



## DEACTIVATION MECHANISMS OF OXYGEN EVOLVING ANODES AT HIGH CURRENT DENSITIES

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**Abstract**—Observed deactivation mechanisms of oxygen evolving DSAs<sup>®</sup> in strongly acidic, sulphate-based electrolytes have been described and separated into classes, in order to clarify the reasons of their occurrence as a function of operating conditions. Laboratory tests (particularly accelerated life tests) are briefly illustrated; they have been intensively used for the identification of experimental conditions, able to affect the catalytic activity and electrode stability. Other deactivation mechanisms and their combinations, usually observed on industrial electrolytic processes (main use of these electrodes is in fast electrogalvanizing plants, operating at high current densities), are described and commented on the basis of laboratory tests, the goal being a general understanding of deactivation mechanisms, and their connection with industrial operating conditions. The resulting scheme has been very helpful to obtain modified electrocatalytic coating and electrode structures, able to operate for long time with good and stable performances.

**Key words:** DSA<sup>®</sup>, oxygen evolution, wear mechanism, passivation, electrogalvanizing processes.

### 1. INTRODUCTION

DSAs<sup>®</sup> (dimensionally stable anodes) are very well known in the electrochemical industry. The application on a valve metal substrate of a mixed metal-oxide coating, having catalytic properties for a selected anodic reaction, allows a long and stable operation of the activated anode thus obtained, in several important industrial applications, such as chlorine production. Nowadays, DSAs<sup>®</sup> are experiencing an increasing utilization also in the field of oxygen evolution, which represents the anodic reaction for many processes. DSAs<sup>®</sup> may operate under very different conditions, varying from mild conditions (acid-water electrolysis, metal electrowinning, cathodic protection, electro-organic synthesis, etc.)(1) to very severe conditions, such as fast electroplating processes, operated at high current densities on EGL (electro galvanizing lines) plants(2).

Our attention is focused on the performance of DSAs<sup>®</sup> used in the latter group, and particularly in processes like Zn or Sn electroplating(3) of steel strips, utilized for example in the car or food industry, or Cu-foil(4) production for the electronic industry. The DSAs<sup>®</sup> utilized in these fields, in fact, operate at medium-high current densities ( $8\text{--}15\text{ kA m}^{-2}$ ), at temperatures ranging from 40 to 60°C and in acidic, sulphate-based electrolytes (sulphate-based electrolytes being needed in order to avoid chlorine evolution at the anode, whose handling could be very difficult).

The service life of these anodes is strictly dependent on the operating conditions, the high current density (needed to make the process economical) being an important deactivation factor. According to

the prior art, fast electrogalvanizing processes use either soluble or insoluble anodes, the latter being based on massive lead or its alloys (Pb-Ag, Pb-Sb)(5), which show several disadvantages in comparison with DSAs<sup>®</sup>, mainly because they cannot be operated at high current densities. Furthermore, lead alloys are not dimensionally stable, since they slowly dissolve in the electrolytes, leading to problems such as changes in the gap between anode and cathode and product contamination by lead(4), just to name some.

Notwithstanding their superiority over lead alloys, also DSA<sup>®</sup> deactivation occurs under severe operating conditions. To give an example, taking as a reference time the average service life of a DSA<sup>®</sup> used for chlorine production, it can be noted that during the same lapse of time an anode of the present DSA<sup>®</sup> generation used in EGL processes (where it can operate for about 8000 h, at  $8\text{ kA m}^{-2}$  before deactivation), will be recoated from 6 to 8 times.

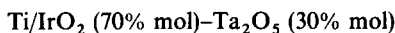
Considering this, it appears that the understanding of the deactivation mechanism, and its connections with the loss of catalytic activity, become of primary importance in view of the target of increasing the service life, the short term goal being at least the doubling of the present one.

### 2. COATING FOR OXYGEN EVOLUTION

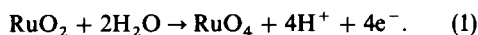
The utilized coating, based on mixed oxides of Ir and Ta, has been described originally in [6]. A detailed structural analysis of this family of coatings is reported in [7, 8], and more recently in [9, 10].

The Ti base structure may have various shapes and geometries, depending on the process. The metal surface is suitably treated in order to receive the active coating, which is applied as a solution of precursor salts using one of the several equivalent techniques, widely described in the literature (brush, roller, spray, *etc.*). After drying at moderate temperature, the precursor salts are thermally decomposed, to obtain the corresponding metallic oxides, one of them,  $\text{IrO}_2$ , being the catalytic and conducting component, the other  $\text{Ta}_2\text{O}_5$ , behaving as the stabilizer and dispersant of the catalyst. The application is repeated several times, up to the reaching of the wanted load.

In principle, many other catalysts could be used. In [7, 8] are described the properties of various couplings between noble metal oxides ( $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{PtO}_x$ —catalytic part) and valve metal oxides ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Ta}_2\text{O}_5$ —stabilizers) applied as a paint on the substrates of different valve metals (Ti, Zr, Ta, Nb). An analysis of the behaviour of various coatings, applied on Ti (which is the best choice as a substrate, for technical and economical reasons) confirms that the best coating for oxygen evolution in acidic solutions is:



based on the concept of anodic efficiency ( $A \text{ h mol}^{-1}$  of active component that can be supplied) and stability. The choice relies on both concepts. Taking into consideration the catalytic activity alone, the best coating would have been  $\text{Ti}/\text{RuO}_2-\text{TiO}_2$ , which, in acidic solutions, usually produces Tafel slopes of  $40 \text{ mV dec}^{-1}$ , vs.  $60 \text{ mV dec}^{-1}$  of the  $\text{Ti}/\text{IrO}_2-\text{Ta}_2\text{O}_5$  coating (or  $120 \text{ mV}$  at high current densities). Unfortunately, the  $\text{RuO}_2$ -based coating is unstable, since the catalyst is oxidized[11] according to the following reaction:



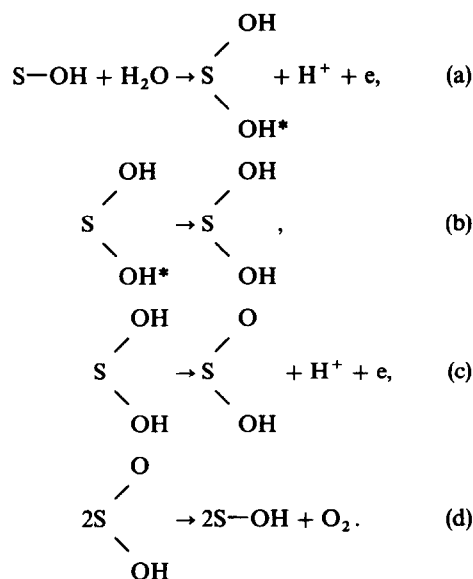
Also  $\text{PtO}_x$  is less stable than  $\text{IrO}_2$  in the same conditions. The composition indicated for the optimum coating corresponds to the maximum of normalized anodic charge ( $\text{C mol}^{-1} \text{ IrO}_2$ ), as obtainable from measurements with cyclic voltammetry (*cv*). This means that the optimum composition is associated with the maximum available population of catalytic sites (related, within certain limitations, to the real surface), obtained by the addition to the coating of the  $\text{Ta}_2\text{O}_5$  component, whose role should be that of promoting and optimizing the status of dispersion of the catalyst.

X-ray diffraction analysis shows that coatings of the  $\text{IrO}_2-\text{Ta}_2\text{O}_5$  types are constituted by a mixture of pure crystalline  $\text{IrO}_2$ , and by a second  $\text{Ta}_2\text{O}_5$  component in the amorphous phase due to the temperatures used for the coating preparation.

The coating surface shows a particular morphology: together with the classical mud-cracked structure, several superficial crystalline agglomerates are present, composed of pure  $\text{IrO}_2$ , whose formation is due to epitaxial growth on the crests of the support, and is to be connected to the type of surface treatment, to the type of coating solution and to the general procedure of thermal decomposition.

These crystalline formations tend to disappear from the surface during the operations, and this is probably connected to the change of the superficial composition observed in time. A certain stabilization of the surface is also shown by experiments in *cv*.

As mentioned above, a typical Tafel plot of  $150 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ , at  $60^\circ\text{C}$  (frequently used parameters in our life tests) shows the presence of two slopes of 60 and  $120 \text{ mV dec}^{-1}$ , in accordance with the behaviour reported in the literature for a system based on  $\text{IrO}_2$  in acidic solutions. In this environment, the oxygen evolution reaction (*oer*) can be described by several equivalent mechanism. A general one has been proposed in [12]:



According to this mechanism, and the experimental determination of the two Tafel slopes, at low current density ( $b = 60 \text{ mV dec}^{-1}$ ) the rate determining step (RDS) is (b) (rearrangement of unstable intermediate  $\text{OH}^*$  before further oxidation), whereas at high current densities ( $b = 120 \text{ mV dec}^{-1}$ ) the primary discharge of water molecules, (a) in the previous scheme, becomes the slow step.

### 3. PERFORMANCE OF THE SYSTEM $\text{Ti}/\text{IrO}_2-\text{Ta}_2\text{O}_5$ : DEACTIVATION PHENOMENOLOGY

A sharp difference between the lifetimes obtained in lab tests and those of the real industrial plants is observed.

In the laboratory, despite the extremely severe working conditions, the number of parameters is limited and all variables are under control. On real plants, the situation is much more complicated, *eg* by the fact that some unknown organic substances, added to the galvanic bath to improve the cathodic deposit characteristics, may play a dramatic influence on the DSA® life, by formation of soluble complexes with coating components, or by precipitation and masking of the surface, *etc.*

### 3.1. Lab tests

According to the reasons mentioned above, lab tests are utilized only as a background for the interpretation of the behaviour and failure observed on plants.

Lab tests are made in thermostated glass cells, using Zr plates as counter electrodes. The electrodes are placed one in front of the other, with suitable separators to avoid gas mixing. The coating under study is usually applied to a Ti plate; an active area of 1 cm<sup>2</sup> is selected from the rest of the surface and exposed to the solution. The test is over when the cell voltage increase from the beginning is 2.5 V: when this occurs, the cell voltage usually increases very fast, in a short time.

If the coating is of particular interest, Tafel plot determinations, superficial voltammetric charge, X-rays fluorescence analyses, *etc.*, are periodically made. In other cases, when for example destructive determinations are requested, testing on several samples is started in parallel, and then samples are taken at different times.

Operating conditions are very different from those used on plants, otherwise tests would last too long. In order to accelerate the deactivation, the electrolyte concentration, the temperature, and the current density are properly increased. Operating in this way, a particular deactivation mechanism is forced, and this could lead to an erroneous evaluation of the coating, or some other phenomena occurring at medium current densities could be masked. It is for this reason that, when a coating is tested at medium-low current densities, the data obtained at high current densities must at least be carefully reinterpreted. The set of life tests presently used in our lab is listed in Table 1.

A diagram representing the behaviour (service life) of a standard coating, obtained from lab tests, as a function of current density and temperature, is reported in Fig. 1. Both parameters are strongly influencing. Temperature has shown such an important effect that, without a careful control ( $\pm 1^\circ\text{C}$ ), the reproducibility is affected.

Service life seems to be slightly influenced by the acid concentration. For instance, keeping both temperature and current density constant (at 60°C at 20 kA m<sup>-2</sup>), a standard coating tested in 1 M Na<sub>2</sub>SO<sub>4</sub> at pH = 2 (for H<sub>2</sub>SO<sub>4</sub>) shows a service life 10% shorter than that of a twin coating tested in 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, but it is not yet clear if this falls in

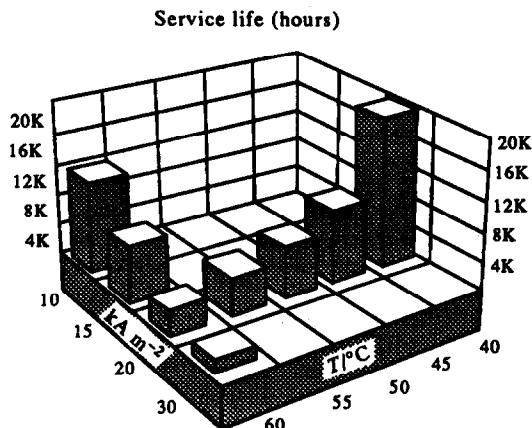


Fig. 1. Service life as a function of current density and temperature.

the range of normal experimental variations or if it is the indication of an effective trend. In [13] it is reported that the lives of the electrodes tested in 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, at 20°C, are 5–10 times longer than those of the same electrodes tested in 270 g l<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution, at 60°C.

Our opinion is that variations in temperature can play an important role. A smaller difference in the service life, such as that observed in our experiments, appears more realistic. The shortening can be explained in terms of conductivity of the solutions (poor conductivity can lead to high electric fields in the solution, with consequent poor distribution of the current) rather than in terms of electrolyte nature.

### 3.2. Deactivation mechanism

Proceeding from lab tests to the general behaviour observed in industrial situations, the deactivation mechanism can be classified into five large classes, which clearly are not to be considered as rigidly separated:

- metal base passivation;
- coating consumption;
- coating deattachment;
- mechanical damages;
- mixed mechanism.

By means of this general scheme, thought for oxygen evolving anodes, a large number of failures

Table 1. Summary of life tests

Test	Purpose	Conditions		
		[H <sub>2</sub> SO <sub>4</sub> ] (g l <sup>-1</sup> )	Temperature (°C)	Current density (kA m <sup>-2</sup> )
A	<ul style="list-style-type: none"> <li>Comparison of various configuration</li> <li>Optimization of production</li> <li>Quality control</li> </ul>	150	60 ± 1	30
B	<ul style="list-style-type: none"> <li>Detection of phenomenological behaviours</li> </ul>	From pH = 2 (in Na <sub>2</sub> SO <sub>4</sub> ) up to 150	40–70	10–30
C	<ul style="list-style-type: none"> <li>Coating evaluation in different experimental conditions and in presence of added substances</li> </ul>	Variables		

occurring in different processes can usually be interpreted. For instance, passivation can explain the rapid deactivation of anodes based on  $\text{SnO}_2\text{-Sb}_2\text{O}_5$  coating, such as those described in [14], utilized in water treatment.

Factors governing the beginning of a particular deactivation mechanism can be either external (related to the process), or internal to the coating. The latter, once clearly identified, can be eliminated with a good chance of success by a proper fabrication of the coating itself.

**3.2.1. Passivation.** Passivation is the most frequent deactivation mechanism associated with operations at high current densities. The general time dependence of electrode potential is shown in Fig. 2.

For a long time, the electrode behaviour is apparently normal. Only a slight increase of the potential, and a different mode of gas evolution (beginning with uniform evolution of fine bubbles, which gradually changes to uneven distribution of large ones), from the surface is observed. Deactivation occurs with a sudden increase of electrode potential, that rapidly reaches very high values, signifying a complete electrochemical failure.

This behaviour is well known, and is traditionally attributed to the formation of an insulating layer of  $\text{TiO}_2$  at the interface between the metallic base and the active coating. This kind of failure is strictly related to current density, as shown in Fig. 3, and at the moment of deactivation a certain amount of catalyst remains non-utilized on the electrode

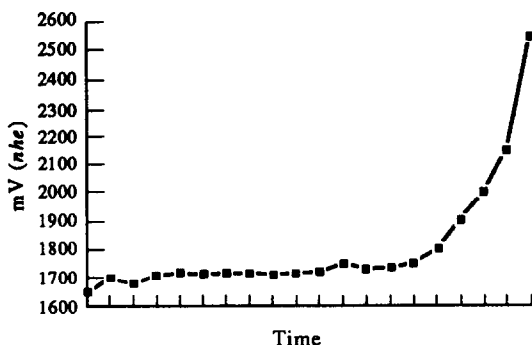
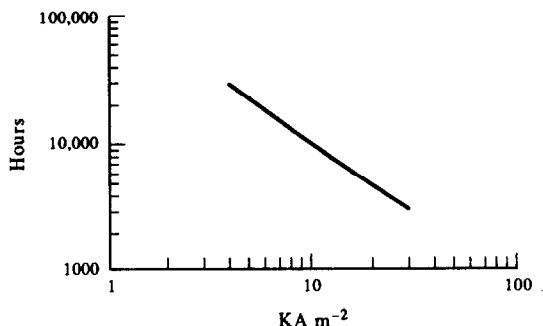


Fig. 2. General time dependence of electrode potential.



150 gpl  $\text{H}_2\text{SO}_4$  -  $60^\circ\text{C}$

Fig. 3. Dependence of service life on current density, at constant electrolyte concentration and temperature.

surface. The wear rate,  $r$ , defined as described in [6]:

$$r = \text{initial loading (g NM m}^{-2}\text{)}/i(\text{kA m}^{-2}\text{)x(hours),}$$

takes this concept into account.

The mechanism of oxide formation has been mentioned by several authors[15–17], who gave a quantitative treatment of the growth rate of the passivation layer obtained by thermal or anodic oxidation, in terms of rate of ionic transport inside and through the films existing on the electrode.

The situation for a DSA<sup>®</sup> can be depicted as shown in Figs 4 and 5, where the three kinds of transport and two possible patterns of oxide forma-

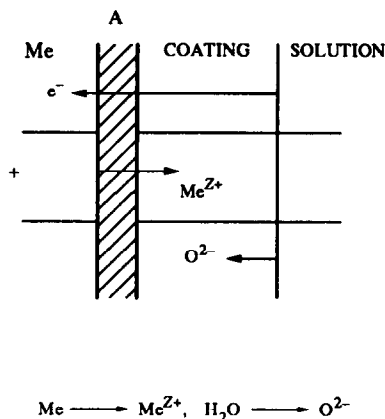


Fig. 4. Electron and ion transport inside the coating. It is hypothesized the existence of an additional layer A (whose composition differs from that of the coating) formed during the thermal decomposition cycle of precursor salts.

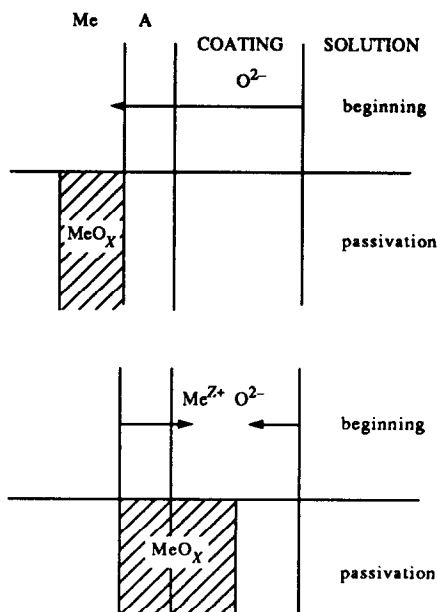


Fig. 5. Two possible patterns of passive layer growth, promoted by ionic transport through the layer A, already described in Fig. 4.

tion are reported. In a simplified scheme, the existence of an additional layer, A, between the metal and the coating is hypothesized. The layer composition differs from that of the coating, and is formed during the thermal decomposition of precursor salts. Referring to Fig. 5, in case (a) only the oxygenated species, generated at the interface coating/solution, is transported through the film toward the metal-coating interface. In case (b), both metal ions and oxygenated species migrate into the coating in different directions, forming an oxide layer that can grow inside the coating itself.

Electrical conductivity will still be possible—see for example [18]—at certain conditions: for instance, if the formed layer is an insulator, the electronic current will flow, providing that it is thin enough (few Ångström) to render electron tunnelling possible. In other cases, if the formed layer is a semiconductor oxide (where defects dominate), the general theory of semiconduction applies. The driving force promoting the mechanism of ionic transport is the strong electric field existing inside the coating, across the interface A. The situation is obviously in dynamic evolution. Passivation occurs when the conditions of electronic conductivity cease to be respected, *ie* when the insulating layer has become too thick, or when defects disappear.

Nucleation of the oxide film begins from preferential sites; the growth then continues laterally. The free surface will gradually decrease, increasing the current density in the conductive portions, and accelerating their deactivation, until all the surface will be completely covered.

The structure of the oxide formed at the interface is extremely variable: amorphous or polycrystalline, anhydrous or hydrated films can be obtained. Formation of amorphous anatase has been observed[19], as well as mixtures of anatase and rutile[20], or just rutile phase[21], depending on the preparation procedure. In the case of thermal oxidation, Ti metal heated in air shows the formation of a surface oxide consisting only, at least for temperatures between 350 and 900°C, of rutile phase[22], whereas inner layers are composed of various suboxides, depending again on the preparation procedure.

Since the coating for O<sub>2</sub> evolution, produced by thermal oxidation, is conductive, it is assumed that a superficial film of TiO<sub>2-x</sub> is formed on the metal, said film being conductive through defects, but not so conductive as the external coating is. Deactivation by passivation will occur when the previous film is transformed into stoichiometric TiO<sub>2</sub>, where the vacancies are completely filled, by O<sup>2-</sup> transport across the coating. Following another hypothesis[23], it is assumed that the layer formed at the interface during coating fabrication—indicated with A in Fig. 4—consists in a mixed Ir(x)Ti(1-x)O<sub>2</sub> oxide.

It is reported in [24] that mixed oxide films of this type, formed by anodic oxidation of Ir-implanted Ti alloys, exhibit a transition from semiconducting to metallic behaviour, for a particular ratio of Ir/Ti. In this case, deactivation would happen in correspondence of stripping[23] of noble metal from this interface, as a result of ionic transport through the film.

Experimental evidence of the formation of a passivated layer at the interface, on a deactivated anode can be obtained by cross-section SEM and EDX microanalysis, and *ac/dc* impedance measurements.

Passivation is promoted by several sources. Impurities (inorganic and organic) contained in the electrolyte are among them. Typical examples are the precipitation on the anode surface of insoluble SrSO<sub>4</sub>, or alpha-MnO<sub>2</sub> or beta-PbO<sub>2</sub>; the latter being a poor conductor is less harmful, but can contribute to affect the uniformity of current distribution, if the precipitate is heavy. The organic impurities will be discussed later.

Also the coating could, in principle, become a source of deactivation if, for instance, it becomes less catalytically active. In this case, in order to keep constant the wanted reaction rate (current density), the current distribution becomes unhomogeneous and in the portions of the surface working for this reason at high current density, a high electric gradient at the interface is produced, leading to passivation. A method for clarifying if this hypothesis is realistic, is to follow the time evolution of the (b) Tafel slope during a life test. Figure 6 shows this kind of analysis, obtained at 60°C and 150 g l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (reference electrode Hg/HgSO<sub>4</sub>). Tafel slopes are ohmic drop corrected, and obtained with a Potentiostat/Galvanostat model M273A—EG&G PAR by means of an M352 software and current interruption.

The same diagram reports the value of the resistance growing at the interface vs. time. This kind of analysis has been repeated for a series of 25 samples, differing only for slight variations made during the preparation procedure.

The average of the Tafel coefficients for new electrodes is 60 mV dec<sup>-1</sup> or 120 mV dec<sup>-1</sup>, respectively, at low or high current density, in agreement with the above-described general mechanism. These electrodes are commonly employed at high current densities, typically in the region characterized by the initial slope of 120 mV dec<sup>-1</sup>.

The deactivated electrodes show an average Tafel slope of 80–100 mV dec<sup>-1</sup> at low current density, and of about 200 mV dec<sup>-1</sup> at high current density, indicating that the catalyst is still present (confirmed

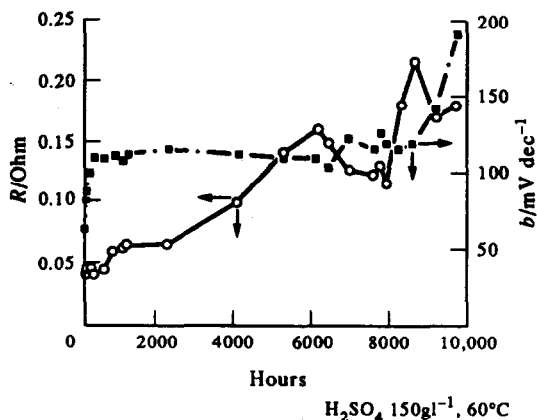


Fig. 6. Time evolution of Tafel slope and resistance growing at the titanium-coating interface.

by XRF measurements), but with a strong decrease of the number of catalytic sites. Tafel slopes obtained at high current densities, higher than  $120 \text{ mV dec}^{-1}$  can be explained assuming the occurrence of reactions parallel to oxygen evolution such as, for instance, passivation or corrosion of the metallic support.

It can be concluded that the only possible source of passivation, internal to the coating, is a loss of catalytic sites or either conductivity.

**3.2.2. Coating consumption.** Coating consumption is the most probable deactivation mechanism at medium–low current densities, where the coating has the possibility of exhibiting all its life, since passivation is less possible. Of course, coating consumption also exists at high current densities.

#### Chemical consumption

It occurs via interactions with electrolyte components or impurities contained. For instance, phosphates[25] or chromates can react preferentially with the Ta component. Organic impurities, complexing agents, such as EDTA or Thiourea will react with precious metals, forming with them stable complexes, or organic cyano reagents (*ie* acetonitrile) will react with Ta. The situation with organic substances is rather complicated, and each case requires a particular study. In Table 2, a tentative classification of possible effects, related to functional groups contained in the organic molecule is reported. As a general rule, all the substances able to promote the consumption of at least one component of the coating, changing the surface ratio, will promote the mixed deactivation mechanism of consumption and passivation.

#### Electrochemical consumption

From a general point of view, for a DSA<sup>®</sup>, oxidation and dissolution of noble metal oxide are possible at the high potentials reached by the electrode. Stability of the Pt group metal oxide depends on the effective conversion of the precursor salt, and particularly on the thermal cycle.

For a coating containing  $\text{RuO}_2$ , dissolution via electrochemical oxidation is possible—see reaction

(1). For a coating containing  $\text{IrO}_2$  a similar reaction is not likely. In [26] a slow corrosion rate of  $\text{IrO}_2$  is reported, in conditions of  $\text{Cl}_2$  evolution, whereas in [27] the anodic dissolution of an  $\text{IrO}_2$  film anodically grown on Ir metal, by potential multicycling is reported. However, in this case anodic dissolution is obtained, polarizing the electrode thus obtained in  $0.5 \text{ M H}_2\text{SO}_4$  at sufficiently high potentials [higher than  $2.0 \text{ V(nhe)}$ ], in order to promote the formation of soluble  $\text{IrO}_4^-$ .

In view of these facts, and keeping in mind that a DSA<sup>®</sup> for  $\text{O}_2$  evolution never reaches these high potentials during its life, we can exclude the occurrence of anodic dissolution with measurable rate. At the end of its life, when a quick potential increase occurs (see Fig. 2) Ir oxidation becomes possible, but at this point deactivation has already occurred, for different reasons from Ir dissolution.

#### Erosion

Coating adherence to the substrate and mechanical consistence (the bonding between the coating particles) are usually very good. In spite of this, erosion is possible, mainly because the coating is porous and the gas evolution at the surface is very fast and can induce the detachment of some coating particles, weakly bonded.

**3.2.3. Coating detachment.** As a general rule, the bonding between the metal base and the coating is involved. Detachment is promoted by all those factors able to weaken this bonding. Also for this mechanism, several possibilities are identified.

#### Chemical attack of base metal

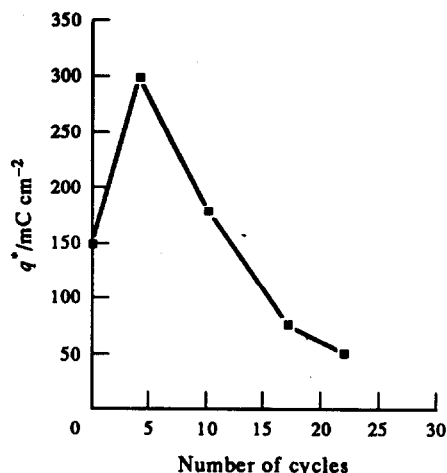
It is usually promoted by the coating porosity (superficial cracks) that increases with time. If the acidic electrolyte is able to reach the base, and the electrode is polarized, nothing happens. Also when the electrode is abandoned unpolarized in the electrolyte, a certain protection given by the coating itself is observed.

When  $\text{F}^-$  ions are present (few ppm are sufficient to promote the attack), the situation becomes much more critical, since even during polarization the Ti

Table 2. Possible effects of organic substances

Group	Aliphatics			Aromatics		
	NP	B	D	NP	B	D
Hydrocarbons	×				×	
With functional groups:						
One functional group						
Usually	×					
–OH			×		×	
			( $\text{CH}_3\text{OH}$ )			
–COOH						
–NH <sub>2</sub>					×	
–NO <sub>2</sub>				×		
–CN			×			
–Cl					×	
–SO <sub>3</sub> H						
Two or more						
Usually		×	×		×	×
		(*)	(*)		(*)	(*)

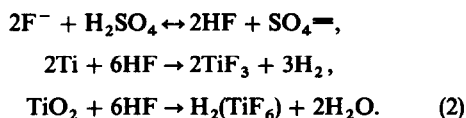
Legend: NP = no problems; B = blanketing; D = dissolution; and (\*) chelation.



$\text{H}_2\text{SO}_4$  150  $\text{g l}^{-1}$  – 60°C – 400  $\text{mV s}^{-1}$

Fig. 7. Superficial voltammetric charge measured in the reported conditions vs. the number of polarity reversal in a 100  $\text{g l}^{-1}$  solution of  $\text{Na}_2\text{SO}_4$  containing 70  $\text{g l}^{-1}$  of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at 60°C.

base, oxidized or not, is dissolved.  $\text{F}^-$  is able to depolarize, forming[28] strong complexes with Ti: they behave like HF, in agreement with the sequence:



Fluorides come from several sources: one of the major contaminants is  $\text{SrCO}_3$ , used to treat the electrolytes for  $\text{Pb}^{2+}$  removal. There is evidence that Ca and Al ions present in the electrolytes may somehow neutralize the  $\text{F}^-$  action, by forming complexes with them.

The problems connected with the presence of  $\text{F}^-$  are very difficult to solve, and the study of electrode configurations, stable to their action is an open and challenging research area.

#### Detachment for internal gas evolution

It is caused when the reaction front moves from the surface into the coating, since, for example, portions of the surface are covered by precipitated impurities etc. Pressure generated by gas evolution inside the pores can be very high, leading to mechanical rupture of the coating.

#### Detachment for massive internal oxide growth (spalling)

##### Detachment for current reversal

The phenomena may happen during the shut down of an electrogalvanizing line. At the moment of interruption, an inversion of polarity is generated (for example, Zn or Sn are dissolved in acid, becoming the site of the anodic reaction), and on the DSA® surface ions can be deposited, together with the discharge of  $\text{H}_2$ . Some tests carried out in our lab showed that the inversion does not affect the DSA® performance when the electrolyte is simply  $\text{H}_2\text{SO}_4$ , but when foreign ions are contained, the effect of several polarity reversals can be very dangerous, because metals are deposited into the surface cracks, during cathodic mode, and then dissolved again during anodic mode. This cycling results in coating damage, due to mechanical weakening. Figure 7 reports the superficial voltammetric charge vs. the number of cycles. It can be seen that, at the beginning, Zn deposition promotes the increase of porosity, which is then progressively reduced, because the coating is mechanically removed.

All the deactivation mechanisms related to the detachment from the base, are strongly related to the superficial profile of the surface. A proper profile, will lower this kind of damage. The importance of the profile is stressed for example in [29].

**3.2.4. Mechanical damages.** Mechanical damages are a trivial—but extremely probable—cause of deactivation. For example, in the EGL plants, where the steel strip runs at high speed, abrasions frequently occur, because the gap between anode and cathode is very narrow. Furthermore, the welding between the end of a coil and the beginning of the next, quite often breaks up, leading to severe shots and damages. Mechanical damages can destroy a good coating, in a few seconds. Practical solutions to these damages are needed. In [30] some examples are given.

**3.2.5. Mixed mechanism.** They are the most probable in the practice. For example, a poor electrode design (*ie* having an improper current distribution), combined to the presence of high  $\text{F}^-$  levels, can lead to the total deactivation of DSAs®, in the parts where the current density is high (here current and  $\text{F}^-$  are both accumulated). The result is the corrosion of the base metal, the local loss of active coating, and an uneven Zn profile on the steel strip. This is a typical example of DSAs®, considered deactivated even if 90% of the surface is still active. Problems of current distribution are frequently treated on

Table 3. Tentative generalization of deactivation mechanisms

Mechanism	Medium current density	High current density
Mechanical damages	Always possible	Always possible
Catalyst consumption	Very probable	Possible in presence of impurities
Passivation	Unlikely	Very probable
pH	Non-influencing	
Temperature	Very affecting	
$\text{F}^-$	Extremely dangerous	
Others (Sr, Pb, ...)	To be evaluated	
Current reversal	Very affecting in presence of metals (Cu, Zn)	

an empirical basis, by means of various kinds of masking, but finite element analysis is now widely adopted, in order to obtain a better electrode design.

#### 4. CONCLUSIONS

Table 3 reports a tentative scheme for the generalization of deactivation mechanisms. Their understanding is considered fundamental in order to improve the performance of the electrodes (increase of service life), through an additional increase of resistance of passivation, coating stability and protection from fluorides attack.

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