on the modified electrode. The oxidation current on the reverse scan is absent. This phenomenon indicates some follow-up chemical reaction occurs.

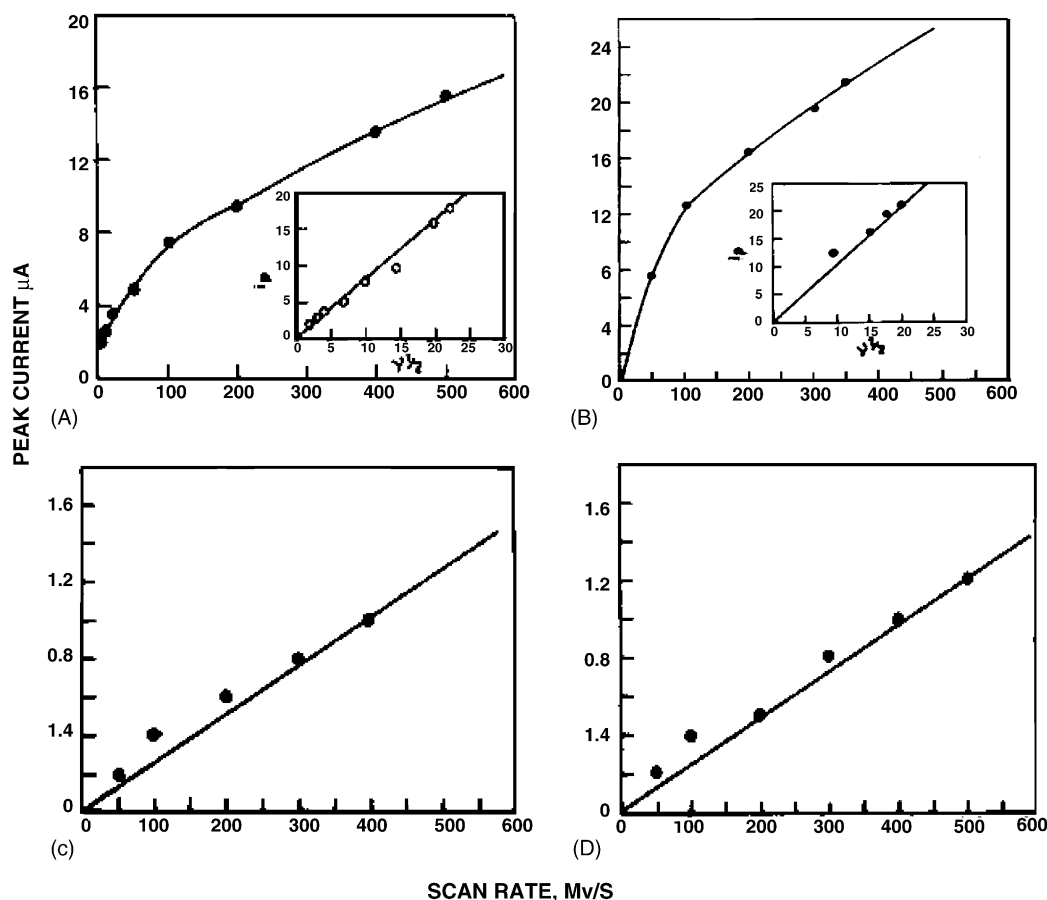


Fig. 3. Peak current dependence on scan rates for the four electrode configurations (A–D) modified with ferrocene in 0.5 M sulphuric acid at ambient temperature (pH 2).

The cathodic current increases with increase in concentration of NO_g .

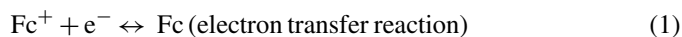
Fig. 5 represents the amperometric curve recorded for electrode configuration A for different additions of NO. The experiment was conducted at a constant potential of -0.380 V. Each addition corresponds to 0.6×10^{-4} M of NO. The current due to electrocatalytic reduction of NO increases with increase in concentration of NO. This method is of interest for practical applications of this analytical procedure.

Fig. 6A–D represent peak current (i_p) versus concentration graph for the modified electrodes A–D. Linear relationship is observed in all the cases.

In all the results mentioned above basically four different modification procedures have been employed to incorporate ferrocene onto the electrode surface. The modification has been confirmed by the cyclic voltammograms representing the near reversible features of ferrocene electron transfer (Fig. 2A–D). In all the cases $E_{\text{FWHM}} > 90.6$ mV. Non-zero ΔE_p corresponds to relative lowering of electron transfer kinetics. The situation corresponds to that of destabilizing/repulsive interactions. The reasons are: in an ensemble of attached species slight variation in surface structure during solvation causes a narrow spectrum of E'_0 surface value rather than a unique value [16]. Surface activity coefficients vary with coverage Γ_0 and Γ_R [17]. Anson proposed “interaction parameters” that are responsible for nar-

rowing down or broadening of peaks. Broadening of peak is due to surface immobilized species with repulsive or destabilizing interaction and narrowing of peaks < 90.6 (E_{FWHM}) is due to attractive interaction between the species. The peak current (Fig. 3A–D) dependence with scan rate varies with the nature of the modification procedure. The configurations C and D represent a monolayer of MUA functionalised with ferrocene carboxylic acid and Fc + CD. Hence, the electron transfer observed corresponds to a surface process and peak currents are proportional to scan rate. In the case of A and B the peak currents are linearly proportional to square root of scan rate indicating surface effects within the multilayer films.

The mechanism for the reduction of NO is proposed as follows:



During the reduction scan the ferrocenium ions are reduced at the electrode surface. The NO molecules oxidize the ferrocene molecules to Fc^+ ions and itself gets reduced to NO^- which causes the increase in reduction current when NO is present. Since NO molecules chemically oxidize the ferrocene molecules, during the reverse scan no Fc species is available for oxidation. Hence, the reverse current becomes very insignificant.

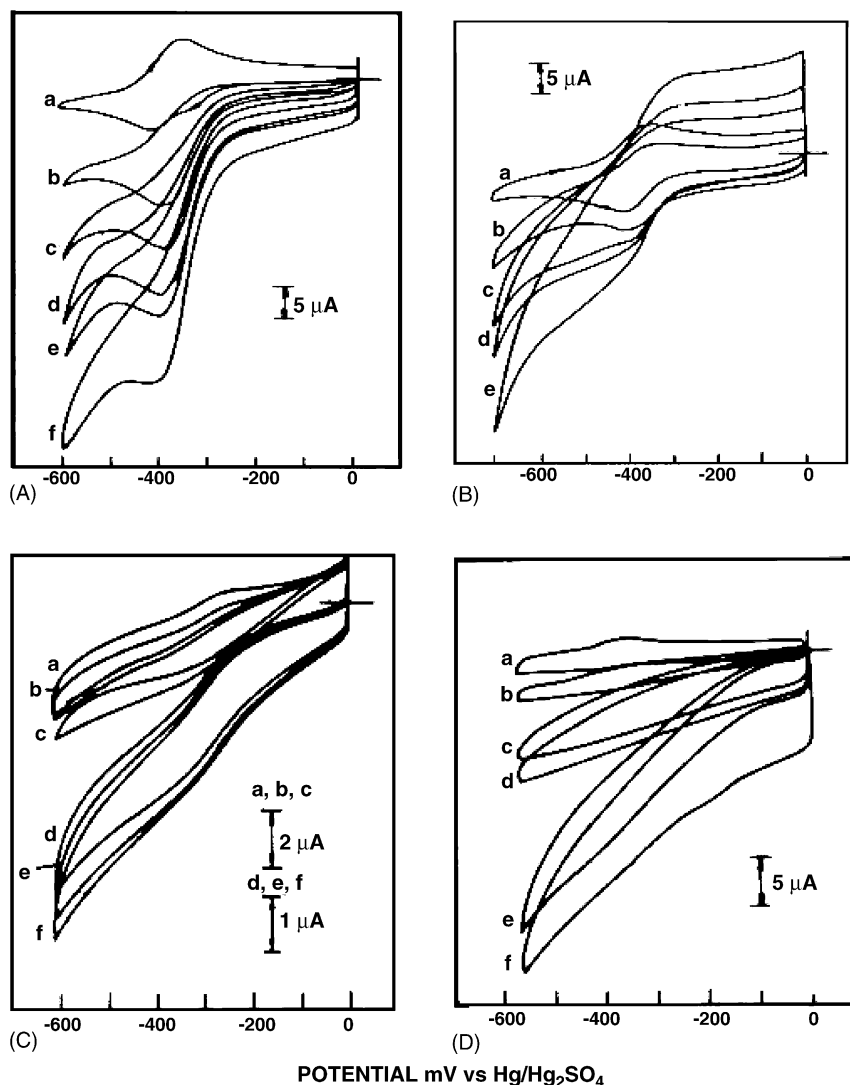


Fig. 4. Electrocatalytic reduction of NO gas at 50 mV/s for different concentrations of NO: (a) 0 M, (b) 0.61×10^{-4} M, (c) 1.18×10^{-4} M, (d) 1.72×10^{-4} M, (e) 2.23×10^{-4} M and (f) 2.71×10^{-4} M for the four modified electrode configurations (A–D), respectively, in 0.5 M sulphuric acid at ambient temperature (pH 2).

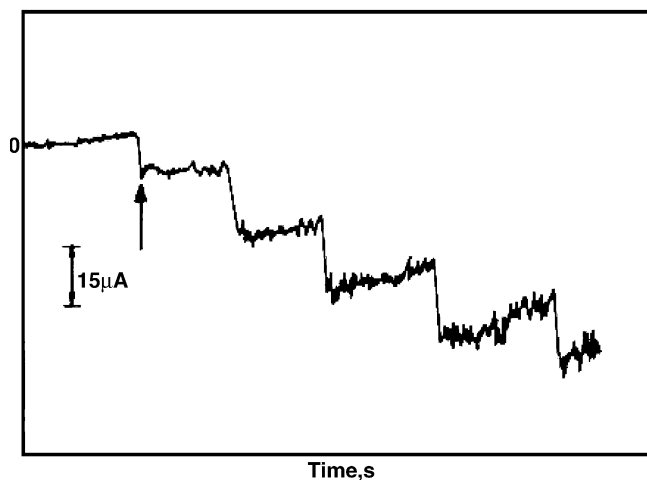


Fig. 5. Amperometry recorded at -0.380 V for different additions of NO. Each addition corresponds to 0.61×10^{-4} M. An arrow represents one point of addition. The electrode configuration A (Au/ferrocene + Nafion) was used for the analysis in 0.5 M sulphuric acid (pH 2).

3.1. Identification of the chemical step

The chemical step in the EC mechanism is identified as follows:



The formation of NO^- intermediate has been reported already [18]. NO has an odd number of valence electron and forms nitrosyl ion (NO^+) by losing one electron and forms nitroxyl anion (NO^-) by acquiring an electron. Although the chemistry of NO and NO^+ is well documented, that of NO^- is still sketchy due to its instability and short life under normal experimental conditions. Ferrocenyl cations are known to exist in blue colour. The formation of blue coloured ferrocenyl ions was verified by chemical oxidation. When a solution of Fc is treated with NO containing solution, the solution turns blue colour [19]. The blue colour of the ferrocenyl cations is confirmed by chemically oxidizing ferrocene in presence of $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$. This experiment clearly confirms that ferrocenyl cations are gen-

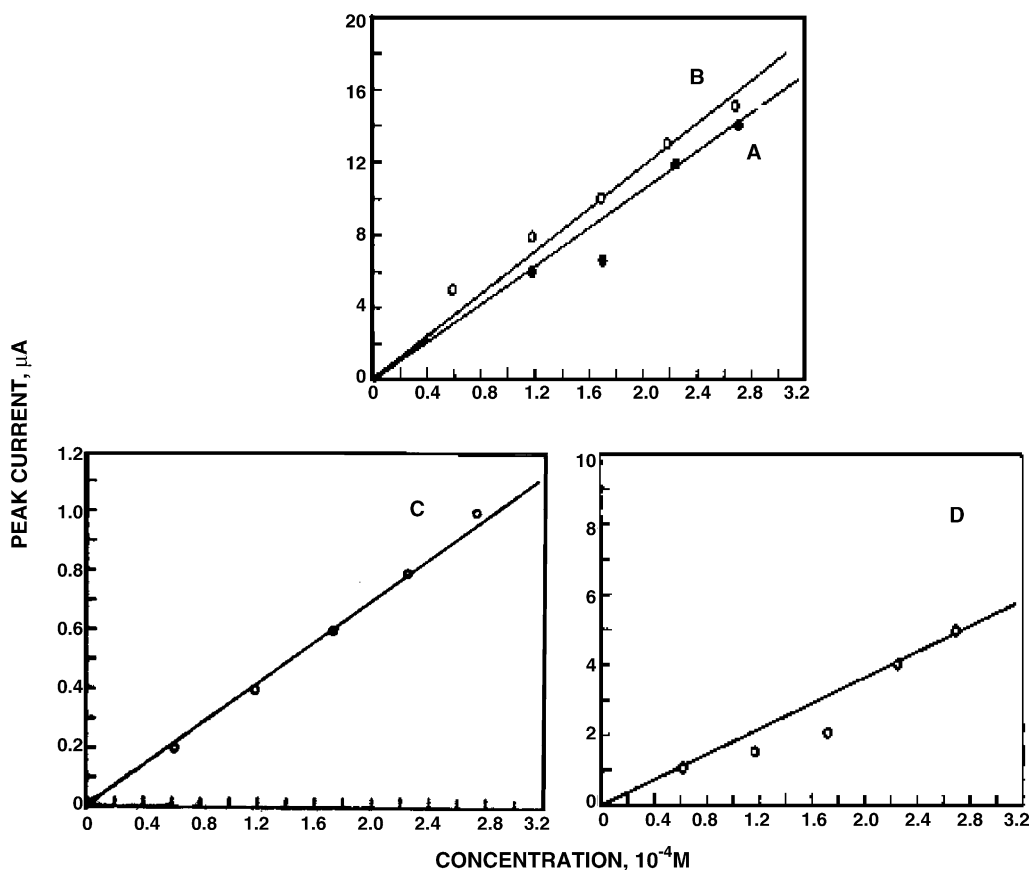
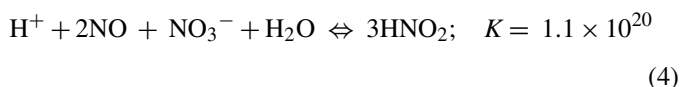


Fig. 6. Linear plots observed for the four configurations (A–D) for different concentrations of NO gas with respect to the reduction currents in 0.5 M sulphuric acid at ambient temperature (pH 2).

erated by the chemical reaction. The formation of ferrocenyl cation is also confirmed by taking UV spectrum of the blue coloured solutions. The spectra showed the presence of maximum at 618 nm in both the cases (blue coloured solution formed by treating ferrocene with NO in acidic medium and ferrocene oxidized by dichromate ions in acidic solution).

3.2. Selective recognition of NO in presence of NO_2^-

In these investigations NO is chemically liberated and a stock solution was then analyzed in a highly acidic solution (pH 2). The same behavior is obtained when NaNO_2 solution is tested in acidic medium. The acid dissociation constant of HNO_2 is 5.1×10^{-4} and its $\text{p}K_a = 3.3$. HNO_2 is the reactive form of nitrite at $\text{pH} < 3$ while NO_2^- acts as the reactive form at $\text{pH} > 3$. NO_2^- can disproportionate in acidic solution as follows:



The rate of this is slow [8] and the aqueous solubility of NO is only 2 mM under normal pressure. Oxygen will not be an interferent as oxygen reduction occurs at high over potentials on gold surface. NO undergoes reduction mediated by ferrocene whose value is sufficiently lower hence there is no question of oxygen interference. This makes this method more promising.

In the present investigation selective recognition of NO over NO_2^- is claimed due to the following:

1. In the entire configuration the presence of Nafion layer prevents the entry of negatively charged species.
2. In acid solution due to disproportionation, NO formed reacts with Fc to give Fc^+ and NO^- .
3. In pH 7.0, no response is observed because of the presence of NO_2^- .

4. Maximum detection limit achieved

The maximum detection limit of $0.1 \times 10^{-4}\text{M}$ is achieved by cyclic voltammetric studies and a detection limit of $0.3 \times 10^{-6}\text{M}$ or 300 nM is reported by DPV studies. In biological situations, the concentration of NO is in the order of nM. The detection limit reported in this work is based on the configurations A and B. In these two configurations the concentration of ferrocene in the modified electrode is 2 mM. The current due to the oxidation of ferrocene species in the modified electrode will be few microamperes. In order to detect nanomolar concentrations, which will give, raise to currents of the order of sub-microampere range in presence of this 2 mM concentration of ferrocene is difficult. Hence, work is in progress to improve the detection limits by decreasing the concentration of the ferrocene in the modified electrode and by using systems that can

Table 1
Performance characteristics of different analytical procedures reported in the literature

Serial number	Electrode material	Modifier	Detection range	Technique	Detection mechanism	Reference
1	Carbon fiber	(a) Nafion; (b) Nafion + Ni porphyrin	1 nM to 40 μ M	Differential pulse amperometry	NO oxidation	[23]
2	Carbon fiber	Poly(<i>N</i> -methyl pyrrole) + iron substituted keggin type hetero polyanion	10^{-7} M to 10^{-3} M; sensitivity 2.65 ± 0.15 nA/ μ M	DPV (analysis of NO in rat brain)	NO oxidation	[24]
3	Pt disk electrode	Pyrrole functionalised Mn(II) trimethoxy carboxy phenylporphyrin	Not given	Pulse technique (NO release from endothelial cells)	NO oxidation	[15]
4	Pt electrode	Pyrrole functionalised Mn(II) trimethoxy carboxy phenylporphyrin	Up to 10^{-7} M	DPV	NO oxidation	[25]
5	Carbon fiber	Ni-porphyrin in orthophenylene diamine	35 ± 7 nM	Amperometry	NO oxidation	[26]
6	Platinized platinum	Nil	Sensitivity 1.3 nA/nM	Amperometry	NO oxidation	[27]
7	Gold	Ferrocene	0.1×10^{-4} M and 300 nM	CV and DPV	NO reduction	This work

sense currents of the order of nanoamperes. Further the use of microelectrodes will also improve the sensitivity and detection limits of the method.

It is difficult to compare our results with the existing literature, because our method is unique and the ferrocene mediated reduction of NO has been reported for the first time. Electrocatalytic reduction of NO has been already reported in presence of water soluble iron and manganese porphyrins [20,21]. In these reports nitrite reduction at pH < 3 is investigated, since nitrite decomposes to NO under acidic conditions as given in Eq. (4), the reduction occurs in two stages. In the first step an electron is transferred to the metal centre, which on further reduction leads to the formation of NH₃ and other products. In these two reports, only the mechanism of reduction of NO has been investigated and the analytical utility of the method is not discussed. NO reduction on gas diffusion electrodes [22] has revealed the formation of NH₃ and N₂ as reduction products depending upon the electrode material. Some of the literature results discussing the analytical protocol for sensing NO gas and our results are compiled in Table 1.

The table clearly shows that all the analytical procedures have been based only on the oxidation of NO. Our results discuss about the analytical procedure for sensing NO based on the electrochemical reduction.

Nitric oxide is a stable free radical with the unpaired electron in this molecule residing in a π^* molecular orbital. This electronic configuration explains the high reactivity of the NO molecule, in particular the ease of oxidation to the nitrosonium ion (NO⁺), the probability of reduction to the nitroxide ion (NO⁻), the facile attack by oxygen leading to the formation of NO₂, and reaction with halogens (X₂) affording XNO. NO⁻ is isoelectronic with O₂, having a triplet ground state. The redox potential for the reversible process $\text{NO} \rightleftharpoons \text{NO}^+ + \text{e}^-$ is strongly solvent-dependent, and in water it is pH-dependent [28–30]. The reduction of NO to triplet and singlet NO⁻ has been quoted as lying between +0.39 and –0.35 V versus NHE, but a recent paper [18] has substantially and authoritatively revised these data to -0.8 ± 0.2 V for ³NO⁻ and -1.7 ± 0.2 V for ¹NO⁻,

respectively, indicating that singlet NO⁻ is inaccessible physiologically. From our results, it has been proved chemically, electrochemically and by UV absorption that Fc⁺ is formed as the intermediate. This indicates the formation of NO⁻ as a result of electron transfer from ferrocene. Hence, E^0 for NO reduction must be more positive than E^0 value for Fc/Fc⁺ conversion. The E^0 value for ferrocene is reported as 400 mV versus NHE [31]. Our values of $E^{0'}$ calculated from $E_{\text{pa}} + E_{\text{pc}}/2$ range from 295 ± 5 mV versus NHE for electrode configurations A, B, D to 380 ± 5 mV for the electrode configuration C, respectively. A discrepancy of nearly 100 mV, observed in the $E^{0'}$ value of the electrode configurations A, B and D is due to the derivatisation process. Ferrocene is linked to the electrode either after complexation with CD or through a multilayer of FC + Nafion. In the case of configuration D ferrocene carboxylic acid is covalently linked to a monolayer of MUA. Hence, the $E^{0'}$ value nearly coincides with the standard electrode potential. Eq. (3) suggests that NO⁻ reduction potential should be more positive than this value. In that case the value of +0.39 V seems to be the right value for ³NO reduction. The revised value of –0.8 V is reported for pH 7.0. However our values correspond to pH 2.0. The pH difference may explain the discrepancy or apparent contradiction with the revised values. The suggested mechanism of reduction is:



Since Fc⁺ formation has been confirmed, NO⁻ reduction is suggested to proceed at a potential close to Fc/Fc⁺ conversion at pH 2.0.

This work has demonstrated the selective sensing of NO in presence of NO₂⁻ by making use of the mediator ferrocene molecules. The sensing is based on electrochemical reduction, which eliminates the interference effects of biological species like ascorbic acid, dopamine, uric acid, etc. The detection limit obtained is in the order of hundreds of nanomolar level. Four different electrode modification procedures have been evolved in this work for the incorporation of ferrocene onto the electrode

surface. The modified electrodes are found to be very stable. The Nafion layer takes care of interference from anionic species and they also enhance the stability of the films. The electrodes can be used for nearly six to eight times without much reduction in the current output values and without leaching problems. The paramagnetic blue ferrocenyl cation formed as the intermediate has been proved by comparing the reaction of ferrocene with potassium dichromate.

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