ELECTROCHEMICAL BEHAVIOUR OF NICKEL
IN AQUEOUS ACETIC ACID SOLUTIONS

Gabriela Elena BADEA[a] and Teodora BADEA[b*]

[a] University of Oradea, Universității 1, 410087 Oradea, Roumania
[b] "Politehnica" University, Calea Griviței 132, 060032 Bucharest, Roumania.

Anodic, cathodic and potential-time studies for Ni in aqueous acetic acid solutions of various concentrations – 0.5, 1.5, 3, 5, 7, 10 and 13 M – have been made by potentiostatic method. Ni shown active-passive transition in acetic acid solutions of concentration 0.5 – 5 and 13 M. In the solution of concentration 7 M and 10 M CH_3COOH, the anodic curves were different, presenting either a continuous increase either an oscillating current. The corrosion of Ni in acid acetic solutions is controlled by the diffusion of the dissolved oxygen at the interface metal/solution. The evolution hydrogen reaction has an insignificant roll in the Ni corrosion. The open circuit potentials after 24 hours of immersion in all acetic acid solutions have shown active values and therefore the spontaneous passivation of Ni is not possible.

INTRODUCTION

The organic acids are used in the industrial synthesis and in the processing of the metallic surfaces. However, the experimental data dedicated to the corrosion resistance of the metals and alloys and the corrosion mechanism in organic acid solutions are less yet.

Electrochemical behaviour of nickel in inorganic aqueous acid solutions made subject of many works,[1-6] but there are less studies devoted to organic acid solutions.[7-10]

The nickel corrosion behaviour in aqueous solutions is characterized by a pronounced tendency to passivation. Therefore, the anodic polarization measurement in potentiostatic conditions, including the passivation potential, the critical current density of passivation and the passive current density are very important for the estimation of the corrosion resistance.

The anodic polarization curve gives the information on the anodic dissolution rate, on the active-passive transition, on the passive state stability and on the metal's behaviour in oxidant medium. To characterize the corrosion of the metallic materials in active state, the cathodic polarization curve becomes essential.

This work is devoted to the investigation of the anodic and cathodic behaviour and of the time dependence of the corrosion potential for Ni in aqueous acetic acid solutions of various concentrations, between 0.5 and 13 M CH_3COOH.

EXPERIMENTAL

The anodic and catodic potentiostatic polarisation curves were recorded for Ni in the aqueous acetic acid solutions, having concentrations: 0.5, 1.5, 3, 5, 7, 10 and 13 M.

For the potentiostatic polarisation measurements a three-electrode glass cell was used. The working electrode was a sheet of nickel of 99.9% purity with geometrical area of 2 cm^2. The electrode assembly was made of Teflon. The electrode surface was polished successively with 1000 and 1200-grade emery papers, washed with acetone, rinsed with distilled water and electrochemical polished in sulphuric acid solution for 1 minute, followed by washing with double distilled water. The counter electrode was a platinum sheet with an area of 4 cm^2. The reference electrode was a saturated calomel electrode (SCE).

The polarization measurements were made with a PS2 potentiostat, using stepwise technique of 40 mV/60 s.

The solutions were prepared using chemically pure reagents and double distilled water. All measurements were made at room temperature (23 ± 1^oC).

RESULTS AND DISCUSSION

The anodic behavior of Ni in aqueous acetic solutions of various concentrations is shown in Fig. 1. The shape of the Ni anodic curves is

* Corresponding author: badea_t@yahoo.com

different, depending on the concentration domain of the acetic acid solutions. The anodic polarization curves obtained in the solutions of 0.5-5 M CH₃COOH, show the common allure of one passivation curve for metals presenting active/passive transition. The corresponding electrochemical parameters are presented in Table 1.

At concentrations $\leq$ 3 M CH₃COOH, the passivation potential, E_p, has the same value of 0.120 V/SCE. In solution of 5 M CH₃COOH, the domain of active-passive transition is lager, extending on 200 mV and on it can be observed two peaks and a minimum. The peak current density (i_{cr}) and passive current density (i_p) increase with acetic acid concentration, reach a maximum value in the solution of 3 M CH₃COOH, after that they decrease. Comparing the values of the i_{cr} and i_p obtained in this study with those reported for anodic behaviour of Ni in 0.5 M H₂SO₄ solution[6] and in HCOOH solutions of different concentrations[8] it has been found the followings: in acetic acid solutions, i_{cr} is smaller with over one magnitude order that pleads for less aggressiveness of the acetic acid solutions; i_p has practical the same value and this means that the passive film has the same chemical nature.

In the domain of the lager concentrations – 7 and 10 M CH₃COOH – the shape of the anodic polarisation curves are different from a classical passivation curve. Thus, in acetic acid solution of 7 M concentration, at the beginning of the anodic polarisation curve, the current increases, reaches a maximum value at 0.040 V/SCE and after a minimum value at 0.200 V/SCE it increases continuously, but without reaching high values, even at 1.4 V/SCE.

At the concentration of 10 M CH₃COOH, the anodic curve of Ni shows more maximum and minimum of current, extending on all potential domain, the currents varying between 82 and 42 μA.cm⁻². In the solution of 13 M CH₃COOH, the anodic curve of Ni shows a similar shape with the obtained in 5 M CH₃COOH solution, but in different parameters: the active-passive transition domain is extended on 400 mV, the passive current density is of twice more and a limiting current appears in the transpassive domain.

Fig. 2 shows the cathodic polarization curves for Ni in acetic acid solutions of various concentrations. Two cathodic reactions must be taken in consideration: reduction of the dissolved oxygen and reduction of the hydrogen ion. The oxygen reduction reaction is controlled by diffusion polarization, being accompanied by a limiting current, which varies about value of 40 μA.cm⁻².

The hydrogen evolution reaction starts at potential values $<$ – 500 mV/SCE. In the potential domain of the hydrogen evolution reaction, the cathodic curves show a mixed control, of charge transfer and of mass transfer. The Tafel domain and a limiting current depend of acetic acid concentration. In Fig. 3 are shown the Tafel lines for hydrogen evolution reaction in 0.5-5 M CH₃COOH solutions. In Table 2 are presented the electrochemical corrosion parameters of Ni deduced from the cathodic polarization curves and potential –time dependence.

Conform to the data presented in Table 2, the acetic acid concentration has a relative small influence on electrochemical corrosion parameters of Ni. The open circuit potential (corrosion potential), measured after 15 minute of Ni immersion ($E_{0.4}$) has nearly the same value, excepting the values corresponding to the solutions of 3 and 5 M CH₃COOH, in which it is more active with about 40-50 mV. After 24 hours of immersion, the open circuit potential (E_{24}) of Ni shifts to positive values with about 40-80 mV, but it remains in active domain in all studied solutions. Therefore, the spontaneous passivation of Ni in acetic acid solutions in presence of dissolved oxygen it is not possible.

The Tafel slopes have high values and enough close, varying in limit of 10 mV. The charge transfer coefficient is less than 0.5, pleading for involving of some adsorption processes in the hydrogen evolution reaction.

The corrosion currents (i_{cor}) calculated from extrapolation of the Tafel line with the open circuit potential ($E_{0.4}$) has small values, being $<$ 1 μA.cm⁻². But in presence of the dissolved oxygen Ni corrosion with hydrogen depolarization is not probable, because the hydrogen evolution reaction starts at a potential with about 400 V more negative than corrosion potential, value which can not reach without polarization from extern current source.

The nickel behaves as a typical active-passive metal in many solutions and conforms to the results obtained and in aqueous diluted solutions of acetic acid (0.5-5 M CH₃COOH). The results may be explained on the basis of literature data concerning to the mechanism of the nickel dissolution and passivation.[3, 7, 11, 12]

Table 1

The electrochemical passivation parameters of Ni in 0.5 - 5 M CH₃COOH
and conductivity (λ) of the solutions

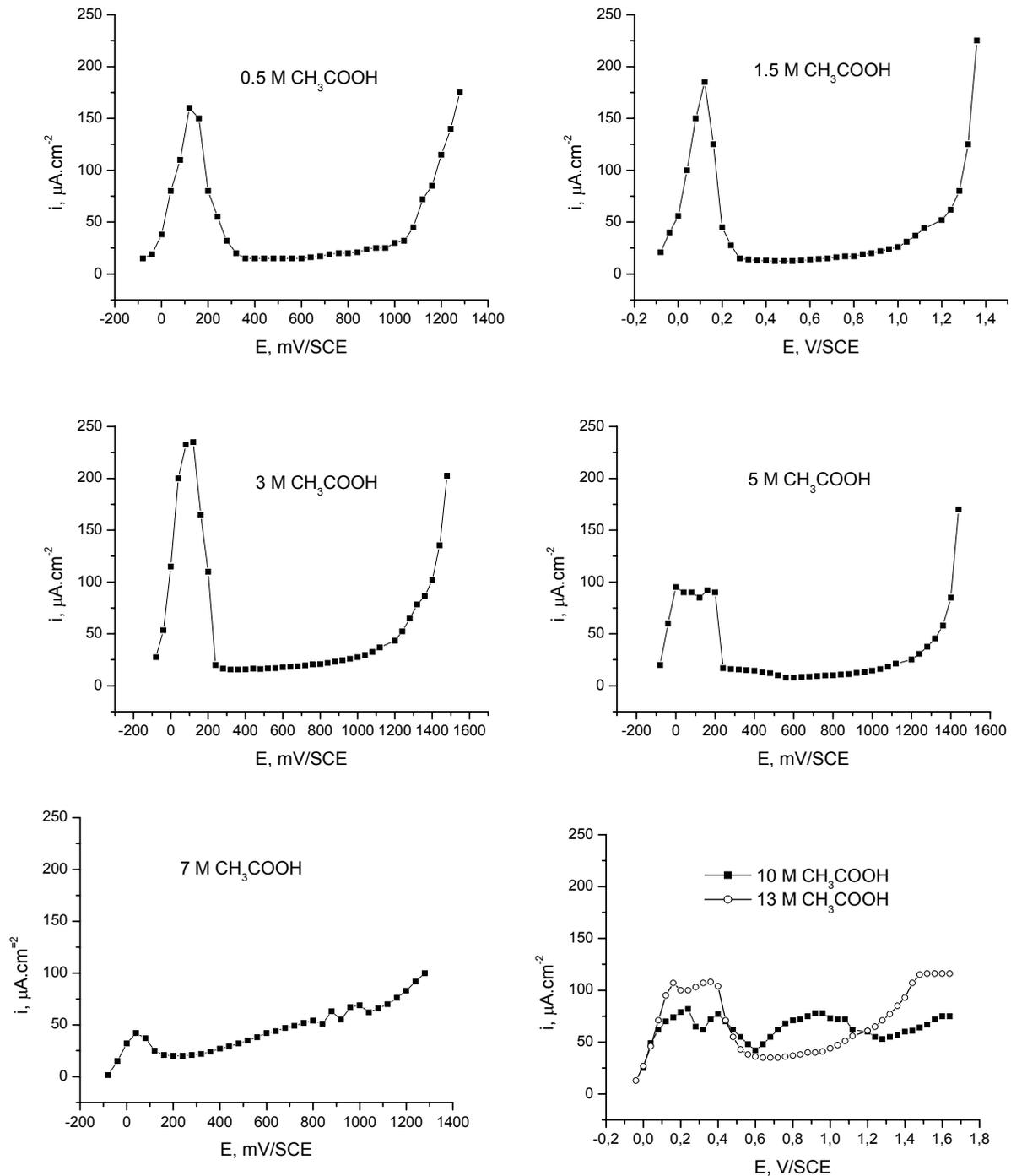| Parameter	Concentration of CH₃COOH			
	0.5 M	1.5 M	3 M	5 M
E_p, V/SCE	0.120	0.120	0.120	0.200
i_{cr}, $\mu A.cm^{-2}$	160	185	235	90
$^1 i_p$, $\mu A.cm^{-2}$	11	14	18	8
$\lambda.10^3.\Omega^{-1}cm^{-1}$	1.20	1.32	1.66	1.35

[1] The passive current density at 0.6 V/SCE.

Fig. 1 – Anodic potentiostatic polarization curves of the Ni electrode in acetic acid solutions of various concentration.
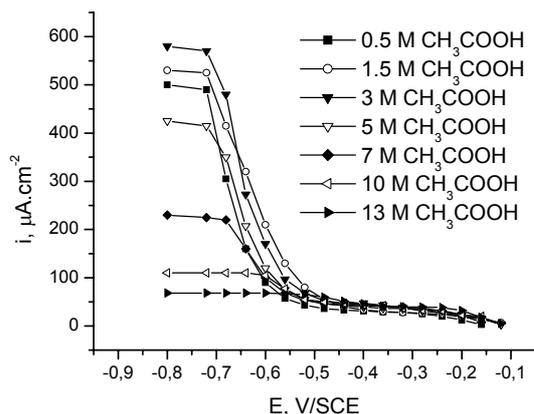
Fig. 2 – Cathodic polarization curves of the Ni electrode in acetic acid solutions of various concentrations.
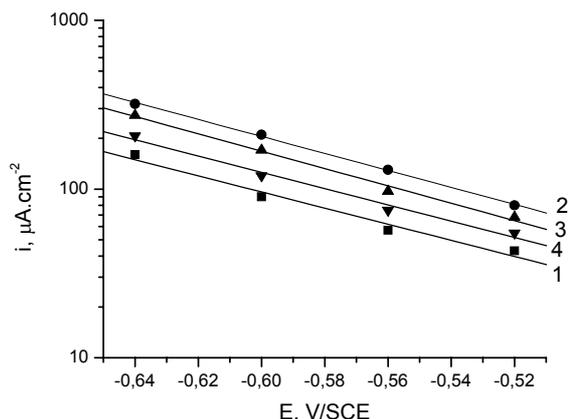

Fig. 3 – Tafel plots of the hydrogen evolution reaction on Ni electrode in acetic acid solutions of concentrations (M): 1 – 0.5; 2 – 1.5; 3 – 3; 4 – 5.

Table 2

The electrochemical parameters deduced from cathodic polarization curves of Ni electrode
in acetic acid solutions of various concentrations

Parameter	Concentration of CH_3COOH						
	0.5 M	1.5 M	3 M	5 M	7 M	10 M	13 M
$^1E_{0.4}$, V/SCE	−0.082	−0.095	−0.133	−0.120	−0.085	−0.075	−0.081
b_c, V.decade^{-1}	−0.209	−0.198	−0.194	−0.207	-	-	-
α	0.28	0.30	0.33	0.28			
$^2i_{cor}$, $\mu A.cm^{-2}$	0.32	0.59	0.69	0.61	-	-	-
i_{L,H_2}, $\mu A.cm^{-2}$	525	810	480	425	225	110	68
i_{D,O_2}, $\mu A.cm^{-2}$	33	40	45	42	43	42	40
$^3E_{24}$, V/SCE	−0.043	−0.045	−0.050	−0.045	−0.045	−0.051	−0.089

[1,3] Open circuit potential of Ni after 15', respectively 24 h of immersion in solution;
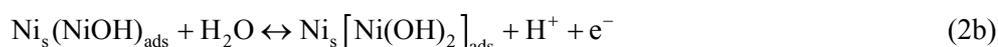[2] Corrosion current corresponding to the hydrogen evolution as cathodic reaction

At the anodic polarization of nickel in aqueous solutions, on his surface have take place the successive, simultaneous and concurrent reactions.

These may lead to the dissolution or passivation of nickel, conform to the following mechanism:[7]

1. Nickel dissolution:

$$Ni + H_2O = Ni_s(NiOH)_{ads} + H^+ + e^- \tag{1.a}$$

$$(NiOH)_{ads} \rightarrow NiOH^+ + e^- \tag{1.b}$$

$$NiOH^+ + H^+ \leftrightarrow Ni^{2+} + H_2O \tag{1c}$$

$$Ni \rightarrow Ni^{2+} + 2e \tag{1}$$

2. Nickel passivation:

$$Ni + H_2O = Ni_s(NiOH)_{ads} + H^+ + e^- \tag{2a}$$

$$Ni_s(NiOH)_{ads} + H_2O \leftrightarrow Ni_s\left[Ni(OH)_2\right]_{ads} + H^+ + e^- \tag{2b}$$

$$Ni_s\left[Ni(OH)_2\right]_{ads} \rightarrow Ni_sNiO + H_2O \tag{2c}$$

$$Ni + H_2O \rightarrow Ni_sNiO + 2H^+ + 2e^- \tag{2}$$
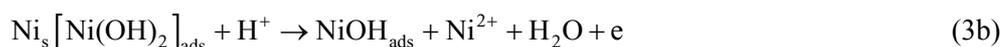
The components of the $CH_3COOH-H_2O$ system there are in two states: free and bound as hydrate.[13] Free state predominates in the outside of the domain 20-80% CH_3COOH (i.e.~3-13 M)

Therefore, in solutions $\leq$ 3 M CH_3COOH, the formation of the species $NiOH_{ads}$ (reaction 2a) and $[Ni(OH)_2]_{ads}$ (reaction 2b) is facilitated by the existence of the free water molecules and when the passivation potential is reached Ni passes in passive state, in accord with reaction (2). This process is inhibited by the increase of the free ions resulted from the acid acetic dissociation, which interact with adsorbed nickel hydroxide, conform to the reactions:

$$Ni_s\left[Ni(OH)_2\right]_{ads} + CH_3COO^- \rightarrow Ni_s\left[NiCH_3COO\right]_{ads} + NiOH^+ + H_2O + e \qquad (3a)$$

$$Ni_s\left[Ni(OH)_2\right]_{ads} + H^+ \rightarrow NiOH_{ads} + Ni^{2+} + H_2O + e \qquad (3b)$$

The increase of the free ions concentration with acetic acid concentration in domain 0.5-3 M CH_3COOH, conform to the conductivity values (Table 1), explains the increase of the critical current density, in accord with reactions (3a) and (3b).

The formation of the adsorbed species $[NiCH_3COO]_{ads}$ in the potential domain of the anodic peak is sustained by the Fukuda and Aramata[14] study on adsorption/desorption of acetate anions on Pt electrode in acid medium ($HClO_4$). They reported a large peak of acetate adsorption/desorption on cyclic voltammogram between 0.1-0.2 V/SCE and suggest that process proceeds as a charge transfer process, conform to the reaction:

$$CH_3COO^- \rightarrow CH_3COO_{ads} + e \qquad (4)$$

At the concentrations $\geq$5 M CH_3COOH, the formation of the adsorbed hydroxide species (conform to the reaction 1a, 2a and 2b) is inhibited by the decrease of the free water molecules. This could explain the extension of the active-passive transition domain in 5 M CH_3COOH or limitation of the anodic reactions in more concentrated solutions of acetic acid.

The existence of the hydrate state, $CH_3COOH-H_2O$, in domain of the concentrations 20-80% CH3COOH, may be an explanation for different shape of the Ni anodic curves in solutions of 7 and 10 M CH_3COOH.

CONCLUSIONS

The electrochemical behavior of Ni in aqueous acetic acid solutions of various concentrations is characterized by the following: the active-passive transition is marked of a distinct peak, at the potential of 0.120 V/SCE in solutions of concentration $\leq$ 3 M CH_3COOH; in solution of 5 and 13 M CH_3COOH the transition domain is extended on 200 mV, respectively 400 mV. The open circuit potential of Ni after 15 min. and 24 hours of immersion is situated in active potential domain in all studied acetic acid solution. Ni corrosion in active state proceeds by oxygen depolarization, without participation of the hydrogen ions resulted from acetic acid dissociation; the moving of oxygen from acetic acid solutions could be a way of increase of the Ni corrosion resistance in acetic acid solutions.

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