

The operation of long-life anodes in amalgam cells

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In recent years, long-life anodes have become a well established type of DSA^(R) anodes for the production of chlorine in mercury cells. They offer considerable benefits compared to 'normal' or conventional metal anodes, i.e. reduced costs for repair, transportation and installation as well as a lower consumption of energy. The reason for the decline in damage incidents is probably the slightly increased electrical resistance of the coating. The reasons for the extended service life of the anodes are the decrease in the generation of oxygen and the improved protection of the titanium substrate against penetrating brine and oxygen diffusion.

1. Introduction

Long-life anodes (LLA) belong to the family of DSA^(R) anodes. 'Normal' DSA^(R) anodes consist of a metal structure usually made of titanium, the substrate, and of an electrochemically active coating manufactured under the Beer [1, 2] patents*. Long-life anodes [3]†, however, are provided with an additional layer, the intermediate layer, between substrate and the coating (Fig. 1). This intermediate layer consists of an electrically conductive titanium dioxide which, in most cases, is deposited on the substrate by plasma spraying. In many cases the intermediate layer is able to protect the anode from being destroyed through short circuits by contact with the amalgam in mercury cell operation. Moreover if the anode is also provided with a special coating (still manufactured under the Beer patents), the service life can be twice as long as that of a 'normal' DSA^(R) anode.

2. The properties of the intermediate layer

The titanium dioxide of the intermediate layer is

partially reduced rutile, i.e. TiO_{2-x}, which shows excellent stability in an oxidizing environment.

The electrical conductivity results from the oxygen deficiency of the crystal lattice. While TiO₂ possesses a specific resistance of more than 10¹⁰ ohm cm, the value for TiO_{1.9995} is reduced to 10 ohm cm and further to 10⁻² ohm cm for TiO_{1.75} [4].

Although TiO_{2-x} is, *per se*, a brittle ceramic material, the LLA anodes are not sensitive to mechanical stress. Wire 3 mm in diameter may be bent through 180 degrees before the intermediate layer chips off while sheet material may be hammered without causing the layer to crumble away. It is, therefore, not necessary for the operating personnel in the cell room to handle the long-life anodes any differently from conventional anodes.

3. Operating characteristics in production cells

3.1. Use of LLA anodes

After showing very promising results in several years of laboratory research and during operation

* These anodes are now patented in a great number of countries in the world.

† The patent rights covering the long-life anode are held by Hoechst AG who have issued a worldwide exclusive licence to Heraeus Elektroden GmbH.

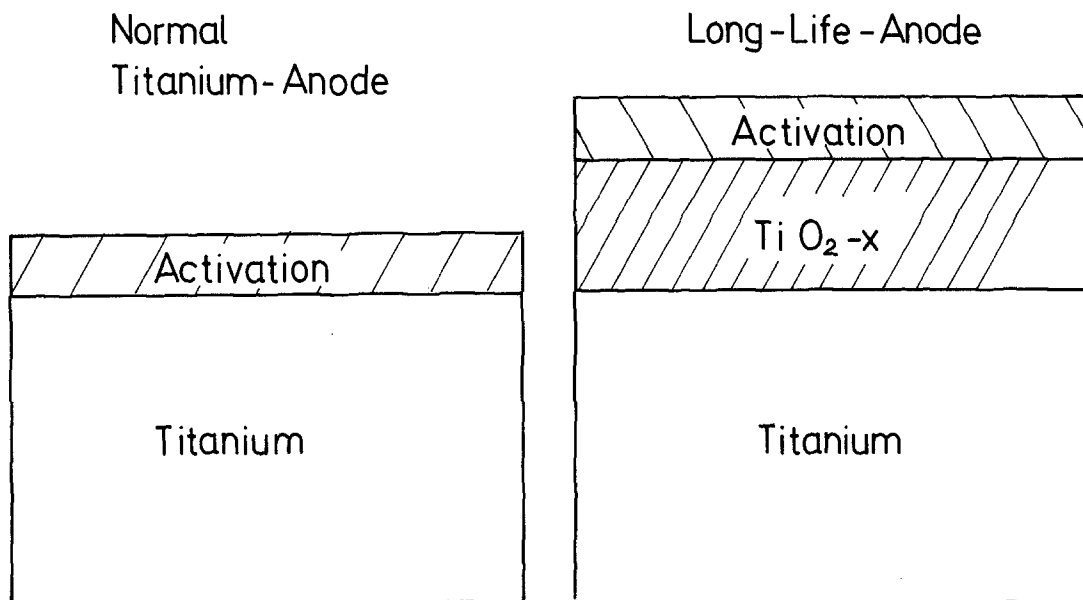


Fig. 1. Schematic drawings of metal anodes.

in individual production cells [5-7], the LLA anodes are now widely used throughout Germany. Therefore, it is now possible to report results that have been obtained from a great number of industrial mercury-cells running under normal production conditions as opposed to specially supervised test-cells, or laboratory cells that are usually operated under conditions far from average for a cell-room.

Data from industrial cells, particularly when collected from several plants, where other parameters may vary strongly, cannot be presented in the exact manner of laboratory experiments. Therefore the reported data are necessarily more qualitative than quantitative. On the other hand these data are accurate enough to estimate and compare the cost reductions that may be obtained under different operating conditions.

As the reduction of costs is the primary aim of LLA anodes, these economic data are evaluated in some detail. In December 1982, about 5900 m² of anode surface were under contract, representing about 623 000 tons year⁻¹ at a current density of 10 kA m⁻², and 85% has already been installed. One third of the total is taken up by test cells being operated in some twenty different plants.

The remaining two thirds are run in three major facilities one of which belongs to the Hoechst AG, the inventors of the LLA anode [3], and the other two are the property of other important producers of chlorine. The planning projections at the end of 1982, provide for about a total of 7300 m² of anode surface; chlorine producers will soon expand their test runs from a few cells to one third or even half of their facilities.

3.2. Advantages of LLA anodes

Experience has confirmed two specific characteristics of the long-life anode:

- (a) The electrodes are not susceptible to short circuits almost wholly eliminating any repairs,
- (b) the service life may reach twice that of an 'ordinary' DSA^(R) anode.

The first statement results from inspection of long-life anode cells: only in a very few exceptional cases could anodes be detected that needed repair.

The second statement can be illustrated by the following example. In a certain cell-room the average life of 'ordinary' DSA^(R) anode-cells is

about 18 months (24 cells). But 7 cells, equipped with long-life anodes, have been running for more than 3 years. More recently, 41 cells were equipped with long-life anodes and none of them has been sent back for recoating.

These improvements lead to some substantial cost benefits.

3.2.1. Reduced maintenance costs. Thus far, no routine repair work on the installed long-life anodes has been required. The intermediate layer, however, will not offer much protection from the consequences of operating errors. In one isolated case the breakdown of process control caused the anodes to be lowered into the mercury and this severely damaged the anodes and necessitated repair. In another case the anode protection device had not been correctly installed; here, too, major repairs had to be made.

3.2.2. Lower k -value. In industrial mercury cells the cell voltage U (in volts) at constant temperature can be estimated from the equation

$$U = 3.15 + k \times I \quad (1)$$

where I is the current density in kA m^{-2} .

The k -factor (k is usually between 0.08 and 0.12 $\text{Vm}^2 \text{kA}^{-1}$) is a linear function of the distance between the anodes and the cathode. From measurements on a 7.5 m^2 -cell [8] the following formula can be derived:

$$k = 0.034 + 0.0215d$$

where d is the electrode gap in mm.

Therefore, the cell voltage drops linearly with the anode-cathode gap, provided the curtain of gas bubbles does not dip into the mercury.

Usually mercury cells are operated with a certain safety distance between the anode and cathode to avoid short circuits. If the anodes are protected against short circuits – either by an anode protection device that lifts the anodes in case of onset of a short circuit or by modifications of the coating as described above – this safety distance may be reduced and thus a lower cell voltage is obtained.

A comparison between 6 long-life anode cells and the rest of the cell room running with normally coated anodes proved that the cells with long-life anodes run about 50 mV (calcu-

lated for 10 kA m^{-2}) lower in voltage than the average for several months. These cells only had a spring loaded soldered protection device. In plants with more sophisticated anode protection devices a smaller voltage reduction (about 25 mV) is expected.

A test is now in progress in which one half of a cell room is running with LLA anodes and the other half with normally coated anodes. The results obtained up to now show a slight reduction of cell voltage.

3.2.3. Lower installation and transportation costs. The extended working life, in many cases double that of normal DSA, reduces the costs for transportation and installation to half of the amount previously experienced.

3.2.4. Lower cell voltage and less cell room contamination. Towards the end of the working life of an anode the cell voltage usually tends to increase somewhat. Doubling the working life will ultimately halve the overall time of operation at increased voltage. At the same time the contamination of the cell room with mercury is considerably reduced as the extended working life permits the cells to be opened less frequently.

3.3. Economic consideration

For each of the points mentioned above it is possible to estimate the savings per ton of chlorine. Although these figures will, of course, vary from plant to plant, a rough estimate assesses the savings at between 1.30 DM and 2.00 DM per ton of chlorine.

Table 1 shows a typical example.

4. Fewer damaged anodes: the reasons

It is not possible to observe the actual events taking place inside an amalgam cell during short-circuiting. Any attempts to explain the events occurring during short-circuiting or near-short-circuiting must, therefore, be based upon plausible assumptions.

The following assumptions are derived from analysing metal anodes that had been damaged and returned for repair. (Several thousands out of

Table 1. Advantages of LLA anodes over 'normal' DSA^(R) anodes

Interpretation/operational data	Cost (DM/t Cl ₂)	Saving (DM/t Cl ₂)
(a) Repair costs (average rate)	0.74	—
If 95% of these costs are eliminated, the resulting saving is	—	0.70
If these costs can be reduced by 50%, the resulting saving is	—	0.37
(b) With LLA anodes it is possible to obtain somewhat more favourable <i>k</i> -factors. Experience from tests shows 25 to 50 mV at 10 kA m ⁻² . The lower value applies to relatively well monitored installations.	—	—
$0.79 \times \Delta U$ (mV) = savings kWh/t Cl ₂		
Savings at 0.07 DM/kWh for 25 mV	—	1.38
(c) Halving of transportation costs, approximately	—	0.05
(d) Halving of installation costs, approximately	—	0.30
(e) During the last two months of the working life the <i>k</i> -factor increases slightly. As a rule, the anodes will be replaced when the increase reaches 0.02 units (200 mV at 10 kA m ⁻²). With a service life of 18 months, approximately $2/18 \times 200$ mV must be added to the mean voltage. As the number of times the anodes must be taken out is halved, one obtains a voltage reduction of 11 mV according to $1/2 \times 2/18 \times 200$ mV	—	0.60

more than about 200 000 that have been returned for reactivation without need for repair.) As, up to now, only a few LLA anodes have been returned this analysis is based on 'normal' anodes only. Therefore Figs. 2, 3 and 4 do not show LLA anodes. According to this experience, the short-circuitings may be subdivided into four categories:

(a) The contact between amalgam and anode is good. In such cases most of the heat generated during the short circuit is released within the anode structure and not in the amalgam-anode contact zone. The coating still remains active, meaning that the temperature at the coating did not exceed 600 to 700° C, as higher temperatures lead to a

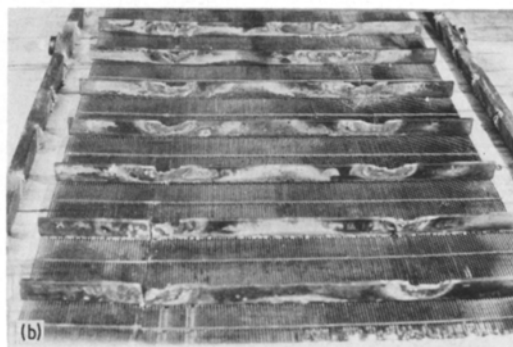
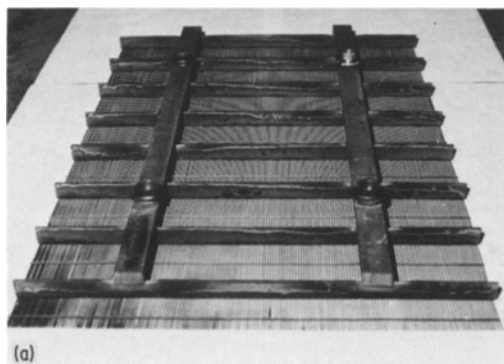


Fig. 2. Damaged anode following good contact between anode and amalgam. (a) shows an anode without damage. (b) shows how the conductor bars are fractured after short circuit.

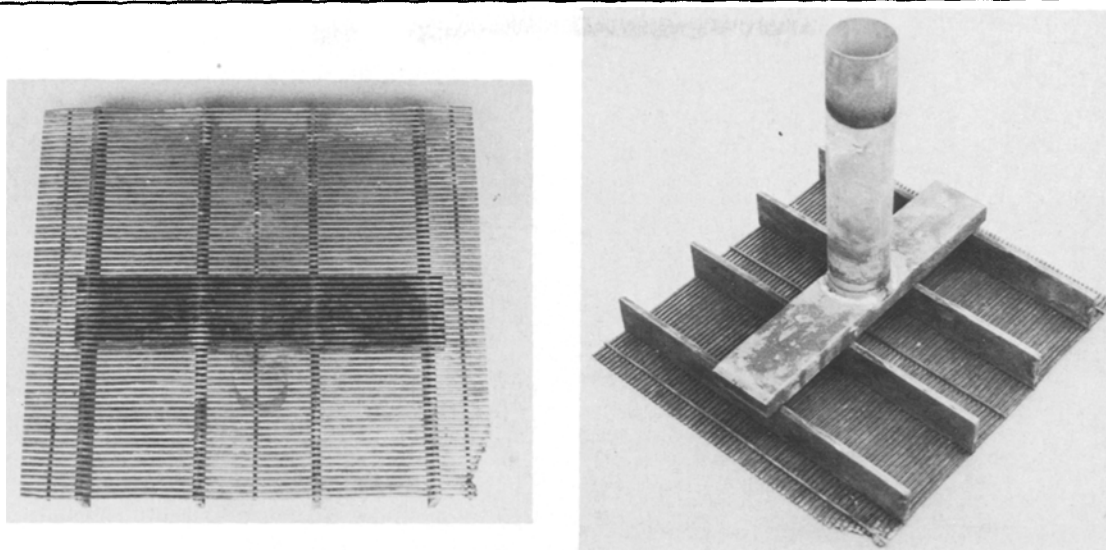


Fig. 3. Damaged anode following poorer contact between anode and amalgam.

disintegration of the active coating [9-11].

The damage then occurs at the welding seams of the current distributors and the lateral distributor when dealing with rod anodes (see Fig. 2). If mesh anodes are used, a destruction of the welding seams near the contacts with the copper bolts is often observed.

(b) The contact between the amalgam and the anode is still intimate but not as good as under (a); the contact area is also reduced. In this case the electrically generated heat is not sufficient to melt the titanium at the seams. In the contact zone between amalgam and anode, however, sufficient heat is generated to vapourize the mercury. If this should lead to arcing, reference is made to (c). If an arc is not formed, the coating normally turns brown and becomes deactivated. Occasionally, small parts of the mesh or of the rods will 'burn' away, (see Fig. 3).

(c) The situation is as described under (b); the heat generated in the amalgam-anode contact zone, however, forms an electrically conductive plasma which will spread as a vast electric arc. This type of short-circuiting causes extensive damage to the grid structure (see Fig. 4).

(d) Occasionally a mercury wave or butter moves through the cell and produces minor short-circuits leading neither to damage nor to an immediate deactivation of the anodes. We will return to this point in the Sections 5.4 and 5.5.

These four types, or categories, of short-circuits represent a reasonable framework within which a good description of damage observed on anodes removed from amalgam cells and returned for repair is possible.

At this point it is interesting to examine the function of the intermediate layer consisting of TiO_{2-x} during the beginning of a short circuit. In the first place, this intermediate layer is an additional resistor connected in series with the resistors representing cathode, anode, the brine in the gap between the electrodes and the anode structure.

This resistor must be compared to the resistance of the entire cell:

R'_A is the surface resistance of the anode (ohm cm^2).

R'_C is the surface resistance of the entire cell (ohm cm^2).

$\frac{R'_A}{S} = R_{sh}$ (ohm) is the actual resistance of that surface part S of the anode section being in contact with the amalgam.

$\frac{R'_C}{F} = R_C$ (ohm) is the resistance and F the total anode area of the entire cell. If small short circuits are considered, R_C is not changed significantly by these small short circuits.

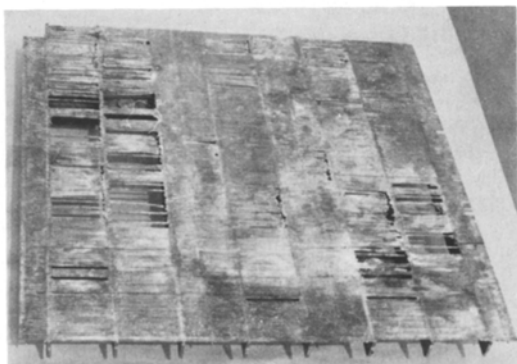
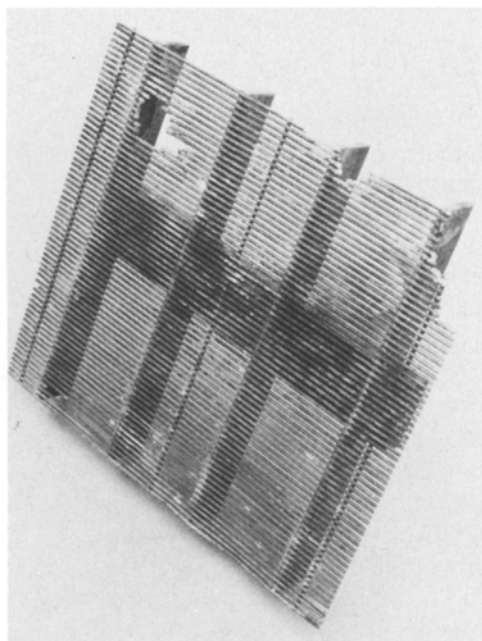
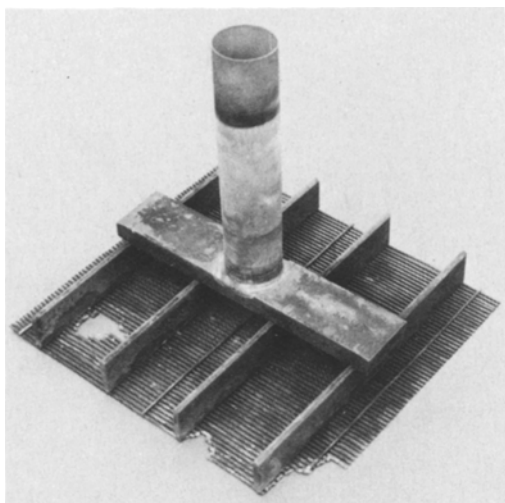


Fig. 4. Anodes damaged by an electrical arc.

i_{sh} is the current passing through the contact zone of the short-circuit.

i_C is the current passing through the cell.

As an example we can consider a cell of 10 m^2 having a voltage of approximately 4 V at 10 kA m^{-2} . The short circuit area is assumed to be 1 cm^2 . This appears to be reasonable to describe the beginning of a short-circuit which can, subsequently, cover a considerably larger area.

The specific resistance of an 'ordinary' DSA^(R) anode coating is about 1 ohm cm [11]; the value for the TiO_2-x intermediate layer is about 0.5 ohm cm . The thickness of the active coating is approximately $10 \mu\text{m}$ and that of the intermediate layer about $100 \mu\text{m}$.

From the above, the following equations are obtained:

$$R_{sh}(\text{ord.DSA}) = 1 \times \frac{0.001}{1} = 10^{-3} \text{ ohm}$$

$$R_{sh}(\text{LLA}) = 0.5 \times \frac{0.01}{1} = 5 \times 10^{-3} \text{ ohm.}$$

At the beginning of a short circuit, a contact-resistance between amalgam and anode surface has to be expected. This would increase R_{sh} . As this has been neglected, the values calculated above are minimum values. R_C is somewhat more complex than an ohmic resistance (cf. Equation 1), but its maximum value is

$$R_C = 4 \text{ V}/100 \text{ kA} = 40 \times 10^{-6} \text{ ohm.}$$

Therefore the maximum short-circuit current can be calculated using the equivalent circuit shown in Fig. 5. Thus the following equation is obtained

$$\frac{R_{sh}}{R_C} = \frac{i_C - i_{sh}}{i_{sh}}$$

both for a cell equipped with 'ordinary' DSA^(R) anodes and for a LLA cell.

Rearranging both the equations and taking into account that $R_{sh} \gg R_C$ and that $R_C(\text{ord. DSA}) = R_C(\text{LLA})$ yields:

$$\frac{i_{sh}(\text{LLA})}{i_{sh}(\text{ord.DSA})} = \frac{R_{sh}(\text{ord.DSA})}{R_{sh}(\text{LLA})}$$

Thus, an increased surface resistance of the short circuiting anode will result in a decreased short-circuit current.

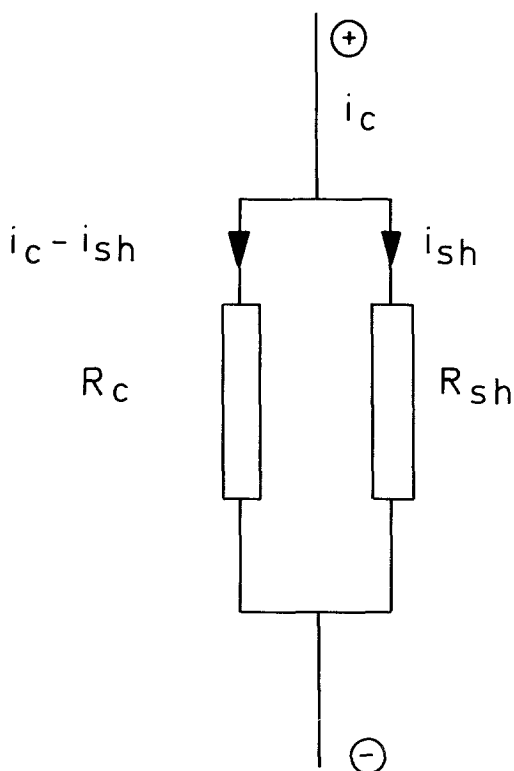


Fig. 5. Equivalent circuit for the situation right after the beginning of a short circuit.

Therefore, using the figures given above, a reduction of short-circuit current to 1/5 can be expected using LLA anodes. Of course, this value varies strongly with the thickness of the intermediate layer.

This example demonstrates that the short-circuit current is much lower with LLA anodes than with 'ordinary' anodes. The ratio of the short circuit currents of LLA anodes and 'ordinary' anodes was measured in a laboratory cell [6]. The ratio thus obtained is approximately 1:2 and of the same order of magnitude as indicated in the above model calculations.

Strictly speaking the resistances of the bus bar feed and distribution system such as copper bars, contacts, copper stems, anode structure are in series with $R_{sh}(\text{ord. DSA})$ or with $R_{sh}(\text{LLA})$. At a current load of approximately 1 kA per copper stem, the voltage drop between the copper stem and the extreme edge of the anode seldom exceeds 70 mV. This corresponds to a resistance of 70 μohm and is thus an order of magnitude below R_{sh} and these resistances were neglected when defining R_{sh} .

This approximate calculation shows that the damage incidents experienced under (a) and (b) will be considerably reduced.

For cases referred to under (c) it is fair to assume that, in many instances, the critical current density required to sustain an electrical arc will not be reached due to the resistance of the intermediate layer. Moreover some of these arguments may also be applied to a situation where the reduction of the short-circuit current depends on the wettability of the anode with amalgam; an incomplete wettability will increase the surface resistance. Notwithstanding the significant differences between the uncoated titanium *per se* (Fig. 6) and the titanium after deposition of the TiO_{2-x} intermediate layer (Fig. 7), it is hardly possible to arrive at conclusions about the wettability of the anodes once both types have been provided with the same active coating (Fig. 8).

Based on the above model calculations, the voltage within the intermediate layer during 'normal' operation of the anodes is approximately 5 mV at 10 kA m^{-2} . In the light of the favourable voltage characteristics mentioned above, this value may well be left out of consideration.

The concepts outlined above show that the long-life anodes are capable of keeping minor short-circuits, which usually constitute the starting point of major damage, from expanding.

5. Reasons for the extended service life of long-life anodes

Several publications deal with the various reasons for the (premature) deactivation of anodes [12–16]:

1. Deactivation due to excessive heat accumulating in the coating and the titanium during short-circuiting;
2. Deactivation due to oxygen diffusion forming a nonconductive TiO_2 layer between the coating and the titanium;
3. Deactivation due to the brine penetrating right through to the titanium substrate, resulting in removal of the coating;
4. Deactivation due to wear of the coating through the oxidation process of water or hydroxyl ions and/or a hypochlorite oxidation into oxygen and/or chlorate.
5. Deactivation due to a reduction of the coating through contacting amalgam and electrolysis in

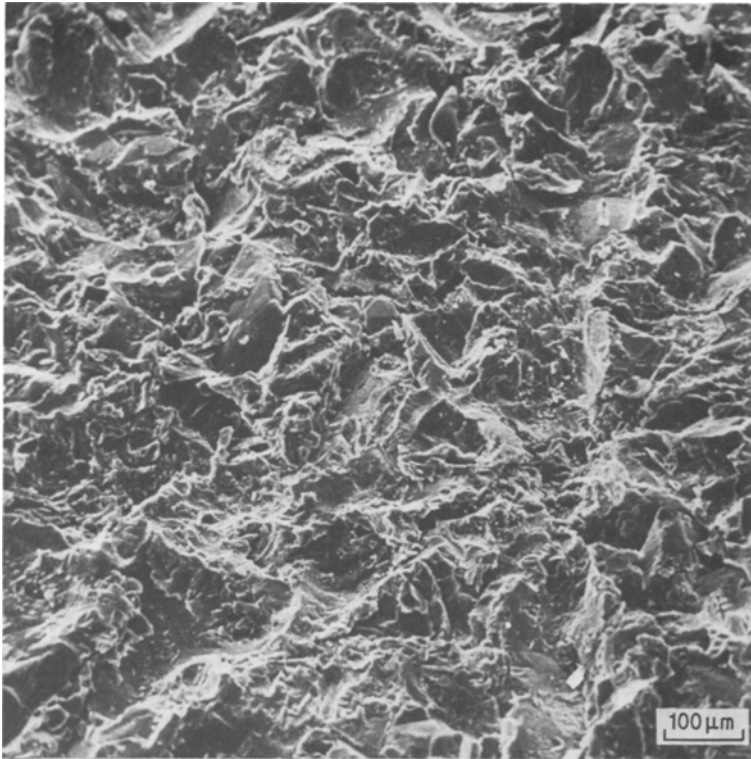


Fig. 6. Titanium before coating.

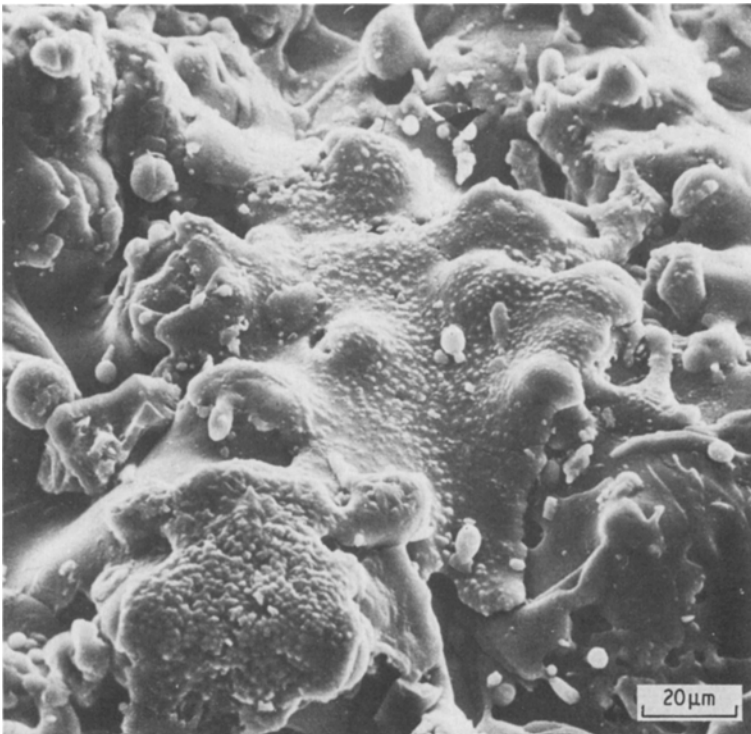


Fig. 7. Titanium coated with TiO_{2-x} .

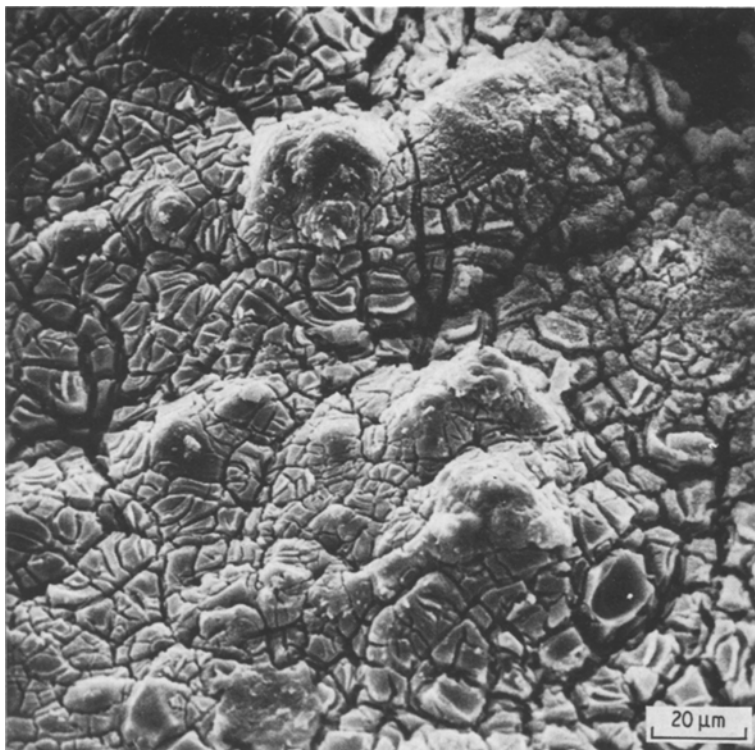


Fig. 8. Titanium coated with TiO_{2-x} and LLA coating.

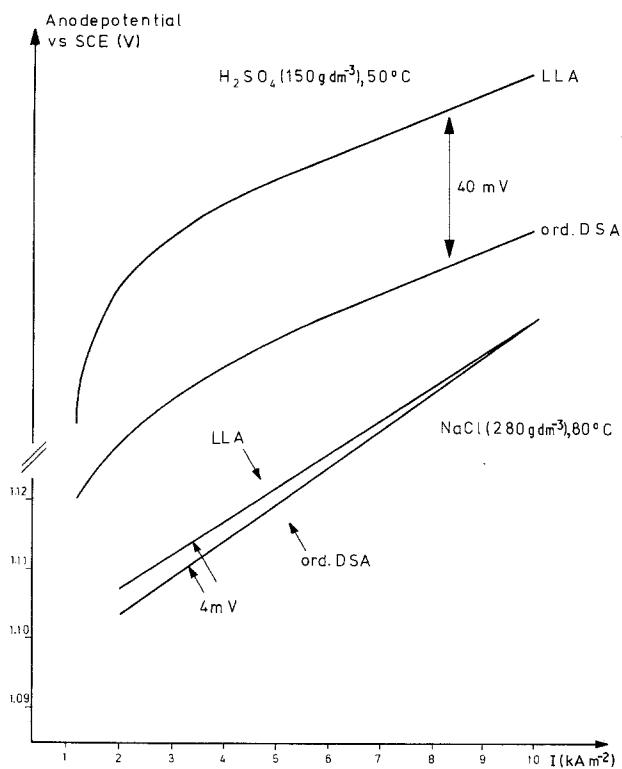


Fig. 9. Voltage/current relation of two types of DSA^(R) coatings (including IR drop).

a strongly alkaline medium.

6. Deactivation by current reversal (after shut-down of a cell).
7. Deactivation due to wear of the coating during the oxidation process turning the chloride into chlorine.

The type of deactivation due to 1 above has already been discussed. It is also immediately apparent that the points 2 and 3, above will play a lesser part in the deactivation process once an intermediate layer of TiO_{2-x} protects the titanium. Points 5, 6 and 7 above should be of comparable importance for both the long-life anodes and the 'ordinary' anodes.

The only one of the above points still to be discussed is 4.

The coating of $\text{DSA}^{(R)}$ anodes is worn off rather rapidly (within a few days) once the anode produces oxygen, i.e. if the anode is operated in H_2SO_4 or NaOH [9, 10]. The addition of another noble metal apart from ruthenium will often lead to an increase of the oxygen potential of the anode [17]; the generation of oxygen, therefore, will be reduced in such cases during the process of chlorine production and thus increase the working life of the anode.

In Fig. 9 a comparison between the current/voltage curves of 'ordinary' $\text{DSA}^{(R)}$ anodes and LLA anodes can be seen.

In brine (chlorine evolution) practically no difference is detectable. In sulphuric acid the

LLA anodes have the higher oxygen over-voltage.

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