

# Material problems encountered in anodic MnO<sub>2</sub> deposition\*

E. PREISLER

*Hoechst AG, Werk Knapsack D 5030 Hürth, Germany*

Received August 1988; revised 11 January 1989

The characteristic material problems in electrolytic manganese dioxide (EMD) deposition concern the electrolysis cell components and, especially, the anodes. Temperature, sulphuric acid concentration, and current density are the most critical parameters which determine the corrosion and life times of the lead, graphite or titanium anodes. The corrosion of lead, even under the cover of electrodeposited manganese dioxide, pollutes the technical product. Graphite anodes are slowly oxidized, a process which limits their life time. The behaviour of titanium as anode material is determined by the conductivities of the TiO<sub>x</sub> interlayer as well as of the manganese dioxide deposits in the layered system Ti-TiO<sub>x</sub>MnO<sub>2</sub>. Passivation and depassivation reactions in conventional EMD electrolysis are described and the improved behaviour of titanium anodes in the suspension bath process is explained.

## 1. Introduction

The material problems specifically encountered in the electrolytic manganese dioxide process are those of the structural materials of the electrolysis cell and, especially, the cathode and anode materials. In other parts of an EMD plant conventional corrosion problems arise from handling of hot and fairly acidic solutions or from the abrasive action of the very hard EMD pieces and powders. These questions will not be discussed here.

For a better understanding of what happens on an anode on which manganese dioxide is deposited electrolytically (EMD) it is necessary to take account of the electrolysis conditions listed in Table 1 for three different process alternatives which differ from each other mainly in the choice of the anode material.

Two special aspects are particularly important to the problems to be discussed here. (1) The electrolyte becomes more acidic as EMD deposition, or Mn depletion, proceeds. Therefore, the electrolyte has to be continuously exchanged for fresh electrolyte to limit the acid concentration to acceptable values. (2) The anodic deposit is not pure manganese dioxide, i.e.  $\beta$ -MnO<sub>2</sub>, or pyrolusite, with an oxygen index very close to 2.00, but contains a certain amount of constitutional or combined water. Furthermore, an adequate reaction equation should indicate that the reaction product contains not only Mn<sup>4+</sup> ions but also a small amount of Mn<sup>3+</sup> ions (sometimes up to 10% of the Mn content). The stoichiometry with respect to H<sub>2</sub>O and Mn<sup>3+</sup> content can be influenced by the electrolysis conditions and these conditions

influence the solid state properties of EMD [1] and determine its electrochemical behaviour in the primary cell [2].

## 2. General demands for anode materials

Table 1 presents three basically different types of anode material each of which has its merits and its disadvantages. All of them should possess the following properties: (a) low corrosion rates even at high working temperature; (b) no passivation; (c) low deposition potential; (d) good mechanical strength to withstand the forces exerted on EMD during temperature changes and during stripping; (e) no contamination of EMD caused by the anodes; (f) repeated use of the anodes; (g) good adherence of, and good electrical contact to, the deposit during electrolysis; (h) ease of deposit recovery; (i) low costs.

The use of an acidic manganese sulphate electrolyte near the boiling point (~105°C) requires excellent corrosion resistance of all structural elements including cathode and anode materials. In order to reduce vaporization losses of the electrolyte and the formation of a sulphuric acid mist above the electrolyte, caused by cathodic hydrogen gas evolution, the surface of the electrolyte is usually covered with a layer of paraffin, of some centimeters thickness, through which the electrodes can be inserted into, and removed, from the cell. Only one plant uses covered cells avoiding the use of paraffin. The advantage can be seen in the protection of the cell-hall atmosphere from hydrogen and sulphuric acid as well as in avoiding accelerated titanium corrosion near the phase boundary between electrolyte and paraffin. The disad-

\* Paper presented at the meeting on Materials Problems and Material Sciences in Electrochemical Engineering Practice organised by the Working Party on Electrochemical Engineering of the European Federation of Chemical Engineers held at Maastricht, The Netherlands, September 17th and 18th 1987.

Table 1. Conditions of electrolysis

Cell body	Rubber-lined steel, glass fibre-reinforced polyester, concrete with glass fibre-reinforced polyester lining or epoxy resin linings		
Anodes	Pure lead or antimonial lead	Graphite	Titanium
Cathodes	Antimonial lead	Graphite, copper, steel	Graphite, lead, copper, steel
Anodic current	0.5–1.2	0.7–1.0	0.7–1.0
Electrolyte	0.5–1.0	0.5–1.0	0.5–1.0
MnSO <sub>4</sub> (mol l <sup>-1</sup> )			
Sulphuric acid (mol l <sup>-1</sup> )	0.5–1.0	0.5–1.0	0.1–0.4
Temperature (°C)	90–95	90–95	90–95

vantage is the more complicated system of electric connections.

Although all three anode options are still being used, it should be stated here that the modern trends in EMD production favour the use of titanium anodes for several reasons. One of these reasons is that the working conditions for titanium anodes are very near to the electrolysis conditions which favour a superior quality of the manganese dioxide.

### 3. Lead anodes

Lead is a soft metal which becomes corrosion protected in sulphuric acid solution by a thin film of lead sulphate. The corrosion rate therefore depends on the dissolution rate of the lead sulphate film, which is low. This film is not very dense. Therefore, at sufficiently anodic polarization lead dioxide is formed. As the electronic conductivity of lead dioxide is high, lead anodes can be used at fairly high current densities with neglect of the ohmic resistance at the interface between the EMD deposit and the lead base metal.

Nevertheless, there are some drawbacks with pure lead anodes: (1) they are difficult to handle because they easily distort; (2) lead dioxide formation still continues during EMD deposition and results in an irregular layer of lead dioxide intergrown with lead sulphate and lower valency lead oxide. When the EMD is stripped part of this corrosion layer is removed from the anode together with the EMD and pollutes the product (Fig. 1).

Pure lead anodes suffer from corrosion because they are not resistant to the deforming forces which cause cracks in the EMD deposit. Thus electrolyte penetrates into the metal/EMD interface and accelerates the corrosion process. In order to reduce these difficulties and to improve the handling of the anode, lead antimony alloys (hard lead) with a higher tensile strength are used in some EMD plants, enabling the construction of anodes of larger dimensions. However, even hard lead alloys have to be renewed after each cyclic because the product takes up more of the

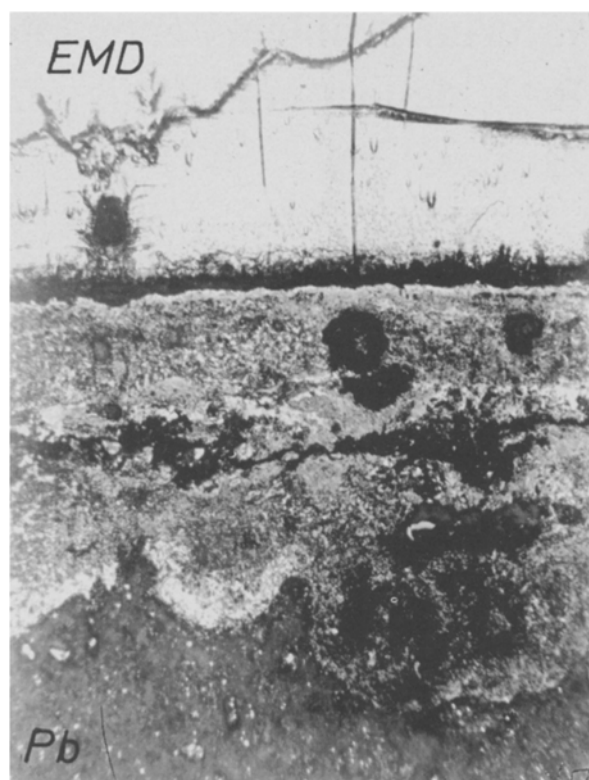


Fig. 1. Corrosion of lead at the interface of lead base and EMD deposit.

corrosion product during the following cycle, though the geometry of the electrode might have allowed a second cycle.

EMD which has been deposited on hard lead alloys cannot be used for the production of alkaline manganese batteries but only for carbon zinc cells. Due to corrosion products the antimony of hard lead builds up a concentration level in the battery which accelerates corrosion of the zinc anode at high alkali concentrations.

### 4. Graphite anodes

The main problem of graphite anodes, as well as of cathodes, is their poor mechanical strength and elasticity. The former can be compensated by choosing relatively thick electrodes (30 mm for anodes, 20–25 mm for cathodes) and by restricting electrode length to about 1100–1500 mm. Lack of elasticity requires much care during stripping of the EMD deposit. If thicker electrodes are used larger cell dimensions are necessary.

Besides these drawbacks there is a further problem which depends on graphite quality and restricts the service life of the anodes. Graphite anodes used in chloralkali electrolysis degrade slowly by anodic oxidation. In the EMD process graphite is attacked even below the EMD layer. This is demonstrated in Fig. 2.

The structure of the surface reveals that the intergranular mass of the graphite electrode corrodes, so that the coarse graphite grains become intimately linked with the EMD deposit. In the stripping oper-

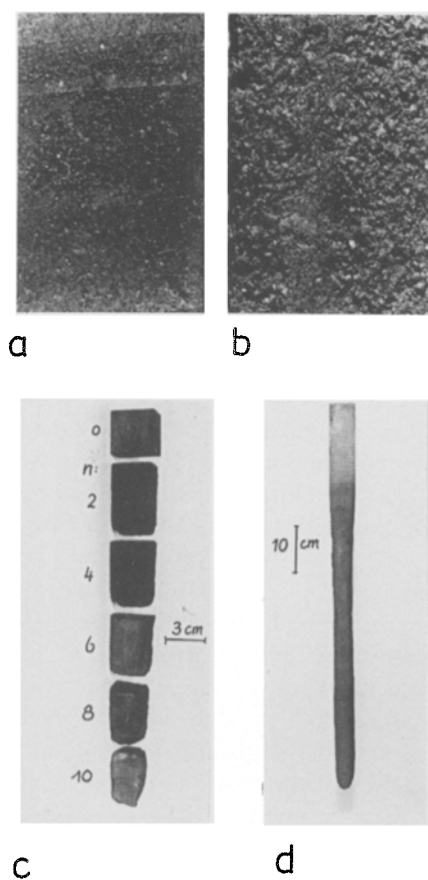


Fig. 2. Oxidative corrosion of a graphite anode during EMD production. (a) Fresh surface; (b) surface after the first cycle; (c) electrode thickness after the  $n$  cycle; (d) profile of an anode after 5 cycles.

ation these coarse grains are stripped together with the EMD, which accelerates the disintegration of the anode.

In practice, a life of from 12 to 20 cycles is achieved before the anodes have to be replaced by new ones.

## 5. Titanium anodes

Modern EMD production technology has changed to titanium anodes. This may be surprising in that titanium – as with niobium, tantalum and zirconium – is a valve metal which, on anodic polarization in aqueous solutions, passivates by forming an oxide layer of remarkable stability.

Yet there are some differences in the behaviour of titanium as compared, e.g. with tantalum. If tantalum is used as an anode in EMD production, no manganese dioxide deposit will be formed. The anodic current density drops immediately below values which are necessary for EMD formation (e.g. below the exchange current density of the MnO<sub>2</sub> redox reaction). With titanium anodes sufficiently high anodic primary current densities are possible and the EMD layer thus formed changes the electronic conditions on the passive TiO<sub>2</sub> layer in a way that prohibits further oxidation of the base metal. If the titanium surface is in contact with an aqueous electrolyte, the electrolyte offers a high ion concentration to the titanium surface

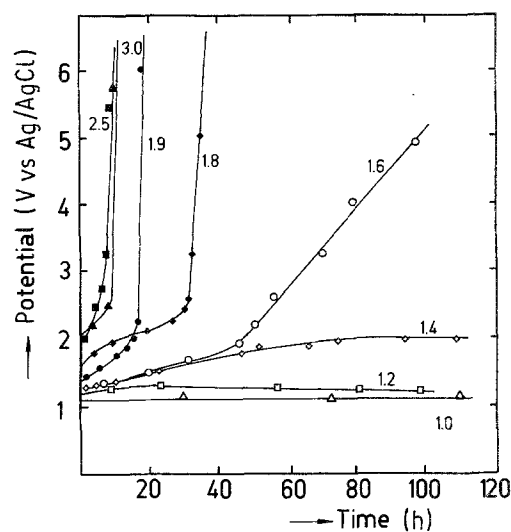


Fig. 3. Potential as a function of time at different current densities at the titanium anode.  $C: 0.4 \text{ mol l}^{-1}$ ; temperature:  $95^\circ \text{C}$ ; platinum cathodes; current densities:  $\text{A dm}^{-2}$ .

and ionic conduction is the predominant transport mechanism across the passive oxide layer, which then grows. Manganese dioxides are n-type semiconductors. A semiconducting MnO<sub>2</sub> layer contacting the passive oxide layer offers a relatively high electron concentration to the TiO<sub>2</sub> surface whilst the redox reaction is moved to the MnO<sub>2</sub>/electrolyte interface. Therefore, only electrons pass the passive layer and its further growth is avoided.

### 5.1. Electrolysis conditions for passivation

This highly simplified explanation disregards the fact that even a titanium anode covered with manganese dioxide may be passivated if MnO<sub>2</sub> electrodeposition is performed at too high current densities or at too low temperatures. Then, after a critical transition times,  $\tau$ , the anode potential begins to rise dramatically. This is shown in Fig. 3 for the case of varying current densities.

We have tried to define sensitivity to passivation by using the reciprocal of  $\tau$ . Figure 4 shows that  $1/\tau$  increases with increasing current density as well as with increasing sulphuric acid concentration at constant current density.

The results of a detailed investigation show that passivation of titanium anodes is favoured by: (a) high current density; (b) high sulphuric acid concentration; (c) low manganese ion concentration; (d) low temperature.

### 5.2. Reversibility

It is not necessary to remove a passivated titanium anode covered with EMD from the cell. In industrial practice it may happen that the sulphuric acid concentration rises to values which at given temperatures and current densities exceed the critical limits and cause an increase in cell voltage corresponding to passivation. In such a case it is only necessary to

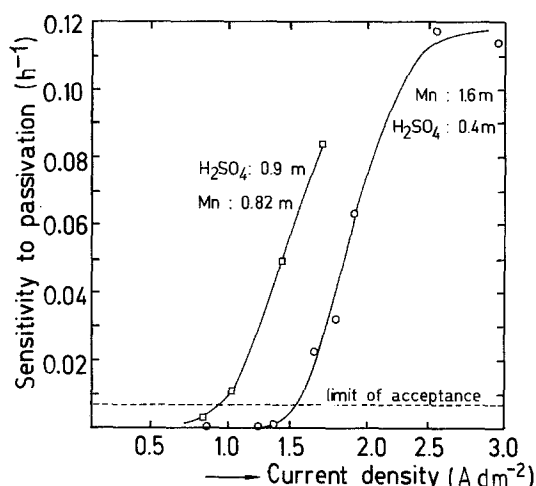


Fig. 4. Sensitivity to passivation as the reciprocal of the time,  $\tau$ , to reach the state of accelerated potential increase. Dependence on current density. Two electrolytes; temperature: 95°C.

adjust the sulphuric acid concentration to values significantly lower than the critical value and, eventually, to assist this by reducing the current density and the anode will resume EMD deposition.

If, as a consequence of a temperature drop, the cell voltage rises and the temperature is afterwards readjusted to the original value the anode also recovers and resumes anodic  $\text{MnO}_2$  deposition. Yet the recovery of the cell voltage needs much more time (several days) than passivation (fraction of an hour).

From these experiments we conclude that the interface  $\text{Ti-TiO}_x\text{-MnO}_2$  is not static but that reactions between Ti and  $\text{MnO}_2$  take place which result in a growth or reduction of the passivation layer. The former proceeds faster, the higher the imposed current density; the recovery of the anode is a very slow process which is governed by solid state diffusion or solid state reactions which may only be accelerated by raising the working temperature.

### 5.3. Technical consequences

Using titanium as anode material implies a set of restrictions: (1) temperature cannot be elevated above 95–98°C; (2) sulphuric acid concentration cannot be reduced readily below 0.25–0.30 mol l<sup>-1</sup> because of the need to react the electrolyte with new ore: low acid concentration requires high electrolyte volumes to be regenerated (which is ineffective); (3) reducing the current density may adversely affect the economy of the electrolysis.

Several proposals have been made to overcome these restrictions, especially the reduction of the effective current density: (a) sand-blasting the anode surface (indentation of the surface by which the true surface becomes enlarged) [3]; (b) pressed titanium chips [4] (rough surface); (c) titanium tubes; (d) sintered titanium plates [5] (rough surface); (e) expanded metal [6] (additional surfaces of the slits); (f) slotted sheets; (g) corrugated sheets [7–9]; (h) sintered titanium strips [10].

The objective is to discover an anode which: (1) gives a highly effective anode surface for a given electrolyte volume; (2) avoids peeling of the EMD deposit during electrolysis; (3) facilitates stripping of the EMD from the anode; (4) avoids deformation of the electrodes; (5) avoids corrosion of the titanium; (6) can be made at a minimum cost.

Sand-blasting, as well as perforation of the titanium sheet, favours adherence. The same applies to sintered titanium. All forms of the anode structure which allows a deposit to grow in an almost annular form around the basis are advantageous. Internal strains in the EMD deposit which cause cracking and descaling are then minimized. This favours rods, tubes, expanded metals and narrow strips. Disadvantageous are all planar structures which must have a remarkable strength to withstand the deforming forces of the deposit.

The corrugated sheet construction, which provides an increase in strength and stability, seems to offer a good compromise but deformations of corrugated sheets are generally more severe and irreversible and may, therefore, limit the dimensions of such anodes.

Sintered titanium strips in parallel mounting suffer from the difficulty of removing the EMD deposit from the space between the strips. This disadvantage is not associated with the V-conformation, so that this construction is one of the most convincing anode forms known to us.

Concerning the costs, sheet anodes may be the cheapest if one can use thin sheets – as is the case with the IMI anode – but cladding such thin sheets (0.7 mm thickness each) produces electrically shielded areas in the tubular channels which, therefore, must be carefully protected from corrosion. The same applies to titanium tubes if they are not completely closed.

### 5.4. The JMC process

EMD deposited at high current densities crystallizes in the  $\epsilon\text{-MnO}_2$  form having a high specific surface and a relatively low electronic conductivity. Battery performance is not good, especially in alkali manganese cells. At lower current densities more  $\gamma\text{-MnO}_2$  is formed; its specific surface is lower, the electric conductivity rises and battery performance is better. Relatively low current densities from 0.7 to 1.1 A dm<sup>-2</sup> represent, therefore, a good compromise between economy and quality.

However, it is known that in the JMC process (Japan Metals and Chemicals Co.) [11] EMD is produced on titanium anodes with current densities of 1.5 A dm<sup>-2</sup>, or even higher, without any passivation of the titanium anodes.

This seems to be contradictory to the conclusion drawn from our experiments. The JMC process uses the addition of fine manganese oxide particles which, surprisingly, being incorporated into the deposit change the structure of the EMD deposit to the  $\gamma\text{-MnO}_2$  variety in spite of the high current density.  $\gamma\text{-MnO}_2$  has a low specific surface and a relatively high

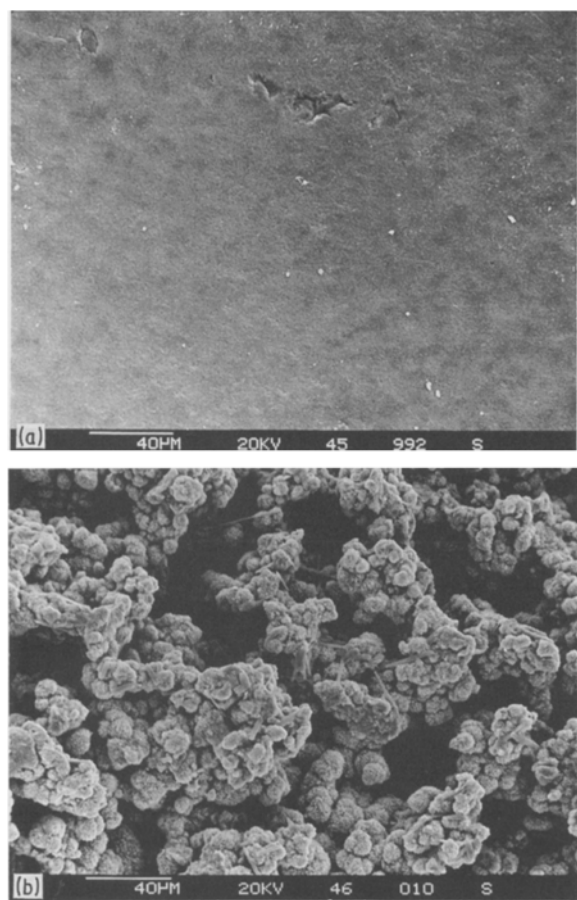


Fig. 5. Scanning electron microscope pictures of electrodeposited manganese dioxide surfaces. (a) Conventional sulphate process; (b) suspended particles process according to JMC Co.

electric conductivity. So it behaves on titanium as a manganese dioxide which has been deposited at a very low current density [1].

The SEM micrographs show that the JMC MnO<sub>2</sub> anode exhibits a very high effective electrode surface as compared with conventional EMD anodes (Fig. 5) and, therefore, was deposited with a low effective current density even in the case of formal current densities up to 2 A dm<sup>-2</sup>.

### 5.5 Activated titanium anodes

Stimulated by the success of RuO<sub>2</sub>-activated dimensionally stable titanium anodes used in chloralkali technology, similar work was carried out to overcome the restrictions for titanium in the EMD process. The idea seems very promising. Nevertheless, there are some problems to be solved. The solid EMD is intimately connected with the anode basis. All electrocatalytic layers of the Beer type (RuO<sub>2</sub>-TiO<sub>2</sub>) are loosely bound to the titanium basis by heating the electrode to 500 or 550°C. On stripping the EMD deposit part of the electrocatalytic layer will be removed together with the EMD.

Therefore it was proposed to create grooves [12], holes and structured surfaces, for example, by producing coarse sintered titanium plates [13] to which such a Beer-type activator could be applied. During

EMD deposition depressions in the electrode would be filled with manganese dioxide which would protect the underlying coating during stripping.

Another idea was to bind a platinum metal coating firmly to the titanium basis by heat treatment at a temperature at which platinum reacts to form a titanium alloy having a thickness of some μm [14]. Without discussing details it should be stated that these coatings are expensive and are not sufficiently stable. Since at a temperature of nearly 100°C a titanium/MnO<sub>2</sub> interlayer is not a static but a dynamic system, small amounts of titanium continuously move to the manganese dioxide and, obviously, some of the noble metal also is transferred to the EMD. Pollution of manganese dioxide by noble metals promotes zinc corrosion in alkaline manganese cells to an intolerable extent.

A more system-compatible activation should produce only such corrosion products as are already constituents of the process. This is, for example, the case for a manganese-titanium alloy containing up to 15% of manganese [15]. A more practical solution of this type is as follows: titanium coated by electro-deposition with a manganese metal layer forms, by heat treatment, a manganese-titanium alloy on the surface of the anode [16]. This alloy, which has a concentration gradient ranging from 0% Mn in the centre to about 20–60% on the surfaces, exhibits an excellent stability against passivation when used as anode for electrodeposition of EMD. A titanium (5–10%)–manganese (0.5–5%)–nickel sintered electrode [17] has proved useful, not only in EMD deposition, but also in metal electrowinning processes.

Another type of activation of titanium anodes was described by Dzaparidze *et al.* [18] who produced a titanium carbide surface on the anode which was sufficiently corrosion resistant and not sensitive to passivation. Formerly Guggs and Dean [19] have shown the suitability of titanium carbide as a possible anode material for the EMD process.

## 6. Discussion of the MnO<sub>2</sub>-Ti passivation phenomena

The experimental facts described here may be explained by the hypothesis that the TiO<sub>x</sub> interlayer between MnO<sub>2</sub> and titanium is a semiconductor which gradually may change to an ionic conductor depending on its thickness and on electrolysis conditions. Manganese dioxide itself is a fairly good n-type semiconductor [20].

The measurement of the electric resistance of solid block samples reveals large differences between the varieties ε, γ and β (Table 2). The passivating layer is clad between a metallic conductor and a semiconductor having a more or less high electron density in the conduction band.

According to our experience, a lower electric resistance of MnO<sub>2</sub> leads to a higher transition time for passivation at critical current densities. A low specific electric resistance indicates a high electron activity in the semiconductor. In this case the electronic equilib-

Table 2. Electric resistance of solid blocks of manganese dioxides

Type	Preparation	Current density (A dm <sup>-2</sup> )	Specific resistance (ohm cm)	Structure	Remark
EMD	Electrochemical	0.9	150	$\epsilon$	
EMD	Electrochemical	0.06	5	$\gamma$	
EMD	Electrochemical suspended particles bath	1.5	10	$\gamma(\epsilon)$	(JMC process)
MD	Thermal (400°C) from EMD (0.9 A dm <sup>-2</sup> )	-	2	$\beta$	
MD	Thermal decomposition of Mn(NO <sub>3</sub> ) <sub>2</sub>	-	0.1	$\beta$	

rium between the phases TiO<sub>2</sub> and MnO<sub>2</sub> may be realized even at relatively high current densities passing through the Ti/TiO<sub>x</sub>/MnO<sub>2</sub> system.

Like other valve metals pure titanium is inevitably covered with a thin layer of titanium oxide which protects it from further oxidation by air or by water. This oxide layer is very thin on a fresh titanium surface. After the formation of the EMD deposit we cannot detect any voltage drop which might be attributed to the ohmic resistance of the primary passive layer if we compare the Ti-EMD electrode with the Pt-EMD electrode. So we assume that electrons can pass this layer by tunnelling.

In thicker passivating layers larger resistances are found. Therefore, charge transfer by tunnelling must change to electronic semiconduction or ionic conduction. The passive layer must be regarded as a semiconductor having conductivities which depend on its thickness, on the potential gradient, and on the type of the contacting phases. We assume that across the passive layer the composition of TiO<sub>x</sub> can vary according to the contacting phases and according to temperature. Similar relations have been described for passive layers on niobium [21].

Electric conduction in stoichiometric TiO<sub>2</sub> layers is due to oxygen transport via oxygen vacancies. Oxygen vacancies are created by dissolution of oxygen in the titanium metal. If on the other side of the oxide layer the oxygen activity is low these vacancies are not refilled with O<sup>2-</sup> ions. In this case the passive layer will become a good electronic conductor. Table 2 shows that different manganese dioxides exhibit remarkably different electronic conductivities. High electronic conductivity implies low oxygen activity and *vice versa*. Therefore, at high current densities or at lower temperatures or with an  $\epsilon$ -MnO<sub>2</sub> contacting the passive layer, the electron concentration in the conduction band of EMD may be too low for carrying the current completely through the TiO<sub>x</sub>/MnO<sub>2</sub> interface. Consequently ion transport becomes important, the oxygen activity rises, oxygen vacancies are filled with oxygen from the manganese dioxide and the passive layer grows. A gradient of  $x$  in TiO<sub>x</sub> is formed.

Interrupting the current for several hours restores equilibrium in the passive layer and lowers the electronic resistance again, which can be seen by the voltage behaviour of the passivated anode (Fig. 6, cycles 4-7) at the end of a cycle and the beginning of the following cycle. The voltage differences are much larger than those that would be caused by just removing the EMD deposit.

Another consideration should be taken into a model for the titanium manganese dioxide electrode: this is the influence of free or combined water in the

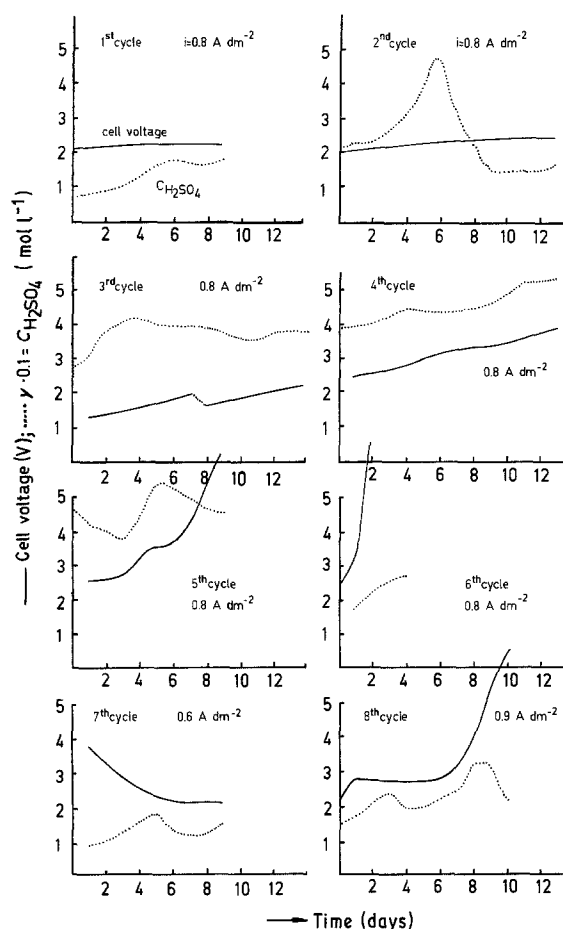


Fig. 6. Cell voltage and sulphuric acid concentration during 8 consecutive electrolysis cycles with 2-mm titanium sheet anodes.

electrode system. If the Ti/TiO<sub>x</sub>/MnO<sub>2</sub> interface is free from water all the relations between passivity and electrolysis conditions described are not valid. A good understanding of Ti-MnO<sub>2</sub> electrodes requires much further work.

## 6. Conclusions

Summarizing one may say that pure titanium is a very attractive anode material for EMD production. Titanium anodes can be formed to most desired shapes because of its mechanical strength. The economy of their use is good as they can work for many years. They are corrosion protected under anodic polarization by a titanium oxide film so they do not pollute the product. The electrodeposition conditions for a good quality EMD are within the range of parameters in which passivation does not usually occur. Possibly the sintered titanium strip anode with zigzag configuration meets the technical demands best.

## References

- [1] E. Preisler, in '3rd Manganese Dioxide Symposium, Graz 1985' (edited by K. V. Kordesch and A. Kozawa), IBA, Cleveland (1985).
- [2] E. Preisler, in 'Dechema Monographs', Vol. 104, Proceedings of the Annual Meeting Fachgruppe Angewandte Elektrochemie, Dortmund 1986. Verlag Chemie, Weinheim (1987).
- [3] The Furukawa Electric Co., and Mitsui Mihonbashi Muromachi, US 3,436,323 (25.7.1986).
- [4] A. L. Fox, US-2,631,115 (6.8.1949).
- [5] A. L. Fox, US-2,608,531 (2.11.49).
- [6] Kerr-McGee Chemical Corp., DE-OS 2 141 447 (18.8.71) US Prior. 25.8.70.
- [7] IMI, US 4,319,977 (3/1982); US 4,380,493 (4/1983).
- [8] Kerr-McGee Chemical Corp. US 4,606,804 (12.12.84).
- [9] Conradty company information sheet, private communication.
- [10] Hoechst, DE-OS 3 521 827 (19.6.85).
- [11] Japan Metal and Chemical Co., Ltd. US-4.405.419 (July 12, 1980) (Jap. priority: 12,1979).
- [12] L. N. Dzaparidze, I. M. Dubov, E. A. Bogdanov, T. A. Čachunashvili, G. T. Gogoladze, A. A. Teisheva, G. N. Rzyzgraeva, M. A. Melnikov-Eichenvald and T. V. Rokva, DE-PS 27 23 406 (mai 24, 77).
- [13] G. Bewer, H. Debroth and H. Herbst, *J. Metals* (1982) 37.
- [14] HOECHST AG/SIGRI GmbH, DE-PS 2 645 414 (8.10.1976).
- [15] R. I. Agladze, K. S. Vanidze and L. A. Zautashvili, SU 891 805 (20.05.80).
- [16] Hoechst AG, Eu-PA-0148 439 (12.12.84) (Prior. DE 21.12.83).
- [17] HOESCH, DE OS 35 10 592 (4.10.84).
- [18] L. N. Dzaparidze, T. A. Tschachunashvili, V. R. Majsuradse, R. V. Tschagunava, Z. J. Kervalishvili, N. G. Sicharulidze, D. G. Otiashvili and A. P. Epik, DE-PS 27 34 162 (28.07.77).
- [19] A. M. Guggs and R. S. Dean (P. R. Mallory & Co.) US 2,636,856 (29.06.1948).
- [20] E. Preisler, *J. Appl. Electrochem.* **6** (1975) 311.
- [21] K. E. Heusler und M. Schulze, *Electrochim. Acta* **20** (1975) 237.