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Effect of coating thickness and surface treatment of titanium on the properties of IrO_2–Ta_2O_5 anodes

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The effect of coating thickness and the effect of surface treatment of the titanium base metal on the surface morphology and electrochemical properties of IrO_2–Ta_2O_5 anodes were investigated. It was observed that for an iridium content of 0.45–1.2 mg cm^{-2} the service life is proportional to the iridium content in the coating. During etching of titanium in 5% HF at 25 °C a surface with macroroughness is formed, while during etching in HCl at 30, 50 and 80 °C a microrough surface with visible pitting is formed. The morphology of the IrO_2–Ta_2O_5 active layer (0.32–0.39 mg Ir cm^{-2}) depends strongly on the pretreatment of the titanium base metal. After etching of titanium in HF, the resulting IrO_2–Ta_2O_5 layer is adherent to the macrorough surface of the titanium base metal. After etching of titanium in HCl the resulting surface of the IrO_2–Ta_2O_5 layer is microrough with partly filled pitting holes. The service life of IrO_2–Ta_2O_5 coating with different roughness does not differ and has a value of 1500 ± 400 h (0.5 M H_2SO_4, 25 °C and $j = 2$ A cm^{-2}).

1. Introduction

Electrode materials containing IrO_2 as the active component have found extensive applications in industrial electrochemistry [1]. The understanding of their electrochemical properties from a fundamental point of view has been the object of several recent papers [1–8].

Vercesi *et al.* [9] investigated the influence of the base metal (Ti, Ta, Zr and Nb) on the performance of IrO_2–Ta_2O_5 electrodes. The chemical and electrochemical stability of the base metal was found to be directly related to the service life of the electrode, measured in 30% H_2SO_4 at 80 °C and 750 mA cm^{-2}. IrO_2–Ta_2O_5 electrodes with tantalum as the base metal had a service life of 1700 h in contrast to a service life of 120 h for electrodes with titanium as the base metal [9]. Nevertheless on a cost/performance basis titanium represents the best alternative and is actually used in almost all conventional DSA applications.

The first operation for the preparation of dimensionally stable electrodes based on titanium sheets, covered with a layer of IrO_2, is the pretreatment of titanium. In the previous work [10] the surface layer structure of titanium treated in hot concentrated HCl solution was investigated. The relative content of TiH_2 on the titanium surface was independently determined by X-ray diffraction and by the vacuum desorption of hydrogen gas from the decomposition of TiH_2 and these values were directly proportional. Observation of the surface of the etched electrodes by electron microscopy showed that TiH_2 formed during the dissolution of titanium in an active region is not regularly distributed over the whole surface area.

In this study the effect of the coating thickness and surface treatment of the titanium base metal on the service life, dissolution rate of iridium, oxygen overpotential and morphology of the Ti/IrO_2–Ta_2O_5 anodes were investigated.

2. Experimental details

The laboratory titanium electrodes, for all tests, were made from a titanium wire of 3 mm diameter (purity 99.9%). Prior to use all the titanium electrodes were degreased and then rinsed with distilled water. The solution of H_2IrCl_6 (in HCl) was mixed with the solution of $TaCl_5$ (in ethanol) to obtain the molar ratio Ir : Ta = 6.5 : 3.5 in the final activation solution. The concentration of iridium (Ir) was 0.26 mol dm^{-3}, the concentration of tantalum (Ta) was 0.17 mol dm^{-3}. The activation of titanium electrodes was described previously [3, 8]. 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. This procedure was repeated until the desired coating thickness (content of iridium per unit surface) was reached. The number of layers ranged from 1 to 13, for the study of the effect of the pretreatment the number of layers was constant (3). After the last coating the electrodes were annealed at a temperature of 450 °C for 1 h. Comninelis and Verscesi [2] observed that IrO_2–Ta_2O_5 coatings can be deposited chemically with high yields (>95%) on a titanium base. 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 titanium wires and from the iridium concentration in the activation solution.

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The service life and the oxygen overpotential in chloride free solutions are the most important properties of the prepared 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 remarkably shorten this service life, thus enabling the testing of a large number of electrodes. The service life and the 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 $j = 2\,\mathrm{A\,cm^{-2}}$) [8].

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

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

where E_1 represents a measured potential between the tested anode and the MSE after ohmic drop elimination, E_2 is the potential fo the MSE against the HE in 0.5 M H_2SO_4 at 25 °C and a pressure of 0.1 MPa (0.696 V [11]) and E_{H_2O} is the standard potential for water decomposition (1.23 V at 25 °C).

The rate of the dissolution of the IrO_2 active layer was determined analytically [8, 12–15]. The morphology of the IrO_2–Ta_2O_5 coating and of the titanium base metal were demonstrated by SEM. The capacity of IrO_2–Ta_2O_5 electrodes was determined during the measurement of the oxygen overpotential by means of rapid current interruption. The time dependence of the potential after interruption was followed on the oscilloscope screen. The capacity was then calculated using

$$C = \frac{j_C}{\left(\dfrac{dE}{d\tau}\right)_{\tau=0}} \qquad (2)$$

where C is the electrode capacity ($\mu\mathrm{F\,cm^{-2}}$), j_C is the current density ($\mu\mathrm{A\,cm^{-2}}$), $(dE/d\tau)_{\tau=0}$ is a slope of the time dependence of the potential ($\mathrm{V\,s^{-1}}$).

3. Results and discussion

3.1. *Effect of the iridium content*

The effect of the coating thickness on the service life of IrO_2–Ta_2O_5 electrodes during an accelerated service life test is shown in Fig. 1. The etching in 30% HCl at 50 °C for 2 h was used as a pretreatment of the titanium base metal. The Ir and Ta concentration and their molar ratio in the activation solution were constant for all coating thicknesses. It can be seen that for an iridium content of 0.45–1.2 mg $\mathrm{cm^{-2}}$ the service life is almost proportional to iridium content in the active layer. This suggests that the active surface layer is uniformly dissolved during the accelerated life test until a sufficient iridium content is present.

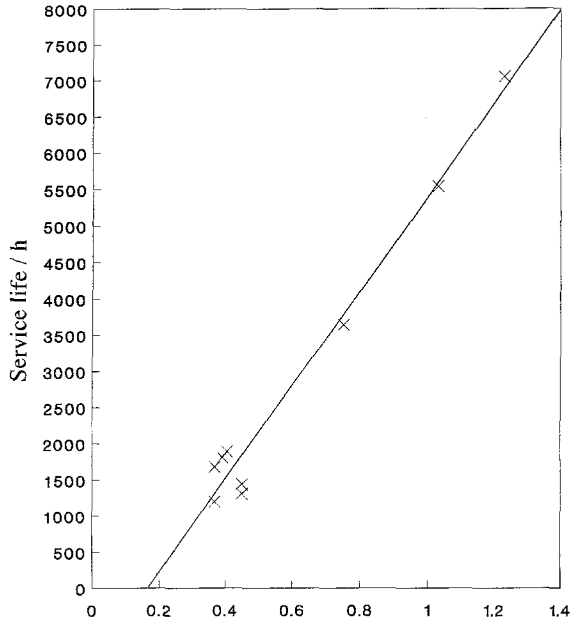

Fig. 1. The dependence of the service life of Ti/IrO_2–Ta_2O_5 anodes (Ir : Ta = 65 : 35) on the iridium content in the active layer.

Tafel plots for oxygen evolution on the Ti/IrO_2–Ta_2O_5 electrodes (Ir : Ta = 65 : 35) for three different coating thickness (iridium content) are presented in Fig. 2. The oxygen overpotential decreases with increasing iridium content, particularly for the higher current densities. The dependence of the oxygen overpotential (for current density, $j = 0.01\,\mathrm{A\,cm^{-2}}$) on the iridium content is plotted in Fig. 3. It is shown that the oxygen overpotential rapidly decreases up to coating thickness ~0.4 mg $\mathrm{cm^{-2}}$, after which the decrease is more gradual. For coating thickness of 1–1.2 mg $\mathrm{cm^{-2}}$ the oxygen overpotential is almost constant.

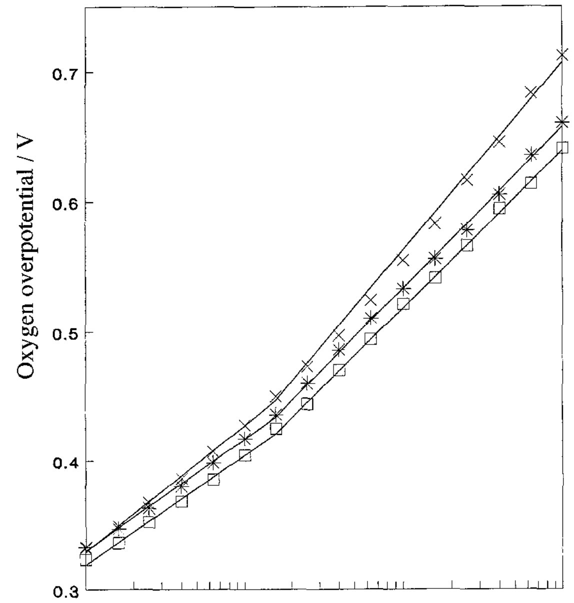

Fig. 2. Tafel plots for oxygen evolution on the Ti/IrO_2–Ta_2O_5 anodes (Ir : Ta = 65 : 35) for three different coating thicknesses: (A) 0.082 mg Ir $\mathrm{cm^{-2}}$, (B) 0.149 mg Ir $\mathrm{cm^{-2}}$, (C) 0.222 mg Ir $\mathrm{cm^{-2}}$. Key: (X) A, (∗) B and (□) C.

For the three different iridium contents (0.082,

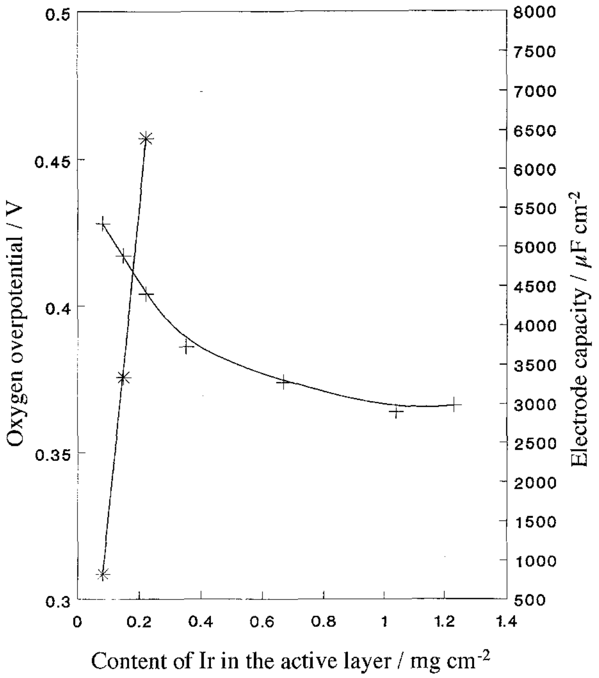

Fig. 3. The dependence of the oxygen overpotential (for $j = 0.01$ A cm^{-2}) and electrode capacity on the iridium content (in 0.5 M H_2SO_4 at 25 °C). Key: (+) η_{O_2} for 0.01 A cm^{-2} and (∗) capacity.

0.149 and 0.222 mg cm^{-2}) the electrode capacities were measured and are shown in Fig. 3. It can be seen that capacity strongly increases with the increase in coating thickness (number of layers deposited). This may be attributed to the fact that the layer of IrO_2–Ta_2O_5 is porous and then, with increasing number of layers, the real surface area increases.

3.2. *Effect of surface pretreatment*

The list of the different pretreatments of the titanium base metal before activation together with the iridium content calculated from the amount of solution (with Ir salt) remaining during coating on the titanium surface are shown in Table 1. Etching in 5% HF at 25 °C (**B**, **F**) and in 30% HCl at 30, 50 and 80 °C (**C**, **D**, **E**) were used as a pretreatment of titanium. The different etching times (**C**, **D**, **E**) were chosen to have the same weight decrease of titanium during the etching (for each temperature).

Table 1. Pretreatment of the titanium base metal

	Pretreatment		*Content of Ir* /mg cm^{-2}
	in HF	in HCl	
A	–	–	0.309
B	2 min in 5% HF at 25 °C	–	0.320
C	2 min in 5% HF at 25 °C	19 h in 30% HCl at 30 °C	0.367
D	2 min in 5% HF at 25 °C	5 h in 30% HCl at 50 °C	0.392
E	2 min in 5% HF at 25 °C	1 h in 30% HCl at 80 °C	0.368
F	30 min at 5% HF at 25 °C	–	0.325
G	30 min in 5% HF at 25 °C	5 h in 30% HCl at 50 °C	0.348

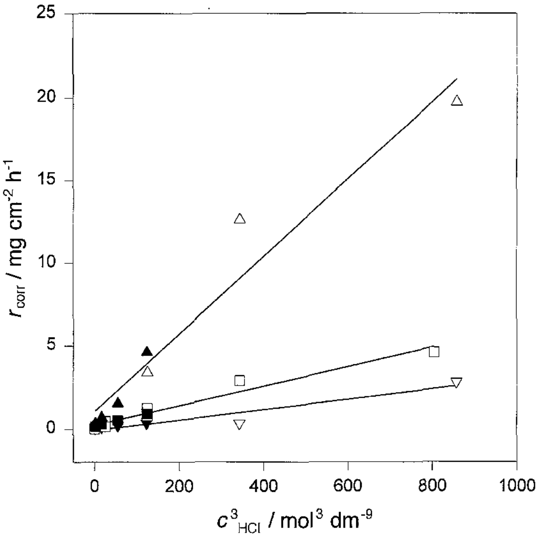

Fig. 4. The dependence of steady state corrosion rate of Ti on the cube of molar concentration of HCl. Key for experimental (open symbols) and theoretical [16] (filled symbols): (▽, ▼) 40 °C, (□, ■) 60 °C and (△, ▲) 80 °C.

The dependence of the steady state titanium corrosion rate on the temperature and concentration of HCl was obtained from the experimental and literature [16] corrosion rates of Ti in HCl. To prevent the access of oxygen to the HCl solution the level was covered with CO_2. The dependence of the steady state corrosion rate, r_{corr}, on the cube of the molar HCl concentration is shown in Fig. 4. It is apparent that steady state corrosion rates can be expressed according to the equation

$$r_{corr} = r_o + kc^3_{HCl} \tag{3}$$

The dependence of $\log k$ and $\log r_0$ on $1/T$ is presented in Fig. 5. Both $\log k$ and $\log r_0$ are linearly dependent on $1/T$ so that the following equations apply:

$$\log k = \log A - S_k T^{-1} \tag{4}$$

$$\log r_0 = \log B - S_r T^{-1} \tag{5}$$

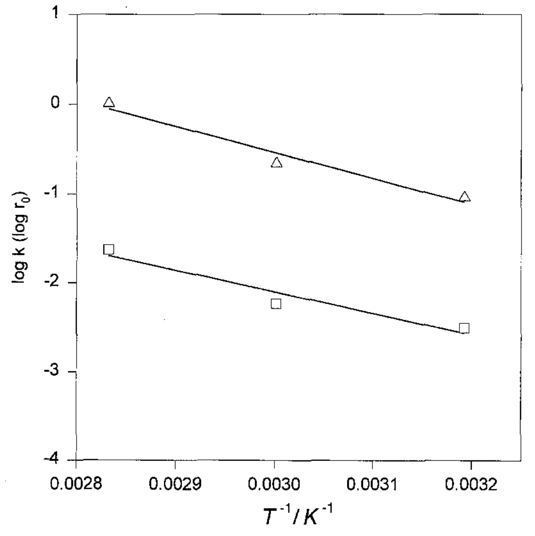

Fig. 5. The dependence of $\log k$ and $\log r_0$ on $1/T$. Key: (□) $\log k$ and (△) $\log r_0$.

A least square fit gives the slopes $S_k = 2874\,\mathrm{K}$ and $S_r = 2404\,\mathrm{K}$ and constants $A = 1.23 \times 10^8\,\mathrm{mg\,mol^3\,dm^9\,cm^{-2}\,h^{-1}}$ and $B = 1.26 \times 10^5\,\mathrm{mg\,cm^{-2}\,h^{-1}}$.

Combining Equations 3, 4 and 5 and introducing A, B, S_r and S_k we obtain the relation for the corrosion rate of titanium in HCl

$$r_{\mathrm{corr}} = 1.26 \times 10^5 \mathrm{e}^{-5536/T} + 1.23 \times 10^8 \mathrm{e}^{-6619/T} c_{\mathrm{HCl}}^3 \qquad (6)$$

where c_{HCl} is HCl concentration ($\mathrm{mol\,dm^{-3}}$), T is temperature (K) and r_{corr} is corrosion rate of titanium ($\mathrm{mg\,cm^{-2}\,h^{-1}}$). The weight decrease of titanium during the etching **C**, **D**, **E** was $\sim$4.5 $\mathrm{mg\,cm^{-2}}$ which represents the titanium layer of an average thickness $\sim$0.01 mm.

The morphology of the titanium electrodes after different pretreatments (Table 1) was demonstrated by scanning electron microscopy and is shown in Fig. 6. Because the titanium surface after etching **C**, **D**, **E** was very similar only the titanium surface after etching **D** is shown. From Fig. 6 it can be seen that the morphology of the titanium surface depends strongly on the pretreatment.

In a previous study [10] it was found that during

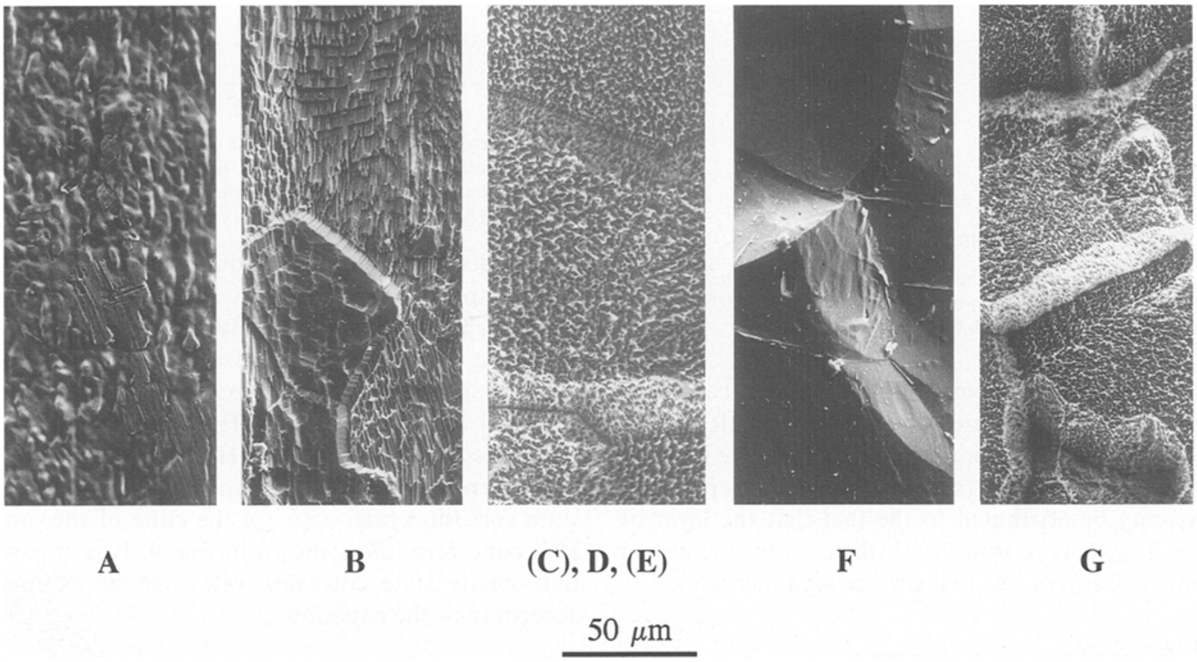

Fig. 6. The morphology of the titanium surface after different pretreatment, 600× (see Table 1).

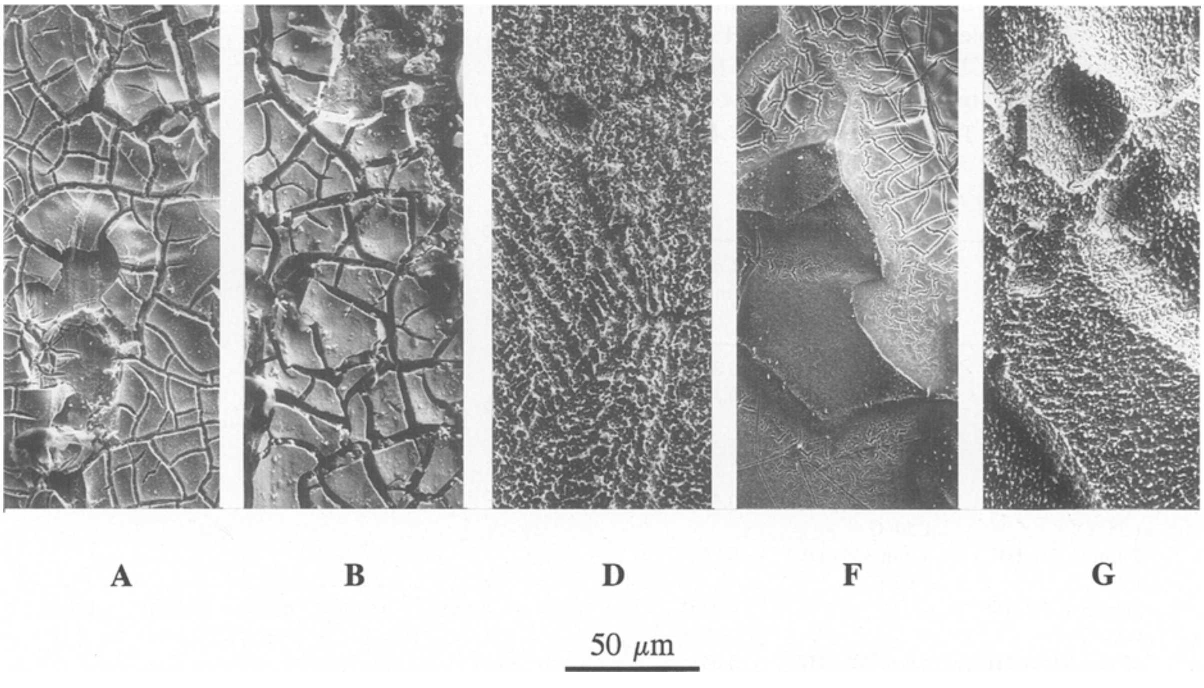

Fig. 7. The effect of different pretreatments (see Table 1) on the morphology of the IrO_2–Ta_2O_5 active layer, 600×.

Table 2. Oxygen overpotential, service life and steady state iridium dissolution rate during accelerated life test (0.5 M *H_2SO_4, 25 °C and $j = 2\,A\,cm^{-2}$*

Pretreatment	η_{O_2}/V (*for 0.01* A cm^{-2})	*Service life* /h		r_{Ir}/µg cm^{-2} h^{-1}	
		1	2	1	2
A	0.394	703	1061	0.12	0.10
B	0.389	1880	1079	0.04	0.10
C	0.390	1193	–	0.08	–
D	0.408	1808	–	0.03	–
E	0.408	1678	–	0.065	–
F	0.412	1455	2036	0.07	0.03
G	0.404	1250	1302	0.09	0.10

etching in hot concentrated HCl a layer of TiH_2 was formed on the titanium surface. From the analysis of microphotographs of the titanium surface etched in HCl (etching **C**, **D**, **E** and **G** in Fig. 6), it is apparent that the titanium hydride formed on the titanium surface, is not uniformly distributed over the surface area. The titanium surface is rough on areas of individual crystals and therefore 'microroughness' is formed.

The X-ray intensities of TiH_2 were negligible after exposure in 5% HF at 25 °C for 2 min (etching **B**) and for 30 min (etching **F**). It follows that during the etching in HF the layer of titanium hydride does not form. During etching in HF (etchings **B** and **F**) the dissolution of whole small titanium crystals takes place while the surfaces of the large individual crystals become smooth and therefore 'macroroughness' is formed.

The effect of etching in HF and HCl on the morphology of the IrO_2–Ta_2O_5 electrodes is expressed in Fig. 7 (600×). The morphology of the active surface layer without any pretreatment (**A**) and after etching in HF (etching **B**) is similar. The active layer contains many large cracks and, on parts of the surfaces, even peels off. Similarly, Roginskaja *et al.* [17] observed a 'dried mud' look which is typical for pyrolytic films.

The electrodes after etching in HCl (etching **D**, **G**) have a completely different structure. The surface of the titanium after pretreatment in concentrated HCl was very rough (Fig. 6). After painting the titanium surface with a solution containing Ir and Ta salts, the rough surface is not completely covered by the coating and the roughness was only slightly decreased. The surface layer of mixed oxides is mainly present in the openings and pores of the rough surface.

From Table 1 it is seen that the amount of solution (with Ir salt) remaining during the coating of the titanium surface increases with the roughness of the titanium. After pretreatment in HF we found 0.32 mg Ir cm^{-2} and after pretreatment in HCl 0.367–0.392 mg Ir cm^{-2}.

Because of the high service life for electrodes with a high iridium content in the active layer and the fact that the service life depends linearly on the iridium content in the active layer, it was decided to investigate the effect of pretreatment for electrodes with the three active layers and corresponding iridium content in the active layer.

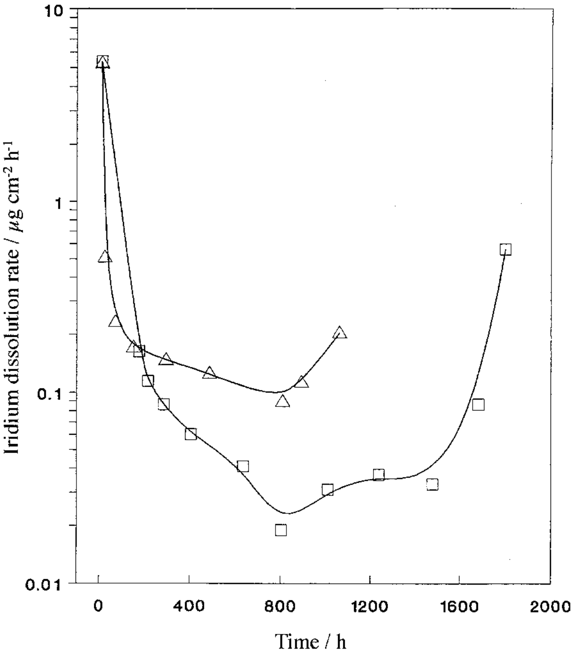

Fig. 8. The time dependence of the iridium dissolution rate for IrO_2–Ta_2O_5 anodes (Ir : Ta = 65 : 35) during the accelerated life test (in 0.5 M H_2SO_4 at 25 °C and $j = 2\,A\,cm^{-2}$). Key (△) pretreatment A and (□) pretreatment D.

As was shown in the previous work [8] the dependence of oxygen overpotential for Ti/IrO_2–Ta_2O_5 anodes on current density in the range 0.0006–1 A cm^{-2} can be expressed by two Tafel equations. The oxygen overpotential (for 0.01 A cm^{-2}) for different pretreatments is shown in Table 2. It is apparent that it does not change significantly with pretreatment.

The effect of the pretreatment on the service life during accelerated life test is shown in Table 2. It was expected that the service life of the electrodes **A** (any pretreatment) and **B**, **F** (pretreatment in HF) would be much shorter than the service life of the electrodes with pretreatment in HF and subsequent etching in HCl (**C**, **D**, **E**, **G**). The reason for this was the fact that the surface of the titanium base metal is not sufficiently rough (**A**, **B**) and that during etching in HF, 'macroroughness' is formed (**F**).

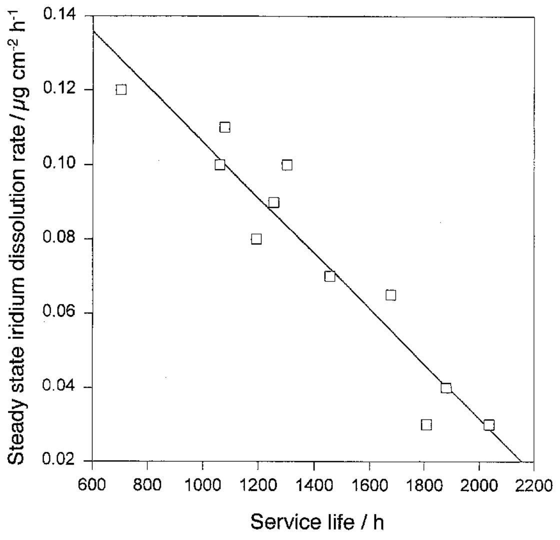

Fig. 9. The dependence of the steady state iridium dissolution rate on the service life during the accelerated life test.

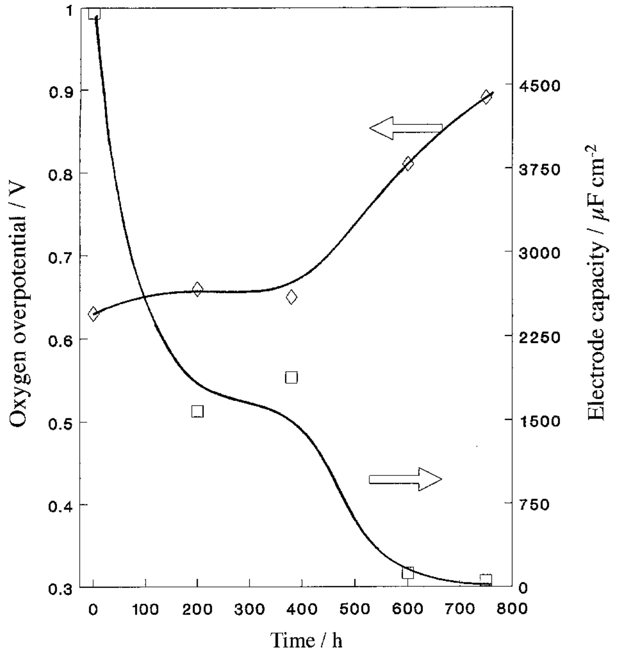

Fig. 10. The time dependencies of electrode capacity and oxygen overpotential (for $j = 1\,\mathrm{A\,cm^{-2}}$) for IrO_2–Ta_2O_5 electrodes with pretreatment **A**. Key: (◇) η_{O_2} for $1\,\mathrm{A\,cm^{-2}}$ and (□) capacity.

From Table 2 a distinct difference between the lifetimes of electrode **A** (700–1000 h) and the lifetimes of the electrodes **B**, **C**, **D**, **E**, **F** and **G** (1200–2000 h) can be seen. This shows that the effect of the surface pretreatment on the service life is relatively low. If the titanium surface is at least pretreated in HF the service life will increase.

The time dependence of the iridium dissolution rate for IrO_2–Ta_2O_5 anodes during the accelerated life test is shown in Fig. 8. As was observed in the previous work [8] the initial dissolution rate for the IrO_2–Ta_2O_5 electrode, with pretreatment in 30% HCl at 50 °C for 2 h, is about two orders higher than the steady state dissolution rate, which is relatively low ($0.03\,\mu\mathrm{g\,cm^{-2}}$).

The steady state dissolution rate is, in the case of electrode **A** (without any pretreatment), much higher ($\sim 0.1\,\mu\mathrm{g\,cm^{-2}}$) than that of electrode **D** ($\sim 0.03\,\mu\mathrm{g\,cm^{-2}}$) and the service life of electrode **A** is lower (Table 2). The increase in surface roughness before activation leads to a higher service life time and a lower steady state dissolution rate. It seems that the lower service life of the anode is in accord with the higher steady state iridium dissolution rate.

Steady state iridium dissolution rate for different pretreatment was plotted as a function of service life in Fig. 9. It is apparent that the service life of the IrO_2–Ta_2O_5 anodes (constant molar ratio Ir/Ta) decreased with the increasing steady state dissolution rate of iridium during the accelerated life test. It may be concluded that the layer of mixed oxides (IrO_2 and Ta_2O_5) dissolves uniformly during the accelerated life test.

Electrode capacity and oxygen overpotential were measured during the accelerated life tests. After a particular time of polarization ($j = 2\,\mathrm{A\,cm^{-2}}$, 0.5 M H_2SO_4, 25 °C) the oxygen overpotential was measured in the current density range of 0.001–$1\,\mathrm{A\,cm^{-2}}$. The capacity was determined by the method outlined above for $j = 1\,\mathrm{A\,cm^{-2}}$. The time dependencies of the electrode capacity and the oxygen overpotential for IrO_2–Ta_2O_5 electrodes with pretreatment **A** are shown in Fig. 10. At the beginning of the accelerated life tests, the oxygen overpotential increases slightly, then reaches the steady state value (for ~200 h) and at the end of the service life it increases strongly. The trend in the capacity is opposite; it decreases from a value of $\sim 6000\,\mu\mathrm{F\,cm^{-2}}$ to the steady state value of 1600–$1900\,\mu\mathrm{F\,cm^{-2}}$. At the end of the accelerated life test the capacity decreased strongly to a value of $\sim 40\,\mu\mathrm{F\,cm^{-2}}$.

From Fig. 10 it may be concluded that the increase in the oxygen overpotential and decrease in electrode capacity during accelerated life test are in accord with the iridium dissolution rate (Fig. 8). The time dependence of dissolution rate, electrode capacity and oxygen overpotential can be divided into three periods.

During the first period the capacity decreases strongly; this is caused by the rapid decrease in the IrO_2–Ta_2O_5 layer thickness (high initial dissolution rate). The slight increase in oxygen overpotential is caused by the change in the ratio Ir : Ta in the coating during dissolution, as previously reported [8].

The second period is characterized by the steady state iridium dissolution rate which is achieved in the end of the first period; the oxygen overpotential and the electrode capacity are almost constant.

For the third period the increase in the iridium dissolution rate is typical and is connected with the rapid increase in the oxygen overpotential and the decrease in the electrode capacity. The amount of IrO_2–Ta_2O_5 active layer is not sufficient to perform oxygen evolution with low overpotential and the electrode surface is covered by the passive oxide layer.

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