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On the use of platinized and activated titanium anodes in some electrodeposition processes

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Abstract Substitution of classical lead anodes containing 6–8% of antimony, 4–6% of tin or 0.75–1.00% of silver in the zinc electrowinning and hard chromium plating bath with platinized and activated titanium anodes is discussed in this paper. Depending on the type of electrochemical processes, the main effects of this substitution are as follows: smaller electrical energy consumption, better current efficiency, increased cell capacity, smaller electrode gap, higher purity of the deposit and savings in manpower and chemicals. Ti/Pt, Ti/Pt-IrO₂, Ti/RuO₂, Ti/Pt-IrO₂-MnO₂, Ti/Pt-IrO₂-PbO₂, Ti/Pt-IrO₂-RuO₂, Ti/MnO₂, Ti/RuO₂-MnO₂ and Ti/PbO₂ coated titanium anodes have been tested in synthetic as well as in industrial electrolytes. At working current densities some activated titanium anodes showed lower overpotential than the lead anode. These electrodes have continued to perform in this way during a one-year test in synthetic and industrial electrolytes so far. No signs of corrosion of the electrodes have been noticed during the test.

Key words Platinized and activated titanium anodes · Zinc electrowinning · Hard chromium plating · Corrosion stability

Introduction

Zinc electrowinning is one of the basic processes of the electrochemical industry. Lead-silver anodes (with 0.75–1.00% of Ag) have been used in zinc production for over 50 years [1–3]. Although these electrodes have the lowest current efficiency for zinc deposition and higher electrical energy consumption when compared to pure lead anodes, they are widely used because of their

high corrosion stability in acid (H₂SO₄) solution and because of the higher purity of the zinc cathodic deposits [4].

In searching for an alloying element for Pb, various other metals were investigated such as: Ca, Th, Sn, Co, Sb, Tl, Sr, Y [5–9], or the anodic oxides formed on Pb under different potentials and pH [10–12], the massive manganese oxide electrode [13] or the Mn-oxide film electrodes prepared by thermal decomposition of manganese(II) nitrate on the Ti and Pt substrate [14, 15], and finally the lead-dioxide-titanium electrodes [16] or the titanium anodes coated with a layer of RuO₂ and TiO₂ [17].

The development of activated titanium anodes for oxygen evolution [based on dimensionally stable anodes (DSAs), widely used in chlor-alkaline electrolysis] can optimize all the requirements in hydrometallurgical processes for pure metals production (Cu, Zn, Co, Cd etc.). Such an anodic material would allow operation with a small and constant gap between electrodes and without contamination of the electrolyte and the metal deposit by lead dissolved from the anodes. In addition, decreased electrical energy consumption and increased cell productivity would be achieved.

One of the basic aims in electrolytic zinc production is to find a high-quality anodic material with high corrosion stability and high cathodic activity for (a) production of high purity metal deposits (elimination of lead contamination of the electrolyte and the metal product, originating from lead anodes), (b) increasing the current efficiency, (c) increasing the capacity of the existing electrolytic plants, and (d) improved morphology of the cathodic metal deposit. This can be achieved by using some types of DSA anodes.

Lead or lead-rich alloy anodes which are insoluble in chromic acid are generally used in electroplating and electrowinning of chromium from the chromic acid electrolyte [18]. Because of the strong passivating properties of the bath, it is generally believed that these materials are immune to acid attack. Practical experience shows, however, that this is not the case.

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Depending on the type of alloy and the operating conditions, the life of lead anodes is between 2 and 5 years [19–21].

When operating correctly, these anodes should be coated with a chocolate-brown film of lead peroxide (PbO_2) [18, 22–25]. In this condition, they will reoxidize much of the Cr^{3+} formed at the cathode back to Cr^{6+} . This will result in an equilibrium being set up between the cathodic reduction of Cr^{6+} and its anodic oxidation, the resulting concentration of Cr^{3+} depending on the relative cathode and anode surface areas. Hence, oxidation of Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ is an important role of the anode to be used, and the lead anode is capable of this action.

Having in mind all the properties which the anode for hard chromium plating should satisfy, the choice of the anodic material is very limited. As a result, any DSA, such as that for chlor-alkaline electrolysis, is investigated. Of course, such anodes should have catalytic activity on the oxidation of chromic ions as well.

Platinized and activated titanium has also been suggested as a more suitable material for this purpose, and indeed does remain uncorroded, but it can only be used in conjunction with a much larger area of lead alloy, since no oxidation of Cr^{3+} occurs at its surface [20–22]. The active components for the coatings for low potential oxygen evolution are carefully selected non-stoichiometric components of some of the platinum metals, predominantly iridium and platinum. These compounds are almost completely inert, even at high electrolyte temperatures and in the presence of free sulfuric acid.

Many investigations of the electrochemical properties of pure RuO_2 and $\text{RuO}_2\text{-TiO}_2$ coatings have been described in the literature [17, 26–30]. While the performance of the RuO_2 anode is fairly good and can even be improved by admixture of valve metals like Ti or Ta, they lose their electrochemical activity after a certain time, in particular undergoing heavy corrosion during anodic oxygen evolution in acid solutions [31]. The activity losses generally manifest themselves as a rapid increase in the potential after a certain time or an end of the service life. In contrast to ruthenium, iridium has lower activity for the oxygen evolution process (i.e.

higher overpotential and Tafel slope) but is far more stable.

In this connection, the present paper is not concerned with the reasons for applying insoluble anodes but rather with the durability of different materials, and in particular the durability of that group of anodes consisting of (noble) metal deposited upon a refractory metal substrate. The suitability of this group of materials in zinc electrowinning and hard chromium plating is discussed as far as possible in relation to both laboratory testing and possibly application.

Experimental

Platinised titanium anodes

Three type of baths were used for the deposition of platinum:

1. Phosphate bath
2. Platinum p-salt ($\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$) bath
3. DNS ($\text{H}_2\text{Pt}(\text{NO}_2)_2\text{SO}_4$) plating bath.

Titanium substrate (rod, $L = 120$ mm, $\phi = 3$ mm) was prepared by the usual methods (etching 10 min in 20% hot HCl, degreasing in ethyl alcohol saturated with NaOH and washing in purified water in an ultrasonic bath) [29]. Compositions and operating parameters of the platinum plating baths are given in Table 1.

Activated titanium anodes

These anodes were produced by thermal decomposition of isopropanol solutions of chlorides of the appropriate precursors. Prior to application of the precursors, the surface of the titanium rods was prepared by sand blasting, followed by the same procedure as for platinum plating. The conversion of chlorides to oxides was performed in air at 500 °C [28]. Four different active coatings were produced: Pt-IrO₂ (Pt : Ir = 60 mol% : 40 mol%), Pt-IrO₂-MnO₂ (Pt : Ir : Mn = 30 mol% : 30 mol% : 40 mol%), Pt-IrO₂-PbO₂ (Pt : Ir : Pb = 30 mol% : 30 mol% : 40 mol%) and Pt-IrO₂-RuO₂ (Pt : Ir : Ru = 30 mol% : 30 mol% : 40 mol%) with a metal content of 10 g m⁻². In the active coatings prepared in this way, platinum exists mainly as a metal, while other metals are in form of nonstoichiometric oxides [32].

In addition, three types of anodes were produced by electrochemical deposition of $\gamma\text{-MnO}_2$ on Pt-IrO₂ and Pt-RuO₂ coating, and on pure titanium substrate. Deposition was performed from a

Table 1 Compositions and operating parameters of the platinum plating baths

Type of bath	Electrolyte composition (g dm ⁻³)	Current density (A dm ⁻²)	Temperature (°C)	
Phosphate	PtCl ₄	3.5	0.1	
	(NH ₄) ₂ HPO ₄	16.0		
	Na ₂ HPO ₄ · 12H ₂ O	80.0		
	NaCl	4.0		
	Na ₂ B ₂ O ₇ · 10H ₂ O	1.5		
Platinum p-salt	Pt(NH ₃) ₂ (NO ₂) ₂	16.5	4.0–5.0	
	NH ₄ NO ₃	100.0		
	NaNO ₂	10.0		
	NH ₃ (ml dm ⁻³)	50.0		
	DNS	H ₂ Pt(NO ₂) ₂ SO ₄		10.0
	H ₂ SO ₄ to correct	pH < 2	2.5	30

solution containing $100 \text{ g dm}^{-3} \text{ MnO}_2 + 10 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ at 90°C and with a current density of 100 A m^{-2} .

Finally, pure titanium substrate was coated by electrochemical deposition of PbO_2 using $3 \text{ M Pb}(\text{NO}_3)_2 + 0.5 \text{ M HNO}_3 + 10 \text{ g dm}^{-3} \text{ Ni}(\text{NO}_3)_2$ solution at current density of 1000 A m^{-2} ; a 0.5-mm thick coating was obtained.

Electrolytes and operating conditions

Polarization measurements of all the anodes were performed in $0.5 \text{ M H}_2\text{SO}_4$ and/or $4.7 \text{ M NaClO}_3 + 1.6 \text{ M NaClO}_4 + 0.01 \text{ M Na}_2\text{Cr}_2\text{O}_7$ solutions.

Corrosion stability tests for all the anodes were performed in appropriate synthetic and/or industrial electrolytes, depending on the process and the type of anode.

For testing and analyzing the anodes of zinc electrowinning, a synthetic electrolyte ($135 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4 + 63 \text{ g dm}^{-3} \text{ Zn}^{+2}$) and an industrial electrolyte: ($135 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4, 63 \text{ g dm}^{-3} \text{ Zn}^{+2}, 50 \text{ mg dm}^{-3} \text{ Fe}^{+2}, 2 \text{ mg dm}^{-3} \text{ Co}^{+2}, 150 \text{ mg dm}^{-3} \text{ Cl}^-, 1 \text{ g dm}^{-3} \text{ CaO}, 0.5 \text{ g dm}^{-3} \text{ Cu}^{+2}, 0.1 \text{ mg dm}^{-3} \text{ Sb}^{+3}, 7 \text{ g dm}^{-3} \text{ Mn}^{+2}, 0.5 \text{ g dm}^{-3} \text{ Ni}^{+2}, 2 \text{ g dm}^{-3} \text{ NH}_4^+, 3 \text{ g dm}^{-3} \text{ MgO}, 0.1 \text{ g dm}^{-3} \text{ Cd}^{+2}$ and $1 \text{ mg dm}^{-3} \text{ As}$ at $40 \pm 1^\circ\text{C}$) were used. Agitation of the solution was provided by a magnetic stirrer. The working electrode (cathode) was of technical aluminum.

Electrodeposition of chromium was carried out in a plating bath containing a high concentration of chromium trioxide (250 g dm^{-3}) and a low concentration of sulfuric acid (2.5 g dm^{-3}) by applying current density of 4.5 kA m^{-2} at $52 \pm 1^\circ\text{C}$. Catalytic anodes based on $\text{RuO}_2\text{-IrO}_2$ catalyst were used and compared to the classical lead anodes.

The characteristics of different anode materials were investigated by cyclic voltammetry (CV) and stationary potentiostatic techniques.

The composition, experiments performed and operating conditions of all electrodes investigated are presented in Table 2.

Results and discussion

Activated titanium anodes in the zinc electrowinning process

The polarization characteristics of the tested anodes were compared to that of the classical Pb anode with 1% of silver, during the oxygen evolution reaction in $135 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ with 63 g dm^{-3} of zinc. The results and the operating parameters are presented in Fig. 1.

The highest activity was found with the anode coated with RuO_2 (curve 1), but the corrosion stability of such an anode was very poor in the oxygen evolution reaction.

It is known [31] that the problem of stability of RuO_2 occurs during anodic gas evolution in acid media. The most serious causes are probably the penetration of the electrolyte through the cracks or pores in the active layer and the dissolution of the active layer or RuO_2 , both of which lead to the formation of a resistive TiO_2 film on the Ti substrate.

Apart from the high catalytic activity for the oxygen evolution reaction from H_2SO_4 solution, the Pt-IrO_2 (curve 2) coating has a significant corrosion stability also. During six months operations with the current density of 575 A m^{-2} in the same electrolyte, the elec-

trode potential remained practically constant ($\Delta E < 20 \text{ mV}$).

In the case of the titanium anode coated with MnO_2 (curve 5), when this is compared to the Pb-Ag anode (curve 7) it shows lower overpotential for oxygen evolution, but during operation it loses its activity because of the growth of the resistive TiO_2 layer on the substrate/coating interface [29, 30]. As a result, after two months of operation, destruction and exfoliation of the coating occurred. However, if RuO_2 or Pt-IrO_2 interlayers were formed on titanium prior to deposition of the MnO_2 layer (curves 3 and 4), the anodes showed better conductivity. In this case, the potential of the anode did not change for some months.

The titanium anode coated with PbO_2 (curve 6), deposited electrochemically, had similar properties to the commonly used anode containing 1% silver. The presence of the nonconductive TiO_2 layer on the substrate/coating interface caused rapid decay of the catalytic activity.

Electrolytic winning of zinc using activated titanium anodes with Pt-IrO_2 coating (curve 2 in Figs. 1 and 2) (with or without the added MnO_2 layers), produced great energy savings due to lower overpotential for the oxygen evolution reaction. The purity of the zinc deposit obtained in this way was greater than in the standard cells with Pb-Ag anodes, which contaminated the electrolyte by dissolution [33]. The presence of chloride and nitrate ions in the electrolyte had no effect on the process, in contrast to the case of Pb-Ag anodes, where they accelerated the anode dissolution. The impurities in the bath solution, particularly the chloride and the nitrate, shortened the life of the lead anodes. In addition, the cathodic current efficiency was improved when the titanium anodes were used (Table 3).

Platinized and activated titanium anodes in hard chromium plating baths

The stability (e.g. the durability) of the anodes was tested in the solution: $4.7 \text{ M NaClO}_3 + 1.6 \text{ M NaClO}_4 + 0.01 \text{ M Na}_2\text{Cr}_2\text{O}_7$, at 52°C ($j = 4.5 \text{ kA m}^{-2}$). The anodes obtained in the platinum p-salt and DNS-plating bath show more than three times the stability of the anodes prepared in the phosphate bath. During 800 h of testing at given current densities, these two anodes did not change their potential significantly.

The anode made in the DNS-plating bath was chosen for further investigation, together with several activated titanium anodes. The polarization measurements were performed in $0.5 \text{ M H}_2\text{SO}_4$ solutions. Figure 2 shows the Tafel plots for oxygen evolution from the investigated anodes. The slopes of Ti/Pt (platinized-DNS bath) (curve 11), Ti/Pt- IrO_2 (curve 2) and Ti/Pt- $\text{IrO}_2\text{-RuO}_2$ (curve 14) anodes (about 30, 40 and 45 mV dec^{-1} , respectively) indicated that oxygen evolution in acid solution occurred at a lower overpotential value than in the case of Ti/Pt- $\text{IrO}_2\text{-PbO}_2$ oxide

Table 2 Composition, experiments performed and operating conditions of all electrodes investigated

No	Composition ^a	Preparation method	Investigated process	Polarization measurement ^b	Corrosion stability test ^b	Cyclic voltammetry ^b	Analyzing in industrial electrolyte ^c
1	Ti/RuO ₂	Thermally	Zn electrowinning Hard Cr plating	Electrolyte A Electrolyte B Electrolyte A	Industrial electrolyte ^c Electrolyte B Industrial electrolyte ^c	– Electrolyte B –	– Current efficiency Purity of Zn deposits Current efficiency Current efficiency
2	Ti/Pt-IrO ₂	Thermally	Zn electrowinning	Electrolyte A	Electrolyte B	Electrolyte B	–
3	Ti/Pt-IrO ₂ -MnO ₂	Pt-IrO ₂ , thermally MnO ₂ electrochemically	Hard Cr plating Zn electrowinning	0.5 M H ₂ SO ₄ Electrolyte B Electrolyte A	Electrolyte B Industrial electrolyte ^c	Electrolyte B –	–
4	Ti/RuO ₂ -MnO ₂	RuO ₂ , thermally MnO ₂ electrochemically	Zn electrowinning	Electrolyte A	Industrial electrolyte ^c	–	–
5	Ti/MnO ₂	Electrochemically	Zn electrowinning	Electrolyte A	Industrial electrolyte ^c	–	–
6	Ti/PbO ₂	Electrochemically	Zn electrowinning	Electrolyte A	Industrial electrolyte ^c	–	–
7	Pb + 1% Ag	Commercial	Zn electrowinning	Electrolyte A	–	–	Purity of Zn deposits Current efficiency
8	Pt	Pure Pt wire	Hard Cr plating	Electrolyte B	–	–	–
9	Ti/Pt-phosphate bath	Electrochemically	Hard Cr plating	Electrolyte C	Electrolyte C	–	–
10	Ti/Pt-p-salt bath	Electrochemically	Hard Cr plating	Electrolyte C	Electrolyte C	–	–
11	Ti/Pt-DNS bath	Electrochemically	Hard Cr plating	Electrolyte C	Electrolyte B Electrolyte C Electrolyte B	–	–
12	Ti/Pt-IrO ₂ -MnO ₂	Thermally	Hard Cr plating	0.5 M H ₂ SO ₄	Electrolyte B	–	–
13	Ti/Pt-IrO ₂ -PbO ₂	Thermally	Hard Cr plating	0.5 M H ₂ SO ₄	Electrolyte B	–	–
14	Ti/Pt-IrO ₂ -RuO ₂	Thermally	Hard Cr plating	0.5 M H ₂ SO ₄	Electrolyte B	–	–
15	Pb + 5% Sb	Commercial	Hard Cr plating	Electrolyte B	–	Electrolyte B	Current efficiency

^a See text for details^b A: 135 g dm⁻³ H₂SO₄ + 63 g dm⁻³ Zn; B: 250 g dm⁻³ CrO₃ + 2.5 g dm⁻³ H₂SO₄, 52 °C (*j* = 4.5 kA m⁻² in corrosion stability tests) C: 4.7 M NaClO₃ + 1.6 M Na ClO₄ + 0.01 M Na₂Cr₂O₇ (*j* = 4.5 kA m⁻², 52°C in corrosion stability tests)^c See text for details of electrolyte composition and operating parameters

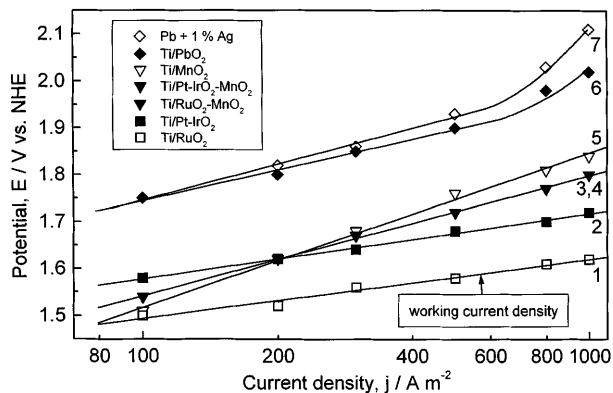


Fig. 1 Polarization characteristics of different anode materials in oxygen evolution reaction: 135 g dm⁻³ H₂SO₄, with addition of 63 g dm⁻³ Zn²⁺, 40 °C (anode designations as in Table 2)

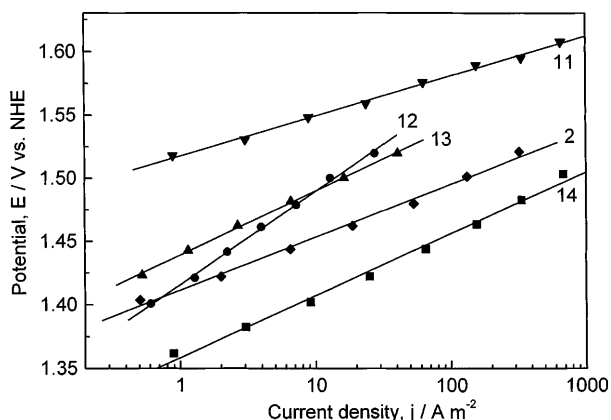


Fig. 2 Polarization characteristics of different anode materials in oxygen evolution reaction: 0.5 M H₂SO₄, 2 Ti/Pt-IrO₂, 11 Ti/Pt (DNS plating bath), 12 Ti/Pt-IrO₂-MnO₂, 13 Ti/Pt-IrO₂-PbO₂, 14 Ti/Pt-IrO₂-RuO₂ anodes, 25 °C (anode designations as in Table 2)

(curve 13) and Ti/Pt-IrO₂-MnO₂ oxide (curve 12) anodes. Higher potential values of the Ti/Pt electrode at the same current densities were caused by the higher surface area of other anodes caused by their sand blasting before the thermal treatment.

Stability tests were performed in the standard chromium electrolyte (250 g dm⁻³ CrO₃ + 2.5 g dm⁻³ H₂SO₄ at 52 ± 1 °C) at a current density of 4.5 kA m⁻². Cell voltage-time dependences were recorded, and results are presented in Fig. 3.

Cell voltage measurements made during long-term electrolysis indicated a steady value of 2.9 V for Pb (the

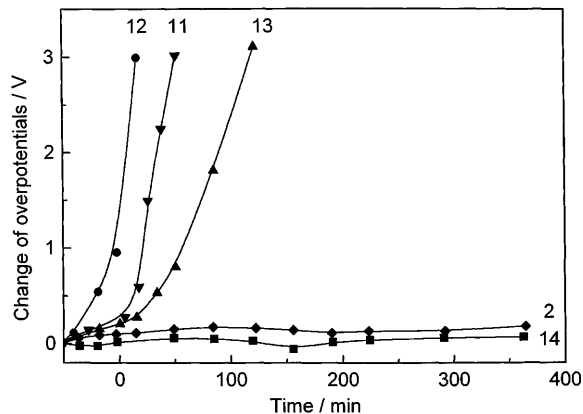


Fig. 3 Corrosion stability of different anode materials in standard chromium electrolyte: 250 g dm⁻³ CrO₃ + 2.5 g dm⁻³ H₂SO₄, *j* = 4.5 kA m⁻², 52 ± 0.1 °C. 2 Ti/Pt-IrO₂, 11 Ti/Pt (DNS plating bath), 12 Ti/Pt-IrO₂-MnO₂, 13 Ti/Pt-IrO₂-PbO₂, 14 Ti/Pt-IrO₂-RuO₂ anodes (anode designations as in Table 2)

same value as for Ti/Pt-IrO₂-PbO₂ or Pb + 1% Ag). For the catalytic anodes (Ti/Pt-IrO₂ or Ti/Pt-IrO₂-RuO₂) it was 2.40–2.50 V initially at an anode current density of 4.5 kA m⁻² and 2.65 V after one month.

Although Pb oxide is the standard anode in hard chromium plating (Mn oxide is sometimes a component of such an anode), the stability of Ti/Pt-IrO₂-PbO₂ (curve 13) Ti/Pt-IrO₂-MnO₂ (curve 12) anodes is poor. This may be attributed to the different natures of Pb (and Mn) oxides. The standard anodes were produced by electrochemical deposition of oxides, in contrast to the investigated anodes where the oxides were obtained by thermal decomposition.

The poor stability of Ti/Pt anodes (curve 11) can be explained by the fact that no oxidation of Cr³⁺ occurs at their surface [20–22]. The concentration of Cr³⁺ increased with time and changed the optimal electrolyte composition, which resulted in the increase of the cell voltage and great energy losses. In fact, the Ti/Pt anode stability was not in question, but its influence on the electrolyte composition.

The cell voltage was found to rise gradually as the Cr⁺³ content in the electrolyte built up in the course of deposition. As the conductivity of the electrolyte containing Cr³⁺ is lower than that of Cr⁺⁶, the rise in the cell voltage is due to an increase in the resistance of the electrolyte [21].

The Ti/Pt-IrO₂ and Ti/Pt-IrO₂-RuO₂ anodes, being those with the best properties, were additionally tested in the same electrolyte, but with higher current

Table 3 Influence of composition of the solution and anode material on cathode current efficiency

Composition of solution		Anode material	
Inlet g Zn/dm ³	Outlet g Zn/dm ³	Pb + 1% Ag Current efficiency (%)	Ti/Pt-IrO ₂ Current efficiency (%)
63	53	92.2	95.9
55	45	85.7	91.1
49	35	83.8	88.3

densities, of 100 A dm^{-2} . During the 50-h stability test, no significant cell voltage changes were observed.

Because of this, Ti/Pt-IrO₂ anode was chosen to be investigated in the real industrial cell for hard chromium plating of the inner tube surface ($L = 100 \text{ mm}$, $\phi_{\text{in}} = 7.6 \text{ mm}$). This type of chromium plating is associated with a number of difficulties, especially in the case of thick deposits. Among the greatest are the unequal thickness of the deposit along the tube and the dissolution of the Pb oxide anode, which necessitates three or more replacements of the anode until the appropriate depth of the deposit is achieved. These difficulties can be eliminated by using a Ti/Pt-IrO₂ anode.

For this purpose, four Ti rods were activated with Pt-IrO₂. Standard Pb oxide anodes were replaced with these anodes, and the hard chromium deposition process was performed with the same operating parameters (current density, temperature, anodic pretreatment, current strike). In some cases the current density increased to twice the optimum for those processes. The anode operations at extremely high current densities were checked in this way.

When Ti/Pt + Ir oxide anode was used, the cell voltage was a few tenths of a volt lower than in the case of the standard Pb oxide anode. In the course of more than 3000 Ah operation no significant changes in the cell voltage were detected.

The polarization characteristics of three different anodes (Pb + 5% Sb, Ti/RuO₂ and Ti/Pt-IrO₂) are presented in Fig. 4. It can be seen that Ti/RuO₂ (curve 1) and Ti/Pt-IrO₂ anodes (curve 2) show much lower polarization in the whole range of current densities, and that this effect is more pronounced with high current densities. Although the Ti/RuO₂ anode has good polarization characteristics, it becomes unstable on long polarization. During electrolysis, a layer of low-conductivity titanium oxide on titanium is formed, and the anode loses its catalytic activity [34, 35]. The Ti/Pt-

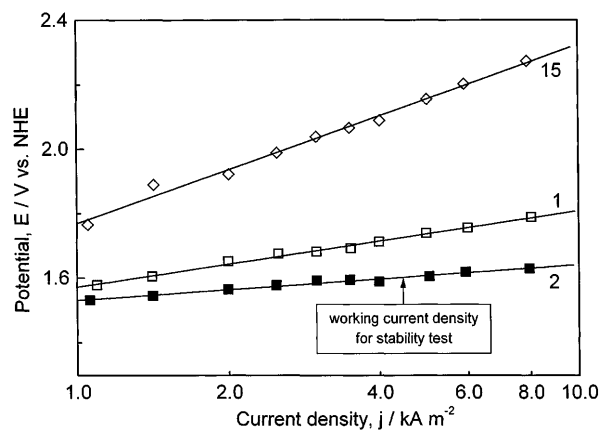


Fig. 4 Polarization characteristics of 1 Ti/RuO₂, 2 Ti/Pt-IrO₂, 15 Pb + 5% Sb in standard chromium electrolyte: $250 \text{ g dm}^{-3} \text{ CrO}_3 + 2.5 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$, $j = 4.5 \text{ kA m}^{-2}$, $52 \pm 0.1 \text{ }^\circ\text{C}$ (anode designations as in Table 2)

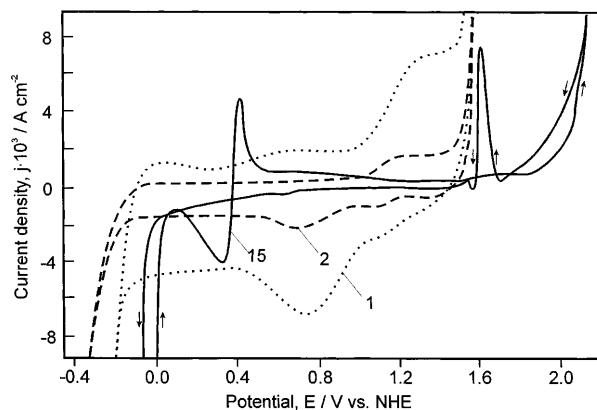


Fig. 5 CVs of 1 Ti/RuO₂, 2 Ti/Pt-IrO₂, 15 Pb + 5% Sb anodes in standard chromium electrolyte: $250 \text{ g dm}^{-3} \text{ CrO}_3 + 2.5 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$, $52 \pm 0.1 \text{ }^\circ\text{C}$ (anode designations as in Table 2)

IrO₂ anode shows better polarization characteristics and is very stable on long polarization. After six months of electrolysis with $j = 4.5 \text{ kA m}^{-2}$, the potential of the Ti/Pt-IrO₂ anode did not change by more than 50 mV.

These three different anodes were investigated by cyclic voltammetry in the same electrolyte. The results are presented in Fig. 5. It is obvious that the Ti/RuO₂ (curve 1) and Ti/Pt-IrO₂ (curve 2) electrodes catalyzed the reaction of oxygen evolution and that the Ti/Pt-IrO₂ electrode was somewhat better for the evolution of oxygen in the range of higher current densities.

It can also be seen that the voltammogram of Pb + 5% Sb electrode (curve 15) has a very complex structure in the potential range 0.0–2.2 V (vs NHE), which is most probably due to the formation of various chemical compounds of lead (oxides or chromate) [19] with the components of the solution and oxygen, and oxidation of Cr⁺³ to Cr⁺⁶ ions.

Under repetitive cycling, the voltammogram of this electrode changes its shape, depending on the cathodic and the anodic potential limits.

CVs of Ti/RuO₂ and Ti/Pt-IrO₂ electrodes have a more simple structure and possess one or two waves prior to oxygen evolution, which are most probably due to oxidation of Cr⁺³ to Cr⁺⁶ ions and/or formation of oxides on the electrode surfaces.

As in the case of zinc, the current efficiency of chromium plating also depends on the anode materials, as can be seen in Table 4.

Table 4 Current efficiency for hard chromium plating ($j = 4.5 \text{ kA m}^{-2}$, $52 \text{ }^\circ\text{C}$)

	Anode material	
	Pb + 1% Ag	Ti/RuO ₂ Ti/Pt-IrO ₂
Current efficiency(%)	11.8	12.0 18.4

Conclusions

The standard lead anodes in the zinc electrowinning and hard chromium plating bath can be substituted by some types of activated titanium anodes. Firstly, the titanium anode coated with Pt, IrO₂ and/or RuO₂ exhibits the best properties, the main effects of the substitution being as follows: smaller electric energy consumption, better cathode current efficiency and smaller electrode gap. In addition, the anodes with an electrochemically deposited Mn oxide overlayer can be successfully used in zinc electrowinning. This Mn oxide overlayer has no influence on the catalytic activity and stability of anodes, but protects the noble metal oxide interlayer from dissolution.

The lowest energy consumption during hard chromium plating can be achieved by using a Ti/Pt–IrO₂ anode. Also, this anode material provides the highest cathodic current efficiency.

Although it has undoubtedly been shown that the process of zinc and hard chromium plating can be improved by using DSA anodes, the mechanism of their performance is not fully understood, e.g. there is a need to increase the cathode current efficiency, which will be a matter of further investigation.

It is obvious that the newly developed but undoubtedly expensive anodes are better than the classical ones from the electrochemical point of view. Their application will depend on economic parameters, but this is beyond the scope of this work.

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