Вісник Дніпропетровського університету. Серія хімія
Bulletin of Dnipropetrovsk University. Series Chemistry
ISSN 2306-871X (Print),
ISSN 2313-4984 (Online)
journal homepage: http://chemistry.dnu.dp.ua

UDC544.653.2

ANODES FOR A TRIVALENT CHROMIUM ELECTROPLATING BATH

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Received 25 November 2013; revised 29 November 2013; accepted 10 December 2013

Abstract

Electrochemical behavior of different anode materials in electrolytes containing trivalent chromium salts was investigated. Some of electrodes (Ti/MnO_2, platinized titanium, materials based on Ebonex®) were shown to be n-type semiconductors. Semiconducting properties of electrodes affects their electrochemical behavior.It was shown that choice of an appropriate anode for a trivalent chromium electroplating bath should be based on compromise between its selectivity and service life. It was found that current efficiency of Cr(VI)-species strongly depends on the nature of anode material. Dimensionally stable anode based on mixture of titanium oxides and ruthenium oxides, PbO_2, Ti/MnO_2 anodes 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. Composite materials based on platinized titaniumor platinized Ebonex® 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.

Keywords: Cr electroplating; semiconductor; anode materials; electrocatalytic activity.

АНОДИ ДЛЯ ГАЛЬВАНІЧНИХ ВАНН ТРИВАЛЕНТНОГО ХРОМУ

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Анотація

Досліджено електрохімічну поведінку різних анодних матеріалів в електролітах, що містять солі тривалентного хрому. Доведено, що деякі електроди (Ti/MnO_2, платинований титан, матеріали на основі Ebonex®) є напівпровідниками n-типу. Напівпровідникові властивості таких електродів впливають на їх електрохімічну поведінку. З’ясовано, що вибір оптимального анодного матеріалу для процесів хромування з електролітів на основі солей тривалентного хрому є компромісом між його селективністю та ресурсом роботи. Встановлено, що вихід за струмом Cr(VI) значною мірою залежить від природи анодного матеріалу. Малозношувані аноди на основі оксидів титану та рутенію, PbO_2, Ti/MnO_2 характеризуються низькими швидкостями утворення сполук Cr(VI). Проте ці матеріали не придатні для використання в процесі електроосадження зносостійкого хрому. Композиційні матеріали на основі платинованого титану або платинованого Ebonex® рекомендовані як аноди для карбамідних електролітів, оскільки вони характеризуються значним ресурсом роботи та задовільними значеннями виходу за струмом сполук Cr(VI).

Ключові слова: електроосадження хрому, напівпровідник, анодні матеріали, електрокаталітична активність.

АНОДЫ ДЛЯ ГАЛЬВАНИЧЕСКИХ ВАНН ТРЕХВАЛЕНТНОГО ХРОМА

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Аннотация

Изучено электрохимическое поведение различных анодных материалов в электролитах, содержащих соли трехвалентного хрома. Доказано, что некоторые электроды (Ti/MnO_2, платинированный титан, материалы на основе Ebonex®) являются полупроводниками n-типа. Полупроводниковые свойства таких электродов оказывают влияние на их электрохимическое поведение. Выяснено, что выбор оптимального анодного материала для процессов хромирования из электролитов на основе солей трехвалентного хрома является компромиссом между его селективностью и ресурсом работы. Установлено, что выход по току Cr(VI) в значительной степе-

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doi: 10.15421/081407

ни зависит от природы анодного материала. Малоизнашиваемые аноды на основе оксидов титана и рутения, PbO_2, Ti/MnO_2 характеризуются низкими скоростями образования соединений Cr(VI). Тем не менее эти материалы не пригодны для использования в процессе электроосаждения износостойкого хрома. Композиционные материалы на основе платинированного титана или платинированного Ebonex® рекомендованы в качестве анодов для карбамидных электролитов, поскольку они характеризуются продолжительным ресурсом работы и приемлемыми значениями выхода по току соединений Cr(VI).

Ключевые слова: электроосаждение хрома, полупроводник, анодные материалы, электрокаталитическая активность.

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 [1–5]. 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: has good corrosion stability; products of anode destruction must not affect the chromium electrodepositionprocess; rates of unwanted reactions that cause change in composition of electrolyte should be minimal (negligible). Most of anode materials are not stable in acidic electrolytes based on Cr(III) compounds. Anodes based on platinum metals or their oxides, compounds of valve metals, PbO_2, MnO_2, SnO_2 are known to be stable in such electrolytes [3; 6; 7]. In this connection, anodic behavior of some anodes in electrolytes containing Cr(III) salts was investigated in this work.

Resultsand 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 [3]. Taking into account that composition changes and accumulation of Cr(VI)-species in a trivalent chromium bath lead to technological parameters deterioration [3; 4; 8; 9] an anode material must be characterized by low activity towards electrolyte components oxidation reactions and high selectivity in reference to oxygen evolution reaction. Thereby, low activity towards Cr(III) electrooxidation is required to choose an appropriate anode.

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 [3; 8; 9]. As one can see, in the range of medium current densities (50–200 mA/cm^2) 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 PbO_2 and MnO_2 destruction are significant at steady-state potential or during anodic polarization. Furthermore, growth of current density up to 50 mA/cm^2 facilitates mechanical destruction of oxide layer by oxygen evolution. In case of dimensionally stable anodes containing RuO_2 (DSA) the main reason of their low service life is electrochemical dissolution of RuO_2 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.

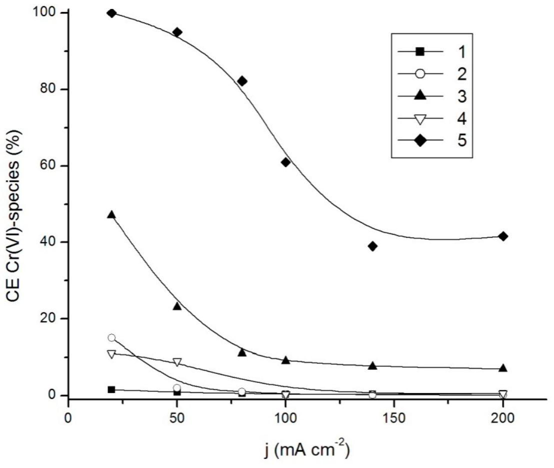


Fig. 1. Current efficiency of Cr(VI)-species at different anodes: 1 – DSA, 2 – Ebonex, 3 – PbO_2, 4 MnO_2, 5 – Pt

As shown in Fig. 1, anodes under trade name Ebonex®, consisting of Magneli phases (titanium "sub-oxides" having the general formula Ti_nO_{2n-1}, where n=4–10 [10; 11]) could be interesting enough owing to low CE Cr(VI) in a wide range of current densities. Ebonex® anodes exhibit high conductivity, good service life [10–13] and electrochemical stability in a wide potential range [13]. Nevertheless, application of Ebonex® as anode material is limited due to high potential values even under low current densities. Specifically, Ebonex® electrodes have been found to lose activity due to over oxidation leading to a more stoichiometric, less conductive surface layer accompanied with increase in potential value with time, especially in solutions containing sulphate-anions [10]. Owing to this, Magneliphases materials are seemingly more commonly used as substrates for active electrocatalytic layer [14–16] among which platinum and other noble metals are often the preferred choice since they exhibit unique catalytic activity.

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, as goes from prior investigation [4]. Important to note that rate of Cr^{3+}-ions electrooxidation on platinized titanium and platinized Ebonex® strongly depends on the method of anode preparation and amount of electrodeposited Pt (Table 1).

Table 1

CE Cr(VI) in a trivalent chromium electroplating bath on different Ti/Pt and Ebonex®/Pt anodes at anodic current density 100 mA/cm^2

Anode	Content of Pt, mg/cm^2	Temperature of treatment, °C	CE Cr(VI), %
Ti/Pt	2	-	30
		410	6
	8	-	29
		410	17
Ebonex®/ Pt	2	-	5
		410	<1
	8	-	<1
		410	11

Interesting enough that surface morphology of platinized titanium and platinized Ebonex® electrodes containing the same amount of Pt is very similar. So, coatings with low amount of Pt are non-uniform and look like islands of Pt on the substrate while electrodes containing 8 mg/cm^{2}represent more uniformly coated by Pt (Fig. 2).

In case of platinized titanium electrodes, decrease in CE Cr(VI) with increasing temperature of treatment was observed. As goes from [17; 18], 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 Fig. 2a, acceleration of Cr^{3+}-ions electrooxidation must be a result of extended surface of active layer.

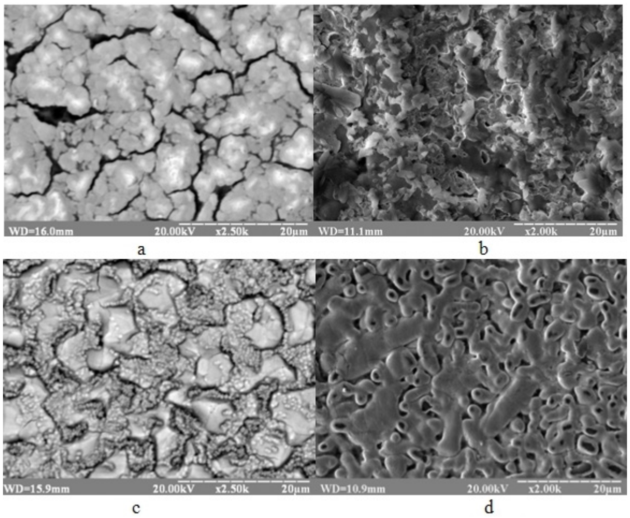


Fig. 2. SEM micrographs of platinum coatings deposited on Ti (a,c) or Ebonex® (b,d). Amount of electrodeposited Pt, mg/cm^2 –2 (a,b), 8 (c,d)

Electrocatalytic activity of Ebonex®/Pt-anodes for oxidation of Cr^{3+}-ions is low, as expected.At anodic current density 100 mA/cm^2 CE of Cr(VI)-species generation not exceeds 11% (Table 1). Non thermally treated anode containing 2 mg/cm^2 of Pt exhibits high CE Cr(VI) in comparison to thermally treated one since electrochemicaly active in this case is areas of metallic Pt that characterized by significant rates of Cr(III)-electrooxidation(Fig. 1, curve 5).

We observed increase in CE Cr(VI) with increasing treatment temperature for Ebonex®/Pt-anodes containing 8 mg/cm^2 of Pt. Important to note that overvoltage of oxygen evolution reaction also increases with increasing temperature of electrode preparation (Fig. 3). Therefore, acceleration of Cr(III) electrooxidation on thermally treated platinized Ebonex® (8 mg/cm^2) is a result of competing oxygen evolution reaction inhibition.

To characterize processes at different electrodes quasi steady-state polarization curves were obtained in electrolyte containing Cr^{3+}-ions (Fig. 4). Curves shown in Fig. 4 characterize several processes among which oxidation of Cr^{3+}-ions and oxygen evolution are main. As goes from Fig. 4, polarization curves obtained at various electrodes are different.

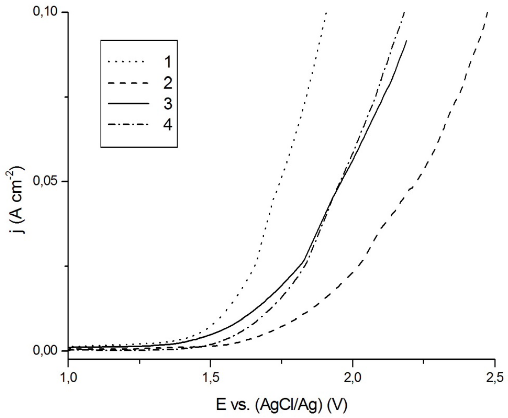


Fig. 3. Polarization curves (5 mV/s) in 1 M $HClO_4$ at platinized Ebonex electrodes containing Pt of 8 (1,2) or 2 mg/cm^2 (3,4) obtained without thermal treatment (1,3) or thermally treated at 410°C (2,4)

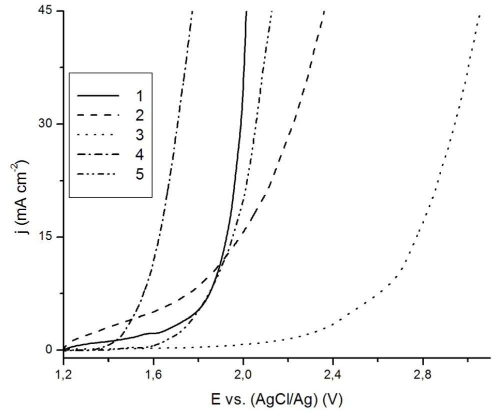


Fig. 4. Polarization curves (5 mV/s) in 0.5 M $Cr_2(SO_4)_3$ at different electrodes: 1 – PbO_2, 2 – MnO_2, 3 Ebonex, 4 – DSA, 5 – Pt

We observed high overpotentials and slopes for polarization curves represented in semilogarithmic scale for Ti/MnO_2 and Ebonex®. Slopes exceeding theoretical values could be a result of high electrode resistance or its semiconducting properties. Taking into account linear character of E–log i dependence, a conclusion about semiconducting properties of electrodes was made up. Impedance measurements were then carried out in order to investigate the semiconducting properties of Ti/MnO_2 and Ebonex® anodes. Solution of 1 M $HClO_4$ was used for impedance measurements to eliminate effects of adsorption. The data recorded at a frequency of 5 Hz obey Mott-Schottky relationship (equation) in a wide range of potentials that denotes the semiconducting properties of investigated electrodes:

$$C^{-2}=\frac{2}{e\cdot\varepsilon\cdot\varepsilon_0\cdot N}\left(E-E_{FB}-\frac{k\cdot T}{e}\right),$$

where:C – capacitance of electrode; e– charge of electron; N – donor concentration; E_{FB}– flatband potential; k – Boltzmann constant; T – absolute temperature; εandε$_0$ – permittivity of semiconductor and vacuum, respectively.

As goes from equation slope of C^{-2} – E plot characterizes donor concentration in semiconductor while intercept of the plot also depends on flatband potential.

Data calculated from Mott-Schottky plot are represented in Table 2. Investigated materials behave as highly doped n-type semiconductors since positive slope of the C^{-2} – E plot was observed and donor concentrations exceeded 10^{18} cm^{-3}. Anodic polarization above flatband potential leads to carrier depletion and decrease in semiconducting component of electrode capacitance.As a result, the slope of polarization curve represented in semilogarithmic scale increases.

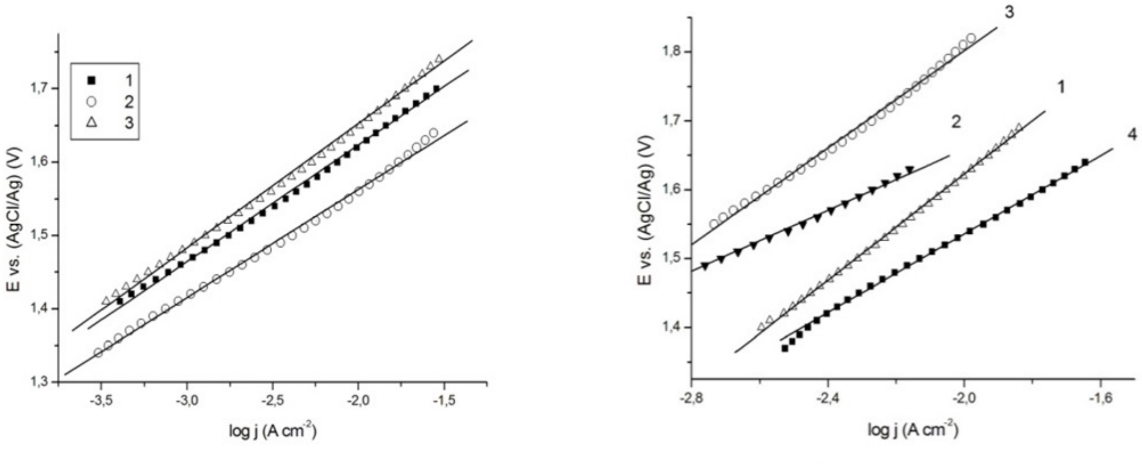
Table 2

Slopes of E–log i dependences (b) and semiconducting characteristics of Ti/MnO_2 and Ebonex® anodes

Anode	b, V	E_{FB}, V	N, cm^{-3}
Ebonex®	0.582	0.422	8×10^{24}
Ti/MnO_2	0.778	0.871	9×10^{19}

Fig. 5 exhibit E–log i dependences obtained for platinized titanium and Ebonex® 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/cm^2 equals 0.121 V. This coincides with theoretical value of Tafel slope for oxygen evolution reaction when stage of first electron transfer is limiting [7]. In other cases, the slopes are higher than theoretical value due to semiconducting properties of anodes.

According to impedance measurements both platinized titanium and Ebonex® electrodes are n-type highly doped semiconductors. In case of Ti/Pt, flatband potential of electrode obtained without thermal treatment is rather higher (Table 3). 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/cm^2 of Pt is characterized by the least value of donor concentration. Probably, for electrodes containing high amount of Pt processes of platinumthermal diffusion occurs with low rate since the surface of such materials is more uniformly coated by Pt (Fig. 2c).



a b

Fig. 5. Polarization curves (5 mV/s) represented in semilogarithmic scale for platinized titanium (a) and platinized Ebonex® (b)anodes with Pt content of 2 (1, 2) and 8 mg/cm^2 (3, 4), obtained without thermal treatment (1, 4) and thermally treated at 410°C (2, 3)
Solution – 1 M $HClO_4$

Table 3

Slopes of E–log i dependences (b) and semiconducting characteristics of Ti/Pt anodes

Amount of Pt, mg/cm^2	Temperature of treatment, °C	b, V	E_{FB}, V	N×10^{-23}, cm^{-3}
2	-	0.157	0.788	6.8
	410	0.147	0.487	16.0
8	410	0.167	0.510	2.0

Thermal treatment of platinized Ebonex® electrodes leads to increase in flatband potential and decrease in donor concentration(Table 3). Increase in flatband potential with thermal treatment is caused by thermal diffusion of Pt both along the surface and deep into substrate. Decrease in donor concentration after thermal treatment is a result of Ebonex® oxidation with formation of more stoichiometric Ti–O compounds, first of all rutile [5; 19; 20].

As goes from obtained data electrochemical behavior of platinized electrodes strongly depends on preparation procedure through change of morphology and semiconducting properties. So, decrease in donor concentration leads to increase in overvoltage of oxygen evolution for platinized titanium or Ebonex® electrodes. In case of electrodes with low amount of Pt this phenomena results in acceleration of Cr(III) electrooxidation.

Conclusions

Thereby, such anodes as DSA, PbO_2, Ti/$MnO_2$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 trivalent chromium electroplating bath was shown to be both platinized Ebonex® and platinized titanium 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/cm^{2}of Pt, thermally treated at 410^{0}C are recommend hard chromium electrodeposition from a Cr(III) electroplating bath since they contain low amount of Pt and characterized by high selectivity towards water oxidation reaction.

Materials and Methods

Electrooxidation of Cr(III)-ions was carried out in a thermostated cell (t=25±1°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$KCr(SO_4)_2 \times 12H_2O$ + 0.15 M $Al_2(SO_4)_3$ + 0.3 M Na_2SO_4 + 0.5 M H_3BO_3 + 0.6 M$HCOOH$ + 0.5 M $(NH_2)_2CO$, pH = 1.5 [21]. Cr(VI)-species concentration in the electrolytes was determined by amperometric titration using ammonium iron(II) sulfate.

Current efficiency of Cr(VI)-species was calculated using equation:

$$CE_{Cr(VI)} = \frac{n \cdot F \cdot m_{Cr(VI)}}{I \cdot t \cdot \mu_{Cr}} \cdot 100\ \%,$$

where:n – number of electrons, $m_{Cr(VI)}$ – total amount of Cr(VI)-species, determined by the amperometric titration (g), I – current (A), t – duration of electrolysis (s), F – Faraday constant (C mol^{-1}), μ_{Cr} – Cr molar mass (g mol^{-1}).

Cu-foil with geometric area of 1 cm^2 was used as a cathode.

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. Fist the surface of Ti plate was prepared mechanically by an abrasive paper; after rinsing it was degreasing with 5 M KOH at room temperature; after removal of degreasing solution it was chemically etched in 8 M HCl at 80°C for 60 min; then the surface was washed and thin layer of platinum was electrodeposited from the electrolyte: K_2PtCl_6 – 25.004 g/l; $NaNO_2$ – 100 g/l; solution of NH_3 (ρ = 0.915 g/cm^3) – 20 ml; at temperature – 70°C. Electrodes containing 8 mg/cm^2 Pt in active layer were obtained at cathodic current density – 30 mA/cm^2; the ones containing 2 mg/cm^2 Pt were deposited at 20 mA/cm^2. Some of electrodes were thermally treated in the air at 410^0C for 1 h using tube furnace [9; 22].

Monolithic block of Ebonex® (density – 8.5 g/cm^3, porosity – 12–18 vol.%), supplied by Atraverda Ltd., measuring 90mm×240mm×3mm was used in the current study. TheEbonex® was cut into 10mm×10mm square samples using a diamond-cutter.

Platinized Ebonex electrodes with platinum content of 2 and 8 mg/cm^2 were obtained by methods described in [23] and [19] respectively.

Ti/MnO_2 and PbO_2-anodes were obtained according to [3] and [24] respectively.

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°C. The procedure was repeated till uniform layer of oxide coating was obtained. The RuO_2 vs. TiO_2 ratio was 30 to 70%.

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.

Morphology of the surface of platinized electrodes was studied by scanning electron microscopy (SEM) technique using of a REM-106I microscope.

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