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Preparation of oxygen evolving electrodes with long service life under extreme conditions*

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Among the numerous base metals tested for DSA® type electrodes (e.g., titanium and its alloys, zirconium, niobium etc.), tantalum is a potentially excellent substrate owing to its good electrical conductivity and corrosion resistance, and the favourable dielectric properties of its oxide. Nevertheless, a DSA® type electrode fabricated on a tantalum substrate would be very expensive due to the high cost of the metal. To prepare an anode combining the excellent properties of tantalum at reasonable price, a new material has been developed in our laboratory. This consists of a common base metal (e.g., Cu) covered with a thin tantalum coating. This tantalum layer was obtained by molten salt electroplating in a $LiF–NaF–K_2TaF_7$ melt at 800 °C. Thus, an anode of the type Metal/$Ta/Ta_2O_5–IrO_2$ with a surface load of $22\,g\,m^{-2}$ IrO_2, submitted to the severe test conditions used in this work, exhibits a standardized lifetime tenfold greater than one made with ASTM grade 4 titanium base metal. Thus, this type of electrode might be advantageously employed as an oxygen evolution anode in acidic solutions.

Keywords: *oxygen evolution*, *long life electrodes*, *tantalum*

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1. Introduction

For several industrial electrochemical processes, involving oxygen evolution in acidic media such as electroplating, electrowinning, electrosynthesis, salt-splitting, the selection of anodic materials is a critical problem [1]. DSA®-type electrodes, made with a titanium base metal coated with a platinum group metal catalyst, are now widely used as anodes. The material, commercially available, has the formula $Ti/Ta_2O_5–IrO_2$ with 70 mol % IrO_2 [2]. However, the service life of this anode, operating under an anodic current density of 10 kA m^{-2} in an acidic medium, such as sulfuric acid 30 wt % at 80 °C, is generally short, that is, less than 100 h. It is known that the electrocatalytic oxide film, thermally formed for such DSA® anodes, generally exhibits a cracked mud-cake surface [3]. This structure, which gives rise to a high surface area, is, however, the source of passivation phenomena. Actually, anodic polarization of the titanium base metal gives an insulating film of titanium dioxide between the substrate and the active layer. Passivation can be induced by acidic solution penetration through cracks and pores to the titanium substrate. The deactivation behaviour is then due to the corrosion properties of titanium in acid solutions. Therefore, the passivating titanium dioxide film, which grows rapidly, leads to electrocatalyst losses and increases the electrode overvoltage during electrolysis.

Amongst the other refractory metals (e.g., Zr, Hf, Nb, Ta) available for anode base metal preparation, tantalum is the most suitable anode material owing to its excellent corrosion resistance in aggressive media due to its protective oxide film [4]. Actually, the Ta_2O_5 film spontaneously formed under oxidizing conditions exhibits an amorphous structure, and is strongly adherent to the metal, extremely thin and self-limiting of its own growth thickness. This behaviour ensures base metal stability and prevents electrocatalyst loss during electrolysis [5]. Moreover, tantalum has a lower electrical resistivity (13 $\mu\Omega$ cm) than titanium (42 $\mu\Omega$ cm). Nevertheless, tantalum has two great drawbacks: it has a very high density

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(16 654 kg m^{-3}) and a high cost (740 \$ kg^{-1}) compared to the common titanium base metal (4450 kg m^{-3} and 250 \$ kg^{-1}).

To decrease the cost of the anode material, a thin layer of tantalum, coated on a common base metal (e.g., copper), which offers the same protection [6], may be employed. Among the numerous tantalum-coating techniques (e.g., explosion cladding, chemical vapour deposition, vacuum deposition or cathodic sputtering) molten salt electroplating (MSE) is a particularly attractive technique [7]. By contrast with other competitive coating techniques, MSE, which has excellent throwing power, gives dense, coherent and thin tantalum coatings with deposition rates up to 100 μm h^{-1}. Taxil *et al.* [8–10] have optimized tantalum electrodeposition conditions in molten fluoride baths.

The behaviour of an anode can be quantified by the stability of its working potential with respect to a reference electrode. This can be defined as the ability of the electrode to maintain its working potential constant under galvanostatic conditions in long-term performance. In practice, the voltage between the working electrode and the counter electrode is measured as a function of time. Unfortunately, the estimation of the real service life of electrodes needs very long experiments. Thus, this parameter is often estimated by accelerated tests which have the advantage of providing a quick answer on a laboratory scale [11].

In this work, a comparative study of the stability of different anodes of the type M/Ta_2O_5–IrO_2 has been undertaken. Recently, Mraz and Krysa [12] studied the service life of Ti/Ta_2O_5–IrO_2 anodes for electroflotation but different conditions for accelerated life tests than those described in the present work were used. The base metal, M, was either pure titanium or titanium alloys or a common metal (e.g., copper) coated by MSE techniques with tantalum. Pure titanium and titanium alloys of similar costs have been tested for comparison with the composite Cu/Ta substrate.

2. Experimental details

2.1. *Tantalum thin coating electroplating*

The thin coating of tantalum on a common base metal (e.g., copper, steel and nickel) was carried out by classical molten salt electroplating. A dense, smooth and adherent tantalum coating was obtained under galvanostatic conditions at a cathodic current density of 80 mA cm^{-2}. Two soluble tantalum anodes 99.9 wt % (Goodfellow Ltd) and a copper substrate cathode were used. The tantalum anode dimensions were 100 mm × 100 mm × 2 mm; the base metal was a plate of 100 mm × 12 mm × 1mm. The melt was prepared using the binary eutectic LiF–NaF (60–40 mol %) (Cerac Inc.) with 40 wt % K_2TaF_7 (Alfa Gmbh), the operating temperature being 800 °C. Before electrodeposition, the cathode base metal was hot degreased by a chlorinated solvent and then electropolished in the appropriate electrolyte bath. The electrochemical polishing operation ensures perfect levelling of the metal surface. It was achieved by anodic dissolution under galvanostatic electrolysis, where the base metal plate anode, that is, the substrate, was immersed in an electrolytic solution between two large area nickel cathodes. The electrochemical polishing conditions, which depend on the metal used as substrate, are listed in Table 1. The molten salt cell is detailed in Fig. 1.

A nickel crucible containing the fluoride melt was introduced to a cell made from Hastelloy®-X and set in a resistance furnace. The operating temperature was controlled at ± 5 °C.

The cathode was introduced and removed from the reactor, without entry of air and moisture, by means of an antechamber which was closed by a large gate valve. The cell was closed by means of a water-

Table 1. Conditions for the electrochemical polishing of various base metals and alloys used as substrates [*17*]

Metal or alloy	*Electrolyte composition*		*Anodic current density, j_a /mA cm^{-2}*		*Duration, Δt /min*
Carbon steels	H_3PO_4 85 wt % CrO_3 (cryst.)	1000 ml ≈30 g	250	(65 °C)	45
Mild steels	EtOH 96 vol % $HClO_4$ 70 wt % EGME*	700 ml 200 ml 10 ml	10	(up to 35 V)	15
Stainless steels (e.g., AISI 304, 316L)	H_3PO_4 85 wt % H_2SO_4 96 wt % H_2O	600 ml 300 ml 100 ml	300	(20–25 °C)	30
Nickel (e.g., Gr. 200)	H_3PO_4 85 wt % H_2SO_4 96 wt % H_2O	600 ml 300 ml 100 ml	300	(20–25 °C)	30
Copper (e.g., CDA 110)	H_3PO_4 85 wt % H_2O	750 ml 250 ml	300	(20–25 °C)	30
Molybdenum 99.8 wt %	H_3PO_4 85 wt % H_2SO_4 96 wt % H_2O	24 ml 46 ml 930 ml	1300	(30 °C)	3–5

* EGME: Ethylene glycol monobutyl ether.

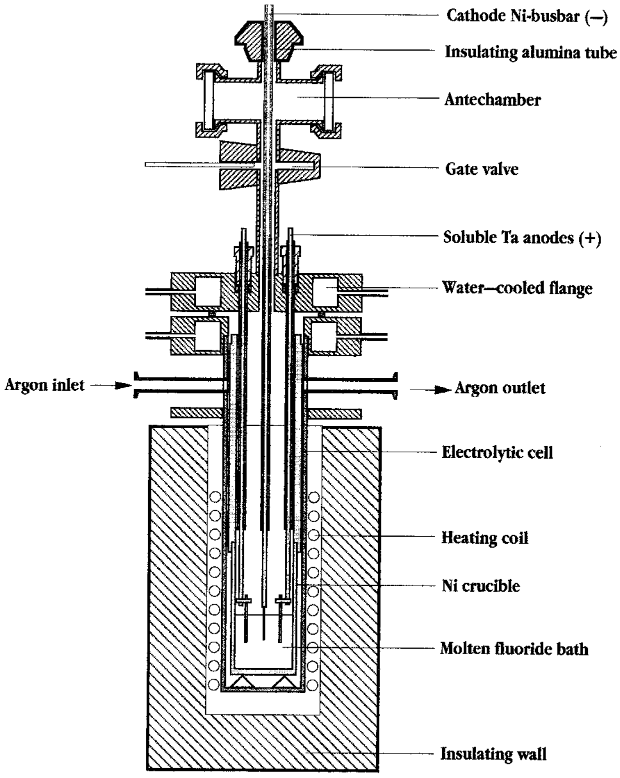

Fig. 1. Molten salt electrolytic cell.

cooled flange setup, the tightness being ensured by an O-ring gasket. The components of the apparatus were selected to achieve a vacuum-tight cell at high temperature. The inert atmosphere within the cell was produced by an argon stream purified by passing it through a water–oxygen trap. Before premelting of the electrolyte, the reactor was purged from background contaminants by high vacuum pumping. As the temperature reached the electrolyte melting point the vacuum circuit was switched to a pure argon stream.

The electrodes were held by nickel busbars electrically insulated from the reactor by alumina tubes (Degussa Corp.). Electrical power supply was provided by a large scale galvanostat (Solired). Typical operating parameters were a current intensity of 2.1 A and a cell voltage of 0.3 V.

2.2. *Anode preparation*

For all laboratory tests plates with dimensions close to 100 mm × 12 mm × 1 mm were used as electrodes. The main properties and characteristics of the base metal, except tantalum previously described, are listed in the Table 2.

Before activation, the base metal was treated following a three step classical procedure. (i) First, the electrode surface was sandblasted with corundum 125 μm powder under 5 bar pressure. Then, the plates were immersed in distilled water in an ultrasonic bath in order to remove incrusted corundum crystals. (ii) Secondly, the dried samples were treated by chemical etching to remove the oxide layer and achieve good surface enhancement. The etching solutions, which depended on the nature of the base metal, are listed in Table 3. (iii) Finally, the active layer was deposited from the precursor solution by thermal treatment. The solution of precursor was obtained by dissolution of 430 mg of hydrogen hexachloroiridate(iv) and 280 mg of tantalum(v) chloride (Alfa Gmbh) in 10 cm^3 of a mixture 1:1 by volume of ethanol-isopropanol. The deposition of the coating mixture was performed by dipping the plates in the solution for 20 s. After each immersion, the plates were dried in hot air at 120 °C in order to evaporate the solvent and then annealed in air, in a muffle furnace, at temperature T_1 for 5 min. After the last coating, the electrodes were calcinated at temperature T_2 for 2 h. The firing temperatures T_1 and T_2 were closely dependent on the base metal oxidation kinetics.

Taking into account the nature of the base metal, the thermolysis temperature, T_1, was chosen to be lower for tantalum than for titanium substrate (Table 3). Tantalum metal is more sensitive to oxidation than titanium [13].

The surface mass density, σ, of iridium dioxide catalyst was measured by weighing. It was assumed that only pure and stoichiometric iridium dioxide was formed. Actually, accurate surface analysis of the electrocatalytic oxide mixture by means of X-ray fluorescence and X-ray diffraction techniques were conducted [2, 14]. Diffractogramms showed peaks of the pure stoichiometric conducting oxide IrO_2 and

Table 2. Characteristics of titanium and alloys base metals [*18*]

Base metal (*Supplier*)	*Chemical composition** /wt %	*Bulk density, ρ* /kg m^{-3}
NF T40 (Weber Métaux)	O 0.1, Fe 0.1, N 0.03, C 0.1	4500
ASTM grade 4 (Signer Titanium AG)	O 0.4, Fe 0.5, N 0.05, C 0.1	4500
ASTM grade 7 (IMI Titanium Ltd)	Ti 99.8–Pd (0.12–0.25)	4510
NF TA6V4 (Goodfellow Ltd)	Ti 90–Al 6–V 4	4420
NF TD12ZE (Goodfellow Ltd)	Ti 77.5–Mo 12–Zr 6 – Sn 4.5	5070

* Impurities or alloying elements.

Table 3. Etching treatment of base metal and preparation of the electrocatalytic oxide layer

Base metal	*Etching medium*	*Oxide layer preparation*
Titanium and alloys	Immersed in hydrochloric acid 37 wt% at boiling point during 30 min	Immersion into soln. 10 s Drying in hot air 120 °C during 5 min Thermolysis at $T_1 = 450\,°C$ during 5 min Final calcination at $T_2 = 490\,°C$ during 2 h
Tantalum	Immersed in hydrofluoric acid 40 wt% at 20 °C during 1 min	Immersion into soln. 10 s Drying in hot air 120 °C during 5 min Thermolysis at $T_1 = 420\,°C$ during 5 min Final calcination at $T_2 = 450\,°C$ during 2 h

a second phase, which is amorphous, so that no characteristic peaks occurred, but only broadened peaks recorded. This is typical of Ta_2O_5, for which the annealing temperature and the preparation conditions did not promote crystallization.

2.3. *Accelerated life tests*

Electrochemical measurements were made in a $200\,cm^3$ thermostated undivided glass cell (Methrom A.G.) using a PAR model 273 potentiostat/galvanostat.

The performance of the anodes was studied by means of accelerated life tests previously described by Comninellis *et al.* [11]. The aim of these tests was to compare the operating life of different electrodes related to their preparation mode. The test was conducted as follows: the anode was inserted into a thermoretractable sheath and then a small window of $0.2\,cm^2$ area was opened. Then, the electrode was anodically polarized in 30 wt % H_2SO_4 at 80 °C under galvanostatic conditions, using a large zirconium plate cathode ($20\,cm^2$) as counter electrode. The electrode gap was maintained at $(3.0 \pm 0.2)\,cm$. A progressive current scan of $0.5\,kA\,m^{-2}\,min^{-1}$ was imposed on the anode until the final current density $j_a = 50\,kA\,m^{-2}$ was reached; the cell voltage was measured as a function of time. Any drift of the potential difference was recorded and evaluated. The end of the life, for a given electrode, was determined after a 2 V increase in the cell potential. At this moment, the electrode was considered to be inactive. In order to check the reliability of the results, at least three identical experiments were performed for each set of preparation parameters. A standardized lifetime was defined as the ratio of the lifetime over the surface mass density of iridium dioxide.

3. Results and discussion

3.1. *Tantalum coating compared to titanium alloys*

We considered various titanium alloys which were selected according to the following criteria: (i) commercial availability, (ii) alloying elements with a valve action (e.g., Mo, Zr, V) or (iii) good corrosion resistance in both acidic and oxidizing media (e.g., Pd). These alloys were compared in terms of lifetime of the resulting anodes with a tantalum coating on copper prepared as reported in Section 2.1.

Table 4 lists both the preparation mode of each anode material by the procedure described in Section 2.2., their lifetime and standardized lifetime. The surface mass density of catalyst being critical, this parameter was previously optimized for each base metal. The anode lifetime plots against the surface mass density of the coating IrO_2 have a typical parabolic form [2], in which the vertex gives the coordinates of the optimal lifetime and its abscissa the optimal load of catalyst. However, before the vertex the anode lifetime is quite proportional to the surface mass density of IrO_2. Nevertheless, this quasilinear region strictly depends on the nature of the base metal or alloy composition. For instance, the plot is linear in the range 4 to $12\,g\,m^{-2}$ for pure titanium as it has been shown recently by Krysa *et al.* [15], between 3 and $15\,g\,m^{-2}$ for the ASTM grade 7 and in the range 3 to $26\,g\,m^{-2}$ for tantalum of high purity (99.9 wt %).

Table 4. Service life of M/Ta_2O_5–IrO_2 (30–70 mol %)

Average errors are mentioned with a confidence interval of 95%

Base metal	*Catalyst surface mass density*, σ $/gIrO_2\,m^{-2}$	*Number of application*	*Lifetime*, Δt /h	*Standardized lifetime*, Δt^* $/h\,g_{Iro_2}^{-1}\,m^2$
ASTM grade 4	16.9 ± 0.5	16	17 ± 1	1.0 ± 0.6
ASTM grade 7	16.6 ± 0.5	15	31 ± 2	1.9 ± 0.1
NF T40	8.4 ± 0.5	10	62 ± 3	7.4 ± 0.6
NF TA6V4	12.9 ± 0.4	20	83 ± 4	6.3 ± 0.4
NF TD12ZE	14.7 ± 0.5	20	100 ± 5	6.7 ± 0.4
Cu/Ta (50 μm)	22.0 ± 0.6	20	240 ± 12	10.1 ± 0.6

The results clearly show that: (i) the copper tantalum coated substrate gives the best lifetime, (ii) the chemical composition of the titanium base metal leads to different lifetimes of metal/Ta_2O_5–IrO_2- type anodes. For similar amounts of catalyst (10–12 $g\,m^{-2}$) the titanium alloys (NF T40 and NF TA6V4) give the same results (6–7 $h\,g^{-1}\,m^2$). By contrast, NF TD12ZE needs more catalyst (15 $g\,m^{-2}$) in giving the same order of magnitude of standardized lifetime (7 $h\,g^{-1}\,m^2$). Finally, the classical titanium base metal ASTM grade 4 gives a standardized lifetime about sixfold less than the other titanium alloys (1 $h\,g^{-1}\,m^2$) excepted grade 7.

If overall lifetime is taken into account, NF TD12ZE and NF TA6V4 show relatively good performances: 100 h and 83 h, respectively. As a general rule, use of a titanium base metal such as NF T40, NF TA6V4 and NF TD12ZE for M/Ta_2O_5–IrO_2 type anodes gives better results than classical ASTM grade 4 and grade 7.

3.2. *Correlation between corrosion rate of titanium alloys and lifetime*

Explanation of the difference in titanium alloy lifetime when undergoing oxygen evolution in acidic media can be linked with the corrosion resistance of these base metals. A comparison between lifetime and the corrosion resistance of the titanium alloys in the chemical etching solutions used during anode pretreatment and in 30 wt % boiling sulfuric acid is shown in Fig. 2. Corrosion dissolution rates were measured by immersion tests performed on metal coupons according to the NACE Standard [16]. The tantalum base metal, owing to its very low corrosion rate in the two media equal to $8 \times 10^{-5}\,g\,m^{-2}\,min^{-1}$, was not taken into account in this correlation.

A good correlation exists between lifetime and the corrosion rate of base metal in the electrolyte. ASTM grades 4 and 7 base metal exibit poor duration. In contrast, with ASTM grades 4 and 7 titanium alloys such as NF T40, NF TA6V4, and NF TD12ZE exhibit standardized lifetimes six to three times greater. Finally, tantalum coated copper exhibits lifetimes tenfold longer than ASTM grade 4, and about 2.4 to 4 times greater than titanium alloys.

4. Conclusion

A comparative study of M/Ta_2O_5–IrO_2 type anodes for oxygen evolution in acidic medium has been performed by means of accelerated service life tests at high current density (e.g., 50 $kA\,m^{-2}$). The base metals considered were pure titanium, titanium alloys and tantalum thin coatings (100 μm thick) deposited on copper by molten salt electroplating.

Results show that Cu/Ta/Ta_2O_5–IrO_2 anodes have lifetimes tenfold greater than for pure titanium. This behaviour is related to the excellent corrosion properties of tantalum.

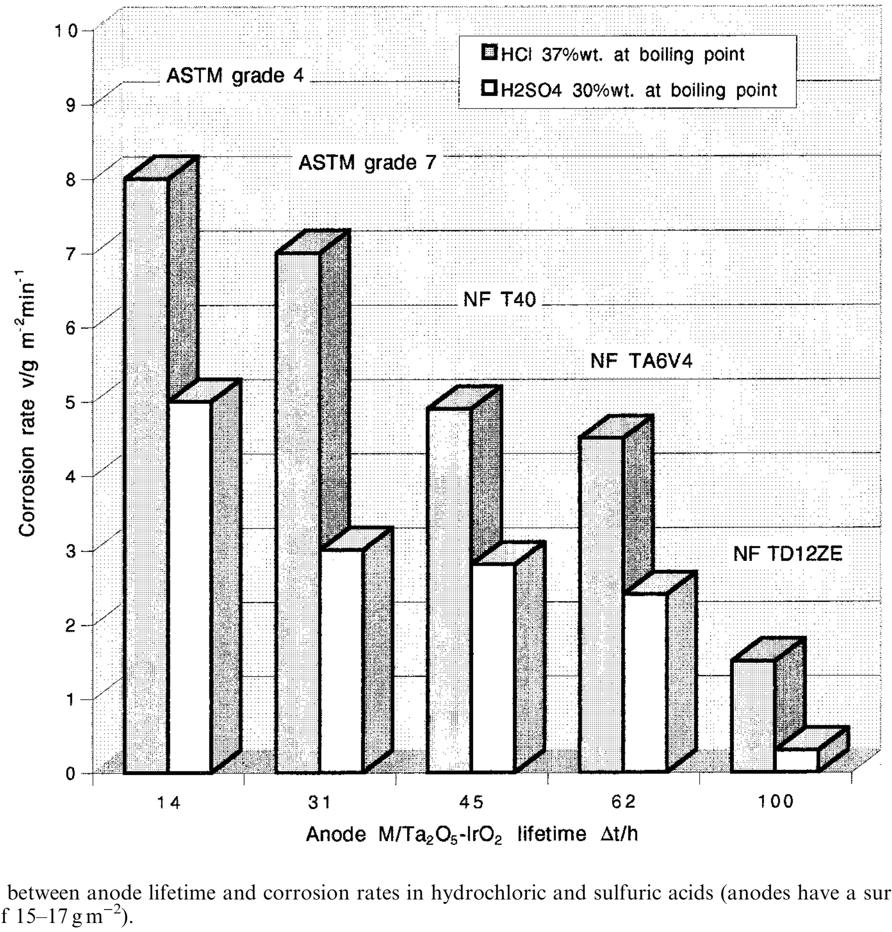

Fig. 2. Correlation between anode lifetime and corrosion rates in hydrochloric and sulfuric acids (anodes have a surface mass density of IrO_2 in the range of 15–17 $g\,m^{-2}$).

Nevertheless, the temperature used for the thermal treatment is not satisfactory, due to the high sensitivity of tantalum to oxidation. Future work should integrate an experimental procedure for optimizing the thermal treatment during the catalytic oxide layer preparation.

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