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ANODIC DECOMPOSITION OF COMPLEXING AGENTS IN ELECTROLYTES BASED ON Cr(III) SALTS AT COMPOSITE TiO_X/PtO_Y ELECTRODES

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Abstract. The kinetics of complexing agents anodic decomposition in electrolytes based on Cr(III) salts was investigated. In Cr(III) electrolytes urea was shown to be fixed in complexes with Cr^{3+}-ions. It was found that the main way of free carbamide degradation was hydrolysis characterized by a high rate ($k = 4.5 \cdot 10^{-3}$ min^{-1}). Decrease in formic acid concentration during electrolysis at composite TiO_x/PtO_y-anodes was insignificant.

Keywords: Cr(III) electrolytes, complexing, urea hydrolysis, formic acid, composite TiO_x/PtO_y-anodes.

1. Introduction

Replacement of highly toxic and oxidative electrolytes based on chromic acid by the ones based on Cr(III) salts affords an opportunity to reduce expenses on wastewater treatment [1, 2]. In a trivalent chromium electroplating bath along with oxygen evolution anodic oxidation of Cr(III)-complexes with generation of Cr(VI)-species is possible [3]. Disengaged ligands can undergo anodic decomposition. Taking into account that composition changes lead to technological parameters deterioration it is important to study the kinetics of untoward reactions.

2. Experimental

Cr(VI)-species concentration in the electrolytes was determined by amperometric titration [4]. Electrolysis was performed in a divided cell, shown in Fig. 1, at anodic and cathodic current densities of 100 mA/cm^2.

The concentration of urea in the electrolyte was determined by spectrophotometric method based on urea interaction with para-aminodimethylbenzaldehyde. In the presence of Cr^{3+}-ions photometric measurements were carried out in relation to solution containing the same quantity of trivalent chromium as in an assay. Such determination is possible due to kinetic inertness of trivalent chromium complexes that are characterized by a low rate of ligand exchange [5].

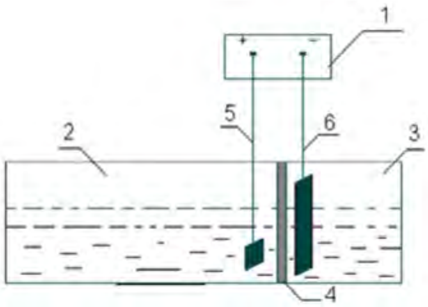

Fig. 1. Experimental setup for determination of Cr(VI) current efficiency: power supply (1); anodic compartment of the cell (2); cathodic compartment of the cell (3); membrane (4); anode (5) and cathode (6)

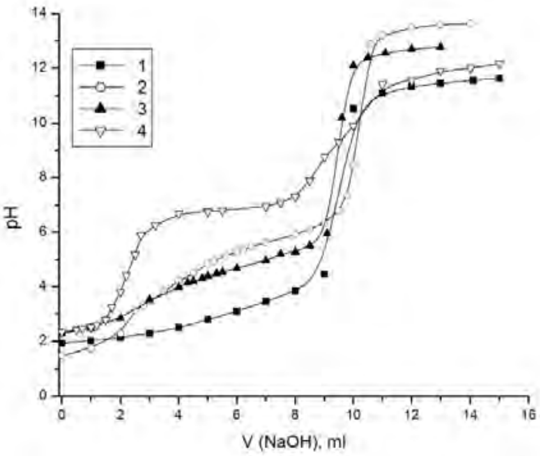

Fig. 2. Potentiometric titration curves of the mixtures of HCOOH and H_2SO_4 in different solvents: water (1); acetone (2); ethanol (3) and methanol (4)

Formic acid concentration in the electrolyte was determined by potentiometric titration. Since electrolyte contains sulfuric acid too and their pK differ one from another less than 4 unities, potentiometric titration should be carried out in nonaqueous solvent. Fig. 2 shows titration curves of the formic and sulfuric acids mixtures in water, acetone, ethanol and methanol. The titration curves performed in acetone, ethanol and methanol were found to have two titration hops. In the trivalent chromium containing solutions results reproducibility of the titration in acetone strongly decreases because of response time increasing. The most suitable solvent was found to be methanol due to its high inductive capacity.

Composite TiO_x/PtO_y anodes have been prepared by platinum electrodeposition on specially pre-treated Ti plates from the electrolyte: K_2PtCl_6 – 25.004 g/l; $NaNO_2$ – 100 g/l; solution of NH_3 (r = 0.915 g/cm^3) – 20 ml; at cathodic current density – 20 mA/cm^2 and temperature – 343 K.

3. Results and Discussion

In Cr(III) electrolytes urea is known to be fixed in complexes with Cr^{3+}-ions, nevertheless the information about the equilibriums taking place in such solutions has not been found. Due to the importance of this question we have investigated Cr^{3+}-ions and carbamide complexing reactions.

Aqueous solution of chromium perchlorate is characterized by two spots of maximum absorption in the visible portion of spectrum. The first one (at pH = 1.5; λ = 580 nm) is related to the electron transition in the system of central ion therms, and the second one (at pH = 1.5; λ = 410 nm) – electron transitions in the system of central ion therms and oscillations of coordination bond electrons (Fig. 3, curve 1).

Urea added to the solution causes the bathochromic shift of both absorption maximums by 10 nm and increase of absorption strength what denotes complexing between Cr^{3+}-ions and urea (Fig. 3, curve 2).

Composition of the complex was ascertained by the relative yield curve plotting. Since trivalent chromium forms mononuclear complexes with urea [6] one set of samples was prepared, where urea concentration was changing from $1.0\cdot10^{-2}$ mol/dm^3 up to $12.0\cdot10^{-2}$ mol/dm^3 during the constant pH, ionic strength and Cr^{3+}-ions concentration is equal to $2.0\cdot10^{-2}$ mol/dm^3. Then the deviation of absorbance from additivity was measured. Since the relative yield curve is linear Cr^{3+}-ions and urea form complex $[Cr((NH_2)_2CO)(H_2O)_5]^{3+}$ (Fig. 4).

To find out stability constant of the complex $[Cr((NH_2)_2CO)(H_2O)_5]^{3+}$ a set of samples with Cr^{3+}-ions – urea ratio 1:1 was prepared. In terms of zero ionic strength stability constant of the complex was found to be equal to 1.4 ± 0.2 [7]. Though, the thermodynamic stability constant of $[Cr((NH_2)_2CO)(H_2O)_5]^{3+}$ is low, this complex may be found in the solution over a long period of time due to its kinetic steadiness.

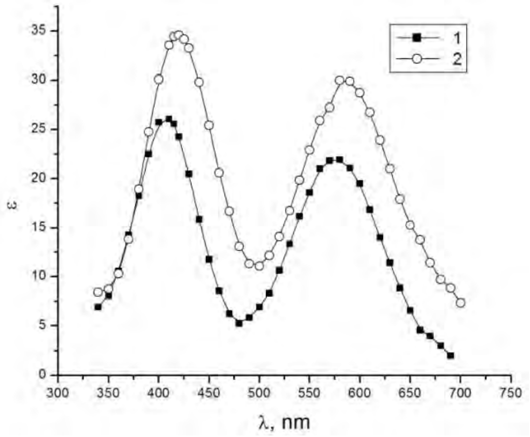

Fig. 3. Spectrum of aqueous solution of chromium perchlorate and Cr(III)- urea complex: C (Cr^{3+}) = $12\cdot10^{-3}$ mol/l (1) and C (Cr^{3+}) = $12\cdot10^{-3}$ mol/l (2); C (urea) = 0.144 mol/l, pH = 1.5, temperature 293 K

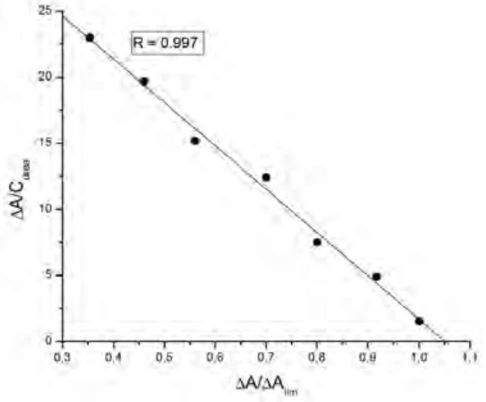

Fig. 4. The relative yield curve; pH = 1.5, λ = 420 nm, l = 1 cm, temperature 293 K

After anodic decomposition of Cr(III)-complexes free carbamide can undergo different reactions. It is well known that urea hydrolyzes in an acidic medium. The kinetics of this process has been studied. The order of the reaction has been found to be first, which is in agreement with [8-13]. In chromium-free electrolyte reaction rate constant is $4.4\cdot10^{-3}$ min^{-1} (T = 308 K, pH = 1.5) (Fig. 5).

The kinetics of the urea hydrolysis does not change in the Cr(III) electrolyte and due to the kinetic inertness of trivalent chromium complexes the rate constant is $4.5\cdot10^{-3}$ min^{-1} (Fig. 6).

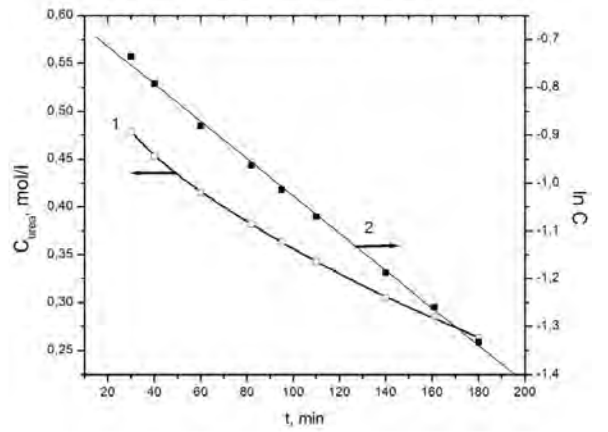

Fig. 5. Carbamide hydrolysis kinetic curve (1) and its semilogarithmic anamorphosis (2) in Cr(III)-free electrolyte; pH=1.5, temperature 308 K

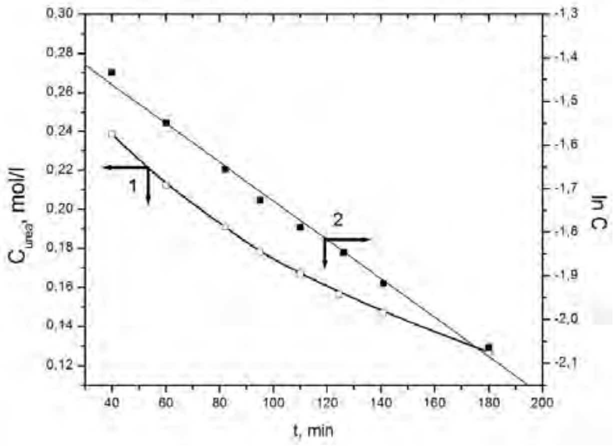

Fig. 6. Carbamide hydrolysis kinetic curve (1) and its semilogarithmic anamorphosis (2) in Cr(III) electrolyte; pH = 1.5, temperature 308 K

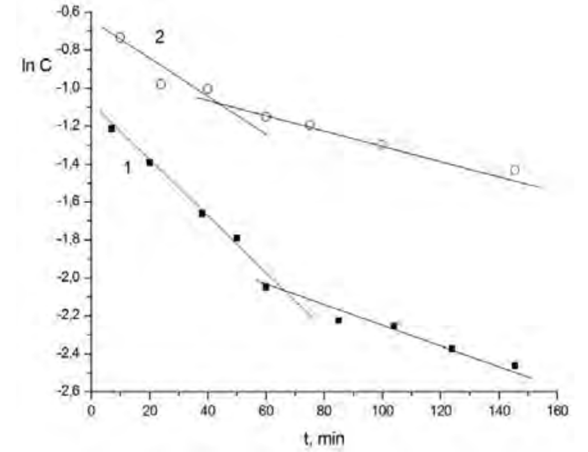

Fig. 7. Dependence of urea integral concentration on electrolysis time at composite TiO_x/PtO_y in solutions containing: 0.5 mol/l urea + 0.6 mol/l formic acid + 1 mol/l Cr^{3+} (1) and 0.5 mol/l urea + 0.6 mol/l formic acid (2); pH = 1.5 *i*=100 mA/cm^2, temperature 308 K

The difference between urea initial concentrations in solution containing Cr(III) compounds and the Cr(III)-free one is probably caused by the complexing between urea and Cr^{3+}-ions.

Thus, in the Cr(III) electrolytes only free urea hydrolyzes and the rate of this process is significant.

Along with chemical interactions electrochemical oxidation of urea is possible. As an anode material was chosen composite TiO_x/PtO_y due to long service life.

Dependence of electrolysis time on concentration of free-urea for both containing Cr(III) salts and Cr(III)-free electrolytes is shown in Fig. 7. In both electrolytes most of the reactions that urea undergoes at Ti/Pt anode are first-order reactions. When concentration of free urea is significant the total reaction rate is high. The rate constants were found to be equal to $8.7 \cdot 10^{-3}$ min^{-1} and $1.5 \cdot 10^{-2}$ min^{-1} for Cr(III)-free and electrolyte containing Cr(III) salts respectively. Interestingly enough when concentration of free urea is diminished the rate constant of the process is similar to the rate constant of the hydrolysis.

The main products of urea electro-oxidation are nitrate- and nitrite-anions [14-17]. The absence of their negative effect on cathodic process confirms insignificance of urea electrochemical oxidation.

After Cr(III)-complexes decomposition anodic oxidation of formic acid is possible. Fig. 8 shows the decrease in formic acid concentration during electrolysis.

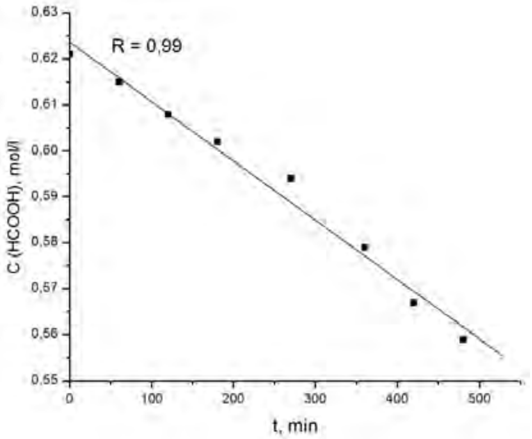

Fig. 8. Effect of electrolysis time on formic acid concentration at composite TiO_x/PtO_y; *i* =100 mA/cm^2, temperature 308 K

The decomposition of formic acid was observed to follow zero-order kinetics, which is in agreement with [18]. This process is characterized by a low rate (rate constant is $1.29 \cdot 10^{-4}$ mol·l^{-1}·min^{-1}). During 8 h of electrolysis concentration of formic acid dropped from 0.621 mol/dm^3 down to 0.560 mol/dm^3. It is less than 10 wt %. So we did not observe dramatic loss of formic acid caused by the electrochemical oxidation reactions.

4. Conclusions

The main way of urea decomposition is acidic hydrolysis, which is characterized by a high rate. The loss of formic acid during electrolysis is insignificant. Thereby, for optimization of anodic process composite TiO_x/PtO_y-electrodes are recommended to be used.

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АНОДНИЙ РОЗКЛАД КОМПЛЕКСОУТВОРЮВАЧІВ НА КОМПОЗИЦІЙНИХ TiO_X/PtO_Y-ЕЛЕКТРОДАХ В ЕЛЕКТРОЛІТАХ НА ОСНОВІ СОЛЕЙ Cr(III)

Анотація. *Досліджено кінетику анодного розкладу комплексоутворювачів в електролітах на основі солей Cr(III). Показано, що в електролітах хромування на основі солей Cr(III) карбамід зв'язаний у комплекси з* Cr^{3+}*-йонами. Встановлено, що основним маршрутом розкладу карбаміду є кислотний гідроліз, який перебігає зі значною швидкістю* ($k = 4{,}5\cdot10^{-3}$ *хв*$^{-1}$). *Досліджено зменшення концентрації мурашиної кислоти під час електролізу на композиційних* TiO_x/PtO_y*-анодах.*

Ключові слова: *електроліти на основі Cr(III), комплексоутворення, гідроліз карбаміду, мурашина кислота, композиційні* TiO_x/PtO_y*-аноди.*