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Long service life IrO_2/Ta_2O_5 electrodes for electroflotation*

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$Ti/IrO_2-Ta_2O_5$ electrodes prepared by thermal decomposition of the respective chlorides were successfully employed as oxygen evolving electrodes for electroflotation of waste water contaminated with dispersed peptides and oils. Service lives and rates of dissolution of the $Ti/IrO_2-Ta_2O_5$ electrodes were measured by means of accelerated life tests, e.g. electrolysis in 0.5 M H_2SO_4 at 25 °C and $j = 2\,A\,cm^{-2}$. The steady-state rate of dissolution of the IrO_2 active layer was reached after 600–700 h ($0.095\,\mu g\,Ir\,h^{-1}\,cm^{-2}$) which is 200–300 times lower than the initial dissolution rate. The steady-state rate of dissolution of iridium was found to be proportional to the applied current density (in the range 0.5–$3\,A\,cm^{-2}$). The oxygen overpotential increased slightly during electrolysis (59–82 mV for $j = 0.1\,A\,cm^{-2}$) and the increase was higher for the lower content of iridium in an active surface layer. The service life of Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) in industrial conditions of electrochemical devices was estimated to be greater than five years.

List of symbols

a	constant in Tafel equation (mV)
b	slope in Tafel equation ($mV\,dec^{-1}$)
E	potential (V)
f	mole fraction of iridium in the active layer
j	current density ($A\,cm^{-2}$)
l	number of layers
m_{Ir}	content of iridium in the active layer ($mg\,cm^{-2}$)
r	dissolution rate of the IrO_2 active layer ($\mu g\,Ir\,h^{-1}\,cm^{-2}$)
T_c	calcination temperature (°C)
η_{O_2}	oxygen overpotential (mV)
$\Delta\eta_{O_2}$	difference in oxygen overpotential (mV)
τ_A	service life in accelerated service life tests (h)
τ_S	service life in accelerated service life tests related to $0.1\,mg\,Ir\,cm^{-2}$ (h)
τ_p	polarization time in accelerated service life tests (h)

1. Introduction

Ti/IrO_2 anodes, although they are rather expensive, have recently been used in the electrochemical industry for cleaning processes. This is because they can be successfully employed as oxygen evolving electrodes in neutral or weakly acid solutions where conventional Ti/RuO_2 anodes cannot be used due to their short lifetime in solutions with a low concentration of chloride ions. The Ti/IrO_2 anodes are used for the removal of cations (at the cathode) in waste water or for the disposal of harmful substances from waste water by oxidation at this anode.

Another application is their utilization for electroflotation of waste water contaminated with dispersed peptides and oils. Stainless steel is used as a stable cathode. The usual current density applied to both electrodes is 0.01–$0.02\,A\,cm^{-2}$. The size of bubbles (H_2 and O_2) generated electrochemically (50–100 μm) ensures the high efficiency of the electroflotation (99.5%) and thus enables a decrease in the content of contaminants from an input concentration of 1–$10\,g\,dm^{-3}$ to an output concentration of 1–$10\,mg\,dm^{-3}$.

Oxides for use as anodes are mainly prepared by thermal decomposition of the respective chlorides [1, 2]. It was shown that the electrocatalytic performances differ dramatically for samples prepared by thermal decomposition of precursors dissolved in different media [3, 4]. Angelinetta *et al.* [5, 6] investigated the properties of mixed oxides prepared by thermal decomposition of $RuCl_3 + IrCl_3$ onto titanium as a support using isopropanol as a solvent ('nonaqueous' mixed oxides) [5] and water as a solvent ('aqueous' mixed oxide) [6]. In particular, surface enrichment appears to be a result of low homogenization of the mixed oxides: this was found to be minimal for the samples prepared in isopropanol [5] and higher for those from water [6]. The electrocatalytic properties of nonaqueous mixed oxides appear to be slightly better [6].

In this work the properties of $Ti/IrO_2-Ta_2O_5$ electrodes for electroflotation prepared by thermal decomposition of precursors dissolved in ethanol–

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water solution were investigated. Emphasis was placed on the requirement of low oxygen overpotential and long service life.

2. Experimental details

The laboratory titanium electrodes for all tests were made from a titanium wire of 3 mm diameter (purity 99.9%). The electrode surface was treated before activation in concentrated HCl at 50–60 °C for 5 h. Activation solutions with a molar ratio of Ir : Ta from 1 : 0 to 3 : 7 were used (chlorides of Ir and Ta). The activation of the titanium electrodes was carried out by immersing the titanium wire into the activation solution. The solutions are relatively stable and it was possible to prepare them several hours before coating of the titanium wire. The content of iridium in each layer and, therefore, the iridium loading in the coating was determined from the weight decrease of the activation solution before and after each immersion of the titanium wires and from the iridium concentration in the activation solution. After each immersion of the titanium wires (activation) the wet surface was dried by hot air and then annealed at a temperature of 450 °C for 10 min. After the last coating the electrodes were annealed at 450 °C for an hour.

The service life and oxygen overpotential in chloride free solutions are the most important properties of the electrodes. Due to the fact that the service life of Ti/IrO_2 electrodes in industrial conditions should be greater than five years it is necessary to ensure laboratory conditions which will shorten this service life, enabling accelerated testing of a large number of electrodes. The service life and rate of dissolution of the IrO_2 active layer were measured by means of accelerated life tests, e.g. electrolysis in 0.5 M H_2SO_4 at 25 °C and $j = 2\,\mathrm{A\,cm^{-2}}$. To study the performance of new electrodes on the laboratory scale Comninellis and Vercesi [7, 8] used also accelerated life tests (in 30% H_2SO_4 at 80 °C at $j = 750\,\mathrm{mA\,cm^{-2}}$. The experimental conditions (0.5 M H_2SO_4 at 25 °C and $j = 2\,\mathrm{A\,cm^{-2}}$) lead to very short laboratory service life, approximately 100 times shorter than in industrial electroflotation devices. The end of the service life for a given electrode was determined as the time at which the anode potential increased significantly (about 4 V).

The oxygen overpotential of prepared Ti/IrO_2–Ta_2O_5 anodes was measured in 0.5 M H_2SO_4 at 25 °C and 60 °C; a platinum wire was used as a cathode (as well as for the accelerated life tests) and SCE was used as a reference electrode. The values of oxygen overpotential were expressed by the relation:

$$\eta_{O_2} = E_1 + E_2 - E_{H_2O} \qquad (1)$$

where E_1 represents a measured potential between the tested anode and SCE after ohmic drop elimination, E_2 is a potential SCE against HE in 0.5 M H_2SO_4 at 25 (60) °C and a pressure of 0.1 MPa (0.266 V at 25 °C and 0.242 V at 60 °C) and E_{H_2O} is the standard potential for water decomposition (1.23 V at 25 °C and 1.20 V at 60 °C).

The rate of the dissolution of the IrO_2 active layer was determined analytically. It was necessary to use a very sensitive analytical method because of the very low dissolution rate. Therefore a catalytic method was chosen for the determination of iridium [9–11]. The basis of this method is the catalytic effect of iridium on the reaction:

$$2Ce^{4+} + As^{3+} = 2Ce^{3+} + As^{5+} \qquad (2)$$

When iridium is not present in the solution the rate of Reaction 2 is negligible. All chemicals used have to be very pure because of the interference of other platinum metals (Ru, Rh, Os) and of impurities (Fe, Bi, Cr, Cu, Ni). Because the Ce^{4+} ions are yellow the rate of reaction can be followed spectrophotometrically as the decrease of absorbance with time. For the determination of iridium in the concentrated solutions (10–100 mg Ir dm^{-3}) a spectrophotometrical method with PAN [12] was used. These solutions were then diluted and used as standard solutions for the catalytic determination of iridium.

During the accelerated life test Ti^{4+} ions are present in the electrolyte due to the anodic corrosion of the titanium base metal. The quantity of Ti^{4+} ions was very small and it was proved experimentally that this amount had no catalytic effect on Reaction 2. In some cases (especially at the end of accelerated life tests) the electrolyte for determination of iridium had a weak yellow colour. This was caused by the

Table 1.

f	l	m_{Ir} /mg cm^{-2}	*Tafel parameters for* η_{O_2}				τ_A /h	τ_S /h
			a_1	b_1	a_2	b_2		
			25 °C					
0.3	8	0.44	560	91	754	196	52	11.8
0.5	8	1.70	519	76	620	150	5317	313
0.6	10	1.07	482	62	590	130	1376	130
0.65	10	1.04	486	61	584	126	5536	534
0.65	13	1.23	498	66	583	122	7049	574
0.7	7	0.71	519	70	612	146	4870	686
1	8	1.06	518	82	804	305	143.1	13.5

Calcination temperature (all electrodes): 450 °C.

Table 2.

f	l	m_{Ir} /mg cm^{-2}	T_c /°C	τ_A /h	τ_S /h
0.65	3	0.41	450	2501	610
0.65	3	0.41	500	3140	766
0.65	3	0.41	550	1890	461

formation of peroxotitanic acid. The peroxotitanic acid affected the determination of dissolved Ir and it was removed by reduction with SO_2.

3. Results and discussion

3.1. *Service life and oxygen overpotential*

According to previous work [7, 8, 13] it is known that some of the iridium can be replaced by tantalum. In this section the results obtained with different molar additions of tantalum to the base iridium activated solutions are presented. The results of the measurement of the oxygen overpotential and service life for anodically polarized electrodes with different molar fractions of iridium (the rest is tantalum) in the active layer on the titanium anodes are summarized in Table 1.

The content of iridium in an active layer was not constant for all the prepared electrodes. To compare the service life of the electrodes the τ_A values were converted to τ_S values corresponding to 0.1 mg Ir cm^{-2}. The dependence of oxygen overpotential on current density in the range 0.0006–1 A cm^{-2} was expressed by two Tafel lines:

$$\eta_{O_2} = a + b \log j \qquad (3)$$

with a slope b_1 and a constant a_1 for lower current densities and with a slope b_2 and a constant a_2 for higher current densities. The intersection between the two Tafel lines lies between $j = 0.01$ A cm^{-2} and $j = 0.05$ A cm^{-2}.

The values of service life were maximum for surface layer compositions of 65–70% IrO_2 and 30–35% Ta_2O_5. Tafel constants, a and b, determined for the oxygen overpotential do not show much scatter for the mole fractions of iridium in the range 0.5 to 0.7 and are minimum for an active surface layer composition of 60–65% IrO_2 and 35–40% Ta_2O_5. Similarly, in the search for a DSA®-type electrode for oxygen evolution Comninellis and Vercesi [7, 8] found that Ti/IrO_2 (70 mol %)–Ta_2O_5 (30 mol %) is by far the best composition. Active layers with higher fractions of iridium (0.8) were also tested, but the active surface layer was not adherent to the titanium surface.

The theoretical service lives for Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) in industrial conditions (25 °C, $j = 0.02$ A cm^{-2}) were calculated to be approximately 50–100 years. The real service life was estimated to be from five to 10 years. The sets of Ti/IrO_2 anodes (2 m^2), (1.23 mg Ir cm^{-2}, 13 layers, 65 mol % IrO_2 + 35 mol % Ta_2O_5) have been working in a cell for more than four years. The flow rate of contaminated water through the cell is 12–16 m^3 h^{-1}, $U = 4$–6 V and $I = 300$ A.

3.2. *Effect of calcination temperature*

To investigate the effect of calcination temperature, the set of electrodes (see Tables 2 and 3) was, after the final coating, annealed at three different temperatures of 450, 500 and 550 °C for an hour. The effect of calcination temperature on the service life of Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) is shown in Table 2. There is a maximum for a calcination temperature of 500 °C. The service life was also sufficiently long for a calcination temperature of 450 °C. Tafel plots for oxygen evolution on the Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) electrodes for two different calcination temperatures are presented in Fig. 1 and the Tafel parameters for oxygen overpotential at 25 °C and 60 °C are summarized in Table 3. The oxygen overpotential increases slightly with calcination temperature. This is similar to the observation of Trassati [14], who found that the electrochemical activity in oxygen evolution at Ti/IrO_2 electrodes increases with decreasing calcination temperature (in the range 350–550 °C). The decrease of oxygen overpotential in 0.5 M H_2SO_4 for 60 °C compared to that for 25 °C can be attributed to the fact that the charge transfer rate increases with temperature.

3.3. *Iridium dissolution rate*

The time dependence of the dissolution rate for a Ti/IrO_2 anode with iridium mole fraction of 0.65 (1.23 mg Ir cm^{-2}, $T_c = 450$ °C) is shown in Fig. 2. The slowly changing steady-state rate of dissolution of the IrO_2 active layer was reached after 600–700 h

Table 3.

f	l	m_{Ir} /mg cm^{-2}	T_c /°C	Tafel parameters for η_{O_2}							
				a_1	b_1	a_2	b_2	a_1	b_1	a_2	b_2
				25 °C				60 °C			
0.65	3	0.35	450	500	73	643	197	430	55	541	153
0.65	6	0.67	450	500	76	619	167	432	58	517	135
0.65	3	0.35	500	550	80	710	208	467	64	564	153
0.65	6	0.67	500	524	75	667	201	457	63	537	148

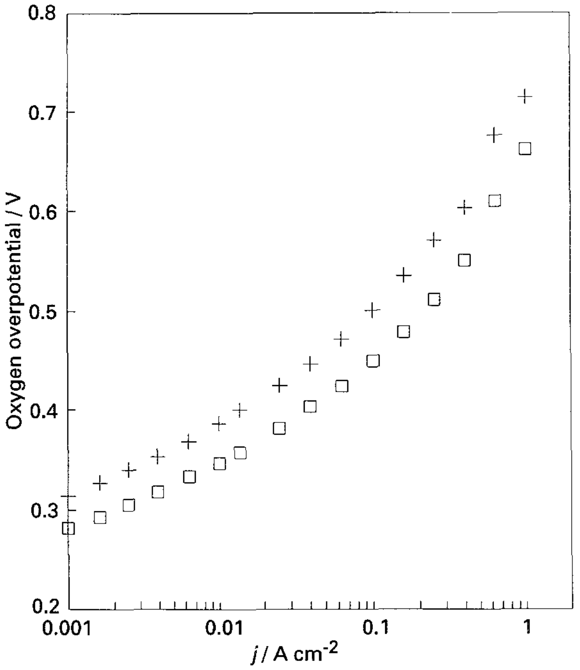

Fig. 1. The dependence of oxygen overpotential on current density for Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) for 25 °C for two different calcination temperatures, $m_{Ir} = 0.35\,mg\,cm^{-2}$. Calc. temp.: (□) 450 °C; (+) 500 °C.

($0.095\,\mu g\,Ir\,h^{-1}\,cm^{-2}$) which is 200–300 times lower than the initial dissolution rate. This rate then slowly decreases and after 4000 h is $0.03\,\mu g\,Ir\,h^{-1}\,cm^{-2}$. Interruption of electrolysis for longer than 1 h has considerable influence on the iridium dissolution rate. Continuing electrolysis after interruption results in a rapid increase in iridium dissolution.

The effect of current density on the steady-state dissolution rate is shown in Fig. 3. The current density was initially changed after the steady-state rate of dissolution was achieved. From Fig. 4 it follows that the steady-state rate of Ir dissolution is proportional to the applied current density in the range 0.5–3 A cm^{-2}.

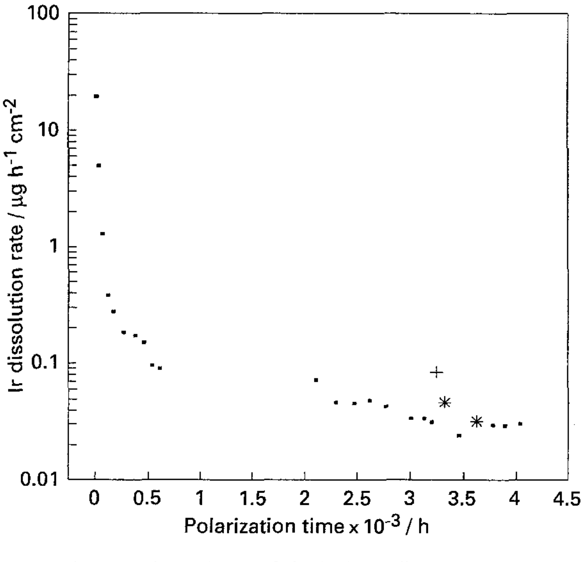

Fig. 2. The time dependence of the iridium dissolution rate (0.5 M H_2SO_4 at 25 °C and $j = 2\,A\,cm^{-2}$, ratio Ir : Ta = 6.5 : 3.5, $1.23\,mg\,Ir\,cm^{-2}$, 13 layers). Increase in iridium dissolution rate after interruption for (+) 2 h and (∗) 2 days.

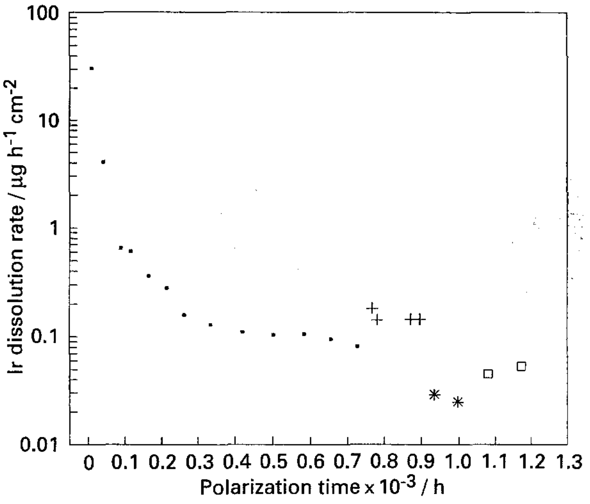

Fig. 3. The time dependence of the iridium dissolution rate, the effect of current density (0.5 M H_2SO_4 at 25 °C, ratio Ir : Ta = 6.5 : 3.5, $1.23\,mg\,Ir\,cm^{-2}$, 13 layers). Current density: (∗) 0.5, (□) 1, (●) 2 and (+) 3 A cm^{-2}.

Iridium dissolved in the electrolyte may be deposited at the cathode during the accelerated life test. This was determined by the following experiment. A tantalum cathode was used instead of platinum during accelerated life test. After 4000 h of polarization the tantalum cathode was removed and deposited iridium was dissolved in a mixture of concentrated HCl and HNO_3. The spectrophotometrically [12] determined amount of iridium deposited at the tantalum cathode ranged between 1–2% of the iridium dissolved during the accelerated life test.

The relative experimental error of catalytic determination of iridium was in the range 4–5% [11] and, therefore, the amount of iridium deposited at the cathode during the accelerated life tests was not considered.

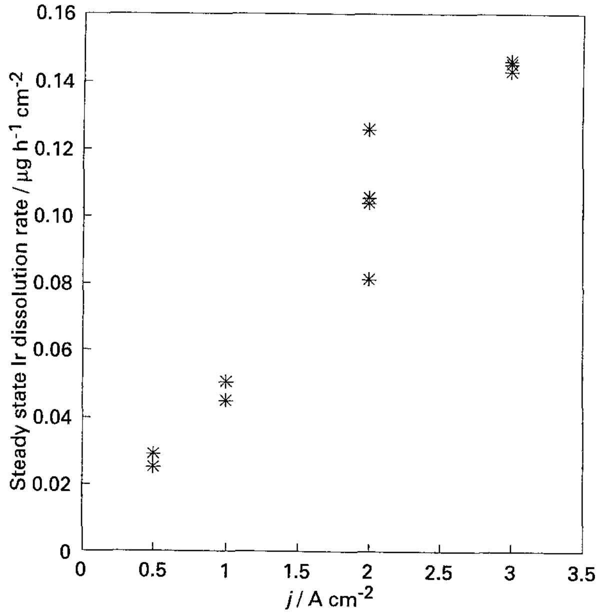

Fig. 4. The dependence of the steady-state iridium dissolution rate on current density.

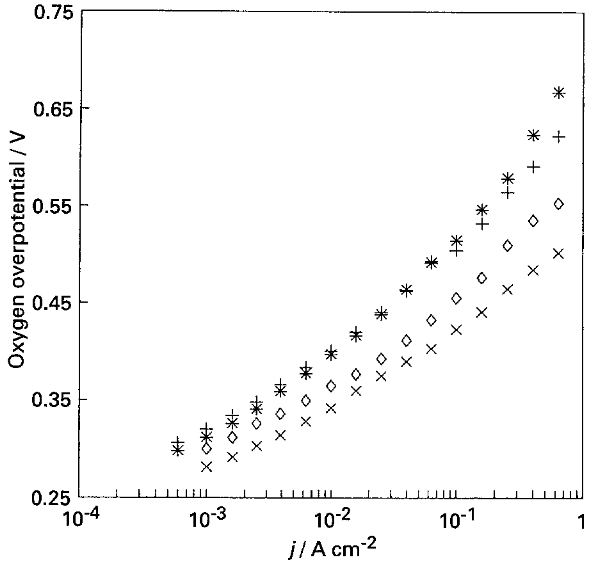

Fig. 5. The dependence of oxygen overpotential on current density for IrO_2/Ta_2O_5 electrodes A and B (0.5 M H_2SO_4 at 25 °C, ratio Ir : Ta = 6.5 : 3.5). (A) 0.84 mg Ir cm^{-2}, 7 layers: (×) new electrode, (+) after 1050 h polarization. (B) 1.23 mg Ir cm^{-2}, 10 layers: (◇) new electrode, (∗) after 860 h polarization.

3.4. *Change of η_{O_2} with polarization time*

The oxygen overpotential was measured at the beginning of electrolysis and also when the steady-state rate of iridium dissolution was achieved (Fig. 5). Parameters for these electrodes, as well as differences in overpotential, are given in Table 4. The differences in overpotential is given as a difference between the oxygen overpotential at the steady state and the oxygen overpotential measured at the beginning of electrolysis for the same current density. The oxygen overpotential increases slightly during electrolysis (about 59–82 mV for $j = 0.1\,\mathrm{A\,cm^{-2}}$) and this increase is higher for the lower content of iridium in an active surface layer (Fig. 5, electrodes A and B). The reason for the increase in the oxygen overpotential is the fact that the electrochemical active surface area changes during electrolysis. Rolewicz *et al.* [13] observed that the mole fraction of iridium in the active surface layer of IrO_2/Ta_2O_5 electrodes during accelerated life tests (80 °C, 30% H_2SO_4 at $j = 0.75\,\mathrm{A\,cm^{-2}}$) decreased from 0.7 to 0.42 during first 5% of service life and then was constant. Table 1 shows that, with decrease in the mole fraction of iridium, the oxygen overpotential increases. The present results show that the very high iridium dissolution rate at the beginning of the accelerated life test is responsible for the decrease in the mole fraction of iridium.

Table 4.

	f	l	m_{Ir} /mg cm^{-2}	τ_p /h	$\Delta\eta_O$ for $j = 0.1$ A cm^{-2}	
					/mV	/%
A	0.65	7	0.84	1050	82	19.3
B	0.65	10	1.23	860	59	12.9

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