SHORT COMMUNICATION

Effect of coating thickness on the properties of IrO_2–Ta_2O_5 anodes*

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1. Introduction

This study describes an experimental investigation of the effect of the coating thickness on the surface morphology and the electrochemical properties of IrO_2–Ta_2O_5 anodes. Electrode materials containing IrO_2 as the active component have found extensive applications in industrial electrochemistry [1]. Their fundamental electrochemical properties have been studied recently by several authors [1–8]. Savinell et al. [9] used cyclic voltametry and a determination of electrochemical active area to characterize Ti/IrO_2 electrodes of different loading. They found that the voltametric charge and the electrochemical active surface area (EASA) are linearly dependent on the loading of IrO_2 (in the range 0.88–2.7 mg IrO_2 cm^{-2}).

Krysa and Mraz [8] reported (similarly as Comninelis and Vercesi [3,4]) that IrO_2–Ta_2O_5 coating (molar ratio of Ir:Ta = 6.5:3.5) is so far the best electrocatalyst for oxygen evolution. In previous work [10] the effect of surface treatment of titanium on the properties of IrO_2–Ta_2O_5 was investigated. It was found that the morphology of IrO_2–Ta_2O_5 coating with the thickness corresponding to 0.32–0.39 mg Ir cm^{-2} depends strongly on the pretreatment of the titanium base metal.

2. Experimental details

The first operation for the preparation of dimensionally stable electrodes based on titanium sheets (wires), covered with an active layer is the titanium pretreatment in hot concentrated HCl solution [1, 11]. The second operation is the deposition of the IrO_2–Ta_2O_5 coating. The experimental conditions for the preparation were described previously [10]. Etching in 30% HCl at 50 °C for 2 h was used as a pretreatment. An activation solution with a molar ratio of Ir:Ta = 6.5:3.5 was used (mixture of H_2IrCl_6 in HCl, $c_{Ir} = 0.26$ mol dm^{-3} and $TaCl_5$ in ethanol, $c_{Ta} = 0.17$ mol dm^{-3}). After each immersion of the titanium wires or sheets (activation) the wet surface was dried by hot air and then annealed at 450 °C for 10 min. This procedure was repeated until the desired coating thickness (content of iridium per unit surface) was reached.

The oxygen overpotential of prepared Ti/IrO_2–Ta_2O_5 anodes was measured in 0.5 M H_2SO_4 at 25 °C

[10]. The capacity of IrO_2–Ta_2O_5 electrodes was determined during the measurement of the oxygen overpotential by means of rapid current interruption [10].

A powder diffractometer with source CoK_α, voltage 35 kV at 20 mA current, speed 0.5 deg min^{-1} was used for X-ray diffraction measurement. The morphology of the IrO_2–Ta_2O_5 coating and of the titanium base metal was observed by scanning electron microscopy (SEM) Hitachi S-450 (Japan).

3. Results and discussion

Comninelis and Vercesi [3,4] observed that IrO_2–Ta_2O_5 coatings can be deposited chemically with high yields (> 95%) on a titanium base. The Ir content in each layer and therefore the Ir 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 Ir concentration in the activation solution. The concentration of Ir and Ta and their molar ratio in the activation solution were constant for all coating thicknesses. Thus the different Ir content in the coating indicates a different coating thickness.

In the range 0.0006–1 A cm^{-2} the dependence of the oxygen overpotential on current density can be expressed by two Tafel equations with constant a and slope b. The intersection between these two lines lies between $j = 0.01$ and 0.05 A cm^{-2}. Tafel parameters for oxygen evolution together with the oxygen overpotential for current density $j = 0.01$ A cm^{-2} on the Ti/IrO_2–Ta_2O_5 electrodes (Ir:Ta = 6.5:3.5) for various coating thickness are presented in Table 1. It is shown that the oxygen overpotential rapidly decreases for the first three layers after which the decrease is more gradual. For a coating thickness of 1.0–1.2 mg cm^{-2} the oxygen overpotential is almost constant.

For three different iridium contents (0.082, 0.149 and 0.222 mg cm^{-2}) the electrode capacities were measured and are shown in Table 1. It can be seen that capacity strongly increases with increase in coating thickness (number of layers deposited). This may be attributed to the porous structure of the IrO_2–Ta_2O_5 layer and then, with increasing number of layers, the electrochemically active surface area (EASA) increases. Similarly Savinell et al. [10]

Table 1. Tafel parameters for oxygen evolution and the initial electrode capacity depending on the thickness of IrO_2–Ta_2O_5 coating ($Ir:Ta = 6.5:3.5$)

Number of layers	c_{Ir} /mg cm^{-2}	Tafel parameters for η_{O_2}/V				η_{O_2}/V (for 0.01 A cm^{-2})	C /μF cm^{-2}
		a_1	b_1	a_2	b_2		
1	0.082	0.625	0.099	0.707	0.148	0.428	819
2	0.149	0.590	0.087	0.657	0.123	0.417	3340
3	0.222	0.574	0.085	0.639	0.120	0.404	6395
10	1.040	0.486	0.061	0.584	0.126	0.364	–
13	1.230	0.500	0.062	0.580	0.124	0.366	–

observed an increase in EASA (Zn^{2+} ion adsorption) of Ti/IrO_2 electrodes with increasing IrO_2 loading; this was expressed by the ratio EASA/loading $= 101.5 \pm 6.4\,cm^2\,mg^{-1}$.

In the previous study [10] it was shown that for an iridium content of 0.45–1.2 mg cm^{-2} the service life is proportional to the Ir content in the coating. This suggests that the active surface layer is uniformly dissolved during the accelerated service life test until a sufficient iridium content is present. For lower Ir content in the coating (<0.4 mg cm^{-2}) the reproducibility of the service life is not good. This can be explained as follows. Krysa and Mraz [8] observed that the initial Ir dissolution rate is about several orders higher than the steady state dissolution rate which implies that the decrease in Ir content (by dissolution) is particularly rapid at the beginning of the accelerated life tests. From the time dependence of the iridium dissolution rate ([10], Fig. 8) the amount of Ir dissolved during accelerated life test (2 A cm^{-2}, 0.5 M H_2SO_4, 25 °C) can be calculated. For the first 200 h this loss is near 0.18 mg Ir cm^{-2} and represents a significant part of the initial coating thickness.

The time dependence of oxygen overpotential and electrode capacity during polarization at 1 A cm^{-2} in 0.5 M H_2SO_4 and 25 °C for 1 layer (0.082 mg Ir cm^{-2}) in the coating is shown in Fig. 1. The oxygen overpotential was measured continuously during polarization and the electrode capacity was determined by the method outlined previously [10]. Figure 1 shows that the oxygen overpotential increases slightly during polarization prior to a large increase at the end of service life. The trend in the capacity is opposite, decreasing from a value of $\sim$600 μF cm^{-2} to 200–230 μF cm^{-2} (for 1 h) and finally to 40 μF cm^{-2}.

The time dependence of oxygen overpotential and electrode capacity during polarization at 1 A cm^{-2} in 0.5 M H_2SO_4 and 25 °C for two layers (0.149 mg Ir cm^{-2}) in the coating is shown in Fig. 2. Similarly as for 0.082 mg Ir cm^{-2}, the time dependencies of oxygen overpotential and electrode capacity are opposite and can be divided into three periods. During the first period the capacity strongly decreases (from 3200 to $\sim$600 μF cm^{-2}); this is caused by the rapid decrease in the IrO_2–Ta_2O_5 thickness layer (high initial dissolution rate). The second period is characterized by the steady-state dissolution rate of iridium which is ob-
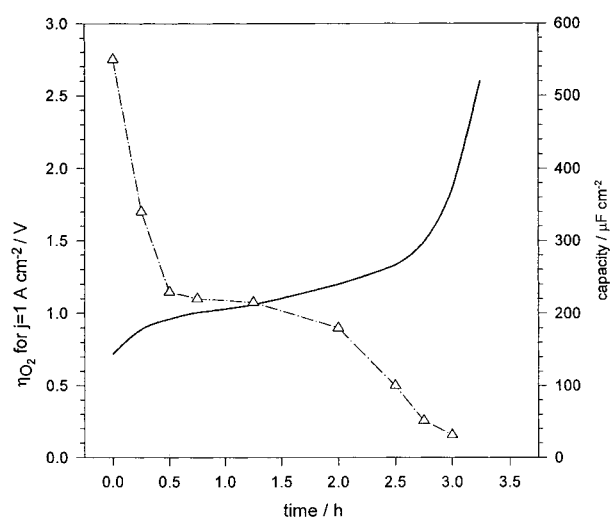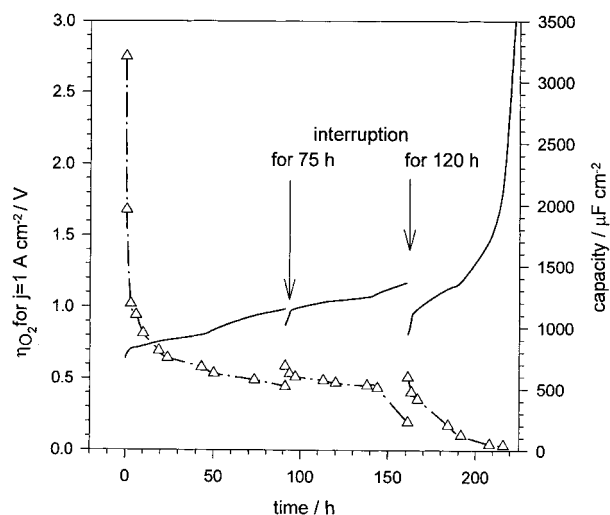

Fig. 1. Dependence of electrode capacity and oxygen overpotential on polarization time at 1 A cm^{-2} in 0.5 M H_2SO_4 at 25 °C for 0.082 mg Ir cm^{-2} in the coating. Key: (——) overpotential; ($-\cdot\triangle\cdot-$) capacity.

served at the end of the first period; the electrode capacity is fairly constant (500–600 μF cm^{-2}). For the third period the rapid increase in the oxygen overpotential and the decrease in the electrode capacity (to $\sim$40 μF cm^{-2}) is typical. The amount of

Fig. 2. Dependence of electrode capacity and oxygen overpotential on polarization time at 1 A cm^{-2} in 0.5 M H_2SO_4 at 25 °C for 0.149 mg Ir cm^{-2} in the coating. Key: (——) overpotential; ($-\cdot\triangle\cdot-$) capacity.

Table 2. Time-dependence of total dissolved iridium and Ir content for two coating thickness

Time /h	Dissolved Ir /mg cm^{-2}	Ir in the coating (1 layer) /mg cm^{-2}	/%	Ir in the coating (2 layers) /mg cm^{-2}	/%
0	0	0.082	100	0.149	100
24	0.063	0.019	23	0.086	58
72	0.075	0.007	8.5	0.074	50
156	0.085	–	–	0.064	43
200	0.089	–	–	0.060	40
300	0.097	–	–	0.052	35

IrO$_2$–Ta$_2$O$_5$ active layer is not sufficient to perform oxygen evolution with low overpotential and the electrode surface is covered by a passive oxide layer. The polarization was interrupted twice (for 75 and 120 h). It can be seen that after interruption capacity is higher and the oxygen overpotential is lower than before interruption. At present there is no reasonable explanation for this and the phenomenon will be further investigated.

Service life for one layer in the coating was 3–10 h, for two layers it was 225 h. The service life decreased much more than the coating thickness (from 0.145 to 0.082 mg Ir cm^{-2}). In our previous study [8] it was found that the iridium dissolution rate during accelerated life testing increases linearly with current density. The time dependence of iridium dissolution rate was recalculated from polarization at 2 A cm^{-2} ([10], curve D in Fig. 9) to polarization at 1 A cm^{-2}. The amount of dissolved iridium from the coating during polarization at 1 A cm^{-2} was then calculated from the iridium dissolution rate. The calculated time dependence of the amount of dissolved iridium as well, as the Ir content in the coating during polarization at 1 A cm^{-2}, are shown for two initial coating thicknesses in Table 2.

From the relation between the time dependence of the Ir content for an electrode with two layers in the coating (Table 2) and the service life for that electrode the amount of Ir (IrO$_2$–Ta$_2$O$_5$ coating thickness) which is not sufficient to perform oxygen evolution with low overpotential can be estimated as $\sim$0.06 mg Ir cm^{-2}. The amount of Ir in the coating (one layer) after 24 h polarization is 0.019 mg Ir cm^{-2}. This amount is lower than 0.06 mg Ir cm^{-2} and is therefore not sufficient to carry out oxygen evolution with low overpotential; this is the reason why the service life for one layer in the coating must be lower than 24 h.

X-ray diffraction was used to characterize the structure and composition of surface layers on titanium during pretreatment in HCl and deposition of a pyrolytic film of IrO$_2$–Ta$_2$O$_5$ (Fig. 3). It is apparent that during dissolution in HCl titanium hydride, TiH$_2$, with cubic crystallographic structure is formed. The layer of TiH$_2$ is stable even after immersion in the activation solution and exposure at 80–100 °C. After annealing at 450 °C the TiH$_2$ layer decomposes and crystalline IrO$_2$ with tetragonal structure is formed, whereas Ta$_2$O$_5$ is present in the amorphous form.
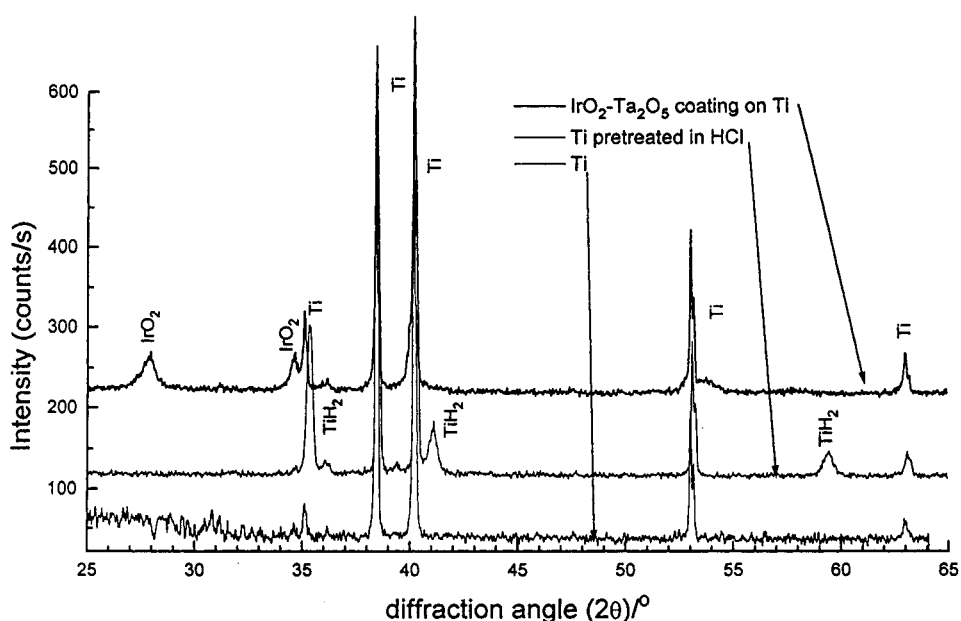
Fig. 3. X-ray intensities of Ti base metal, Ti after pretreatment in HCl and Ti after deposition of IrO$_2$–Ta$_2$O$_5$ coating and annealing at 450 °C.
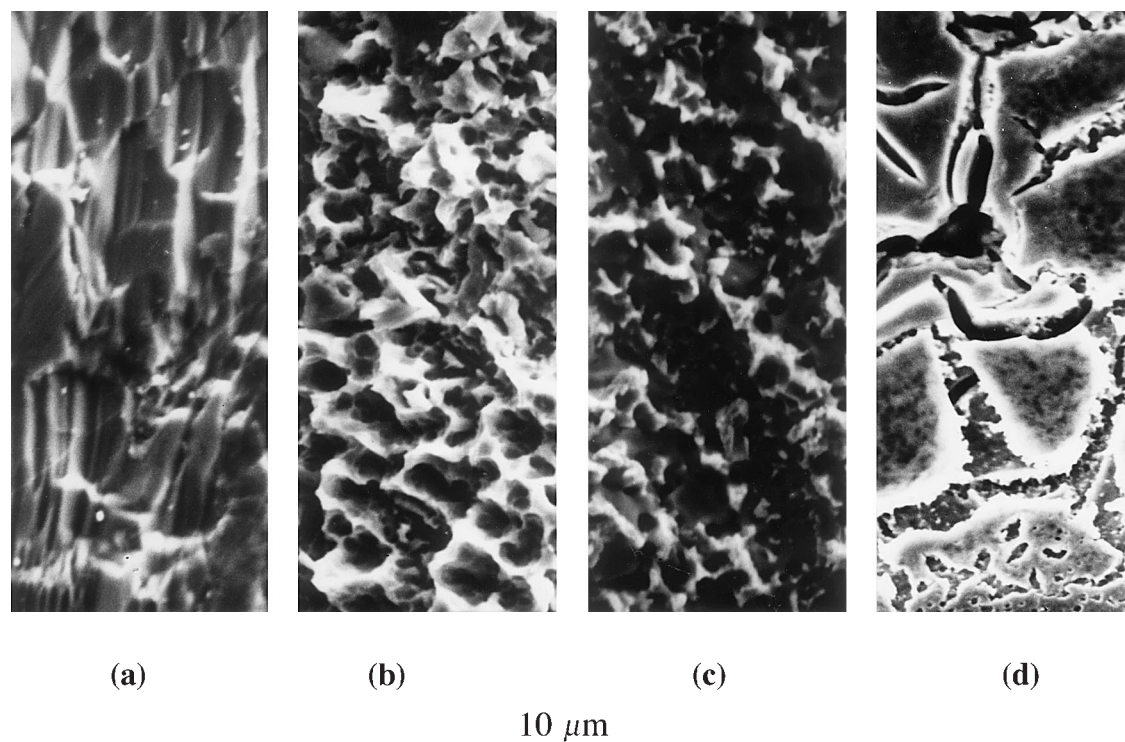
(a)   (b)   (c)   (d)

10 μm

Fig. 4. Effect of coating thickness on morphology of the IrO_2–Ta_2O_5 coating (2500×). (a) Ti base metal, (b) Ti after etching in 30% HCl at 50 °C for 2 h, (c) three layers (0.36 mg Ir cm^{-2}), (d) six layers (0.65 mg Ir cm^{-2}).

The morphology of titanium (a), pretreated titanium (b) and the IrO_2–Ta_2O_5 coating (c, d) is shown in Fig. 4. During pretreatment of titanium in HCl a rough surface at the microscale is formed with visible pitting holes. For three active layers (0.36 mg Ir cm^{-2}) the resulting surface of the IrO_2–Ta_2O_5 is microrough with partly filled pitting holes and is similar to the surface of pretreated titanium. For six active layers (0.65 mg Ir cm^{-2}) the morphology of the surface is not dependent on the morphology of the titanium base metal. The structure of the IrO_2–Ta_2O_5 surface is typical for pyrolytic films and similar to the 'dried mud' appearance observed by Roginskaya *et al.* [12].

Acknowledgement

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