Cr(VI) Ion Reduction Reaction on Nickel and Stainless Steel Electrodes in Acid Medium

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The reduction of Cr(VI) ion in 0.5 M H_2SO_4 deaerated solutions with different concentrations of K_2CrO_4 on nickel and 18Cr-10Ni stainless steel electrodes have been studied by potentiostatic polarisation technique depending on the chromate concentration in solution. The kinetic parameters -Tafel slope, charge transfer coefficient and limiting current density -were evaluated comparatively. For the solutions containing ≤5 mM K_2CrO_4 the Tafel slopes are higher on stainless steel than on nickel (around -135 mV·dec⁻¹ for nickel and -165 mV·dec⁻¹ for stainless steel). Moreover, by increasing the chromate concentration the Tafel slopes increase on nickel and decrease on stainless steel. The low Tafel slope values of -75 mV·dec⁻¹ obtained on stainless steel electrode in the potential region -0.5÷ -0.75V vs. SCE could be due to a decrease of the charge transfer process rate because of the presence of a physical barrier. The values for the reaction rates are slightly higher for nickel than for stainless steel electrodes on all the studied potential range. The reaction product is soluble trivalent chromium, excepting the solution with 500 mM K_2CrO_4, when a $Cr(OH)_3$ film may cover the electrode surface that determines the decrease of the reaction rate.

Keywords: Cr(VI) reduction, nickel, stainless steel, acid medium

Due to continuous increasing of industrial activities, environmental pollution is an up to date problem. The latest restrictions imposed by new environmental legislation require effective initiatives for pollution reduction, not only in gaseous emissions and industrial aqueous effluents but also proper soil decontamination.

Depending on the nature of the pollutants, the industrial wastewater treatment is carried out using primary, secondary or tertiary methods. An efficient alternative is considered the application of electrochemical technologies for pollutant removal, due to their advantages such as versatility, environmental compatibility and potential cost effectiveness [1].

Heavy metal ions, chromium being one of them, which are discharged in the environment, are not biodegradable and represent a threat to human health.

The causes of the environment contamination with chromium compounds are results of its practical applications. The uses of chromium or chromium compounds are find in various practical domains, such as: in metallurgy as an alloy constituent in stainless steels, in chrome plating, in some anodizing processes; in dyes and paints; as catalyst; potassium dichromate is a chemical reagent used for cleaning laboratory glassware and as titrating agent, as corrosion inhibitor or as a mordant (i.e. a fixing agent) for dyes in fabric; chromium sulphate, $Cr_2(SO_4)_2$, is used as a green pigment in paints, in ceramic, varnishes, inks and in chrome plating; in medicine and pharmacy, as a dietary supplement or slimming aid, usually as chromium (III) chloride, chromium (III) picolinate, or as an amino acid chelate, such as chromium (III) D-phenylalanine [2].

Chromium has the ability to form stable compounds in a range of oxidation states from –2 to +6, Cr(III) and Cr(VI) are the most common oxidation states present in the environment. Between them Cr(VI) is considered extremely dangerous being carcinogenic and mutagenic and capable of displaying considerable diffusion rates through soils and aquatic environments, as well as being a strong oxidizing agent readily absorbed through the skin, even in small quantities it irritates plant and animal tissues [3, 4]. Chromium trivalent Cr(III) is required in trace amounts for sugar metabolism (Glucose Tolerance Factor) and its deficiency may cause a disease called chromium deficiency [5, 6].

Nowadays there is an increased interest for limitation of the Cr(VI) uses as well as for developing procedures for the removal of the toxic hexavalent chromium from waste waters. Many of these procedures rely on the reduction of Cr(VI) to Cr(III), which is much less toxic and can be easy adsorbed at a variety of inorganic and organic materials at neutral pH [7, 8]. However, none of them form insoluble species of the pollutant, such that its separation is not feasible from the wastewater through a direct precipitation method [9].

Among the electrochemical processes, the directly or indirectly reduction of Cr(VI) present as the hexavalent chromium (dichromate) anion uses as cathodes carbon steel [10] / stainless steel [11], lead [12, 13], gold [14], titanium [11, 15, 16] or copper [17, 18] as well as carbon substrates such as porous carbon [16, 17, 19-23] or reticulated vitreous carbon (RVC) [24]. The kinetics chromate reduction reaction on platinum electrode in acid solutions showed that is an autocatalytic process at higher chromate concentrations (50 and 500 mM) [25-27].

The aim of this paper is the study of Cr(VI) ions reduction reaction in 0.5 M H_2SO_4 deaerated solutions on nickel and 18Cr-10Ni stainless steel electrodes using potentiostatic polarization method depending on the chromate concentration in solution. The kinetic parameters – Tafel slope, charge transfer coefficient and limiting current density –were evaluated comparatively.

Experimental part

Electrochemical investigations were carried out by linear sweep voltammetry using a Zahner IM6e (Germany)

potentiostat, connected to a PC for data acquisition and control.

The measurements were performed at room temperature, 24 ± 1 ^{o}C, in a conventional three-electrode electrochemical cell using polycrystalline nickel and 18Cr-10Ni stainless steel (18% Cr; 10% Ni; 0.04% C; 0.33% Si and Fe) (with the geometrical area of 2 cm^2) as working electrodes, a platinum sheet (active surface area of 4 cm^2) as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was polished with alumina paste, rinsed and dried prior to all measurements. All the potentials were recorded with respect to the reference electrode. The potentiodynamic polarization technique was performed with a scan rate of 20 mV·min^{-1}.

The solutions (0.5 M H$_2$SO$_4$ without and with different additions of K$_2$CrO$_4$) were prepared from the chemically pure reagents and double distilled water. Before measurement the solutions were deaerated with purified nitrogen for one hour. The experimental conditions were chosen to be similar to the rinse water produced from electroplating plants.

Results and discussions

Linear voltammetric curves, obtained on Ni and 18Cr-10Ni electrodes in 0.5 M H$_2$SO$_4$ deaerated solutions in the absence and in the presence of various chromate concentrations are shown in figure 1 and figure 2, respectively. In order to evaluate the Cr(VI) ion reduction reaction the polarization curves were recorded by sweeping the applied potential in cathodic direction from 150 mV to -950 mV vs. SCE for nickel electrode and to -800 mV vs. SCE for stainless steel electrode.
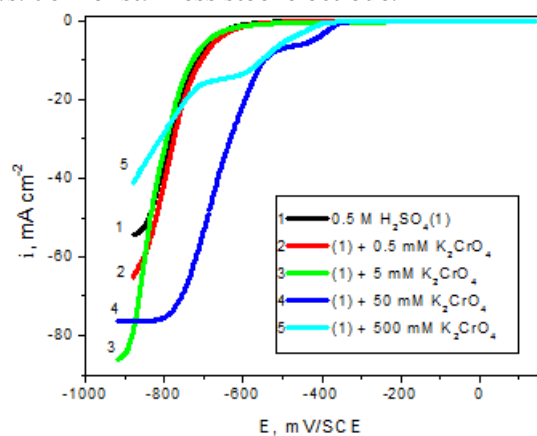

Fig. 1. Cathodic potentiostatic polarization curves on Ni electrode in 0.5 M H$_2$SO$_4$ solutions in the absence and presence of various K$_2$CrO$_4$ concentrations (0.5-500 mM)
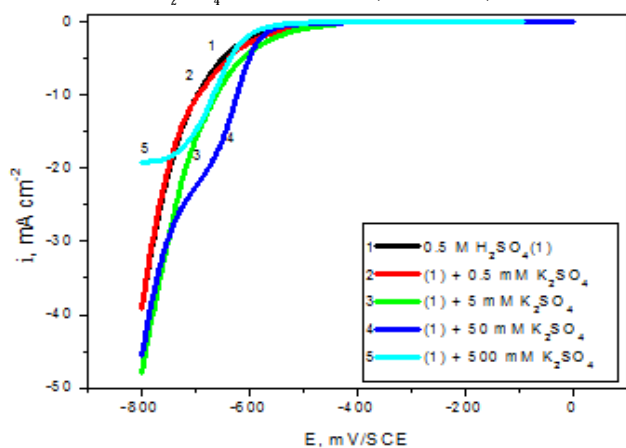

Fig. 2. Cathodic potentiostatic polarization curves on 18Cr-10Ni stainless steel electrode in 0.5 M H$_2$SO$_4$ solutions in the absence and presence of various K$_2$CrO$_4$ concentrations (0.5-500 mM)

The cathodic current density increases with the increase of electrode potential in the negative direction. The polarization curve recorded on Ni electrode for 0.5 M K$_2$CrO$_4$ in 0.5 M H$_2$SO$_4$ solutions is similar to the curves obtained in the absence of K$_2$CrO$_4$. With the increase of K$_2$CrO$_4$ concentration a cathodic reduction limiting current can be observed, at potential values which are shifted in cathodic direction with the increase in K$_2$CrO$_4$ concentration from -320 mV to -440 mV and -600 mV respectively.

On stainless steel electrode the curves corresponding to K$_2$CrO$_4$ concentrations ≥5 mM show a shoulder, the potential being shifted in cathodic direction with the increase of K$_2$CrO$_4$ concentration from -475 mV, to -660 mV and -760 mV respectively. As observed also in the case of nickel electrode, on stainless steel electrode the curve obtained in the solution containing 0.5 mM K$_2$CrO$_4$ presents a similar shape with the one for 0.5 M H$_2$SO$_4$ solution background.

The cathodic Tafel plots for Ni and 18Cr-10Ni stainless steel electrodes are depicted in figures 3 and 4, respectively.

As can be seen, the cathodic Tafel lines on both studied electrodes show different behaviour for different potential ranges. All curves recorded for solutions with K$_2$CrO$_4$ concentration > 5 mM have two slopes corresponding to different potential ranges.

In the first potential range chromate reduction reaction takes place, while in the second potential range the chromate reduction is superposed over the hydrogen evolution reaction. The corresponding Tafel parameters
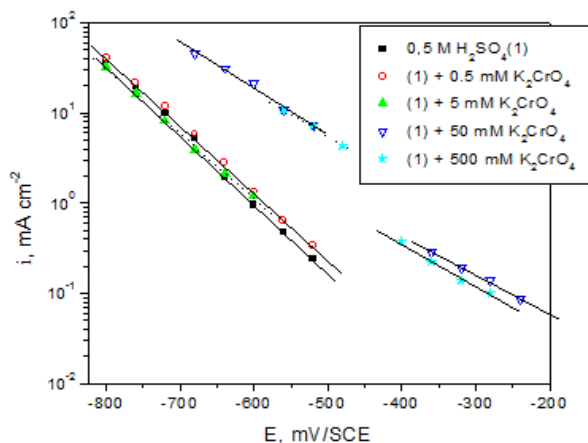

Fig. 3. Cathodic Tafel plots on Ni electrode, in 0.5 M H$_2$SO$_4$ solutions in absence and in presence of various K$_2$CrO$_4$ concentrations
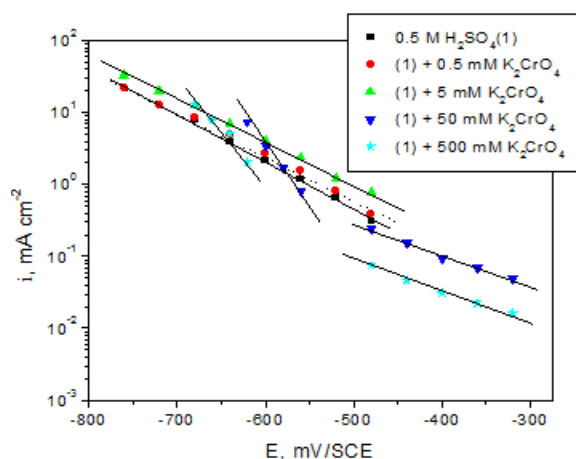

Fig. 4. Cathodic Tafel plots on 18Cr-10Ni stainless steel electrode, in 0.5 M H$_2$SO$_4$ solutions in the absence and in the presence of various K$_2$CrO$_4$ concentrations

K$_2$CrO$_4$ conc., mM	First step (−0.3÷−0.5 V)			Second step (−0.5÷−0.75V)		
	$b_{e,1}$, mV·dec^{-1}	α	$i_{L,1}$, mA·cm^{-2}	$b_{e,2}$, mV·dec^{-1}	α	$i_{L,2}$, mA·cm^{-2}
0	-	-	-	−126	0.468	54.35
0.5	-	-	-	−132	0.447	65.22
5	-	-	0.49	−138	0.427	86.07
50	−236	0.250	6.60	−196	0.301	76.09
500	−210	0.281	14.60	−201	0.293	41.30

Table 1
ELECTROCHEMICAL PARAMETERS OF THE CATHODIC PROCESSES ON NICKEL ELECTRODE, IN 0.5 M H$_2$SO$_4$ SOLUTIONS AT VARIOUS K$_2$CrO$_4$ CONCENTRATIONS

K$_2$CrO$_4$ conc., mM	First step (−0.3÷−0.5 V)		Second step (−0.5÷−0.75V)	
	$b_{e,I}$, mV·dec^{-1}	α	$b_{e,II}$, mV·dec^{-1}	α
0	-	-	−165	0.357
0.5	-	-	−163	0.362
5	-	-	−169	0.349
50	−227	0.260	−75	0.936
500	−244	0.242	−75	0.756

Table 2
TAFEL PARAMETERS FOR THE TWO CHARGE TRANSFER STEPS OF THE CATHODIC PROCESSES ON 18Cr-10Ni STAINLESS STEEL ELECTRODE IN 0.5 M H$_2$SO$_4$ SOLUTIONS AT VARIOUS K$_2$CrO$_4$ CONCENTRATIONS

(Tafel slope, *b*, and charge transfer coefficient, α) as well as the limiting current density (i_L) are given in tables 1 and 2.
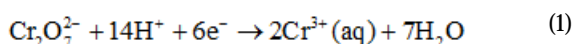
In the first potential range, the Tafel slopes, corresponding to chromate reduction reaction, have similar values for both studied electrode materials, those values being relative high and in consequence leading to low values for a parameter. It is possible that the reaction is accompanied by an adsorption intermediate step. Also, in the first potential range, the limiting current density can be clearly distinguished in the case of Ni electrode, for solutions containing ≥ 5 mM K$_2$CrO$_4$; it increases nearly linear with chromate concentration logarithm.

In the second potential range, corresponding to hydrogen evolution reaction superposing over chromate reduction, the Tafel slope values and their variation with chromate concentration are different for both electrodes. For the solutions containing ≤ 5 mM K$_2$CrO$_4$, the Tafel slope has values close to the one obtained for the background solution, namely higher on stainless steel than on nickel (around -135 mV·dec^{-1} for Ni and -165 mV·dec^{-1} for stainless steel). By increasing the chromate concentration, the Tafel slopes values are increasing on Ni and decreasing on stainless steel. This suggests that for both studied electrodes there are differences in the reaction mechanism.
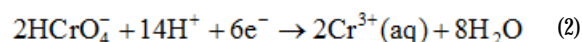
The low Tafel slope values of -75 mV·dec^{-1} obtained on stainless steel electrode in the potential region -0.5÷ -0.75V vs. SCE could be determined by the decrease in charge transfer process rate because of the presence of a physical barrier. For all studied potential ranges, the values for the reaction rates are slightly higher on nickel than on stainless steel electrodes.

For comparison, figure 5 shows the variation of the cathodic current density with chromate concentration at two potential values on both electrodes. The reaction rate, on both electrodes, decreases at 500 mM K$_2$CrO$_4$ concentration.
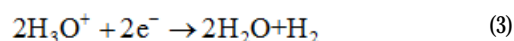
The theoretical distribution of the predominant chemical species Cr(VI) depends on *p*H and chromium concentration [26]. In solutions containing ≤ 5mM Cr(VI) the predominant species is Cr$_2$O$_7^{2-}$ [25], which reduces in the electro-chemical reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O \qquad (1)$$

At concentrations ≥ 50 mM Cr(VI) the predominant species is HCrO$_4^-$ [25] that reduces in the total electrochemical reaction:

$$2HCrO_4^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+}(aq) + 8H_2O \qquad (2)$$

At cathode the hydrogen evolution reaction can also take place:

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2 \qquad (3)$$

In case of the solution containing 500 mM K$_2$CrO$_4$, the decrease of the current density (fig. 5) is probably due to the formation of an adsorbed film of Cr(OH)$_3$; the explanation is related to the fact that the high rate consumption of hydrogen ions in reaction (2) leads to the pH increase near electrode surface and thus to hydroxide precipitation. This hydroxide film on electrode surface acts as an inhibiting barrier, determining the decreases of the reaction rate.
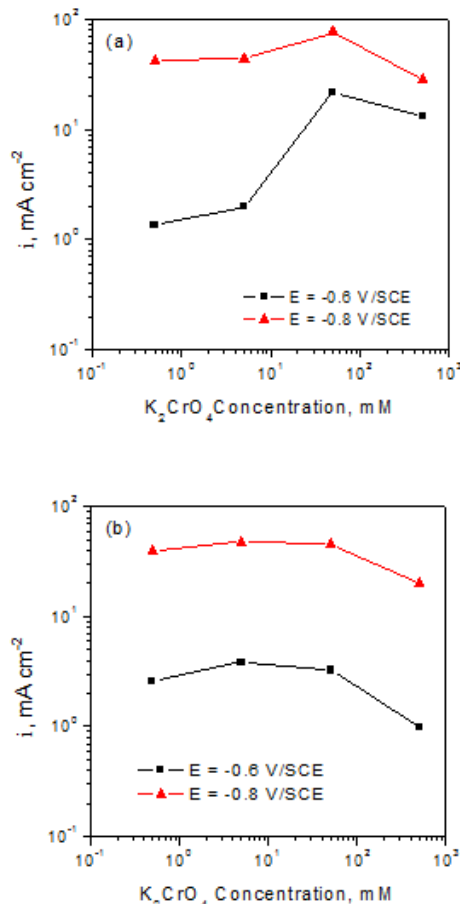

Fig. 5. Cathodic current density dependence of chromate concentration at two potential values on (a) Ni and (b) 18Cr-10Ni stainless steel electrodes

Conclusions

This paper presents the results obtained in the study of Cr(VI) ions reduction reaction in 0.5 M H_2SO_4 deaerated solutions containing different chromate concentrations by potentiostatic polarization technique on nickel and 18Cr-10Ni stainless steel electrodes.

The electrochemical parameters for Cr(VI) reduction in 0.5 M H_2SO_4 deaerated solutions containing different concentrations of chromate, depend on the electrode nature, potential range and on the chromate concentration. In the electropositive potential range, where the only reaction is the chromate reduction, the Tafel slopes as well as the current density values are comparable on the nickel and stainless steel electrodes. Differences between the Tafel slope values appear in the electronegative potential range, where the hydrogen evolution reaction is superposed on the Cr(VI) electroreduction. The reaction product is soluble trivalent chromium, except the solution with 500 mM K_2CrO_4, when a $Cr(OH)_3$ film may cover the electrode surface and determines the decrease of the reaction rate at this concentration.

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