

Electrocatalysis of NADH oxidation at a glassy carbon electrode modified with pyrocatechol sulfonephthalein

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Abstract

The pyrocatechol sulfonephthalein (PS) modified glassy carbon (PS/GC) electrode, which was prepared by adsorption of PS on glassy carbon electrode surface, shows electrocatalytic activity toward NADH oxidation with an overpotential of ca. 310 mV lower than that of the bare electrode and a great enhancement of the anodic currents. The electrocatalytic rate constant (k) was determined using rotating disk electrode measurements in Britton–Robinson buffer solution at pH 7.0. It is found that the k is dependent on NADH concentration, the relation between k^{-1} and c_{NADH} can be fit to the line regression equation: $10^5 k^{-1} (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{-1} = 1.62286 + 0.65286 c_{\text{NADH}} (\text{mmol dm}^{-3})$ with correlation coefficient of 0.99964. The experimental results also indicate that the presence of Ca^{2+} and Mg^{2+} in electrolyte can drastically enhance the electrocatalytic currents of NADH oxidation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electrocatalysis; Chemically modified electrode; Mediator; NADH; Pyrocatechol sulfonephthalein

1. Introduction

The electrochemical oxidation of nicotinamide adenine dinucleotide (NADH) to its oxidized form (NAD^+) at a bare electrode surface is highly irreversible and takes place at considerable overpotential although the reversible potential for NADH oxidation is estimated to be -0.56 V (vs. saturated calomel electrode (SCE), pH 7.0). In addition, the direct oxidation of NADH is often accompanied by electrode fouling and interfering background currents in real samples and sometimes leads to the formation of enzymatically inactive forms NAD^+ .

A number of approaches have been employed in an effort to accelerate the kinetics of NADH oxidation, because NADH is utilized by several hundred different dehydrogenase, if NADH oxidation to enzymatically active NAD^+ can be efficiently and effectively achieved, it is possible to develop a wide range of different amperometric enzyme electrodes for a wide range of substrates. One of efficient ways to circumvent the high overpotential for NADH oxidation is use of mediators which can undergo fast redox reactions with NADH. Much efforts [1–3] has been dedicated to identifying materials which could be employed as mediators. These include quinones [4], catechols [5], redox dyes [6–8], ferrocene derivatives [9], inorganic metal complexes [10,11], conducting organic salt [12] and conducting polymers [13–20].

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Even though many compounds have been found to mediate the electron transfer for NADH oxidation, there is still a great deal of interest in the development of new materials for the electrocatalytic oxidation of NADH, especially alternative approaches for immobilization of the mediator on electrode surface, in order to further lower the overpotential for NADH oxidation and also to find more efficient and stable chemically modified electrodes for electrocatalytic oxidation of NADH. In the present work, we report the electrocatalytic oxidation of NADH at pyrocatechol sulfonephthalein modified glassy carbon (PS/GC) electrode and the effects of some divalent cations on this electrocatalytic process. The PS/GC electrode can lower the overpotentials of about 310 mV for NADH oxidation, and the apparent rate constant k (at $c_{\text{NADH}} \rightarrow 0$) for chemical reaction between the NADH and PS is estimated to be $6.16 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is higher than the values obtained with most other mediators, although still smaller than that obtained by Murthy and Anita [21] at TCNQ modified pyrolytic graphite electrode, where TCNQ is 7,7,8,8-tetracyanoquinodimethane.

2. Experimental

NADH was obtained from Sigma and was used as received without further purification. PS (dye content ca. 90%) was purchased from Shanghai Chemical Factory (Shanghai, China). Prior to use, it was recrystallized twice from water. All other chemicals were of analytical grade. The electrochemical experiments were performed in 0.1 mol dm⁻³ Britton–Robinson (B–R) buffer solution. B–R buffer solution contains in 1 l of water 3.92 g H₃PO₄, 2.40 g CH₃COOH and 2.47 g H₃BO₃. The 0.1 mol dm⁻³ NaOH was used to control the solution at different pH. All solutions were prepared with doubly deionized water and deaerated with highly pure nitrogen for 20 min before the electrochemical experiments, and a continuous

flow of nitrogen was maintained over the sample solution during experiments. The experimental temperature was controlled at $25 \pm 0.1^\circ\text{C}$ with a Type 501 thermostat (Shanghai, China).

The electrochemical experiments were carried out with an EG&G PAR 273 potentiostat/galvanostat using M270 electrochemical analysis software in a three-electrode cell configuration comprising a PTFE-shrouded glassy carbon electrode (3-mm diameter) as the working electrode, an SCE as a reference electrode and a coiled platinum wire serving as the counter electrode. The continuous scanning stability of the PS/GC electrode was tested using a ZF-3 potentiostat programmed by a ZF-4 waveform generator and a LM-20A recorder (Shanghai, China) was used to record the cyclic voltammograms. The working electrode was polished with metallographic abrasine paper (No. 6, Shanghai, China) first, the progressively with fine slurries of 1-, 0.3-, and 0.05- μm alumina powder to mirror finish. After thoroughly rinsing, the electrode was cleaned in an ultrasonic cleaner for about 15 min, firstly with ethanol and finally with distilled water, to eliminate any trace of alumina. Prior to use, the polished electrode was treated by placing in 1.0 mol dm⁻³ NaOH solution with applying potential of +1.2 V for 5 min, followed by potential cycling from -0.2 to +1.0 V in buffer solution (pH 7.0) for 5 min. For rotating disk electrode measurements, a PAR M616 disk electrode system was employed. In this case, a glassy carbon disk electrode (3-mm diameter) from PAR was used as the working electrode, and the procedures of the treatment is the same as the above.

The PS/GC electrode was prepared by dipping a bare glassy carbon electrode, which was treated by above procedures, into a 5×10^{-3} mol dm⁻³ PS solution for some time. The surface coverage depends on the dipping time. After PS adsorption layer formed on the electrode surface, the electrode was rinsed thoroughly with water and dipped into the buffer solution to test its electrochemical behavior and examine electrocatalytic activity toward NADH.

3. Results and discussion

3.1. Electrochemical responses of PS/GC electrode

As reported previously [22], the PS can be adsorbed on the surface of glassy carbon electrode forming the PS/GC electrode. When the electrode was scanned in B–R buffer solution (pH 7.0) in potential range of -0.35 to $+0.7$ V, a couple of well-defined redox peaks were observed (Fig. 1, curve a), with a formal potential of 172 mV at a scan rate of 20 mV s⁻¹. The electrochemical responses of the PS/GC electrode were those anticipated for a surface-confined redox couple, because the peak currents were directly proportional to the scan rates at least up to 200 mV s⁻¹, and the peak to peak potential separation was small, although not

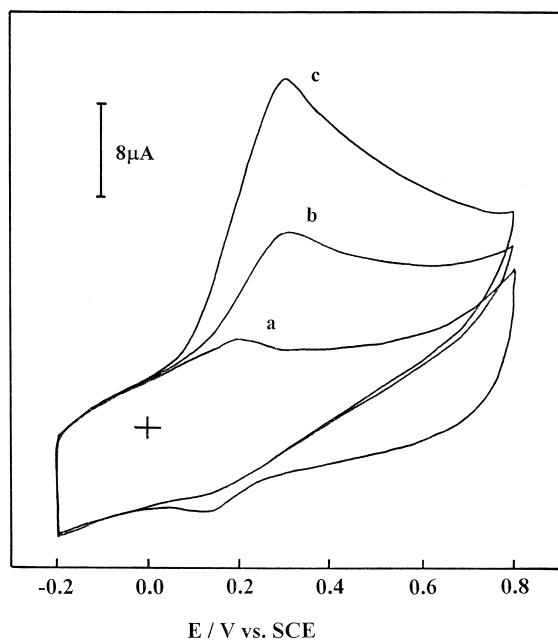


Fig. 1. Cyclic voltammograms of PS/GC electrode at 100 mV s⁻¹ in (a) 0.1 mol dm⁻³ B–R buffer solution (pH 7.0) and (b) in the presence of 1.0×10^{-3} mol dm⁻³ NADH and (c) 1.0×10^{-3} mol dm⁻³ NADH + 10×10^{-3} mol dm⁻³ MgCl₂. The displayed curves (b) and (c) have been subtracted the voltammetric response of directed oxidation of NADH at unmodified GC electrode in B–R buffer solution (pH 7.0) at the same scan rate.

Table 1
The dependence of k_s on the solution pH

pH	5.3	7.0	8.3
k_s (s ⁻¹)	11.8	10.2	4.1

zero. The potentials separation between anodic and cathodic peaks was 4 mV at a scan rate of 20 mV s⁻¹. The value of separation was increased with increasing of scan rates, the value becomes 24 mV, for example, at a scan rate of 200 mV s⁻¹. The apparent heterogeneous charge transfer rate constant, k_s , of a surface-confined redox couple can be evaluated from cyclic voltammetric experiments from the various separation of the anodic and cathodic peak potentials with the scan rate following the treatment developed by Laviron [23]. The dependence of k_s , which was obtained using Laviron's method at case of $\Delta E_p/n < 200$ mV, on the solution pH is shown in Table 1.

The stability of PS/GC electrode was examined by repetitive scans in B–R buffer solution (pH 7.0) at a scan rate of 100 mV s⁻¹. The height of peak currents remains at 90% of the value of the first cycle after 5 min repetitive scanning (about 15 cycles). The currents remain 85% of that for first cycle after 50 min continuous scanning (about 143 cycles), and then almost no changes in height and separation of cyclic voltammetric peaks were observed after 110 min of repetitive scanning (about 314 cycles).

The redox response of the PS modified electrode was pH dependent, the anodic and cathodic peak potentials shift in the negative direction with an increase in solution pH. The relation between formal potential, $E^{0'}$ and solution pH can be fit to the line regression equation $E^{0'} \text{ (mV)} = -51.4 \text{ pH} + 538.7$, the slope is -51.4 mV per pH unit with a standard deviation of 5.2902 and correlation coefficient of 0.9988 , and the intercept at the $E^{0'}$ -axis is 538.7 mV with a standard deviation of 0.8491 and correlation coefficient of 0.9988 (number of

data points = 11). The slope of -51.4 mV per pH unit is close to the anticipated Nernstian value of -59 mV. It can be therefore concluded that an equal number of electrons and protons ($2e, 2H^+$) is involved in the process of electrode reaction.

3.2. Electrocatalytic oxidation of NADH at PS/GC electrode

Since several redox dyes are known to act as a highly active electron-transfer mediator for the electrocatalytic oxidation of NADH, it was expected that the PS/GC electrode may similarly be used to catalyze oxidation of NADH. To test the electrocatalytic activity of the PS/GC electrode toward NADH oxidation, their cyclic voltammetric responses were obtained in pH 7.0 B–R buffer solution in the absence and presence of NADH. The results are presented in Fig. 1. In the absence of NADH (curve a), a couple of well-defined redox peaks for the PS on the electrode surface can be observed. The cathodic and anodic peak potential is $+158$ and $+174$ mV, respectively. The formal potential is $+166$ mV. On addition of 1.0×10^{-3} mol dm^{-3} NADH, there is a great enhancement of the anodic current, and in addition, almost no cathodic current is observed in return wave (curve b), simultaneously, the anodic peak potential shifts in the positive direction by about 116 mV. This behavior indicates that the PS/GC electrode has a strong electrocatalytic effect on NADH oxidation. Under the same experimental conditions, the direct oxidation of NADH at unmodified GC electrode shows an irreversible wave with an anodic peak potential around $+600$ mV (not shown here), and such unmodified electrode rapidly become deactivated, the oxidation peak shifts to significantly more positive values. At the PS/GC electrode, the anodic peak potential for oxidation of NADH is at $+290$ mV, a decrease in overpotential of approximately 310 mV is achieved. After tested the electrocatalytic activity of a series of aro-

matic diamines toward NADH oxidation, Kitani et al. [24,25] proposed the mechanism of NADH oxidation catalyzed by mediators involves transfer of the 4-hydrogen of NADH to mediator. In terms of this hydride transfer mechanism, the essential features required of a NADH mediator are a site for hydride transfer and the ability to delocalized the charge within the mediator. From the molecular structure of PS, one can find that PS can meet the two essential requirements as a NADH mediator.

The stability of electrocatalytic activity of the PS/GC electrode toward NADH oxidation was tested by repetitive scanning of the electrode in buffer solution (pH 7.0) containing 1.0×10^{-3} mol dm^{-3} NADH. During the initial cycles (about 10 cycles), the electrocatalytic currents decrease quickly with increasing scanning number. This behavior is found at almost all mediators catalytic system for NADH oxidation. After the initial period, the electrocatalytic currents change slowly and reach a relatively stable value, remain ca. 75% of first cycles. After this time, no visible change in height of the electrocatalytic currents can be detected within 8 h continuous scanning. This indicates that the PS/GC electrode is stable enough to be used in NADH measurements.

The cyclic voltammograms of PS/GC electrode at various scan rates obtained in buffer solution (pH 7.0) containing 1.0×10^{-3} mol dm^{-3} NADH indicate that the catalytic oxidation peak potential for NADH shifts slightly to positive direction with increasing the scan rates. The positive shift of oxidation peak potential suggests a kinetic limitation in the reaction between the PS and NADH. To study the relationship between the anodic peak currents for NADH oxidation and the scan rates, the signals for direct oxidation of NADH at bare GC electrode were systematically subtracted from the cyclic voltammograms of NADH oxidation at PS/GC electrode at correspondence scan rates. The plot of anodic subtracted currents against the square roots of the scan rates shows a good linearity, so it can be stated that the oxidation of

NADH at PS/GC electrode, at sufficient overpotential, is controlled by diffusion of NADH in solution.

The amount of PS on the GC electrode surface can be controlled by the dipping time of the electrode in PS solution during preparation of the PS/GC electrode. Surface coverage, Γ , can be calculated with the equation:

$$\Gamma = Q/nFA \quad (1)$$

where Q is the amount in coulombs of consumed charge obtained from integrating the peak area in cyclic voltammograms under the background correction, the other symbols have their usual meaning. In the calculation, the geometric area A was employed, thus, the value reports represent upper limits. The dependence of Γ on the dipping time of GC electrode in PS solution is shown in Fig. 2. The value of Γ increases rapidly with increasing of dipping time when the time is less than 10 min, then the Γ increases slowly with time. From the plot, one can estimate the coverage of ca. 2.3×10^{-10} mol cm^{-2} for PS monolayer on GC electrode. The effect of Γ on the electrocatalytic peak current for NADH oxidation was studied, the catalytic current increases with increasing of Γ up to

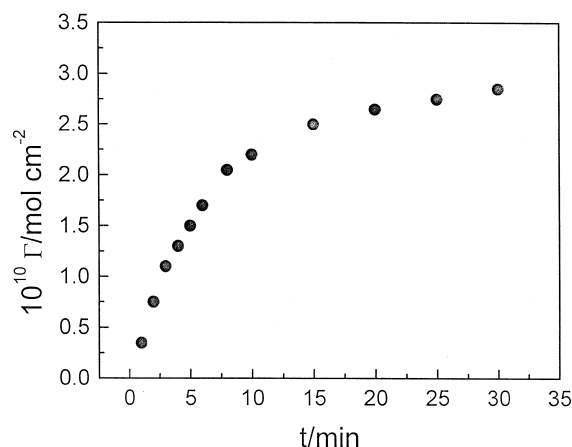


Fig. 2. The dependence of PS coverage on GC electrode surface on the dipping time for the electrode in 5×10^{-3} mol dm^{-3} PS solution.

about 2.2×10^{-10} mol cm^{-2} (this value corresponds the dipping time of about 10 min, and the same as the coverage of PS monolayer on GC electrode), whereas the catalytic current levels off for Γ above 2.2×10^{-10} mol cm^{-2} . We can tentatively give explanation as following. Before the PS on GC electrode surface reaches the monolayer, the catalytic reaction sites increase with increasing of the Γ , thus the electrocatalytic currents increase with increasing of the Γ . The catalytic reaction sites increase slowly after the PS on GC electrode surface reaches the monolayer although PS can take place the multilayer adsorption because the catalytic reaction between PS and NADH just occurs at the interface of PS and electrolyte, so the catalytic currents no longer increase with Γ . Based on these results and to ensure that the electrocatalytic current for NADH oxidation at PS/GC electrode was independent of Γ , a dipping time of 15 min, which corresponds the Γ of 2.6×10^{-10} mol cm^{-2} , was employed in the experiments.

Although the apparent rate constant (k) for the chemical reaction between NADH and PS can be evaluated by cyclic voltammetry according to the method proposed by Andrieux and Saveant [26], the use of rotating-disk electrode measurements typically provides more accurate results. In the present case, the rotating-disk electrodes experiment was carried out by fixing the potential at +300 mV, then the steady state currents was measured at various rotational speed. Fig. 3A presents the plots of electrocatalytic currents (i_{cat}) against the square roots of rotational speed ($\omega^{1/2}$) for electrocatalytic oxidation of NADH at the PS/GC electrode. The currents increase with increasing of rotational speed, but lacks the linearity at high rotational speed, which suggests that the reaction is limited by kinetics and not by transport. The catalytic currents i_{cat} corresponding to the mediated reaction is a function of the Levich current i_{Lev} representing the mass transfer of NADH in the solution and the kinetic current i_{K} corresponding to the electron transfer between NADH

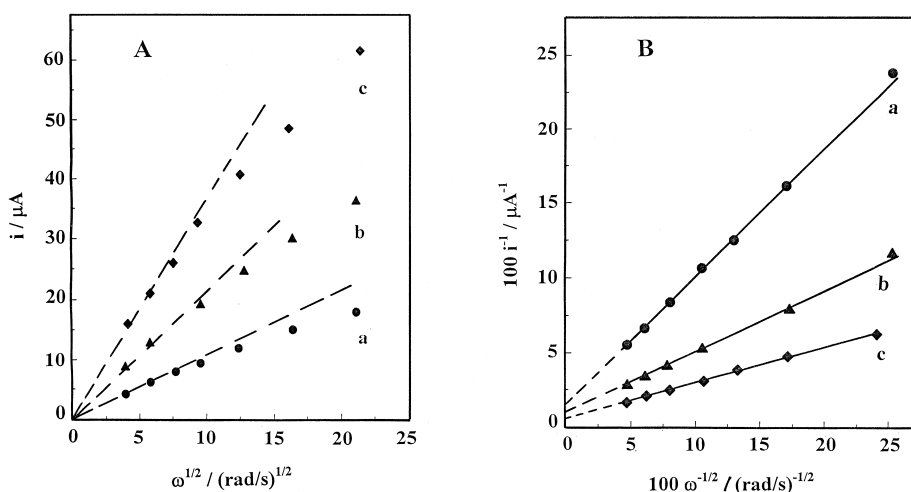


Fig. 3. (A) Plot of the electrocatalytic currents, i , for NADH oxidation at +0.30 V at a PS/GC electrode as a function of $\omega^{1/2}$. The NADH concentration was (a) 0.5×10^{-3} mol dm $^{-3}$, (b) 1.0×10^{-3} mol dm $^{-3}$ and (c) 1.5×10^{-3} mol dm $^{-3}$. (B) Double-reciprocal plots of the data in (A).

and PS. The value of k can be obtained from the so-call Koutecky–Levich plot using the following expression [27,28]:

$$\frac{1}{i_{\text{cat}}} = \frac{1}{i_{\text{Lev}}} + \frac{1}{i_{\text{K}}} \quad (2)$$

and

$$i_{\text{Lev}} = 0.62 n F A D^{2/3} \nu^{-1/6} c_{\text{NADH}} \omega^{1/2} \quad (3)$$

$$i_{\text{K}} = n F A k \Gamma c_{\text{NADH}} \quad (4)$$

where c_{NADH} is the bulk concentration of NADH, ω is the rotational speed, ν is the kinematic viscosity, Γ is the surface coverage of PS, k is the apparent rate constant for the chemical reaction of PS and NADH and all other parameters have their usual meanings. The Koutecky–Levich plot, obtained from the data in the Fig. 3A, is shown in Fig. 3B. Such plot shows the well-behaved linear dependence between the $1/i_{\text{Cat}}$ and $1/\omega^{1/2}$. From the intercept of the plot, the value of the k can be obtained (the data are shown in Table 2).

Table 2
The dependence of k on the NADH concentration

$10^3 c_{\text{NADH}}$ (mol dm $^{-3}$)	0.5	1.0	1.5	2.0	2.5	3.0	3.5
$10^{-4} k$ (dm 3 mol $^{-1}$ s $^{-1}$)	5.2	4.4	3.8	3.5	3.1	2.8	2.6

From Table 2, we can conclude that the value of k decreases with increasing of the NADH. A line can be obtained when one do the plot of k^{-1} against NADH concentration, c_{NADH} . The value of 6.16×10^4 dm 3 mol $^{-1}$ s $^{-1}$ for k at zero concentration of NADH can be calculated by extrapolating the line to $c_{\text{NADH}} = 0$. This value is higher than that obtained with most other mediators. The relation between k^{-1} and c_{NADH} can fit to the line regression equation: $10^5 k^{-1}$ (dm 3 mol $^{-1}$ s $^{-1}$) $^{-1} = 1.62286 + 0.65286 c_{\text{NADH}}$ (mmol dm $^{-3}$), the slope is 1.62286 with a standard deviation of 0.01744 and correlation coefficient of 0.99964, and the intercept is 0.65286 with a standard deviation of 0.0078 and correlation coefficient of 0.99964 (number of data points = 7). A similar phenomenon, the k decreased with increasing of the NADH concentration and the linearity between k^{-1} and c_{NADH} , has been previously reported for the electrooxidation of NADH at electrodes modified with different mediators [18,29,30]. In order to rationalize such a concentration dependence of the rate constant, Gorton et al. [30] has suggested that a charge transfer complex between NADH and the mediator is involved in the electrocatalytic process. Although we have

Table 3
The dependence of the $k(c_{\text{NADH}} \rightarrow 0)$ on the formal potential, $E^{0'}$

Mediator	$E^{0'}$ (mV)	$k(c_{\text{NADH}} \rightarrow 0)$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	pH	Ref.
PS	166	6.16×10^4	7.0	This work
PTOB	5	4.36×10^3	7.0	[29]
PNB	-67	1.29×10^3	6.8	[19]

not explored this specific aspect in this study, it is plausible that a similar mechanism might be operative.

Comparing the electrocatalytic activity of PS films toward NADH electrooxidation with that of poly(toluidine blue o) (PTOB) [31] and poly(nile blue A) (PNB) [19], one can find that PS films is more efficient because the apparent rate constant for chemical reaction between NADH and the mediator is larger in the case of PS. The values of $k(c_{\text{NADH}} \rightarrow 0)$ are presented in Table 3. This can be explained through the different formal potential among them, the formal potential of PS film is more positive than that of PTOB and PNB. The formal potentials of these mediators are also shown in Table 3.

3.3. The effects of cation on the electrocatalytic oxidation of NADH

Katz et al. [32] reported that the presence of Ca^{2+} in the electrolyte can drastically enhance the electrocatalytic current of NADH oxidation at pyrroloquinoline quinone (PQQ) monolayer modified electrodes. These authors suggested Ca^{2+} and PQQ can form the complex, $\text{Ca}^{2+} \cdots \text{PQQ}$, and formation of the ternary complex between the $\text{Ca}^{2+} \cdots \text{PQQ}$ and NADH could be more efficient in the electrocatalytic reaction than formation of complex between immobilized PQQ and NADH. The Ca^{2+} ions might provide a favourable orientation of NADH molecules for its electrocatalytic process. Pariente et al. [18] recently also reported that the Ca^{2+} and Mg^{2+} ions can significantly enhance the anodic currents of NADH electrocatalytic

oxidation at GC electrode modified with electrodeposited films derived from 3,4-dihydroxybenzaldehyde. In order to examine whether the electrocatalytic activity of PS/GC electrode toward NADH oxidation was affected by presence of cations, we carried out experiments where a variety of cations were deliberately added to the electrolyte.

Curve c in Fig. 1 shows the effect of Mg^{2+} cation on the electrocatalytic activity of PS/GC electrode toward NADH oxidation. In presence of Mg^{2+} cation, the anodic electrocatalytic current at +290 mV was enhanced considerably (about two times) comparison with curve b. A apparent rate constant of $6.43 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ was obtained for the reaction of NADH at PS/GC electrode in presence of $10 \times 10^{-3} \text{ mol dm}^{-3} \text{Mg}^{2+}$, which is higher than that obtained in absence of Mg^{2+} (Table 2). In order to compare results obtained from different electrodes, the anodic currents was normalized to the surface coverage (Γ) of PS on glassy carbon electrode (i_p/Γ), and then expressed as a percentage of the value obtained in the absence of deliberately of added ions (control). The results are presented in Fig. 4. From the Fig. 4,

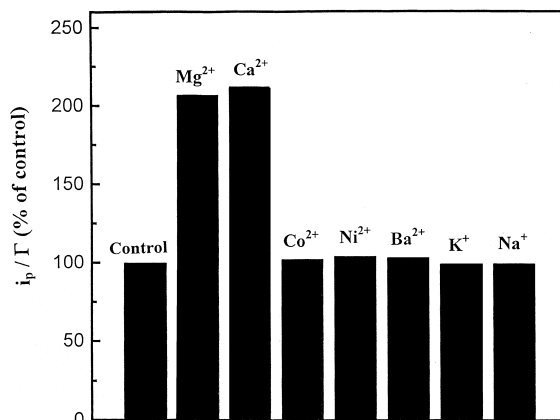


Fig. 4. Surface coverage normalized peak currents for the electrocatalytic oxidation of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ NADH at PS/GC electrode in the presence of $10 \times 10^{-3} \text{ mol dm}^{-3}$ deliberately added ion in 0.1 mol dm^{-3} B-R buffer solution (pH 7.0). The control represents the value obtained for the surface coverage normalized peak currents in the absence of deliberately added ion.

it is clear that the most significant enhancements were obtained in the presence of Mg^{2+} and Ca^{2+} . Some other divalent cations (e.g., Co^{2+} , Ni^{2+} and Ba^{2+}) can also enhance the electrocatalytic current for NADH oxidation but with a smaller effect than Ca^{2+} and Mg^{2+} . Additions of monovalent cations (Na^+ , K^+ and NH_4^+) had no effect on the anodic currents for NADH oxidation. These results are similar to that obtained by Katz et al. [32] and Pariente et al. [18]. We believe that a ternary complex (PS–NADH–ion) is formed during the charge transfer process, which is responsible for the anodic currents enhancement, although the detailed structure of the ternary complex is not clear.

4. Conclusion

The cyclic voltammograms of the PS/GC electrode show the presence of a couple of well-defined redox peaks and the formal potential shifts in the negative direction with increasing the solution pH, with a slope of -51.4 mV per pH unit. The PS/GC shows electrocatalytic activity toward NADH oxidation, with an overpotential ca. 310 mV less than that of the bare electrode. The rate constant was for chemical reaction between NADH and PS was determined using rotated disk electrode measurements, it is found that the value of k decreases with increasing of the NADH concentration, and k is, at zero concentration of NADH, $6.16 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The electrocatalytic reaction is strongly influenced by the presence of Ca^{2+} and Mg^{2+} in electrolyte.

Acknowledgements

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