



AUTOCATALYTIC REDUCTION OF Cr(VI) ON PLATINUM ELECTRODE IN ACID SOLUTION

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Electrochemical reduction of Cr(VI) at Pt electrode in 0.5 M H₂SO₄ deaerated solutions have been studied by potentiostatic polarisation method as a function of chromate concentration (0.5; 5; 25; 50 and 500 mM K₂CrO₄). The kinetic parameters – Tafel slope, charge transfer coefficient and limiting current density were evaluated. The Tafel slopes decrease with chromate concentration, reaching values ≤ 24 mV·decade⁻¹ at concentrations ≥ 25 mM K₂CrO₄ that pleads for an autocatalytic reaction mechanism. The limiting current density has a polynomial dependence of chromate concentration, presenting a maximum at 380-430 mM K₂CrO₄. The reaction product is soluble trivalent chromium, excepting the solution with 500 mM K₂CrO₄, when a Cr(OH)₃ thin film may cover the electrode surface and inhibits the reaction.

INTRODUCTION

Chromium is an inorganic contaminant released to drink water to environment from electroplating facilities, old mining operations, and fossil-fuel power plants. The toxicity and mobility of chromium depends on its oxidation state. Cr(VI) is carcinogenic and highly soluble in water,^{1, 2} while Cr(III) tends to form insoluble complexes with hydroxides and is considered much less toxic³ and even is required in trace amounts for sugar metabolism (Glucose Tolerance Factor).^{4, 5}

The maximum contaminant level for drinking water is 0.1 mg·L⁻¹ total chromium. For this, in present there is an increased interest for limitation of the Cr(VI) uses, as well as in the developing of the procedures for removal of the toxic hexavalent chromium from environment. Many of these procedures rely on the reduction of Cr(VI) to the trivalent state.

Among the electrochemical processes, the indirect reduction of Cr(VI) using soluble anodes of carbon steel⁶ or lead⁷ as well as direct electroreduction of

Cr(VI) using carbon substrates such as porous carbon⁸ or reticulated vitreous carbon (RVC)⁹ were attempted. Also, the reduction process of Cr(VI) to Cr(III) was studied on mercury electrode: the influence of the environment pH was studied by Tondeur *et al.*¹⁰ and Bothukova *et al.*¹¹ studied the effect of ammonium ions on the electrochemical chromate reduction.

The aim of this paper is to study the effects of the concentration on the kinetic and mechanism of the chromate reduction reaction at the Pt electrode in 0.5 M H₂SO₄ deaerated solutions.

EXPERIMENTAL

The measurements were performed in a conventional three-compartment electrochemical cell separated by fritted glass disk, with a PS 2 potentiostat, using the stepwise technique of 20 and 40 mV/60 s. The working electrodes, having the geometrical area of 0.06 cm², were made from polycrystalline platinum. A platinum sheet with an area of 1 cm² was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

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The solutions were prepared from the chemically pure reagents and doubly distilled water. Before the measurement the solutions were deaerated with purified nitrogen for one hour. All measurements were carried out at the room temperature ($24 \pm 1^\circ\text{C}$).

RESULTS AND DISCUSSION

The cathodic potentiostatic polarization curves of the platinum electrode in 0.5 M H_2SO_4 solutions in absence and in presence of various K_2CrO_4 concentrations are shown in Fig. 1.

The curve 1 in Fig.1 corresponds to the fond solution containing dissolved oxygen. The processes that take place, in this case, are the reduction of the dissolved oxygen and hydrogen evolution reaction. In presence of chromate and deaerated solutions, the polarization curves show two potential ranges where the cathodic process is charge transfer controlled and an extended potential range where it is mass transfer controlled. The Tafel lines for these potential regions are shown in Fig. 2 and the corresponding electrochemical parameters are given in Table 1.

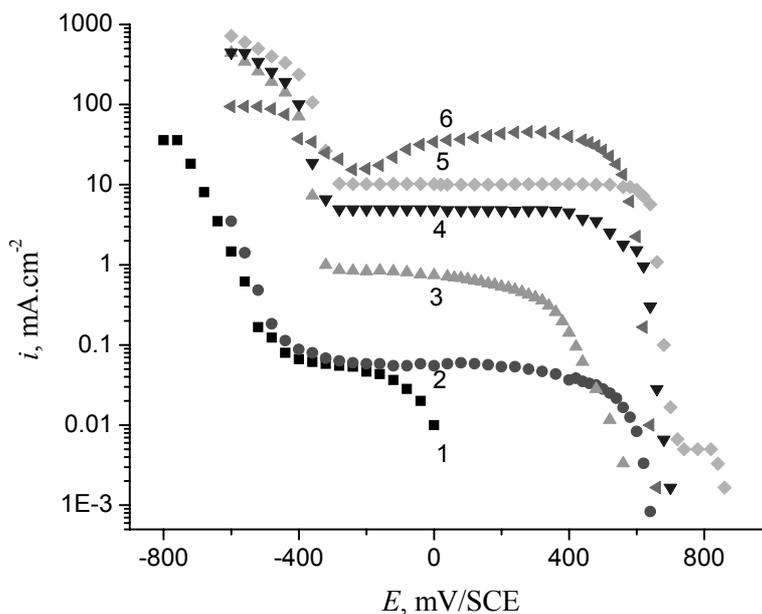


Fig. 1 – Cathodic potentiostatic polarization curves on Pt electrode in 0.5 M H_2SO_4 solutions in absence (1) and in presence of various K_2CrO_4 concentrations. (mM): 2 – 0.5; 3 – 5; 4 – 25; 5 – 50; 6 – 500.

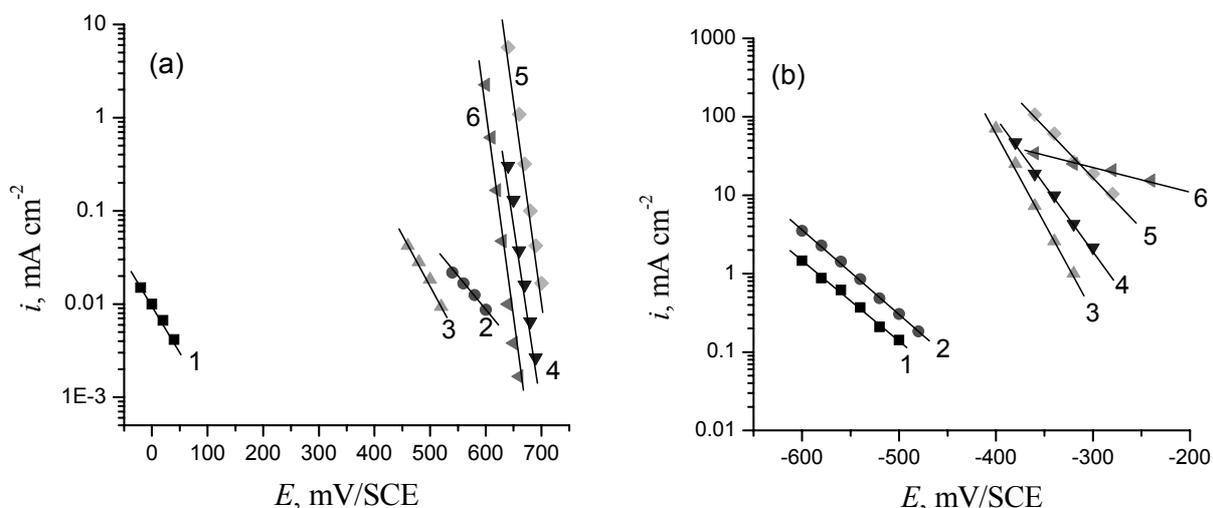


Fig. 2 – Tafel lines for cathodic process on Pt electrode in 0.5 M H_2SO_4 solution in absence (1) and in presence of various K_2CrO_4 concentrations (mM): 2 – 0.5; 3 – 5; 4 – 25; 5 – 50; 6 – 500.

(a) – The first step charge transfer controlled; (b) – The second step charge transfer controlled.

Table 1

Tafel parameters of the cathodic processes on the Pt electrode in 0.5 M H₂SO₄ solutions in presence of various K₂CrO₄ concentrations

Parameter	K ₂ CrO ₄ concentration, mM					
	0	0.5	5	25	50	500
$-b_c$ (a)/mV.dec ⁻¹	108	146	113	24	23	19
αn	0.546	0.404	0.522	2.458	2.565	3.105
$-b_c$ (b)/mV.dec ⁻¹	98	92	43	60	77	355
αn	0.476	0.634	1.372	0.983	0.747	0.166

The Tafel slopes have different variations with K₂CrO₄ concentration in the two potential ranges; they decrease significantly in the first Tafel range and pass to a minimum in the second Tafel range, presenting a high value at the most chromate concentration. Only chromate reduces in the first step, while in the second step evolution hydrogen reaction take places too.

For the first step charge transfer controlled, the (αn) parameter has the value approximate of 0.5 for the solutions of concentration ≤ 5 mM K₂CrO₄, what shows that there are not surface processes. Contrary, at more chromate concentration the (αn) parameter becomes more than 2, indicating a process catalyzed by a surface reaction.

All polarization curves are characterized by the limiting current density of what variation with chromate concentration is polynomial (Fig. 3a); the limiting current increases with chromate concentration, passes through a maximum between 380 and 430 mM K₂CrO₄ concentration after that starts to decreases. Fig. 3b shows a Gaussian variation of the cathodic current density with

chromate concentration at two potential values in the second region of the current increase. This variation presents a maximum at 50 mM K₂CrO₄ concentration.

The diffusion coefficient of Cr(VI) ions calculated from the limiting value for solution containing 50 mM K₂CrO₄ (10 mA·cm⁻², conform to curve 5 from Fig. 1) is equal with $3.45 \cdot 10^{-5}$ cm² s⁻¹. Using this value of the diffusion coefficient, the calculated limiting currents for the other studied chromate concentrations have following values [mA·cm⁻²]: 0.1; 1, 5 and 100 for concentrations of 0.5; 5, 25 and 500 mM K₂CrO₄, respectively. The mean values obtained experimental are: 0.0633; 0.925; 4.833 and 43.667 mA·cm⁻², respectively. The calculated and experimental values are relatively close excepting to the solution containing 500 mM K₂CrO₄ (curve 6 from Fig. 1). In this case, the chromate reduction with high rate (The Tafel slope is -19 mV·decade⁻¹) determines the pH increase near electrode and Cr(OH)₃ precipitation that inhibits the reaction.

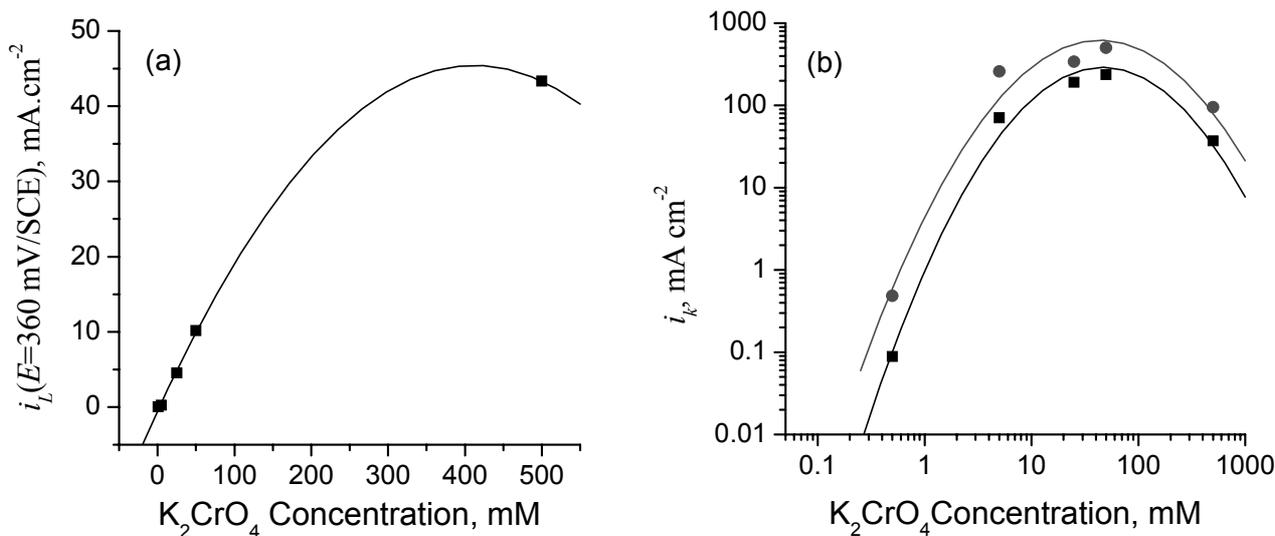


Fig. 3 – Dependence of chromate concentration for: (a) the limiting current density, i_L , and (b) the cathodic current density, i_k , at potential values (mV/.SCE): 1)–440; 2) –520.

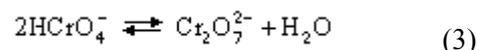
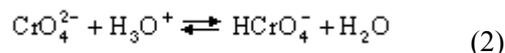
The reaction order, p versus K_2CrO_4 , deduced from calculated and experimental values of the limiting current, according to Fig. 4 and to the relation:

$$\left(\frac{\partial \log i_L}{\partial \log c_{K_2CrO_4}} \right) = p \quad (1)$$

has values of 1 and 1.068, respectively.

The most probable Cr(VI) species in aqueous solutions are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} , of which relative distribution depends on the solution pH and Cr(VI) concentration. In the bulk solution

and at electrode, there are the following equilibriums:



With equilibrium constants:^{11, 12} $K_2 = 6.3 \times 10^{-2}$ and $K_3 = 3.2 \times 10^{-7}$.

The pH values calculated in function of ionic strength of the solutions are given in Table 2 together with the distribution of the Cr(VI) species, calculated as activities (a) from equilibrium constants K_2 and K_3 .

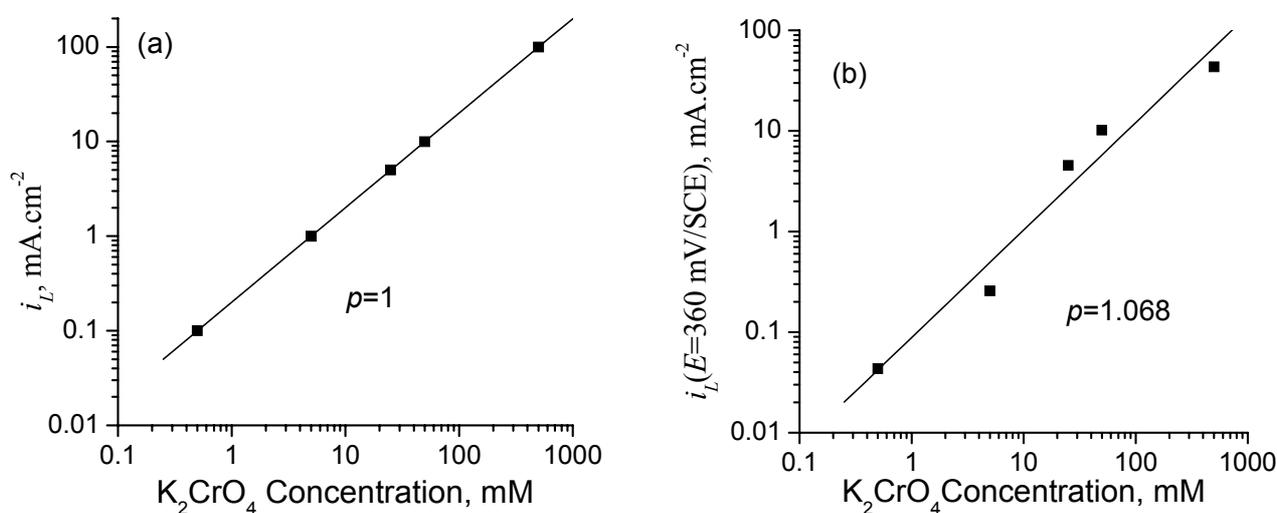


Fig. 4 – Plot of the calculated (a) and experimental (b) limiting current vs. K_2CrO_4 concentration.

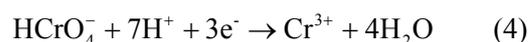
Table 2

The pH values and the Cr(VI) species distribution in the studied solutions

[K_2CrO_4], mM	0	0,5	5	25	50	500
pH	1.418	1.418	1.417	1.415	1.412	1.375
$a(HCrO_4^-)$, mM	-	0.062	0.615	3.00	5.79	37.93
$a \times 10^7(Cr_2O_7^{2-})$, mM	-	0.012	1.210	28.76	107.28	4603.37

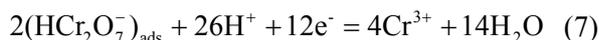
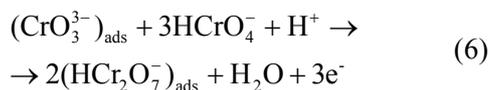
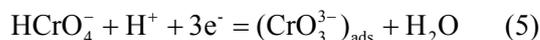
According to the data from Table 2, the concentrations of the $HCrO_4^-$ anion are approximately of 10^7 - 10^5 more than the concentrations of $Cr_2O_7^{2-}$ anion. Conform to the potential-pH diagram^{12, 13} for chromium species, the thermodynamically most stable species in water will be: $HCrO_4^-$ (in pH range 1.20-6.52) and CrO_4^{2-} (at pH>6.52). This means that the predominant specie in all studied solutions is $HCrO_4^-$.

At the concentrations ≤ 5 mM K_2CrO_4 , the $HCrO_4^-$ anion is reduced directly to Cr(III), conform to the reaction:

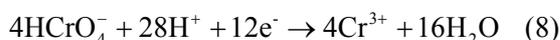


The Tafel slopes for solutions containing ≥ 25 mM K_2CrO_4 have very low values (Table 1) that correspond to a catalytic reaction mechanism.¹⁴ The (αn) parameter is > 2 , indicating a surface reaction that has a catalytic effect and which controls the reaction rate. Taking account of the

thermodynamic potentials for the electrochemical reactions in which are implicated various Cr(VI) species,¹⁴ the probable mechanism, for concentrations ≥ 25 mM K_2CrO_4 , is given by the following reaction succession:



By summarizing of the (5)-(7) reactions it obtains the total reaction (8):



Simplifying with 4 the total reaction (8) it is obtained the reaction (4) that is in accordance with the found reaction order versus K_2CrO_4 , equal with 1 (Fig. 4).

Therefore, HCrO_4^- , the predominant specie in solutions, is reduced fast to the adsorbed intermediate specie $(\text{CrO}_3^{3-})_{\text{ads}}$, conform to the reaction (5). This intermediate is oxidized in presence of the HCrO_4^- anion to dichromate anion, conform to the reaction (6), setting up a catalytic loop. The reaction (6) required more HCrO_4^- concentrations at electrode surface that is possible only in solutions containing ≥ 25 mM K_2CrO_4 . Thus, at high chromate concentrations, this has an autocatalytic effect on his electrochemical reduction.

The decrease of the limiting current with cathodic polarization increasing, in case of the solution containing 500 mM K_2CrO_4 (Fig. 1) is due probably to the formation of an adsorbed film of $\text{Cr}(\text{OH})_3$; at high chromate concentrations, the hydrogen ions are consumed with high rate that leads to the pH increase near electrode surface and the hydroxide precipitation. The hydroxide film on surface electrode acts as an inhibiting membrane for reaction that explains the current density

decrease (Fig. 3a and Fig. 3b) and the high Tafel slope value (-355 mV.decade⁻¹) found for this solution in the second Tafel region (Table 1).

CONCLUSIONS

The kinetics and reaction mechanism of the Cr(VI) reduction on Pt electrode in 0.5 M H_2SO_4 depends on its concentration. The Tafel slope significantly decreases, reaching very low values at high chromate concentration that pleads for an autocatalytic reaction mechanism. The limiting current density has a polynomial dependence of chromate concentration. The reaction product is soluble trivalent chromium, excepting the solution with 500 mM K_2CrO_4 , when a $\text{Cr}(\text{OH})_3$ thin film may cover the electrode surface and that acts as a inhibiting membrane.

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