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**The Corrosion Behaviour Of Cobalt And Nickel In Sulphuric  
Acid Solution Containing Propargylic Alcohol**

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27

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TURQUIE

# The Corrosion Behaviour Of Cobalt And Nickel In Sulphuric Acid Solution Containing Propargylic Alcohol

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## ABSTRACT

In this study, the corrosion behaviour of cobalt and nickel in 0.5 M  $H_2SO_4$  containing propargylic alcohol (PA) solutions was investigated. The current density-potential curves were obtained by using electrochemical potentiodynamic ( $1 \text{ mV.s}^{-1}$ ) and galvanostatic large and small signal pulse polarization techniques. Corrosion rates were determined by extrapolating the anodic Tafel lines and using potentiodynamic ( $1 \text{ mV.s}^{-1}$ ) and galvanostatic small signal pulse polarization techniques by applying the Stern-Geary equation. It has been observed that propargylic alcohol has a very good inhibiting effect on the corrosion of cobalt.

## 1. INTRODUCTION

The corrosion rates of metals and alloys can be determined by using different electrochemical and nonelectrochemical techniques<sup>1-3</sup>. In this study, the corrosion rates of cobalt and nickel were determined by the following methods.

1- Extrapolation of the anodic and cathodic Tafel lines of the current density-potential curves, determined by potentiodynamic ( $1 \text{ mV.s}^{-1}$ ) and galvanostatic large signal pulse polarization applied, to the corrosion potential.

2- Measurement of the polarization resistance was made under potentiodynamic ( $1 \text{ mV.s}^{-1}$ ) or galvanostatic small signal pulse polarization in the vicinity of the corrosion potential, using the Stern-Geary equation.

Propargylic alcohol (PA) was used as an inhibitor for pure iron and iron alloys in acidic media<sup>4-7</sup>. It was reduced on the analytically pure

iron, therefore it didn't have any inhibiting effect for this system<sup>2,3,8</sup>. But it was found that PA had a strong effect on the corrosion of pure iron and iron alloys<sup>1,4-7</sup>. For this reason it was found necessary to investigate the inhibiting effect of this substance on the corrosion of cobalt and nickel in the acidic media.

## 2. EXPERIMENTAL

The Co<sup>x</sup> or Ni<sup>xx</sup>/0.5M H<sub>2</sub>SO<sub>4</sub><sup>xxx</sup> + x mM PA<sup>xxxx</sup> system deaerated by purified hydrogen were investigated by the rotating discs technique at a rotation frequency of 60 rps.

The electrodes were polished with sand paper and washed with doubly distilled water. The solutions were also prepared by doubly distilled water. A Megaphysik multichannel pulse galvanostat system MPI-IM 400 was used for the creation of large and small signal pulse polarizations. The system responses were recorded by a Tectronix storage oscilloscope Type 549. All potentials were corrected for the ohmic drop and given against the standart hydrogen electrode.

## 3. EXPERIMENTAL RESULTS

a) The results obtained with cobalt samples

The current density-potential curves determined by the potentiodynamic (1 mV.s<sup>-1</sup>) and galvanostatic large pulse polarization techniques in the deaerated system for the cobalt specimens are given in Figs. 1 and 2, respectively. The curves were obtained by starting at  $E = E_{cor}$  and moving in anodic and cathodic directions. The corrosion rates determined by extrapolating the anodic and cathodic Tafel lines of those curves described above, to the corrosion potential, are given in Table 1 (column a and b).

Figs. 3 and 4 show the current density-potential curves of cobalt obtained by potentiodynamic (1 mV.s<sup>-1</sup>) and galvanostatic small sig-

x and xx: Materials Research, Marz grade, recrystallized under high vacuum at  $T = 1400^\circ$  K for 2h and cooled with a speed 150°K/h.

xxx : Merck, suprapure

xxxx : Freshly bidistilled

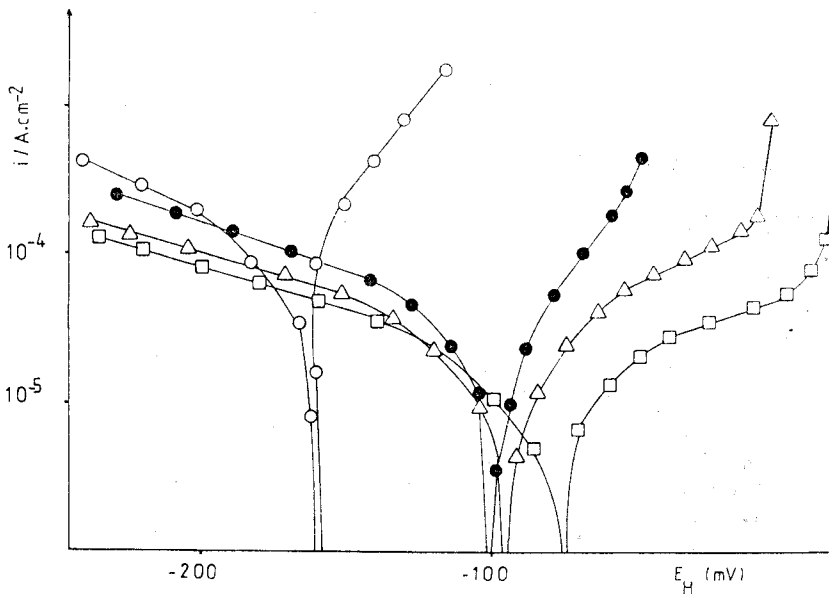


Fig. 1: Quasi-steady state current density-potential curves measured by potentiodynamic ( $|dE/dt| = 1 \text{ mV} \cdot \text{s}^{-1}$ ) technique.

System: Co (Marz)/0.5M  $\text{H}_2\text{SO}_4$  + x mM PA, deaerated,  $\nu = 60 \text{ rps}$ ,  $T = 298^\circ\text{K}$   
 $x = 0$  (○), 0.2 (●), 2.0 (△), 20.0 (■).

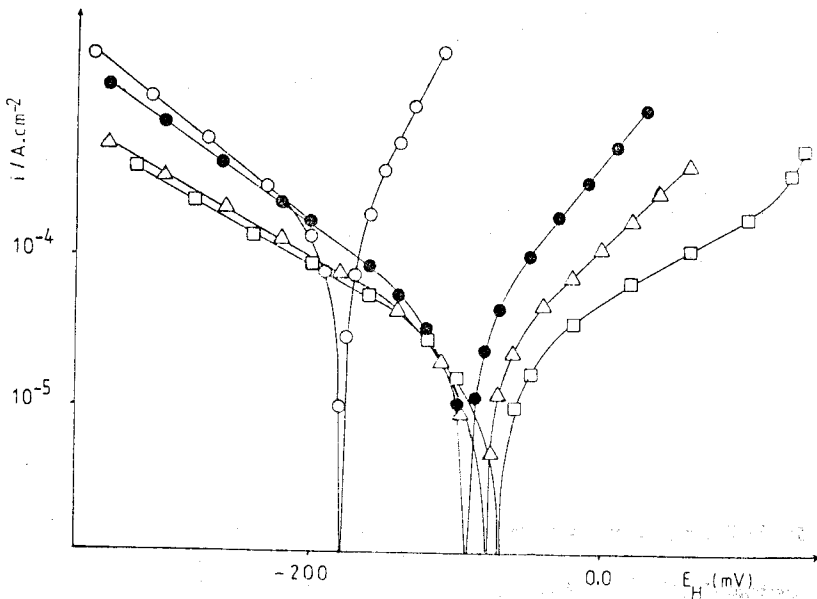


Fig. 2: Non-steady state current density-potential curves measured by galvanostatic large signal pulse polarization technique.

System: Co (Marz)/0.5 M  $\text{H}_2\text{SO}_4$  + x mM PA, deaerated,  $\nu = 60 \text{ rps}$ ,  $T = 298^\circ\text{K}$   
 $x = 0$  (○), 0.2 (●), 2.0 (△), 20.0 (■).

Table 1: Determination of Corrosion Rate ( $\text{mA}\cdot\text{cm}^{-2}$ )

System: Co (Marz)/0.5M  $\text{H}_2\text{SO}_4$  + x mM PA, deaerated,  $\nu = 60$  rps,  $T = 298^\circ\text{K}$   
Methods

x	a	b	c	d
0.0	0.12	0.15	0.27	0.15
0.2	0.03	0.03	0.07	0.04
2.0	0.03	0.03	0.08	0.03
20.0	0.02	0.02	0.06	0.03

- Extrapolation of anodic and cathodic current density-potential curves, potentiodynamic technique ( $|dE/dt| = 1 \text{ mV}\cdot\text{s}^{-1}$ ).
- Extrapolation of anodic and cathodic current density-potential curves, galvanostatic large signal pulse polarization technique.
- Determination of polarization resistance, potentiodynamic technique ( $|dE/dt| = 1 \text{ mV}\cdot\text{s}^{-1}$ ).
- Determination of polarization resistance, galvanostatic small signal pulse polarization technique.

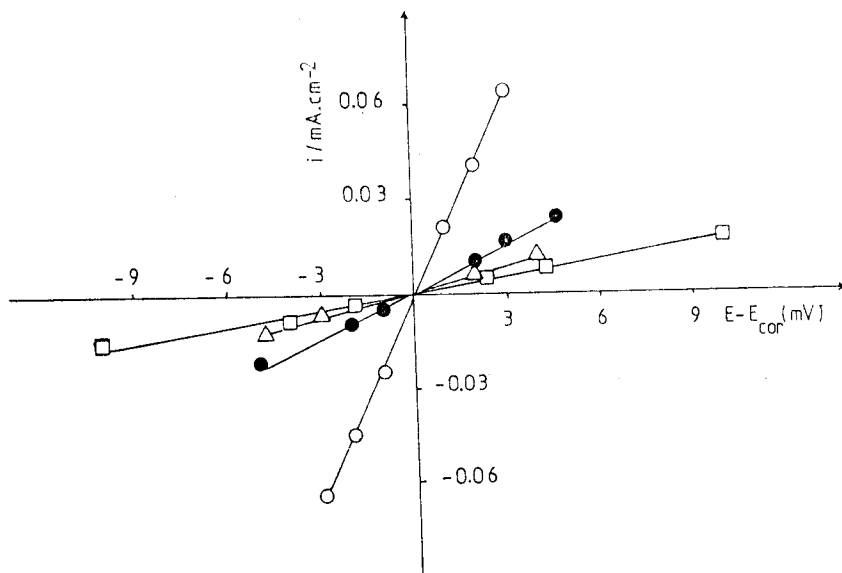


Fig. 3: The linear polarization curves measured by potentiodynamic ( $|dE/dt| = 1 \text{ mV}\cdot\text{s}^{-1}$ ) polarization.

System: Co (Marz)/0.5 M  $\text{H}_2\text{SO}_4$  + x mM PA, deaerated,  $\nu = 60$  rps,  $T = 298^\circ\text{K}$   
x = 0 (○), 0.2 (●), 2.0 (△), 20.0 (■).

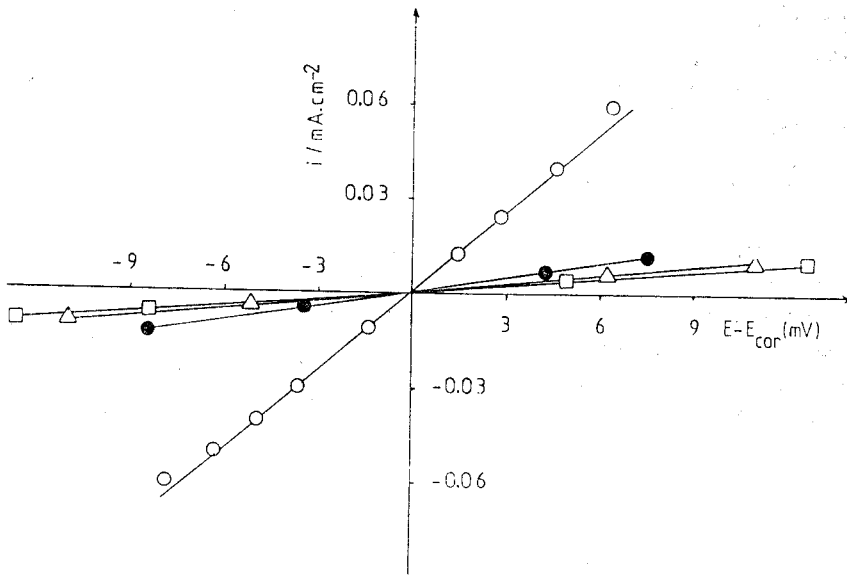


Fig. 4: The linear polarization curves measured by galvanostatic small signal pulse polarization.  
 System: Co (Marz)/0.5M H<sub>2</sub>SO<sub>4</sub> + x mM PA, deaerated,  $\nu = 60$  rps,  $T = 298^\circ\text{K}$   
 $x = 0$  (○), 0.2 (●), 2.0 (△), 20.0 (■).

nal pulse polarization in the vicinity of the corrosion potential, respectively. The corrosion rates of cobalt under these conditions were measured by linear polarization methods under potentiodynamic and galvanostatic small signal pulse polarization conditions, using the Stern-Geary equation. The corrosion rate values are given in Table 1 (column c and d).

In the deaerated 0.5M H<sub>2</sub>SO<sub>4</sub> + x mM PA (pH = 0.6) solution, anodic Tafel slope ( $b_a$ ) was found to be  $40 \pm 5$  mV in both inhibitor-free and the system containing 0.2 mM PA, from the current density-potential curves obtained by potentiodynamic technique. In this conditions, anodic Tafel slope was determined as  $70 \pm 10$  mV, from the current density-potential curves obtained by galvanostatic large signal pulse polarization. In the deaerated 0.5M H<sub>2</sub>SO<sub>4</sub> containing 2 and 20 mM PA solutions, anodic Tafel slopes were obtained as  $110 < b_a < 160$  mV in both techniques.

In the deaerated  $0.5\text{M H}_2\text{SO}_4 + x \text{ mM PA}$  solutions, cathodic Tafel slope ( $b_a$ ) was obtained as  $-130 \pm 10 \text{ mV}$  in both inhibitor-free and the system containing  $0.2 \text{ mM PA}$ . Cathodic Tafel slope was determined as  $-190 \pm 10 \text{ mV}$  in the systems containing  $2$  and  $20 \text{ mM PA}$  in  $0.5\text{M H}_2\text{SO}_4$ .

b) The results obtained with nickel samples

Figs. 5 and 6 show the current density-potential curves obtained by the potentiodynamic ( $1 \text{ mV} \cdot \text{s}^{-1}$ ) and galvanostatic large signal pulse polarization techniques, respectively. The corrosion rates obtained by extrapolating the anodic and cathodic Tafel lines of current density-potential curves to the corrosion potential are given in Table 2 (column a and b).

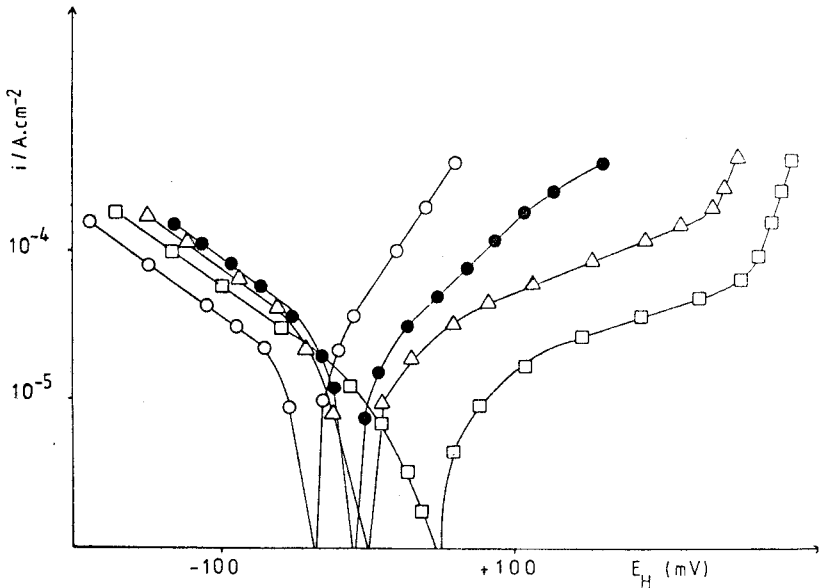


Fig. 5: Quasi-steady state current density-potential curves measured by potentiodynamic ( $|dE/dt| = 1 \text{ mV} \cdot \text{s}^{-1}$ ) technique.  
System: Ni (Marz)/ $0.5\text{M H}_2\text{SO}_4 + x \text{ mM PA}$ , deaerated,  $v = 60 \text{ rps}$ ,  $T = 298^\circ\text{CK}$   
 $x = 0$ (○),  $0.2$ (●),  $2.0$ (△),  $20.0$ (■).



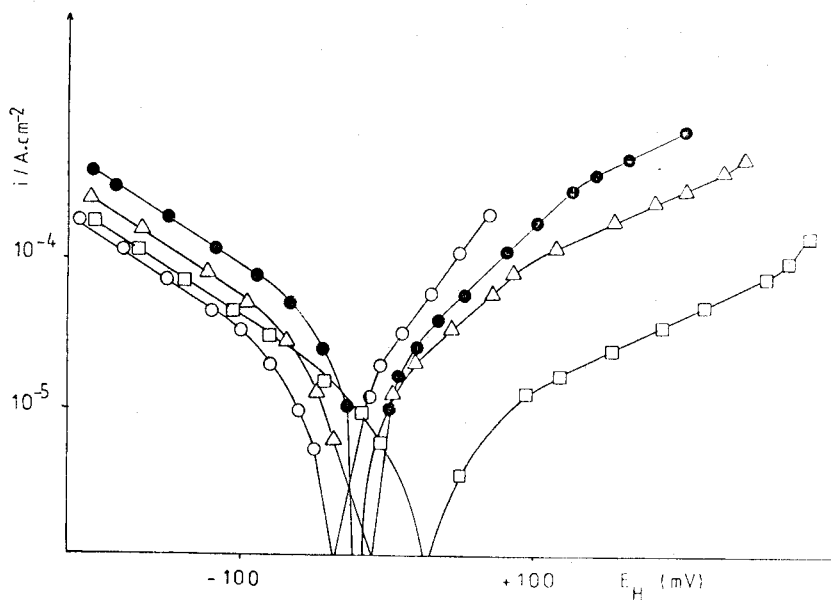


Fig. 6: Non-steady state current density-potential curves measured by galvanostatic large signal pulse polarization technique.

System: Ni (Marz)/0.5M H<sub>2</sub>SO<sub>4</sub> + x mM PA, deaerated,  $\nu = 60$  rps, T = 298°K  
 x = 0 (○), 0.2 (●), 2.0 (△), 20.0 (■).

Table 2: Determination of Corrosion Rate (mA.cm<sup>-2</sup>)

System: Ni (Marz)/0.5M H<sub>2</sub>SO<sub>4</sub> + mM PA, deaerated,  $\nu = 60$  rps, T = 298°K  
 Methods

x	a	b	c	d
0.0	0.014	0.010	0.008	0.014
0.2	0.018	0.021	0.014	0.024
2.0	0.019	0.014	0.022	0.026
20.0	0.010	0.007	0.014	0.010

- Extrapolation of anodic and cathodic current density-potential curves, potentiodynamic technique ( $|dE/dt| = 1$  mV.s<sup>-1</sup>).
- Extrapolation of anodic and cathodic current density-potential curves, galvanostatic large signal pulse polarization technique.
- Determination of polarization resistance, potentiodynamic technique ( $|dE/dt| = 1$  mV.s<sup>-1</sup>).
- Determination of polarization resistance, galvanostatic small signal pulse polarization technique.

Figs. 7 and 8 show the current density-potential curves of nickel obtained by the potentiodynamic ( $1 \text{ mV.s}^{-1}$ ) and galvanostatic small

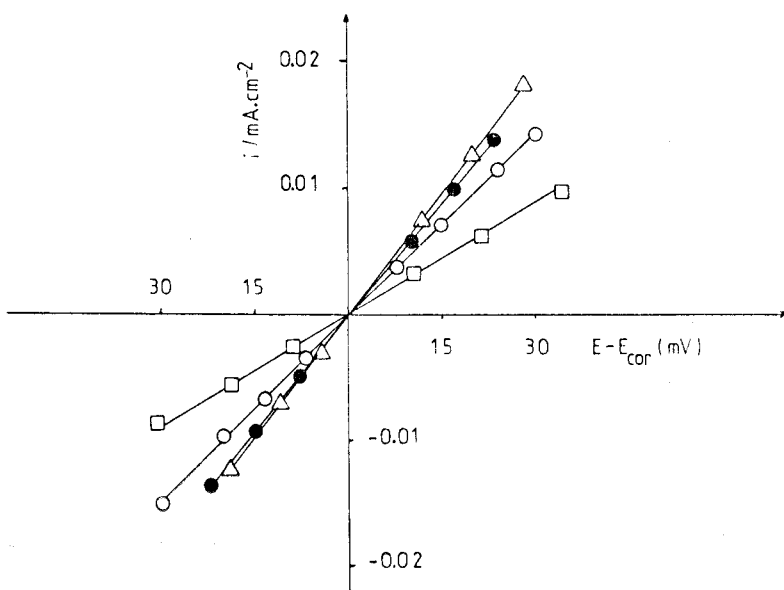


Fig. 7: The linear polarization curves measured by potentiodynamic ( $|dE/dt| = 1 \text{ mV.s}^{-1}$ ) polarization.

System: Ni (Marz)/ $0.5\text{M H}_2\text{SO}_4 + x \text{ mM PA}$ , deaerated,  $v = 60 \text{ rps}$ ,  $T = 298^\circ\text{K}$   
 $x = 0$  (○),  $0.2$  (●),  $2.0$  (△),  $20.0$  (■).

signal pulse polarization techniques in the vicinity of the corrosion potential, respectively. The corrosion rates under these conditions were measured by linear polarization methods under the potentiodynamic and galvanostatic small signal pulse polarization conditions using the Stern-Geary equation, are given in Table 2 (column c and d).

In the deaerated  $0.5\text{M H}_2\text{SO}_4 + \text{mM PA}$  solution, the anodic Tafel slope was  $65 \pm 5 \text{ mV}$  in the PA-free and  $100 < b_a < 220 \text{ mV}$  in the PA containing system. The cathodic Tafel slope under these conditions was  $-140 \pm 10 \text{ mV}$ .

On the other hand, when the concentration of PA was larger than  $2 \text{ mM}$ , then a second anodic Tafel slope was observed. The Tafel slope of this range determined from the current density-potential curves of

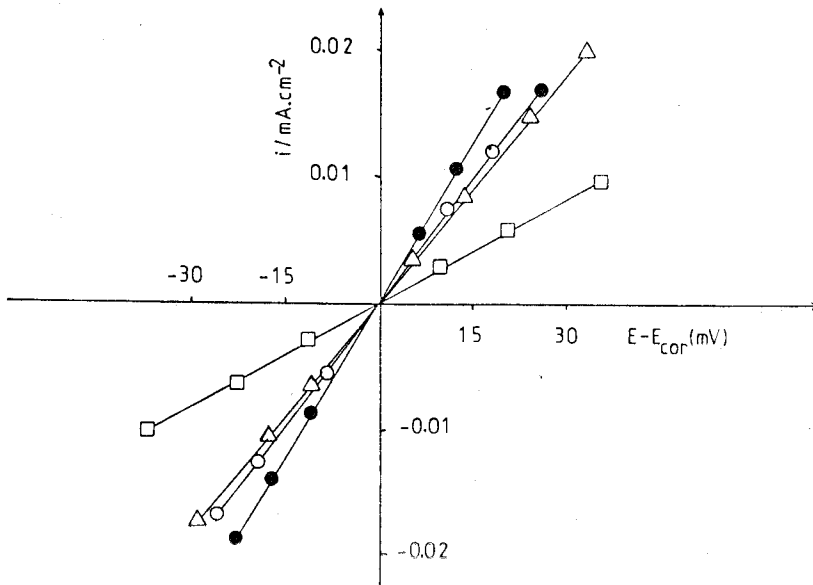


Fig. 8: The linear polarization curves measured by galvanostatic small signal pulse polarization.  
 System: Ni (Marz)/0.5M  $H_2SO_4$  + x mM PA, deaerated,  $\nu = 60$  rps,  $T = 298^\circ K$   
 $x = 0$  (□), 0.2 (○), 2.0 (△), 20.0 (●).

the potentiodynamic ( $1 \text{ mV}\cdot\text{s}^{-1}$ ) method and galvanostatic large signal pulse polarization method were  $40 \pm 5 \text{ mV}$  and  $65 \pm 5 \text{ mV}$ , respectively.

#### 4. DISCUSSION

Figs. 1, 2, 5 and 6 show that the current density-potential curves of cobalt and nickel determined by the potentiodynamic method are in agreement with the current density-potential curves obtained by the galvanostatic large signal pulse polarization technique.

The values given in Tables 1 and 2 respectively show that the  $i_{\text{cor}}$  values for cobalt and nickel determined by all four methods are in agreement. These values clearly indicate that the galvanostatic large and small signal pulse polarization techniques can be used for determining the corrosion rate of cobalt and nickel in aqueous solutions. Similar results have been obtained for analytically pure iron in previous works<sup>2,3,8</sup>

It can be seen in Table 1 that the corrosion rate of cobalt decreases approximately 80 % in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.2 mM PA. The inhibition effect of PA for cobalt does not change with the concentration of PA. On the other hand, PA has not a great effect on the corrosion of nickel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The  $i_{cor}$  values obtained by different methods were tabulated in Table 2.

PA was reduced on the analytically pure iron surface in the sulphuric acid solutions<sup>3</sup>, but it was not reduced or oxidized on the surfaces of cobalt and nickel electrodes. It can be adsorbed on the cobalt and nickel surfaces in the sulphuric acid solution, therefore the corrosion potentials change and become more positive. The current densities decrease at the constant potential in anodic and cathodic ranges with increasing PA concentration.

There is one Tafel zone for cobalt at low potential<sup>9,10</sup>, so that PA changes the slope in this potential range. After desorption of PA, the current increases rapidly. There are two anodic Tafel zones for the nickel oxidation reaction<sup>11-17</sup>. Nickel is oxidized to Ni<sup>+2</sup> in the first and to Ni<sup>+3</sup> in the second range. This situation can be seen from the current density-potential curves shown in Figs. 5 and 6. The second Tafel zone appears when the PA concentration is greater than 2 mM.

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### ÖZET

Bu çalışmada, propargil alkol içeren 0.5 M H<sub>2</sub>SO<sub>4</sub> çözeltilerinde kobalt ve nikelin korozyonu araştırıldı. Bu amaçla, potansiyodinamik polarizasyon ve galvanostatik büyük ve küçük puls polarizasyon teknikleriyle akım-potansiyel eğrileri elde edildi. Korozyon hızları ise, akım yoğunluğu-potansiyel eğrilerinin Tefel bölgelerinin, korozyon potansiyeline ekstrapolasyonu ve Stern-Geary denkleminde yararlanılarak belirlendi.