FABRICATION AND ELECTROCATALYTIC APPLICATION OF NI-MODIFIED ELECTRODE TOWARD DETECTION OF PARACETAMOL

Mostafa Dehghani Mobarake*, Leila Samiee, and Ramin Karami

Renewable Energy Department, Energy Research Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran.

ABSTRACT

In the present work, the modified nickel electrode was electrochemically fabricated and tested for the electro-oxidation of paracetamol in alkaline media. The methods of cyclic voltammetry (CV), chronoamperometry (CA), and impedance spectroscopy (EIS) were used to determine kinetic parameters such as transfer coefficient (α), the catalytic reaction rate constants (k), and the diffusion coefficient of paracetamol in the bulk of solution. The electrochemical results showed that the modified nickel electrode had a high electrocatalytic activity for the electro-oxidation of paracetamol around 400 mV/Ag.AgCl in alkaline media and the diffusion coefficient of paracetamol was obtained to be 3×10^{-6} $cm^2.s^{-1}$. It means that the modified nickel electrode is highly sensitive toward the detection of paracetamol.

Keywords: Ni Electrodes, Paracetamol, Paracetamol Detection, Catalytic Process

INTRODUCTION

Paracetamol was introduced in medicine over 100 years ago [1-8]. Since then paracetamol has been available as a safe effective analgesic and antipyretic drug in the global market. [1]

The quantitative analysis of paracetamol has been achieved using spectrophotometry, liquid chromatography, near infrared transmittance spectroscopy, titrimetry and voltammetry. In addition, several flow injection methods for the determination of paracetamol have been reported using fluorometric [2], UV-Vis spectrophotometry [3], Fourier transform infrared spectrophotometry [4], or electrochemical detection techniques [5]. However, some of these methods are time-consuming, and since paracetamol is electroactive and can be oxidized under suitable conditions, the use of electrochemical detection can be considered appropriate due to its rapid response and high sensitivity capabilities. Furthermore, because of the potential for miniaturization, ease of manufacture, and low cost, electrochemical techniques can be considered as an attractive method for the determination of paracetamol [6, 5].

Craig E. Banks et al. investigated the electrochemical oxidation of N-(4-hydroxy-phenyl) ethanamide (paracetamol) at C60-modified glassy carbon electrodes. This work clearly shows that substrate activation is an important parameter for the study of the C60 filmmodified electrodes, especially in electro-
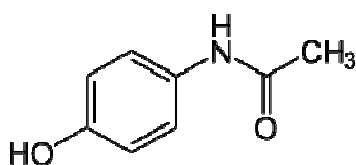
analysis applications. [7]

Nickel modified or nickel alloy electrodes are commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis, the electrolysis of water, and the direct electrochemical oxidation of alcohol [9-16]. One of the most important applications of nickel is the catalysis of the oxidation of alcohols [15, 17].

With the exception of pure nickel, nickel hydroxides and the modified complex of Ni-electrodes have been used for a variety of electro-oxidation [18-25] and reduction pur-poses [26].

Here, we have studied the electrochemical oxidation of paracetamol on a nickel electrode in NaOH solution along with driving the kinetic parameters of the electro-catalytic process.

EXPERIMENTAL

Chemicals

Sodium hydroxide and the nickel rods were received from Merck. Paracetamol was obtained from Borhan Daro Company. Also, all chemicals were analytical grade.

Characterization

Electrochemical studies were carried out in a conventional three-electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solar-tron model 1255 frequency response analyzer. The system is run and controlled by a PC through M270 commercial software via a GPIB interface. A dual Ag/AgCl-Saturated KCl, a Pt wire, and a graphite (G) disk electrode were used as the reference, counter, and working electrodes respectively. All studies were carried

out at 298 ± 2 K. The G disk electrode was polished with 0.05 mm alumina powder on a polishing micro cloth and rinsed thoroughly with doubly distilled water before modification.

Working electrode, Ni/NiOOH rod, was prepared by fifty cycles between 0 to 600 mV at a 100 mV/s scan rate in a 1M NaOH solution.

RESULTS AND DISCUSSION

Figure 1 shows the 50 consecutive cyclic voltamograms of the Ni electrode with 100 mv/s scan rate in 1 M NaOH. In the first scan, a pair of redox peaks appears at 450 mV and 500 mV, which is assigned to Ni^{2+}/ Ni^{3+} redox couple in alkaline media. The entire behavior is in agreement with the previous data in the literature related to the formation and inter-conversion of α- and ß-phases of $Ni(OH)_2$, its transformation to NiOOH, and the enrichment of Ni^{3+} species on or beneath the surface [23-27].
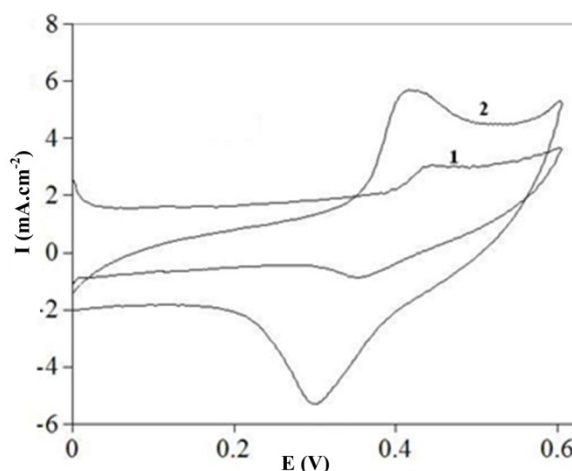

Figure 1: Consecutive 50 cycles voltammogram of Ni/NiOOH electrode in 1 M NaOH at a scan rate of 100 mVs^{-1}. (1) First cycle; (2) Fifty cycle

Upon further cycles, the peaks shift cathodically and stabilize at 430 mV and 480 mV respectively. In the subsequent cycles, both the anodic and cathodic peaks shift negatively and then stabilize; higher energies (potential) are required for the nucleation of NiOOH in the first cycle. The enhanced base line current of the first

cycle is related to the oxidation of Ni to Ni(II).

The current increases with the number of potential scans indicating the progressive enrichment of the accessible electro-active species (Ni^{2+} and Ni^{3+}) on or near the surface. The increased current in anodic wave is a result of oxygen evolution reaction.

After prolonged cycling, the redox peak potentials are stabilized at 388 mV and 471 mV Ag/AgCl.

These changes are probably due to a change [23] in the crystallite structure of the nickel hydroxide and the nickel oxyhydroxide films. It has been reported [24, 25] that at the initial stages of electro-oxidation, α-Ni(OH)$_2$ forms and is then slowly converted to ß-Ni(OH)$_2$ form. It is believed that both of the above phases are non-stochiometric [26, 27]. Figure 2a presents the typical CVs of a Ni-modified NiOOH electrode in 1M NaOH solution at various potential scan rates of 2 to 2000 mVs^{-1}. The peak's currents are proportional to scan rates in the range of 2 to 40 mVs^{-1}. Figures 2b and c show the electrochemical activity of the surface redox couple [28]. According to Equation 1 [28], with respect to the slope of I_p versus v and taking the average of both cathodic and anodic results, surface coverage (Γ^*) was estimated to be around 6.2×10^{-8} mol.s^{-2}.

$$I_p = \left(\frac{n^2 F^2}{4RT} \right) vA\Gamma^* \tag{1}$$

Γ^* value corresponds to the formation of approximately 54 monolayers of Ni/NiOOH surface species.

At higher potential scan rates, it has a $v^{1/2}$ dependency; Figures 2d and e show the dominance of the diffusion controlled processes.

Figure 3 presents the CVs of Ni/NiOOH electrode without (a), in 3 mM paracetamol (b), and in 9 mM paracetamol (c) at the potential scan rate of 10 mVs^{-1}. In the study of electro-oxidation of

paracetamol on Ni electrode, it was [29] revealed that the obtained current of anodic and cathodic were 35 mA.cm^{-2} in a 3 mM solution. The results showed that anodic current rose against cathodic drop in the presence of paracetamol.

Figure 4 showed the effect of paracetamol concentration on the anodic and cathodic current of the above electrode. It is clearly observed that the anodic current increases with paracetamol concentration. The enhancement of the current ratio (anodic:cathodic) from 56:44 to 96:4 has been caused by paracetamol component. Figure 5 (a) depicts the cyclic voltamograms of Ni/NiOOH in 5 mM paracetamol at different scan rates. It was showed that anodic/cathodic currents are proportional to the scan rates in a range of 2 to 2000 mVs^{-1}, as illustrated in Figures 5b and c respectively.

The cathodic peak was not observed at low scan rates, but appeared upon increasing the scan rate. This phenomenon indicates that the electro-oxidation of nickel species to a higher valence state is much faster than the catalytic oxidation of ethylene glycol. At higher scan rates, a new oxidation peak appeared for ethylene glycol oxidation at a potential much more positive than the oxidation potential of Ni(OH)$_2$.

A double-step chronoamperometry has been employed for the investigation of the processes via ErCi mechanism [23]. The chronoamperograms of Ni/NiOOH electrode without (11) and in the presence of (1-15) paracetamol in a concentration range of 1 to 9 mM in 1M NaOH solution at the oxidation potential of 400 and 200 mV are presented in Figure 6A. The plot of net current versus $t^{-1/2}$ was obtained by the elimination of background current via point-by-point subtraction method. It gives a straight line at a level of around 0.27 mA, (Figure 6B). Moreover, a diffusion process controls the transient current.
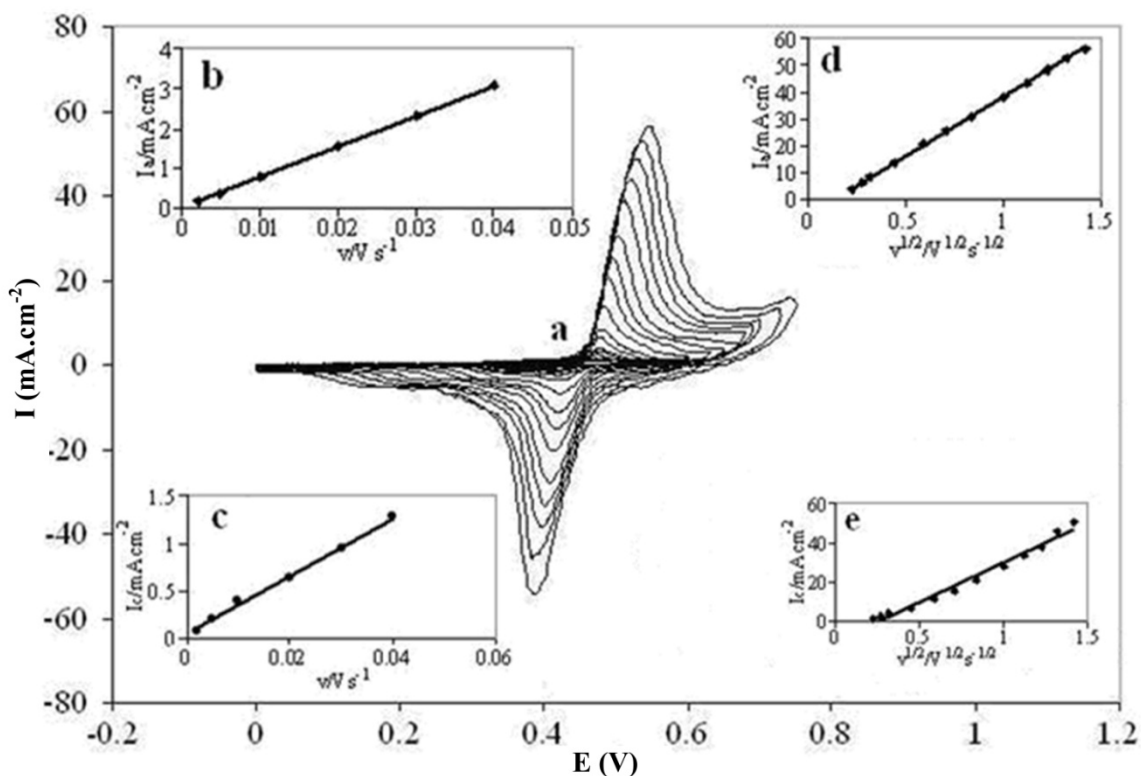
Figure 2: (a) Typical cyclic voltamograms of a Ni/NiOOH electrode in 1 M NaOH in the potential sweep rates of 2, 5, 7, 10, 20,30, 40, 50, 75, 100, 200, 350, 500, 750, 1000, 1250, 1500, 1750, and 2000 mVs⁻¹; (b) the dependency of anodic and (c) cathodic peak currents on the sweep rate at lower values (2-40 mVs⁻¹); (d) the proportionality of anodic and (e) cathodic peak currents to the square roots of sweep rate at higher values (50-2000 mVs⁻¹)
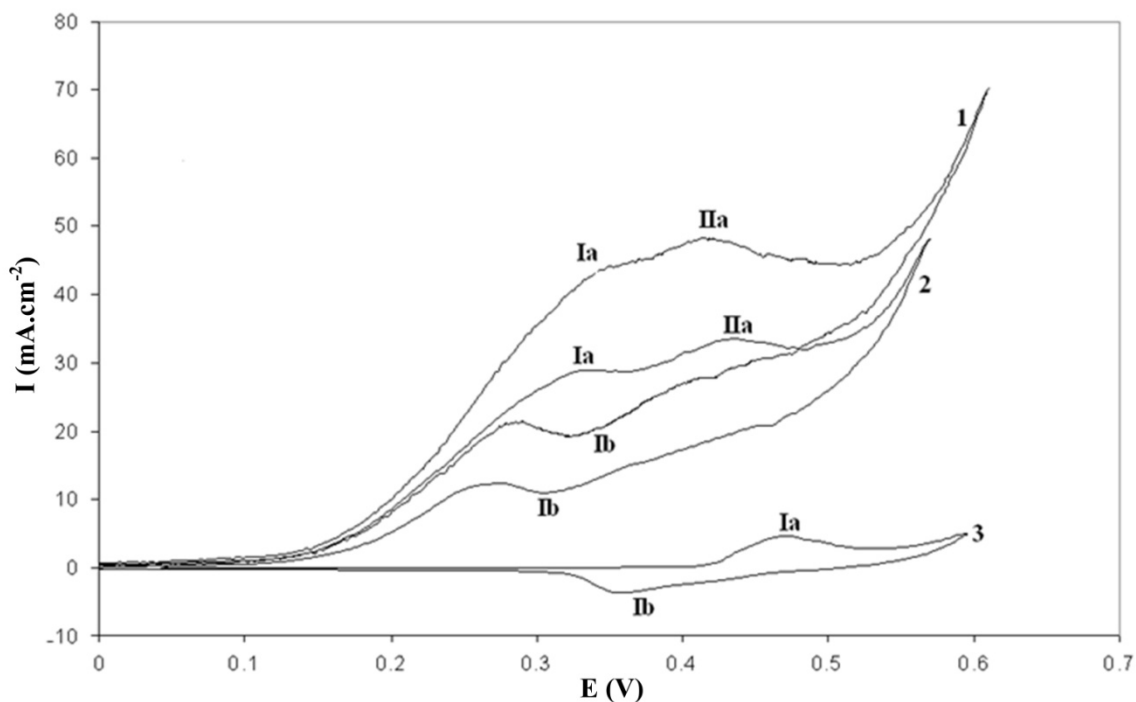

Figure 3: Cyclic voltamograms in the presence of 5 mM (a) and 1mM (b) of paracetamol on Ni/NiOOH electrode and only Ni/NiOOH (C) in 1M NaOH solution. Potential sweep rate was 10 mVs⁻¹.
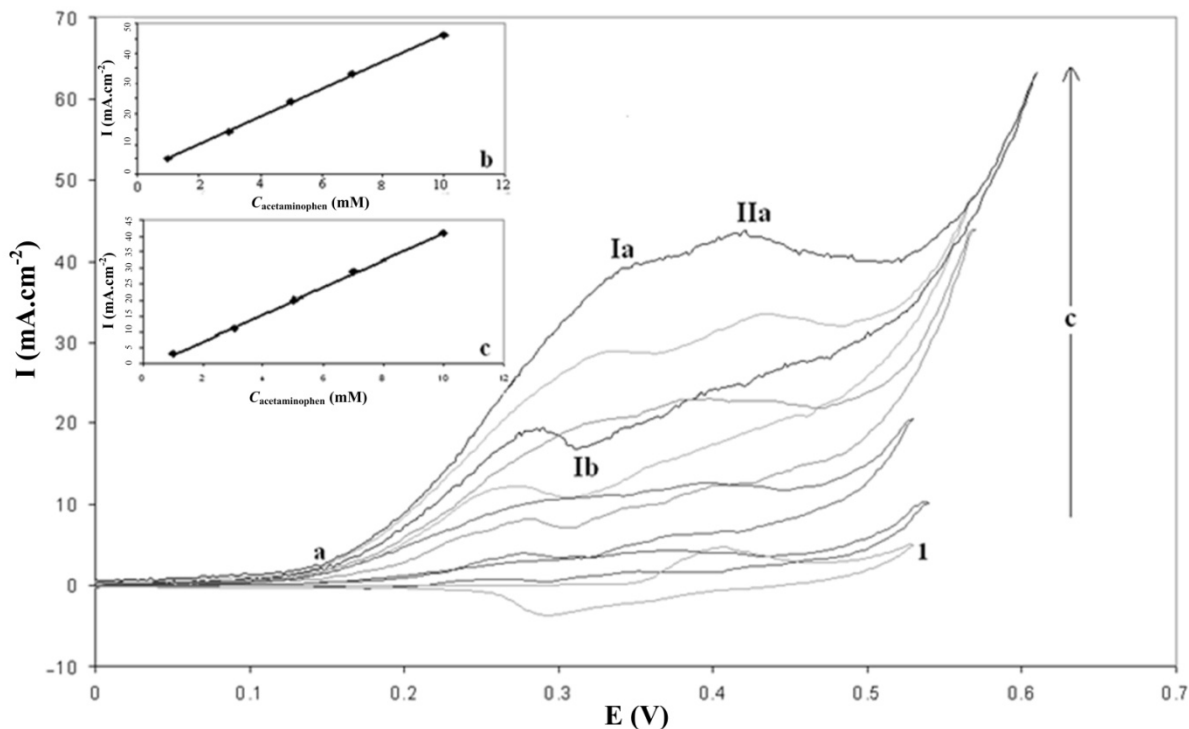
Figure 4: (a) Cyclic voltamograms of the Ni/NiOOH electrode in 1 M NaOH solution in the presence of (1) 1 mM; (2) 3 mM; (3) 5 mM; (4) 7 mM; and (5) 9 mM of paracetamol in the solution. Potential sweep rate was 10 mVs^{-1}; (b) the dependency of the anodic peak current on the concentration of paracetamol in solution; (c) the dependency of the cathodic peak current on the concentration of paracetamol in solution
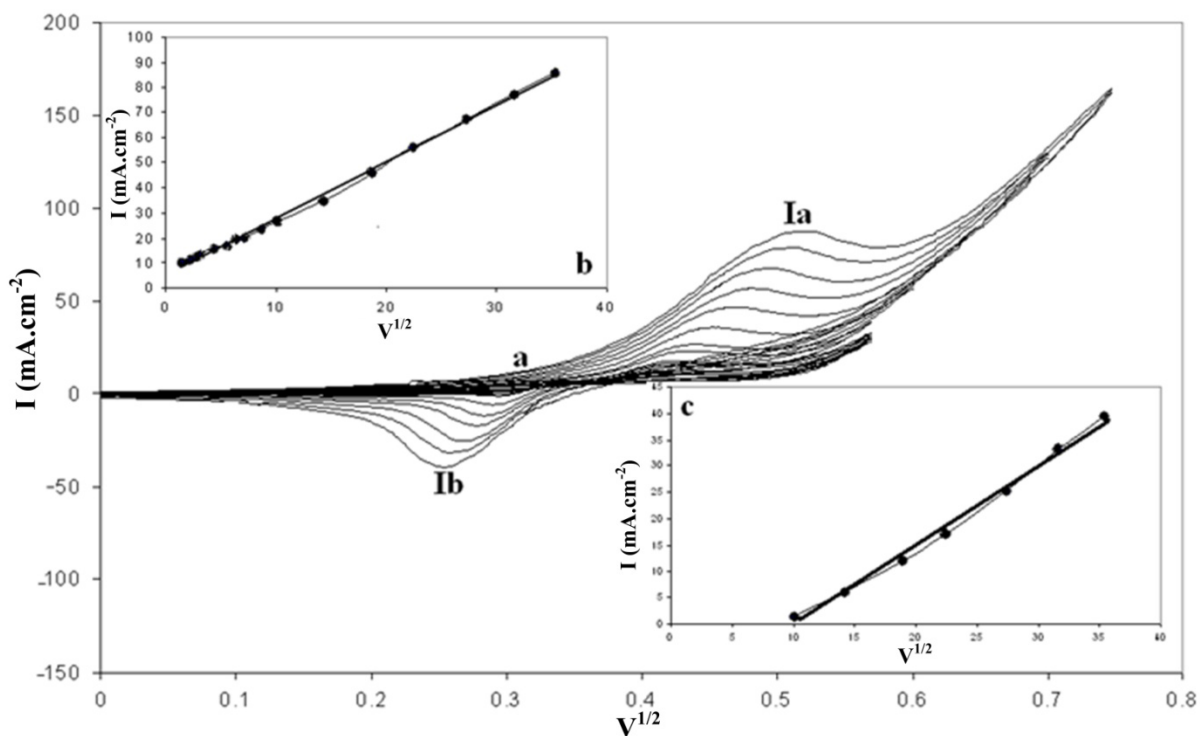

Figure 5: (a) Typical cyclic voltamograms of the Ni/NiOOH in1 M NaOH in the presence of 0.5 mM paracetamol at various potential sweep rates of 2, 5, 7, 10, 20, 30, 40, 50, 75, 100, 200, 350, 500, 750, 1000, 1250, and 1500 mVs^{-1}; (b) the dependence of anodic peak current during the forward sweep on the square roots of sweep rate; (c) the anodic current function ($I/v^{1/2}$) vs. potential sweep rate v
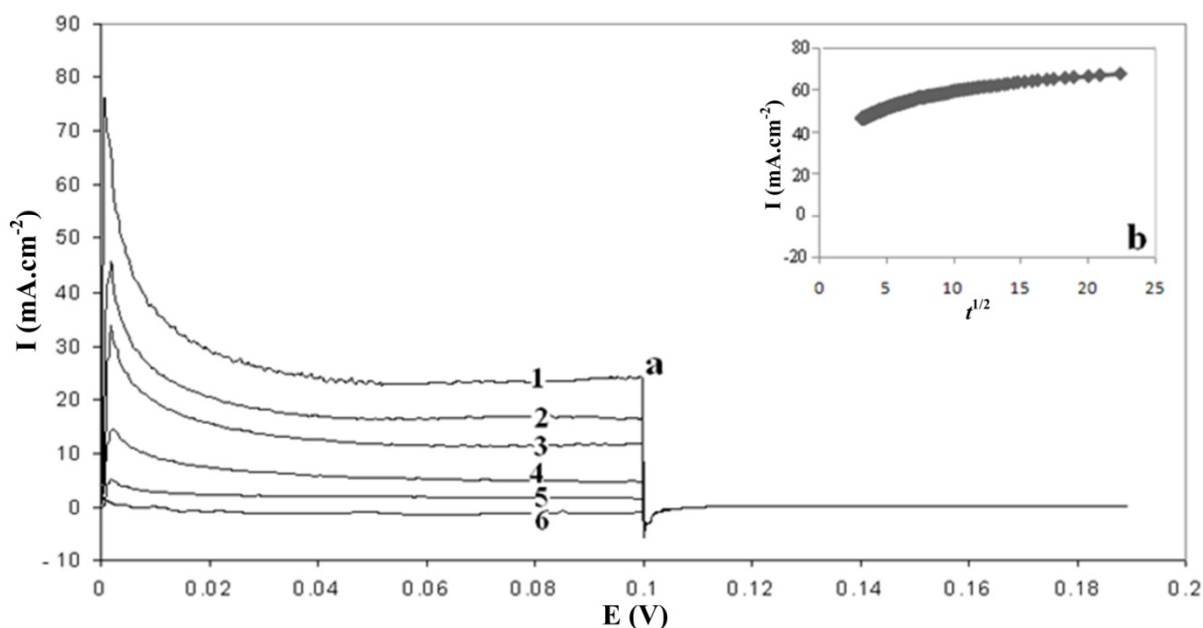
Figure 6: (a) Double steps chronoamperograms of Ni/NiOOH electrode in 1 M NaOH solution with different concentrations of paracetamol of: (1) 0 M, (2) 0.1 M, (3) 0.3 M, (4) 0.5 M, (5) 0.7M, and (6) 0.9 M; potential steps were 400 mV and 200 mV respectively; (b) the dependency of transient current on $t^{1/2}$.
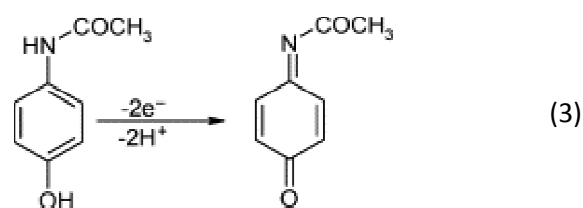
By using Cottrell equation [30] and the slop of I_p versus $t^{-1/2}$, the diffusion coefficient of paracetamol was obtained to be around 5×10^{-7} cm^2.s^{-1}.

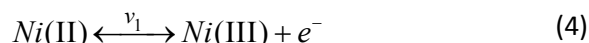$$I = nFAD^{1/2}C \times \pi^{-1/2}t^{-1/2} \qquad (2)$$

The irreversibility of paracetamol oxidation process was proved by the negligible current obtained at 300 mV potential.

A number of mechanisms have been proposed for the electro-oxidation of alcohols on Ni in alkaline solutions. While Fleischmann et al. [16, 31] assumed a catalytic/intermediate role for NiOOH, others [10] reported the methanol oxidation after the conversion of Ni(OH)$_2$ to NiOOH in the course of reaction at anodic scan rates. Vertes and Horanyi [32] criticized Fleischmann mechanism and gave rise to the doubts on the role of NiOOH as an electrocatalyst. In their research, a new oxidation peak for the alcohol at a potential much more positive than the oxidation potential of Ni(OH)$_2$ was obtained; however, the redox peaks were unchanged. Appearance of a new oxidation peak at a more positive potential than the oxidation potential of Ni(OH)$_2$ is due to the elimination of
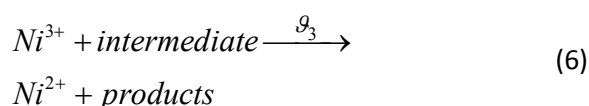
methanol oxidation on the surface of oxide layer. This mechanism is accompanied by the oxidation of paracetamol on the G/Ni electrode.

$$(3)$$

The redox transition of nickel species available in the film is given by:

$$Ni(\text{II}) \xleftrightarrow{v_1} Ni(\text{III}) + e^- \qquad (4)$$

Then, methanol is oxidized on the modified surface via the following reaction

$$Ni^{3+} + acetaminophen \xrightarrow{\vartheta_4} \\ Ni^{3+} - intermediate + e \qquad (5)$$

$$Ni^{3+} + intermediate \xrightarrow{\vartheta_3} \\ Ni^{2+} + products \qquad (6)$$

where, Ni^{3+} sites are regenerated by the power source and on the Ni^{3+} oxide surface by direct electro-oxidation:

$$Ni^{3+} + acetaminophen \xrightarrow{\vartheta_2}$$
$$Ni^{2+} + intermediate$$

(7)

$$Ni^{3+} - intermediate \xrightarrow{\vartheta_5}$$
$$Ni^{3+} + products + e$$

(8)

Equations (5) and (6) are according to Fleischmann mechanism and in Equations (7) and (8), Ni^{3+} is used as the active surface for methanol oxidation.

Methanol oxidation occurs at a more positive potential than the oxidation of $Ni(OH)_2$ according to Equations (7) and (8). The above equation of the Faradic current density can be written as:

$$I_F = (v_1 + v_4 + v_5)F$$

(9)

Figure 7 shows the Nyquist diagrams of Ni/NiOOH electrode at the oxidation peak potential as dc-offset for some selected concentrations of paracetamol. The Nyquist diagrams consisted of two slightly depressed overlapping capacitive semicircles in the high and low frequency sides of the spectrum. While the depressed semicircle in the high frequency region can be related to the combination of charge transfer resistance and the double layer capacitance, the low frequency semicircle is attributed to the adsorption of reaction intermediate on the electrode surface. The equivalent circuit, corresponding to the Nyquist diagram in the presence of paracetamol, was depicted in Figure 8.

To obtain a satisfactory impedance simulation of paracetamol electro-oxidation, it is necessary to replace the capacitor *C* with a constant phase element (*CPE*), *Q*, in the equivalent circuit. The most widely accepted explanation for the presence of *CPE* behavior and depressed semicircles on solid electrodes is the microscopic roughness which causes an inhomogeneous distribution in the solution resistance as well as in the double-layer capacitance [33].
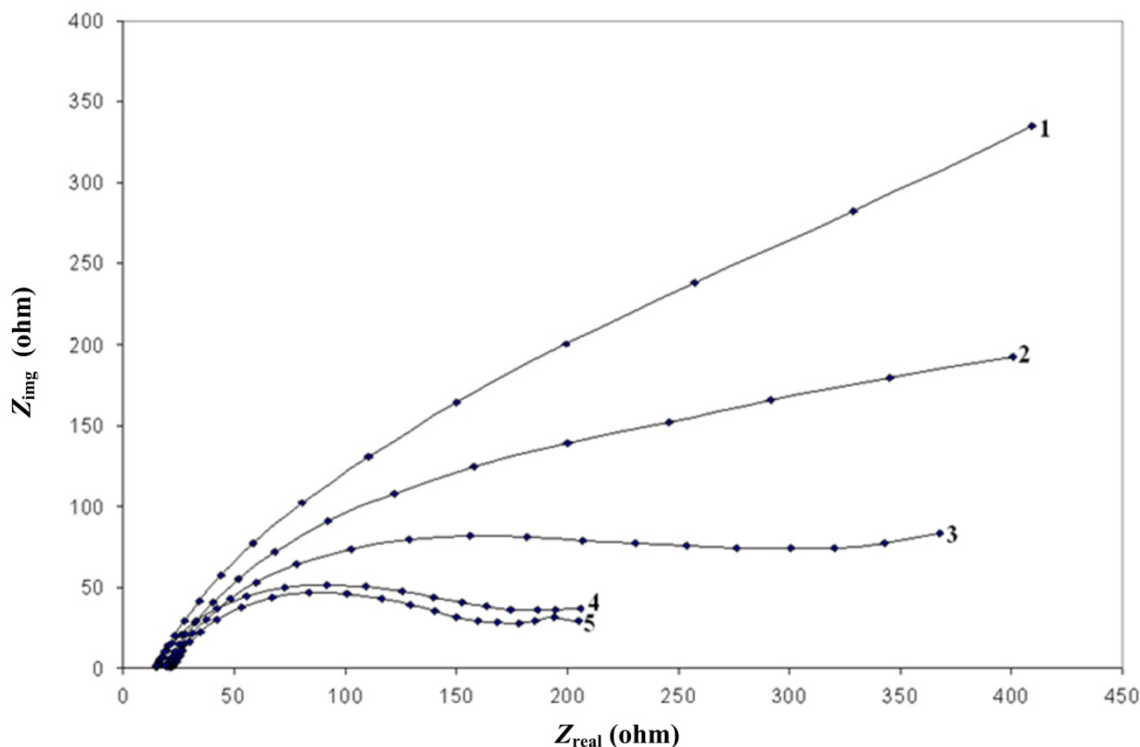

Figure 7: Nyquist diagrams of Ni/NiOOH electrode at different concentrations of paracetamol in 1 M NaOH: (1) 0.1 M, (2) 0.3 M, (3) 0.5 M, (4) 0.7 M, and (5) 0.9 M; DC potential is 450 mV/Ag,AgCl

In this electrical equivalent circuit, R_s, CPE_{dl}, and R_{ct} represent solution resistance, a constant phase element corresponding to the double-layer capacitance, and the charge transfer resistance respectively. CPE_{ads} and R_{ads} are the electrical elements related to the adsorption of reaction intermediates. In this circuit, the charge transfer resistance of the electrode reaction has a simple physical meaning and indicates how fast charge transfer occurs during methanol electro-oxidation at the surface of the electrode.

At a low applied overpotential, the current density of oxidation processes is related to Ni^{2+}/Ni^{3+} redox couple in the presence of paracetamol oxidation and can be given by Equations (7) and (8).
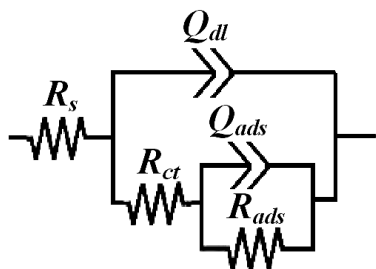

Figure 8: Equivalent circuits compatible with the Nyquist diagrams in Figure 7 for paracetamol electro-oxidation on Ni/NiOOH electrode

In the above sequence of reactions, Equations (3) to (5), k_1 and k_{-1} are obviously potential dependent rate constants and are of the forms of:

$$k_1(E) = k_1^o \exp\left[\frac{\alpha nF(E - E^o)}{RT}\right] \tag{10}$$

$$k_{-1}(E) = k_{-1}^o \exp\left[\frac{(\alpha - 1)nF(E - E^o)}{RT}\right] \tag{11}$$

where, k^o's are the chemical rate constants measured at the equilibrium potential; α is the anodic symmetry factor and the other parameters have their usual definitions as previously defined. The rate equations for the reactions (3) to (5) have the forms of:

$$v_1 = k_1 \Gamma \theta_{II} - K_{-1} \Gamma \theta_{III} \tag{12}$$

$$v_2 = k_2 \Gamma \theta_{III} C* \tag{13}$$

where, Γ is the total number of adsorption sites per unit area of the electrode surface; ϑ's represent the fractional coverage's of different nickel valence states and $C*$ is the bulk concentration of methanol. If the (II) and (III) valence states of nickel meet the below condition:

$$\theta_{II} + \theta_{III} = 1 \tag{14}$$

And if the rates of changes of their coverage as well as the rate of the intermediate compounds satisfy:

$$\frac{d\theta_{II}}{dt} = -\frac{d\theta_{III}}{dt} = \\ -k_1\theta_{II} + k_{-1}\theta_{III} + k_2\theta_{III}C* + k_3\theta_{III}C_i \tag{15}$$

$$\frac{dC_i}{dt} = k_2\theta_{III}C* - k_3\theta_{III}C_i \tag{16}$$

where, C_i is the concentration of the intermediate.

And, by assuming that the steady state approximations dominate, one may obtain:

$$\frac{d\theta_{II}}{dt} = -\frac{d\theta_{III}}{dt} = 0 \tag{17}$$

$$\frac{dC_i}{dt} = 0 \tag{18}$$

One arrives at the values of the coverage:

$$\theta_{II} = \frac{(k_{-1} + 2k_2C*)}{(k_1 + k_{-1} + 2k_2C*)} \tag{19}$$

$$\theta_{III} = \frac{k_1}{(k_1 + k_{-1} + 2k_2C*)} \tag{20}$$

On the basis of this rate equation, the faradic current will be:

$$i_f = \frac{2FAk_1\Gamma k_2C*}{(k_1 + k_{-1} + 2k_2C*)} \tag{21}$$

where, A is the surface area of the electrode and

the corresponding charge transfer resistance is given by:

$$R_{ct} = \left(\frac{di_f}{dE}\right)^{-1} =$$

$$\frac{(k_1 + k_{-1} + 2k_2C^*)^2}{\left[2FA\Gamma k_2C^*k_1\left(\frac{2\alpha Fk_2C^*}{RT} + \frac{k_{-1}F}{RT}\right)\right]} \quad (22)$$

The dependence of R_{ct} on the paracetamol concentration is presented in Figure 9, where an initial sharp drop is terminated with a plateau as the concentration of paracetamol reaches 9 mM. The results are further fitted to Equation (22) to estimate the values of the rate constants. From Equation (22), the values of the rate constants as $k_1 = 2.4 \times 10^{-5}$, $k_{-1} = 6 \times 10^{-3}$, and $k_2 = 3 \times 10^{-3}$ cm^{3}mol^{-1}s^{-1} are calculated.

CONCLUSIONS

The nickel oxide film was prepared electrochemically on electrodeposited nickel in cyclic voltammetry regime and tested for the electro-oxidation of paracetamol in alkaline media. The modified electrodes showed high electrocatalytic activity for the oxidation of paracetamol around 400 mV/Ag.AgCl. Moreover, the results showed an effective response of paracetamol electro-oxidation at the Ni/NiOOH modified electrode. The anodic peak currents for paracetamol oxidation at Ni/NiOOH were linearly proportional to the square root of scan rate. The double-step chronoamperograms of Ni/NiOOH in the presence of paracetamol showed an irreversible process and the dominance of a diffusion-controlled process. The diffusion coefficient of paracetamol was obtained to be 3×10^{-6} cm^2.s^{-1}. The methods of cyclic voltammetry (CV), chronoamperometry (CA), and impedance spectroscopy (EIS) were used to determine kinetic parameters such as transfer coefficient (α), the catalytic reaction rate constants (k), and the diffusion coefficient of paracetamol in the
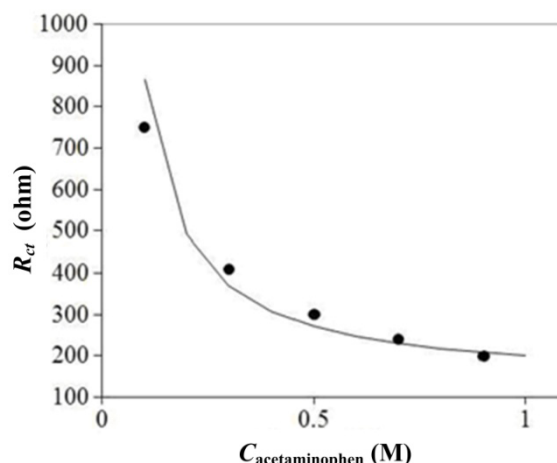
bulk of solution.

Figure 9: The dependence of experimental R_{ct} (•) on paracetamol concentration derived from the data of Nyquist diagrams

ACKNOWLEDGEMENTS

NOMENCLATURE

A : Electrocatalytic activity [mV/reference electrode]

Ag/AgCl : Reference electrode

CA : Chronoamperometry

CV : Cyclic voltammetry

D : Diffusion coefficient [cm^2.s^{-1}]

E : Potencial [volt]

EIS : Electrochemical impedance spectroscopy

F : Faraday constant [9.648x10^4 C/mol]

K : Kelvin (Temperature unit)

k : Catalytic reaction rate constants [cm^3.mol^{-1}.s^{-1}]

R : Ideal gas constant [8.314 J.mol^{-1}.K^{-1}]

R_{tc} : Charge transfer resistance [Ω]

α : Transfer coefficient

Γ* : Surface coverage [mol.cm^{-2}]

REFERENCES

[1] Ameer B., Greenblatt J., "Pharmacological Review of Paracetamol (Paracetamol)", *Ann. Int. Med*. **1974**, 87, 202-2098.

[2] Palgarin J., Bermejo L.; "Flow-injection Stopped-flow Spectrofluorimetric Kinetic Determination of Paracetamol Based on its Oxidation Reaction by Hexacyanoferrate (III)", *Anal. Chim. Acta*. **1996**, 333, 59-69.

[3] Canada M., Reguera P., Ruiz Medina A., "Fast Determination of Paracetamol by Using a Very Simple Photometric Flow-through Sensing Device", *Pharm J. Biomed. Anal.* **2000**, 22, 59-68.

[4] Ramos M., Tyson J., Curran D., "Determination of Acetaminophen by Flow Injection with On-line Chemical Derivatiza-tion: Investigations Using Visible and FT IR Spectrophotometry", *Anal. Chim. Acta* . **1998**, 364, 107-114.

[5] Li M. Jing L., "Electrochemical Behavior of Acetaminophen and its Detection on the PANI-MWCNTs Composite Modified Electrode", *Electrochim. Acta*. **2007**, 52 3250-3256.

[6] Wan Q., Wang X., Yu F., Wang X., Yang N., "Effects of Capacitance and Resistance of MWNT-film Coated Electrodes on Voltam-metric Detection of Acetamino-phen.", *Appl J. Electrochem*. **2009**, 39, 1145-1151.

[7] Sebastian G., Dimitrios K., Kampourisa, Rashid O. K., and Craig E. B., "A Critical Review of the Electro-catalysis Reported at C60 modified electrodes", *Electroanalysis*, **2008**, 20, 1507-1513.

[8] Antolini E., "Formation of Carbon-supported PtM Alloys for Low Temperature Fuel Cells: A Review", *Mater. Chem. Phys*. **2003**, 78, 563-573.

[9] Park K., Choi J., Kwon B., Lee S., Sung Y., Ha H., Hong S., Kim H., Wieckowski A., "Chemical and Electronic Effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy Nanoparticles in Methanol Electrooxidation", *J. Phys. Chem*. **2002**, 106, 1869-1877.

[10] Taraszewska J., Roslonek G., "Electro-catalytic Oxidation of Methanol on a Glassy Carbon Electrode Modified by Nickel Hydroxide Formed by Ex Situ Chemical Precipitation", *J. Electroanal. Chem*. **1994**, 364, 209-213.

[11] Wen T., Lin S., Tsai J., "Sulphur content and the hydrogen evolving activity of NiS_x deposits using statistical experimental strategies", *J. Appl. Electrochem*. **1994**, 24, 233-238.

[12] Fan C., Piron D., Sleb A., Paradis P., "Study of Electrodeposited Nickel-Molybdenum, Nickel-Tungsten, Cobalt-Molybdenum, and Cobalt-Tungsten as Hydrogen Electrodes in Alkaline Water Electrolysis", *J. Electrochem. Soc.* **1994**, 141, 382-387.

[13] Raj I., Vasu K., "Transition metal-based hydrogen electrodes in alkaline solution-electrocatalysis on nickel based binary alloy coatings", *J. Appl. Electrochem*. **1990**, 20, 32-38.

[14] Casadei M. A., Pletcher D., "The influence of conditions on the electrocatalytic hydro-genation of organic molecules", Electro-chim. Acta. **1988**, 33, 117-120.

[15] Berchmans S., Gomathi H., Prabhakara Rao G.," Electrooxidation of alcohols and sugars catalysed on a nickel oxide modified glassy carbon electrode", *J. Electroanal. Chem*. . **1995**, 394, 267-270.

[16] Fleischmann M, Korinek K, Pletcher D; "The oxidation of organic compounds at a nickel anode in alkaline solution"; *J. Electroanal. Chem*. **1971**, 31, 39-49.

[17] Van Effen R. M., Evans D. H., "A study of aldehyde oxidation at glassy carbon, mercury, copper, silver, gold and nickel anodes", *J. Electroanal. Chem*. **1979**, 103, 383-397.

[18] Motheo A. J., Machado S., Rabelo F., Santos Jr. J., "Electrochemical Study of Ethanol Oxidation on Nickel in Alkaline Media", *J. Braz. Chem. Soc*. **1994**, 5, 161-165.

[19] Marioli J. M., Luo P., Kuwana T., "Nickel-chromium Alloy Electrode as a Carbohydrate Detector for Liquid Chromatography", *Anal. Chim. Acta*. **1993**, 282, 571-580.

[20] Marioli J. M., Kuwana T., "Electrochemical Detection of Carbohydrates at Nickel-

copper and Nickel-chromium-iron Alloy Electrodes", *Electroanalysis*. **1993**, 5, 11-15.

[21] Trasatti S., "Electrodes of Conductive Metallic Oxides: Part B", *Elsevier, New York*, **1980.**

[22] Khulbe K. C., Mann R. S., Manoogian A., "Behavior of Nickel-copper Alloy in Hydrogenation, orthohydrogen-parahydrogen Conversion and H_2-D_2 Exchange Reaction", *Chem. Rev.* **1980**, 80, 417-428.

[23] El-Shafei A. A., "Electrocatalytic Oxidation of Methanol at a Nickel Hydroxide/Glassy Carbon Modified Electrode in Alkaline Medium", *J. Electroanal. Chem*. **1999**, 471 89-95.

[24] Briggs G., Snodin P. R., "Ageing and the Diffusion Process at the Nickel Hydroxide Electrode", *Electrochim. Acta*. **1982**, 27, 565-572.

[25] Hahn F., Beden B., Croissant M., Lamy C., "In Situ UV Visible Reflectance Spectroscopic Investigation of the Nickel Electrode-alkaline Solution Interface", *Electrochim. Acta*. **1986**, 31, 335-342.

[26] Desilvestro J., Corrigan D., Weaver M., "Characterization of Redox States of Nickel Hydroxide Film Electrodes by In Situ Surface Raman Spectroscopy", *J. Electrochem. Soc*. **1988**, 135, 885-892.

[27] Barnard R., Randell C., "Studies Concerning Charged Nickel Hydroxide Electrodes. VII. Influence of Alkali Concentration on Anodic Peak Positions", *J. Appl. Electrochem*. **1983**, 13, 89-95.

[28] Bard A., Faulkner L., "Electrochemical Methods"; *Wiley New York*. **2001**, 591.

[29] Danaee I**.**, Jafarian M., Forouzandeh F., Gobal F., Mahjani M.G., *International Journal of Hydrogen Energy*. January **2009**, 34, 859-869

[30] Khulbe K., Mann R., Manoogian A., "Behavior of Nickel-copper Alloy in Hydrogenation, Orthohydrogen-parahydrogen Conversion and H_2-D_2 Exchange Reaction", *Chem. Rev*. **1980**, 80, 417-428.

[30] Fleischmann M., Korinek K., Pletcher D., "The Kinetics and Mechanism of the Oxidation of Amines and Alcohols at Oxide-covered Nickel, Silver, Copper, and Cobalt Electrodes"**,** *J. Chem. Soc., Perkin Trans*. **1972**, 2, 1396-1402.

[31] Bard A., Faulkner L., "Electrochemical Methods, Fundamentals and Applications"; *Chap. 5. Wiley, New York*. **2001**, 209.

[32] Vertes, G., Horanyi, G., Nagy, F., "A New Method for the Electrochemical Oxidation of Alcohols", *Tetrahedron*. **1972**, 28, 37-42.

[33] Losada J., del Peso I., Beyer L. J., "Redox and Electrocatalytic Properties of Electrodes Modified by Films of Polypyrrole Nickel(II) Schiff-base Complexes", *J. Electoanal. Chem*. **1998**, 447, 147-154.