

Anodes For a Trivalent Chromium Electroplating Bath

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Abstract – Electrochemical behavior of different anode materials in electrolytes containing trivalent chromium salts was investigated. It was found that current efficiency of Cr(VI)-species strongly depends on the nature of anode material. Some of Ti/Pt electrodes were shown to be n-type semiconductors. Composite materials based on platinized titanium are recommend as anodes for carbamide-containing electrolytes since they characterized by good service life and admissible values of current efficiency of Cr(VI)-species.

Key words – Cr electroplating, semiconductor, anode materials, electrocatalytic activity.

I. Introduction

Replacement of highly toxic and oxidative electrolytes based on chromic acid by the ones containing Cr(III) salts affords to reduce expenses on wastewater treatment [1-5]. Nevertheless industrial application of a trivalent chromium bath is limited due to lack of appropriate anodes. Since, in case of Cr(III) electrolytes, composition of solution affects process of chromium electrodeposition, anode material must obey strict requirements: (i) has good corrosion stability; (ii) products of anode destruction must not affect the cathodic process; (iii) rates of unwanted reactions that cause change in composition of electrolyte should be minimal. Anodes based on platinum metals or their oxides, compounds of valve metals, PbO₂, MnO₂, SnO₂ are known to be stable in acidic electrolytes based on Cr(III) compounds [2]. In this connection, anodic behavior of some anodes in electrolytes containing Cr(III) salts was investigated in this work.

II. Materials and Methods

Electrooxidation of Cr(III)-ions was carried out in a thermostated cell ($t=25\pm 1^{\circ}\text{C}$) where anodic and cathodic compartments were divided by a porous membrane to avoid the cathodic reduction of Cr(VI)-species. Experiment was carried out in solution containing 1 M $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ + 0.15 M $\text{Al}_2(\text{SO}_4)_3$ + 0.3 M Na_2SO_4 + 0.5 M H_3BO_3 + 0.6 M HCOOH + 0.5 M $(\text{NH}_2)_2\text{CO}$, pH=1.5 [3].

Amount of Cr(VI)-species was determined by the amperometric titration using ammonium iron(II) sulfate.

The two stage procedure of preparation of platinized titanium electrodes including Pt electrodeposition on Ti followed by thermal treatment in the air has been used [4].

Dimensionally stable anodes based on mixture of titanium oxides and ruthenium oxides (DSA) were obtained by pyrolytic decomposition of solution containing chlorides of titanium and ruthenium at 450^oC. Electrochemical measurements were carried out in 1 M HClO_4 with GAMRY Potentiostat/Galvanostat/ZRA Reference 3000 in a three-electrode cell with Pt auxiliary electrode and Ag/AgCl reference electrode.

III. Results and Discussion

In a trivalent chromium electroplating bath along with oxygen evolution anodic oxidation of Cr(III)-complexes with unwanted generation of Cr(VI)-species is possible [1,4]. Taking into account that composition changes and accumulation of Cr(VI)-species in a trivalent chromium bath lead to technological parameters deterioration [1,4] an anode material must be characterized by low activity towards electrolyte components oxidation reactions and high selectivity towards oxygen evolution reaction. Thereby, low activity towards Cr(III) electrooxidation is required to choose an appropriate anode.

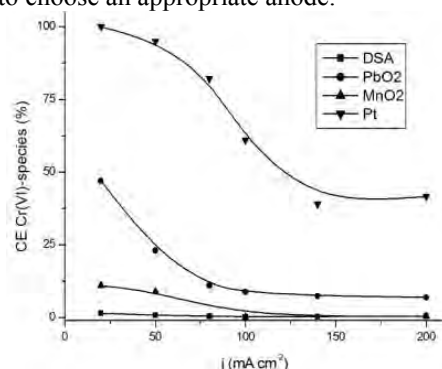


Fig. 1. CE Cr(VI)-species in a trivalent chromium electroplating bath at different electrodes

Fig. 1 shows dependence of current efficiency (CE) of Cr(VI)-species on anodic current density for different anodes. In general, CE Cr(VI) decreases with growth of current density since rate of oxygen evolution increases greatly with current density as against rate of Cr(III) electrooxidation [1,4]. As one can see, in the range of medium current densities (50-200 mA/cm²) most of anodes, except Pt, are characterized by relatively low CE Cr(VI). Important to note that low activity of anode to Cr(III) electrooxidation is an insufficient condition to choose an appropriate anode since long service life is also required. According to this criterion most of oxide materials could be unsuitable owing to high content of reducing agents in the Cr(III) electroplating bath. For example, in such conditions rates of PbO₂ and MnO₂ destruction are significant at steady-state potential or during anodic polarization. Furthermore, growth of current density up to 50 mA/cm² facilitates mechanical destruction of oxide layer by oxygen evolution. In case of DSA the main reason of their low service life is electrochemical dissolution of RuO₂ under high potential, especially in electrolytes without Cl⁻ ions. Thereby, choice of an appropriate anode for a trivalent chromium electroplating bath should be based on compromise between its selectivity and service life. Pt anode not recommend to be applied in a trivalent chromium bath due to high rates of Cr(III)-electrooxidation. Nevertheless, composite anodes based on platinized titanium are interesting enough since they exhibit low electrocatalytic activity towards oxidation of components of electrolyte [5]. Important to note that rate of Cr³⁺-ions electrooxidation on platinized titanium strongly depends on the method of anode preparation and amount of electrodeposited Pt (Table).

TABLE

ELECTROCHEMICAL PROPERTIES OF DIFFERENT Ti/Pt ANODES INCLUDING CE Cr(VI) IN A TRIVALENT CHROMIUM ELECTROPLATING BATH AT ANODIC CURRENT DENSITY 100 MA/CM², SLOPES OF E-LOG I DEPENDENCES (B) AND SEMICONDUCTING CHARACTERISTICS.

Anode	Pt, mg/cm ²	Temperature of treatment, °C	CE Cr(VI), %	b, mV	E _{FB} , mV	N×10 ⁻²³ , cm ⁻³
Ti/Pt	2	-	30	157	788	6.8
		410	6	147	487	16.0
	8	-	29	-	-	-
		410	17	167	510	2.0

As was shown before, coatings with low amount of Pt are non uniform, look like islands of Pt on the substrate and characterized by extended surface while electrodes containing 8 mg/cm² are more uniformly coated by Pt [4].

For Ti/Pt electrodes, decrease in CE Cr(VI) with increasing temperature of treatment was observed. As goes from [6], thermal treatment at temperatures above 400°C leads to interaction between titanium and platinum with formation of intermetallic compounds or mixed oxides. So, decrease in CE Cr(VI) for thermally treated electrodes must be a result of composite formation and reduction of amount of electrochemically active Pt on the surface of electrode owing to its thermal diffusion deep into substrate. CE Cr(VI) on electrodes with different amount of electrodeposited Pt, obtained without thermal treatment, are close, but the value of CE for anode containing low amount of Pt is shade higher. According to SEM data acceleration of Cr³⁺-ions electrooxidation must be a result of extended surface of active layer.

Fig. 2 exhibit E-log i dependences obtained for Ti/Pt anodes. As goes from obtained data overvoltage of oxygen evolution in these cases strongly depends on amount of electrodeposited Pt and temperature of treatment. The slope of the curve for Ti/Pt electrode with amount of Pt 8 mg/cm² equals 0.121 V. This coincides with theoretical value of Tafel slope for oxygen evolution reaction when stage of first electron transfer is limiting [3]. In other cases, the slopes are higher than theoretical value due to semiconducting properties of anodes.

According to impedance measurements Ti/Pt electrodes are n-type highly doped semiconductors. Flatband potential of electrode obtained without thermal treatment is rather higher (Table). Probably, oxide film formed on the surface of Ti during anodic polarization is thin, more nonstoichiometric and differs greatly from one formed during thermal treatment. Increase in amount of electrodeposited Pt (donor of electrons) leads to increase in the flatband potential value. We also observed increase in donor concentration after thermal treatment of electrode, apparently caused by interaction between Pt and titanium oxides. Thermally treated electrode containing 8 mg/cm² of Pt is characterized by the least value of donor concentration. Probably, for electrodes containing high amount of Pt processes of its thermal diffusion occurs with low rate since the surface of such materials is more uniformly coated by Pt [4].

So, decrease in donor concentration leads to increase in overvoltage of oxygen evolution for platinized titanium electrodes. In case of electrodes with low amount of Pt this phenomena results in acceleration of Cr(III) electrooxidation.

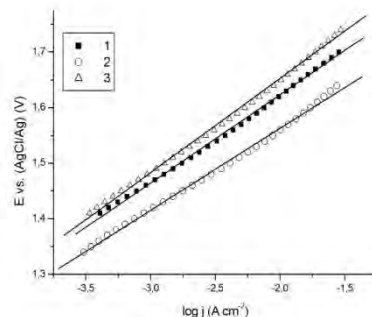


Fig. 2. Polarization curves (5 mV/s) represented in semilogarithmic scale for Ti/Pt-anodes with Pt content of 2 (1,2) and 8 mg/cm² (3), obtained without thermal treatment (1) and thermally treated at 410°C (2,3). Solution – 1 M HClO₄

Conclusions

Thereby, such anodes as DSA, PbO₂, Ti/MnO₂ are characterized by low rates of Cr(VI)-species generation. Nevertheless these materials are not stable in the electrolyte media that limits their application for hard chromium electrodeposition. The most suitable for a Cr(III) electroplating bath was shown to be Ti/Pt anodes owing to good service life and admissible values of CE Cr(VI). Some of these electrodes were found to be n-type semiconductors that effects their electrochemical behavior. Electrodes containing 2 mg/cm² of Pt, thermally treated at 410°C are recommend hard chromium electrodeposition from a Cr(III) electroplating bath.

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