J Solid State Electrochem (2007) 11:601–607
DOI 10.1007/s10008-006-0205-0

ORIGINAL PAPER

A study of the electrocatalytic oxidation of aspirin on a nickel hydroxide-modified nickel electrode

S. Majdi · A. Jabbari · H. Heli

Received: 30 April 2006 / Revised: 12 May 2006 / Accepted: 18 July 2006 / Published online: 11 October 2006

Abstract The electrocatalytic oxidation of aspirin has been investigated on a nickel oxide-modified nickel electrode in alkaline solution. The process of oxidation and its kinetics have been investigated by using cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy techniques and also steady-state polarization measurements. Voltammetric studies have indicated that in the presence of aspirin, the anodic peak current of low-valence nickel species increases, followed by a decrease in the corresponding cathodic current. This indicates that aspirin was oxidized on the redox mediator immobilized on the electrode surface via an electrocatalytic mechanism. The rate constant of the catalytic oxidation of aspirin and the electron transfer coefficient have been found to be 1.15×10^5 cm^3 $mol^{-1}s^{-1}$ and 0.49, respectively. Impedance measurements show that aspirin is diffused into the bulk of the modifier film, and the oxidation process of aspirin occurs in the bulk of nickel oxide film. It has been shown that by using this modified electrode, aspirin can be determined with a detection limit of 4.8×10^{-5} and successfully applied for determination of aspirin in tablet.

Keywords Aspirin · Acetylsalicylic acid · Nickel · Modified electrode · Electrocatalysis · Impedance spectroscopy

S. Majdi · A. Jabbari (✉) · H. Heli
Department of Chemistry, Faculty of Science,
K. N. Toosi University of Technology,
P.O. Box 16315-1618, Tehran, Iran
e-mail: jabbari@kntu.ac.ir

H. Heli
Institute of Biochemistry and Biophysics, University of Tehran,
P.O. Box 13145-1384, Tehran, Iran

Introduction

Aspirin, the prototype of the salicylates, is a nonsteroidal antiinflammatory, analgesic, antipyretic, and antiseptic agent [1] and is known as an acetylsalicylic acid. It has found widespread application in medicine as a chemopreventative for many types of degenerative diseases such as cancers, cataracts, and circulatory diseases. It is also an antioxidant capable of controlling dioxygen metabolite damage, consisting of O_2^-, H_2O_2, and OH. This substance is highly consumed in the world, and its therapeutic action and its toxic effects make it a drug that is subjected to continuous researches [2, 3].

A large number of techniques such as potentiometry [4], spectrophotometry [5], amperometry [6], and chromatography [7] have been reported for the determination of aspirin. However, the development of a simple, specific, sensitive, and inexpensive method for the determination of aspirin is yet highly desirable.

Intensive researches have been directed toward the development of electrocatalysts aiming at lowering the normally large overpotential and rising the faradic current encountered in the electrooxidation of materials. In this context, a great deal of interest has been recently centered on the materials immobilized onto the electrode surface and capable of mediating fast electron transfer under the effect of external electric fields, namely, chemically modified electrodes [8, 9].

Nickel and nickel-based chemically modified electrodes have been widely used in the oxidation and determination of a large number of organics [10–12]. Electrochemical studies using nickel-based electrodes have proved that various electroreactant species can be determined with high rate of heterogeneous electron transfer process, good sensitivity, and reproducibility. In these studies, the pres-

ence of various Ni-based surface species, such as NiO and $Ni(OH)_2$, and the various phases of NiOOH have been detected, and extensive analysis of the composition of the nickel oxide films on the electrodes has also been performed [13, 14]. Formation of a nickel oxide layer on a substance can be performed using several electrochemical methods such as: (a) applying a large number of potential sweeps to a nickel electrode in alkaline solution [10, 15], (b) galvanostatic oxidation of nickel in alkaline media [16, 17], (c) deposition of $Ni(OH)_2$ layers on a negative electrode during the electrolysis of pH-controlled $Ni(NO)_3$ solution without either nickel metal deposition or hydrogen gas evolution [18], and (d) passing on a droplet of Ni^{2+} solution on the surface of the electrode, evaporating the solvent, transferring to an alkaline medium, and potential sweeping in the region of nickel oxide formation [19]. In these manners, a very low soluble nickel oxide layer is attached to the surface.

The purpose of the present work is to study the electrocatalytic oxidation of aspirin on nickel hydroxide-modified nickel electrode in alkaline medium.

Experimental

All chemicals used in this work were of analytical reagent grade from Merck. Acetylsalicylic acid was synthesized and further purified by recrystallization in water/acetone mixture. The standard solutions of acetylsalicylic acid, with concentration in the range of 2×10^{-4} to 1.0×10^{-2} M, were prepared by weight (±0.01 mg) and diluted using deionized water.

Electrochemical measurements were carried out in a conventional three-electrode cell (from Metrohm) powered by an electrochemical system comprising of AUTOLAB system with PGSTAT30 and FRA2 boards (Eco Chemie, Utrecht, The Netherlands). In impedance measurements, the frequency range of 500 kHz to 25 mHz was employed, the ac voltage amplitude was 10 mV, and the equilibrium time was 5 s. The system was run by a PC through the FRA and GPES 4.9 softwares. In all voltammetric measurements, the IR drop compensation was performed by positive feedback. An Ag/AgCl, 3 M KCl (from Metrohm) and a platinum disk (from Azar Electrode, Iran) were used as reference and counter electrodes, respectively. The working electrode was made of nickel-exposing surface area of 0.79 cm^2, which embedded in a glass tube. Modification of the working electrode was carried out by cycling the potential of the electrode in the range of 100–900 mV vs Ag/AgCl electrode for 3 min. All studies were carried out at room temperature.

Results and discussions

The typical cyclic voltammogram of nickel electrode in 0.1 M NaOH solution after polarization at anodic potentials in the potential range of 100–600 mV with a potential sweep rate of 10 mV s^{-1} is represented in Fig. 1a. In the early sweeps, a pair of redox peaks appears at 352 and 456 mV that are assigned to the Ni(II)/Ni(III) redox couples according to:

$$NiOOH + H_2O + e \rightleftarrows Ni(OH)_2 + OH^- \quad (1)$$

The peak-to-peak potential separation in the potential sweep rate of 10 mV s^{-1} is 104 mV, which is larger than that of theoretical value. This can be accounted for the lateral interaction of the immobilized redox couples present on the surface, interaction of electrolyte species with the modifying film, electrostatic factors, and coupled diffusion–migration processes in the bulk of film and/or presence of nonequivalent sites in the film.

Figure 1b illustrates cyclic voltammograms of modified nickel electrode in 0.1 M NaOH solution at various potential sweep rates in a wide range of 2–500 mV s^{-1}. The anodic and cathodic peak currents are proportional to the sweep rate at low values (2–25 mV s^{-1}, Fig. 1c,d). This points out an electrochemical activity of the surface redox transition. From the slope of this line and using:

$$I_p = \left(n^2F^2 / 4RT\right) \nu A\Gamma^* \quad (2)$$

where Γ^* is the surface coverage of the redox species and ν is the potential sweep rate [20], and taking the average of both cathodic and anodic currents, the total surface coverage of the electrode with the modified film of about 3.36×10^{-7} mol cm^{-2} has been derived that corresponds to the presence of more than 200 monolayers of surface species. In the high range of sweep rates (50–500 mV s^{-1}, Fig. 1e,f), this dependency is of square-root form, signifying the dominance of a diffusion process as the rate limiting step in the total redox transition of modified film [10, 21]. This limiting diffusion process which is also reported for other Ni-modified electrodes [22, 23] may occur for the charge neutralization of the film during oxidation/reduction process.

Figure 2 represents cyclic voltammograms of nickel-modified electrode in 0.1 M NaOH solution in the absence (curve a) and presence of 2.0×10^{-3} M aspirin (curve b) recorded at the potential sweep rate of 10 mV s^{-1}. In the presence of aspirin, it was observed that the anodic current and the associated anodic charge increased drastically, while the cathodic current and the corresponding charge decreased. In the presence of aspirin, the anodic charge associated with the anodic peak is quantitatively 94.82% of that of the corresponding cathodic peak, while in the absence of aspirin, this is

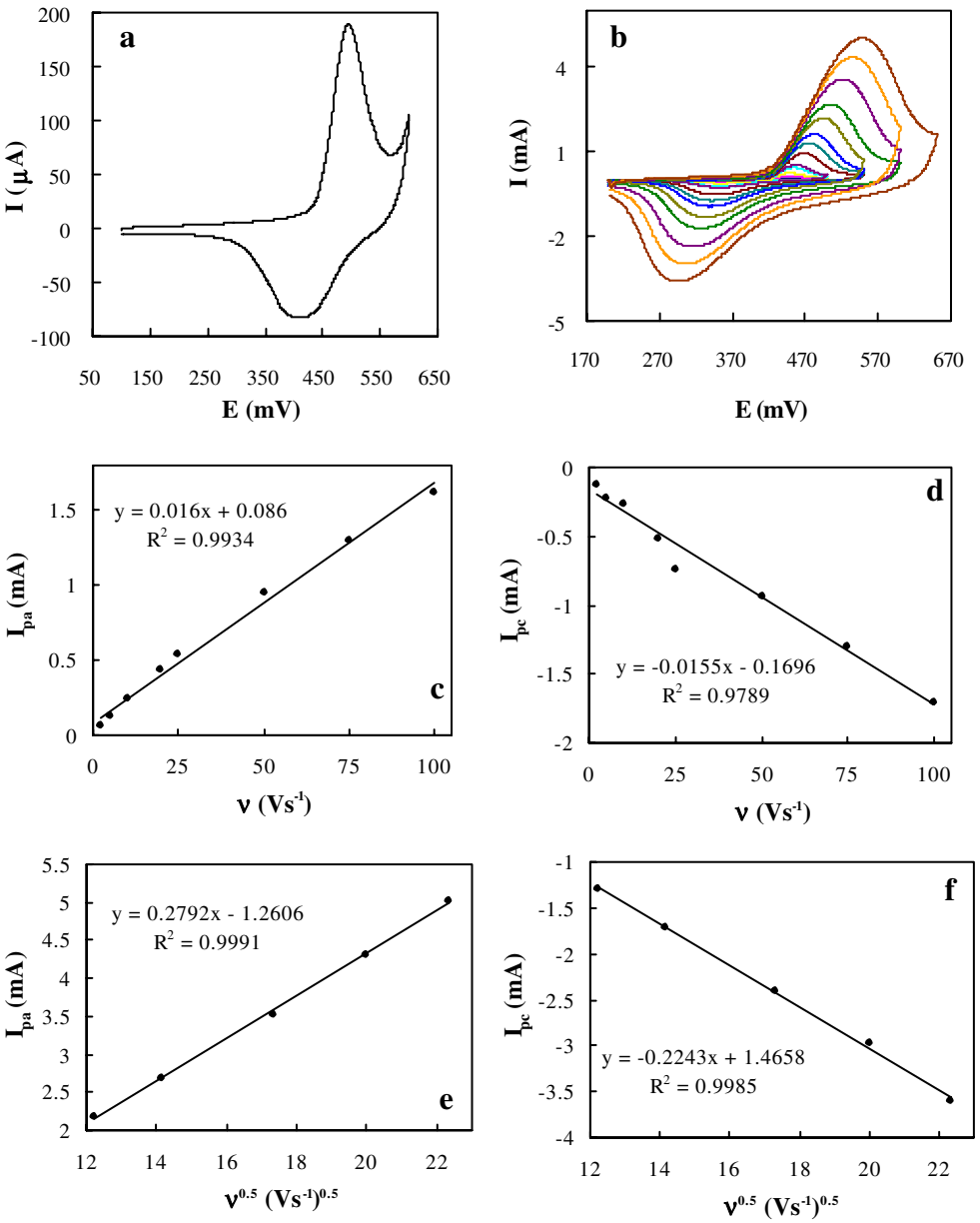


Fig. 1 **a** Cyclic voltammogram of nickel electrode in 0.1 M NaOH solution with a potential sweep rate of 10 mV s^{-1}. **b** Cyclic voltammograms of nickel hydroxide-modified nickel electrode in 0.1 M NaOH solution in the potential sweep rates of 2, 5, 10, 20, 25, 50, 75, 100, 150, 200, 300, 400, and 500 mV s^{-1}. **c**–**f** The dependency of anodic (**c**) and cathodic (**d**) peak currents on the potential sweep rate at lower values (2–100 mV s^{-1}) and the proportionality of anodic (**e**) and cathodic (**f**) peak currents on the square roots of sweep rate at higher values (150–500 mV s^{-1})

34.75%. This indicates that aspirin is oxidized by active nickel moiety via a cyclic mediation redox process. Nickel species is immobilized on the electrode surface, and the one with a higher valence oxidizes aspirin via a chemical reaction followed by generation of low-valence nickel. Along this line, the high-valence oxide is regenerated through the external electrical circuit. Accordingly, aspirin is oxidized via an EC′ mechanism. Moreover, the significant current in the reverse sweep indicates that the reaction of aspirin with high-valence nickel oxide is the rate-determining step of the oxidation process. Another point observed in Fig. 2, curve b, is that the onset potential of oxidation of low-valence nickel oxide is lowered in the presence of aspirin, which reveals the facilitation of oxidation of low-valence oxide by aspirin. Meanwhile, plotting the current function (peak current divided by the square root of the potential sweep rate) against the square root of the potential sweep rate reveals negative slope, which confirms the electrocatalytic nature of the process (Fig. 3, vide infra). The anodic peak current associated with the oxidation of low-valence nickel species is proportional to the bulk concentration of aspirin, and any increase in the concentration of aspirin causes an almost proportional linear enhancement of the anodic peak current (Fig. 2, inset). This proportionality is linear in the range of 4×10^{-4} to 6×10^{-3} M.

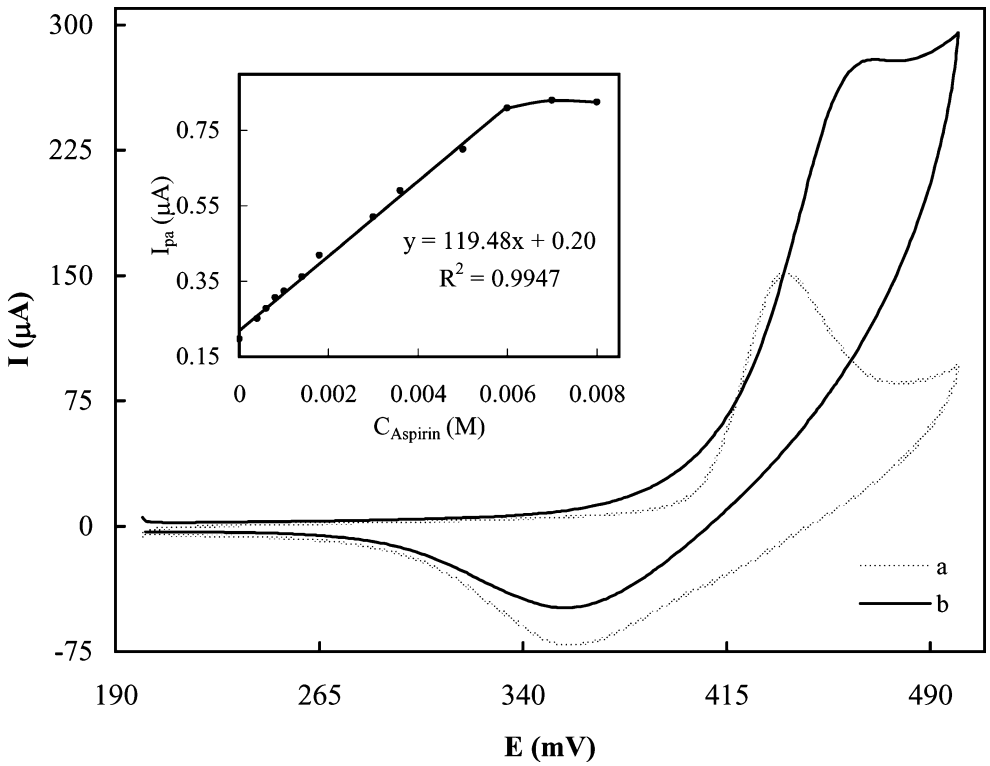


Fig. 2 Cyclic voltammograms of nickel hydroxide-modified nickel electrode in 0.1 M NaOH solution in the absence (**a**) and the presence (**b**) of aspirin in the solution. Potential sweep rate is 10 mV s^{-1}. *Inset*: Dependency of the anodic peak current on aspirin concentration

On the basis of the reported results, the following mechanism can be proposed for the mediated oxidation of aspirin on the modified surface, which is outlined in Scheme 1. The redox transition of nickel species is:

$$Ni(II) \rightleftarrows Ni(III) + e \quad (3)$$

In addition, aspirin is oxidized on modified surface via the following reaction:

$$Ni(III) + Aspirin \rightarrow Intermediate + Ni(II) \quad (4)$$

where the intermediate is further oxidized to the product, 3,6-dioxocyclohexa-1,4-dienecarboxylate or 5,6-dioxocyclohexa-1,3-dienecarboxylate, through the final electron transfer process:

$$Ni(III) + Intermediate \rightarrow Product + Ni(II) \quad (5)$$

Figure 4 indicates a steady-state current–potential curve recorded for the electrocatalytic oxidation of aspirin. A typical S-shape plot has been obtained, and the electron transfer coefficient (α) can be found by plotting E vs log I as α=0.49.

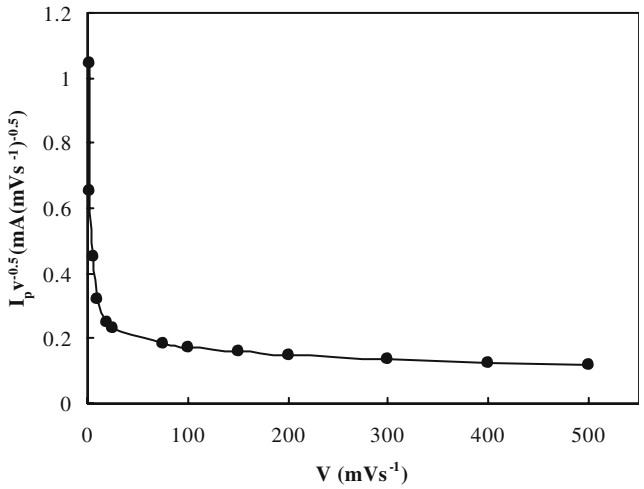
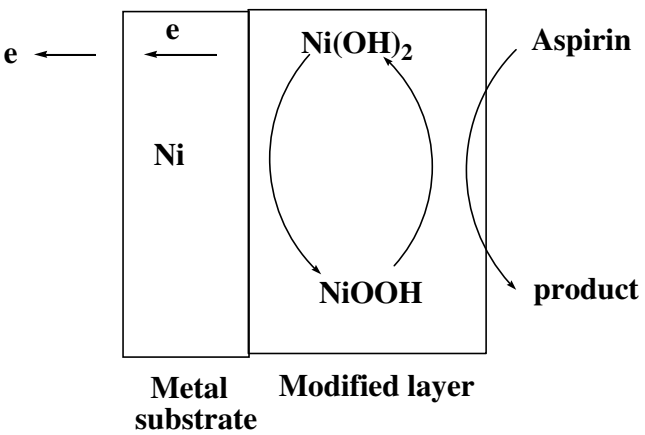


Fig. 3 Current function vs $\nu^{0.5}$ for 0.1 M NaOH solution in the presence of 8×10^{-4} M aspirin



Scheme 1 Mechanism for the mediated oxidation of aspirin on the modified surface

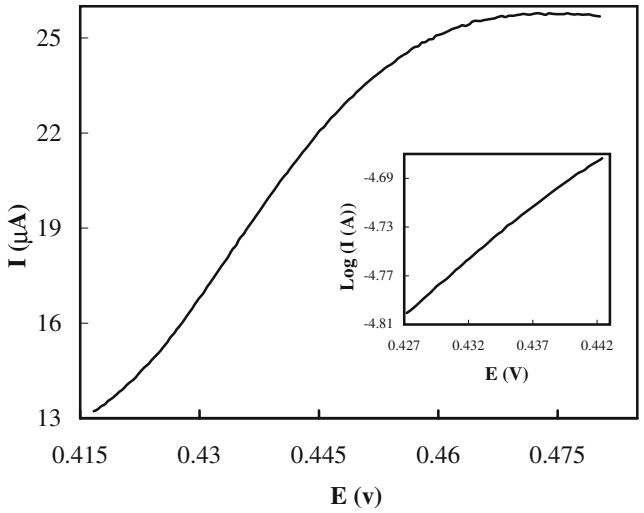


Fig. 4 Potentiodynamic polarization curve for nickel hydroxide-modified nickel electrode in 0.1 M NaOH in the presence of 2.2×10^{-3} M aspirin recorded using a potential sweep rate of 0.005 mV s^{-1}. *Inset*: The corresponding Tafel plot

Double-step chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the catalytic rate constant on the modified surface. Figure 5 shows double-steps chronoamperograms for the modified electrode in the absence (curve a) and presence (curve b–g) of aspirin over a concentration range of 2×10^{-4} to 7×10^{-3} M with applied potential steps of 480 and 228 mV, respectively. The current is negligible when potential is stepped down to 228 mV, indicating that the electrocatalytic oxidation of aspirin is irreversible.

Figure 5, inset a, shows the plot of sampled current at a fixed time interval of 10 s with respect to the concentration of aspirin in the range of 2×10^{-4} to 7×10^{-3} M. A good linear dependency has been observed, and a limit of detection of 4.8×10^{-5} M has been obtained.

Chronoamperometry can also be used for the evaluation of the catalytic rate constant according to [24]:

$$I_{cat}/I_L = \gamma^{1/2}\left[\pi^{1/2} erf\left(\gamma^{1/2}\right) + exp\left(-\gamma\right)/\gamma^{1/2}\right] \quad (6)$$

where I_{cat} and I_L are the currents in the presence and absence of aspirin, and $\gamma=kCt$ is the argument of the error function. k is catalytic rate constant, C is bulk concentration of aspirin, and t is the elapsed time. In the cases where $\gamma>1.5$, and erf($\gamma^{1/2}$) is almost equal to unity, the above equation can be reduced to:

$$I_{cat}/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kCt)^{1/2} \quad (7)$$

From the slope of the I_{cat}/I_L vs $t^{1/2}$ plot, presented in Fig. 3, inset b, the mean value of k for the concentration range of 2×10^{-4} to 8×10^{-3} M of aspirin was obtained as 1.15×10^5 cm^3 mol^{-1} s^{-1}.

Figure 6 represents Nyquist diagrams of the modified electrode recorded at 450 mV dc-offset in the absence (curve a) and presence of 2.2×10^{-3} M aspirin (curve b) in 0.1 M NaOH solution, respectively. In the absence of aspirin, the Nyquist diagram comprises a depressed semicircle at the high frequencies which can be related to the combination of charge transfer resistance of transition of Ni(II)/Ni(III) redox couple and the double-layer capacitance, followed by a straight line with the slope of near 45°. The latter is due to the occurrence of mass transport process via diffusion (see Fig. 1e,f). A similar result has also been reported in the literature [25]. The equivalent circuit compatible with the Nyquist diagram recorded in the absence of aspirin is depicted in Scheme 2. In this circuit, R_s, CPE, and R_{ct} represent solution resistance, a constant phase element corresponding to the double-layer capacitance and the charge transfer resistance associated with the oxidation of low-valence nickel species. In the presence of aspirin, the diameter of the semicircle is decreased. This is due to the instant chemical reaction of aspirin with the high-valence nickel species. The catalytic reaction of oxidation of aspirin that occurred via the participation of high-valence nickel species virtually causes an increase in the surface concentration of high-valence nickel species, and the charge transfer resistance becomes low, depending on the concentration of aspirin in the solution. This behavior is consistent with the result of cyclic voltammetry and chronoamperometry (see Figs. 2 and 5). Moreover, Nyquist diagram in the presence of aspirin at low-frequency region rolls over the real axis, and it also points out a typical finite (Nernstian) diffusion process. The equivalent circuit compatible with this Nyquist diagram is presented in Scheme 3. In this circuit, R_s, CPE, and R_{ct} represent solution resistance, a constant phase element corresponding to the double-layer capacitance and the charge transfer resistance associated with the oxidation of aspirin. W_s is a finite-length Warburg short-circuit term coupled to R_{ct}, which accounts for the Nernstian diffusion. The impedance of this element can be written as [26]:

$$\begin{aligned} Z(\omega) &= R_d[(sin\ h\ w + sin\ \ w) - j[(sinh\ w + sin\ \ w)] \\ &\quad /[x(cosh\ \ x + cos\ \ x)] \\ &\text{where } j = \sqrt{-1},\ \omega \text{ is angular frequency and} \\ &R_d = RTl/z^2F^2ACD \\ &w = (2\omega/\omega_d)0.5 \\ &\omega_d = D/l^2 \end{aligned} \quad (8)$$

where R_d is the diffusion resistance, l is the diffusion thickness, D is the diffusion coefficient, C is the maximum concentration, A is the electrode surface area, and other parameters have their usual meanings. The impedance of this element is the application of "totally absorbing

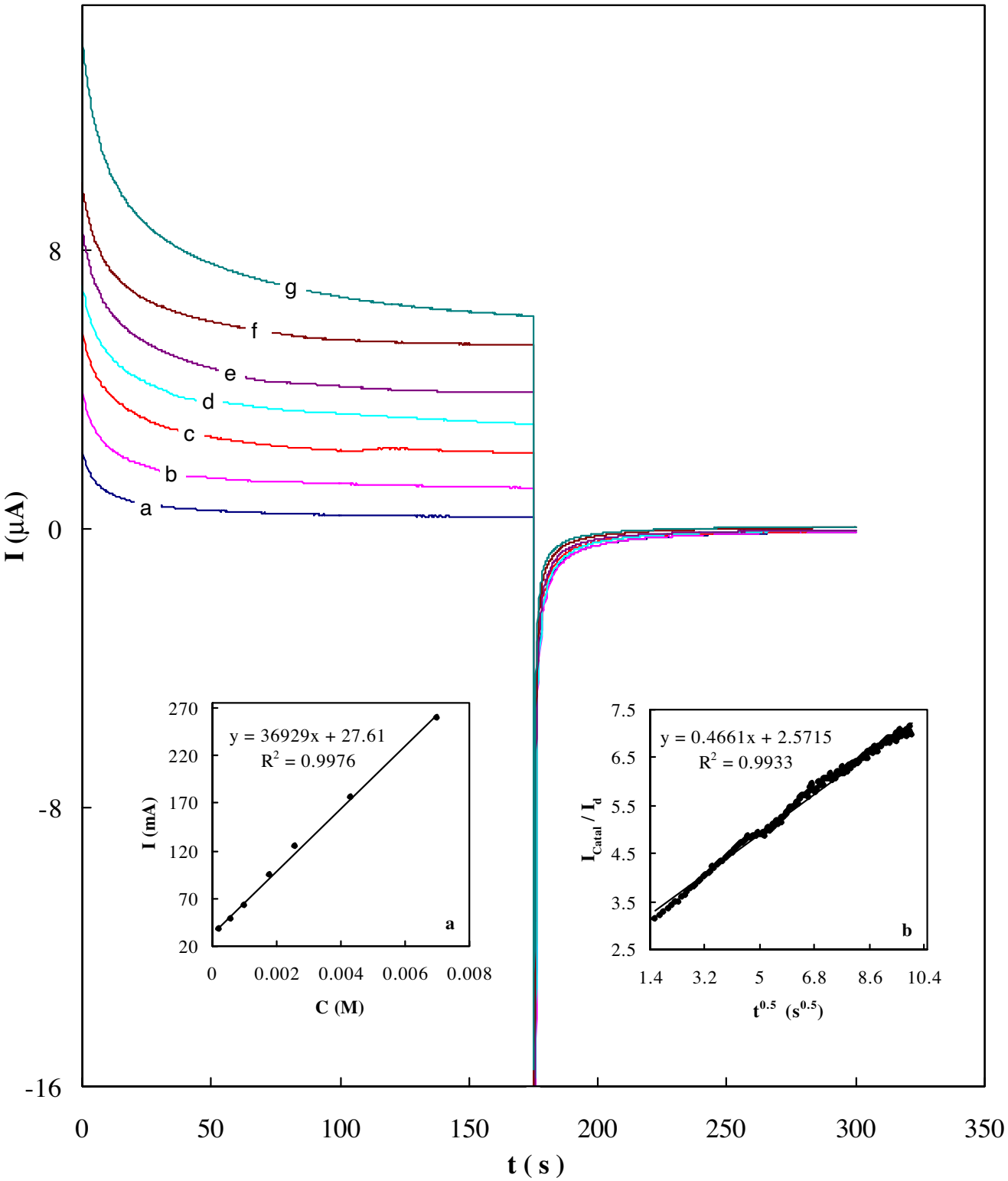


Fig. 5 *Main panel*: Double-step chronoamperograms of nickel hydroxide-modified nickel electrode in 0.1 M NaOH solution with different concentrations of aspirin of: 0 (**a**), 2×10^{-4} (**b**), 6×10^{-4} (**c**), 1.4×10^{-3} (**d**), 2.6×10^{-3} (**e**), 7×10^{-3} (**f**), and 8×10^{-3} M (**g**), respectively. Potential steps were 480 and 228 mV, respectively. **a** Dependency of sampled current at fixed time of 10 s to different concentrations of aspirin of 2×10^{-4}, 6×10^{-4}, 1×10^{-3}, 2.6×10^{-3}, 4.3×10^{-3}, and 7×10^{-3} M. **b** Dependence of I_{cat}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of (**a**) and (**c**) in *main panel*

boundary conditions" on the equation of generalized diffusion impedance [27]. This condition implies that the excess concentration of electroreactant species at the boundary is immediately drained out, or the concentration

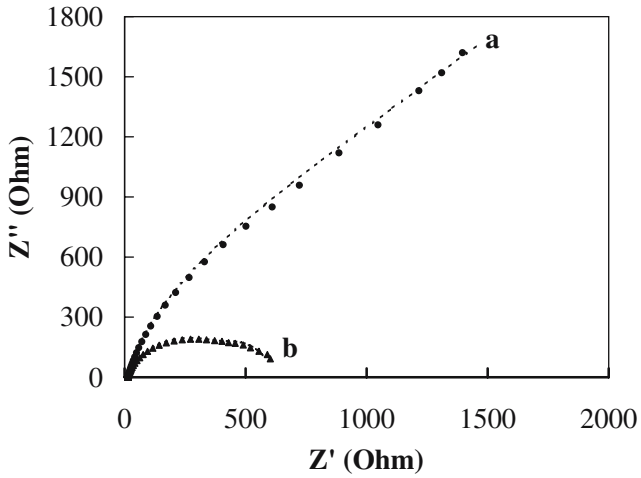
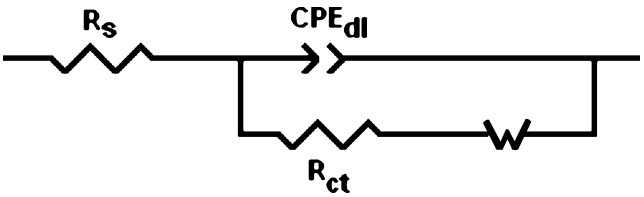


Fig. 6 Nyquist diagrams of nickel hydroxide-modified nickel electrode in the absence (**a**) and presence (**b**) of 2.2×10^{-3} M aspirin in 0.1 M NaOH solution. Bias is 450 mV. *Dots* represent experimental data, and *line* indicates fitting on the equivalent circuits

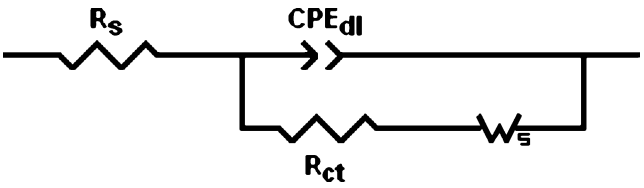
of electroreactant species at the boundary remains at an equilibrium level. The appearance of the short-circuit terminus at the low-frequency region in Nyquist diagram shown in Fig. 6, curve b, implies that aspirin is transferred from the bulk of the solution via a linear diffusion process (because there are no convection or migration effects for transport of aspirin to the electrode surface). This process is followed by permeation of aspirin into the bulk of film and chemical reaction with the high-valence nickel species. Accordingly, while aspirin moves through the bulk of modifier film of nickel oxide, the oxidation of aspirin occurs.

Conclusion

The nickel oxide film was formed electrochemically in a regime of cyclic voltammetry on a nickel electrode and checked for electrooxidation of aspirin in alkaline media.



Scheme 2 The equivalent circuit compatible with the Nyquist diagram recorded in the absence of aspirin



Scheme 3 The equivalent circuit compatible with Nyquist diagram recorded in the presence of aspirin

The modified electrode shows electrocatalytic oxidation of aspirin at around 468 mV vs Ag/AgCl. Aspirin enters to the bulk of the modifier film and oxidizes in the bulk of this film at more negative potentials than the electrooxidation of redox couple Ni(II)/Ni(III). Using cyclic voltammetry and chronoamperometry techniques, the kinetic parameters such as charge transfer coefficient (α) and the catalytic reaction rate constant (k) for oxidation of aspirin were determined. Moreover, the nickel oxide-modified nickel electrode can be used for determination of real samples.

Acknowledgments We gratefully acknowledge the support of this work by K. N. Toosi University of Technology Research Council. The authors are also grateful to Dr. S. Balalaie, Dr. B. Movassagh, and Dr. S. Noroozizadeh for their fruitful comments.

References

1. Florey K (1979) Aspirin in analytical profiles of drug substances. Academic, New York
2. Thiessen JJ (1992) In: Barnett HJM, Hirsh J, Mustard JF (eds) Acetylsalicylic acid: new uses for an old drug. Raven, New York, pp 49–61
3. Nietsch P (1989) Therapeutic applications of ASPIRIN®. Bayer, Leverkusen
4. Kubota LT, Fernández JCB, Rover L, Neto GO (1999) Talanta 50:661
5. Sena MM, Fernández JCB, Rover L Jr, Poppi RJ, Kubota LT (2000) Anal Chim Acta 409:159
6. Junior LR, Neto GO, Fernández JR, Kubota LT (2000) Talanta 51:547
7. Nogowska M, Muszalska I, Zajac M (1999) Chem Anal 44:1041
8. Pournaghi-Azar MH, Sabzi RE (2004) Electroanalysis 16:860
9. Golabi SM, Irannejad L (2005) Electroanalysis 17:985
10. Jafarian M, Mahjani MG, Heli H, Gobal F, Heydarpoor M (2003) Electrochem Commun 5:184
11. Kowal A, Port SN, Nichols RJ (1997) Catal Today 38:483
12. Yousef Elahi M, Heli H, Bathaie SZ, Mousavi MF (2006) J Solid State Electrochem (in press). DOI 10.1007/s10008-006-0104-4
13. MacDougall B, Graham MJ (1981) Electrochim Acta 26:705
14. MacDougall B, Mitchell DF, Graham MJ (1985) J Electrochem Soc 132:2895
15. Burke LD, Twomey TAM (1984) J Electroanal Chem 162:101
16. MacDougall B, Mitchell DF, Graham MJ (1980) J Electrochem Soc 127:1248
17. Ord JL, Clayton JC, De Smet DJ (1977) J Electrochem Soc 124:1714.14
18. Wohlfahrt-Mehrens M, Oesten R, Wilde P, Huggins RA (1996) Solid State Ionics 86–88:841
19. El-Shafei AA (1999) J Electroanal Chem 471:489
20. Bard AJ, Faulkner LR (2001) Electrochemical methods, ch. 14. Wiley, New York
21. Srinivasan V, Weidner JW, White RE (2000) J Solid State Electrochem 4:367
22. Salimi A, Abdi K, Khayatiyan G-R (2004) Electrochim Acta 49:413
23. Roslonek G, Taraszewska J (1994) Electrochim Acta 39:1887
24. Bard AJ, Faulkner LR (2001) Electrochemical methods, ch. 12. Wiley, New York
25. Yang CC (2002) Int J Hydrogen Energy 27:1071
26. Arai H, Muller S, Hass O (2000) J Electrochem Soc 147:3584
27. Bisquert J, Garcia-Belmonte G, Fabregat-Santiago G, Bueno PR (1999) J Electroanal Chem 475:152