

TREATED TITANIUM ANODES FOR THE PRODUCTION OF EMD

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ABSTRACT

The application of treated titanium anodes with special reference to the process know-how on Electrolytic Manganese Dioxide (EMD) is briefly described. The know-how has been developed on a pilot plant scale, using manganese salt solutions and graphite or treated titanium anodes. The results obtained with titanium anodes as well as the significance of employment of chloride route, with special emphasis on the characteristics of the final product, are also presented. Furthermore, the various steps involved in the treatment of titanium anode so as to make it suitable for high current density and high acidity operations in EMD preparation and their significance have been highlighted.

Key words: Manganese dioxide, Electrodeposition, Titanium anode

INTRODUCTION

The customary procedure for the production of EMD [1] is to electrolyse an aqueous solution containing sulphuric acid in the range 0.2-0.5 M and manganese sulphate 0.5-1.0 M using lead or lead based alloys (e.g. Pb-Sb) or graphite as anode. The conditions of electrolysis viz. anode current density, anode pretreatment, temperature, acidity, Mn^{2+} concentration etc. depend much upon the anode material. The deposited manganese dioxide, usually to a thickness of 2.5 cm on the anode, is harvested by stripping suitably. This procedure is having certain disadvantages. It has been found:

- i) to be impossible to obtain the resultant EMD product free from harmful contamination of the oxidation product of the substrate material of lead. Even traces of lead is considered to be deleterious impurity in electrolytic grade manganese dioxide, especially for use in dry cells. In order to minimise this contamination either smooth surface of lead is to be adopted or suitable complexing agents like triethanolamine and sulphur compounds may have to be judiciously incorporated in appropriate quantities in the battery electrolyte at a later stage, so as to complex the lead
- ii) to be extremely difficult to avoid the loss of substrate anode material particularly graphite, as the electrodeposited manganese dioxide is tenaciously adhering onto the anode surface, the adhesion increasing more, with successive removal and deposition of EMD, with increase in acid concentration and anode current density and
- iii) to be difficult to avoid the breakage of graphite while harvesting the EMD deposits, necessitating periodical replacement, thereby increasing the manufacturing cost of resultant EMD. But the purity of EMD is generally good, except the small quantity of inert impurity of graphite/graphitic oxide. The dimensions of the anodes change due to wear with formation of loosely adhering and less conducting graphitic oxide or in other words, the anodes do not preserve the dimensional stability, in addition to contaminating the electrolyte.

Of course, graphite and lead anodes are relatively insensitive to wide changes in concentration and temperature of electrolyte or higher current densities. Platinum and platinum plated titanium electrodes have been tried as an alternative to graphite, lead or lead based alloy anodes. The cost of production of EMD using platinum or platinum plated anode is prohibitive.

Alternatively, electrolysis of manganese chloride (0.64-1 M) - hydrochloric acid (0-0.7 M) has been adopted using platinum plated titanium [2] or highly corrosion-resistant graphite electrodes with some success [3].

Advantages of adopting chloride electrolyte over sulphate electrolyte [4]

(i) Favourable raw materials position (ii) superior quality, fibrous structure (yf EMD) with improved physical, chemical, catalytic and electrochemical properties (iii) consumption of substrate graphite is less, thereby leading to a higher purity and longer life of anode (iv) consumption of EMD in the ultimate application is less for the same performance (v) higher leaching efficiency (vi) less salt crystallisation during electrolysis, and (vii) ease of washing of the final EMD (due to the absence of entrapped sulphate) and (viii) can tolerate higher percentages of Ba^{2+} , Ca^{2+} , Na^{+} and NH_4^{+} ions in the electrolyte without undue influence on the crystal structure of EMD.

As a further development, the utilisation of titanium in rod or plate form, or titanium metal chips or powder in compacted form as anode in such electrodeposition has resulted in the avoidance of the contamination of impurities in EMD deposit, but this procedure simultaneously paved the way for new difficulties to creep in, such as passivation of anode, poor adherence of the deposit and loss of mechanical strength, culminating in frequent stoppage of the electrolytic cell. Some of the drawbacks could be avoided by the employment of expanded titanium metal [5]. However, difficulties associated are in:

- 1) increasing the anode c.d. greater than $1.4 A/dm^2$ (based on solid plate area) at 41 g/l sulphuric acid concentration
- 2) increasing acidity greater than 14 g/l for a higher c.d. of $1.8 A/dm^2$ (based on solid plate area) in prolonged electrolysis without passivation and enhanced electrical energy consumption and
- 3) avoiding the frequent removal of anode from the cell and pre-treatment of the same and loss of titanium metal.

Various treatments were evaluated so as to result in a coating which would obviate the above disadvantages. The coating should possess the following general characteristics: (i) the property of preventing the formation of energy wasting barrier layer on titanium substrate (ii) minimum micro, macro and meso pores and pore size distribution (iii) adequate electrical conductivity (iv) high O_2 and Cl_2 overpotentials, (v) larger surface area with good adhesion (vi) low and stable potential for facilitating the electrochemical deposition of MnO_2 and (vii) providing centres for growth of EMD and relieving stress and keying of EMD. The substrate is subjected to suitable simple pre-treatment procedures, such as physical, chemical and electrochemical, either singly or jointly, to enable increase the productivity of high grade EMD from different electrolytes for quite long periods without damaging the substrate material.

EXPERIMENTAL**Electrolysis**

Commercially pure titanium sheet has been used. The properties of titanium sheet are furnished in Table I.

Table I: ASTM Grade-2, Medium hardness

H ₂ %	C %	N ₂ %	Fe %	O ₂ %	Tensile Strength	Hardness
0.015	0.01	0.03	0.30	0.25	4.43 x 10 ⁷ N/m ² at room temp.	200 VHN

The same has been expanded suitably so as to increase the exposed area in the range 10-75%. Then it is cleaned electrolytically in sodium hydroxide solution of 40-180 g/l for 30 minutes to 1 hour, the temperature being 298°–303°K. It is subsequently coated with manganese dioxide by thermal decomposition of manganese nitrate solution so as to result in an integral coating. The electrode so prepared is employed as an anode in the deposition of manganese dioxide from manganese salt solutions for 100-800 hours.

RESULTS AND DISCUSSION

The efficacy of the treatments could be appreciated from the examples of Tables II and III. It is evident that treated titanium anode can withstand relatively high anode current densities at higher acid concentrations for longer periods without passivation under otherwise constant experimental conditions. The energy saving due to the employment of treated titanium instead of untreated titanium anode is appreciable in chloride and sulphate electrolysis for longer durations.

To postpone passivation, employment of coated titanium anode is very common in other industrial electrolytic processes like alkali-chlorine, chlorate and perchlorate production. In such cases, the anodic product is a

gas or liquid. However, in EMD production, a hard compact solid mass is obtained as an anode product which has to be harvested periodically. During stripping operations the coated material(s) are found to come off along with EMD and recoating may have to be done for efficient functioning of the anode.

The switching over to treated titanium anode would necessitate a higher flow rate of cell electrolyte for EMD preparation as compared with cells using graphite but certainly a slower flow rate as compared with cells fitted with bare titanium.

Pilot plant studies

Based on the optimum conditions arrived at on the bench scale experiments, pilot plant scale investigations on the preparation of EMD using treated titanium anode of capacity ~ 10 kg/day (250 A - chloride electrolyte) have been carried out round the clock with all its associated unit operations in an integrated fashion. The salient features are presented in Table IV for a set of experimental conditions. The typical analysis of the product obtained under such conditions (Table V), X-ray diffraction pattern (Fig. 1), cross-section of the deposit (Fig. 2) showing the fracture running along the individual fibres, needle-like crushed particles (Fig. 3), SEM photographs of crushed material (Fig. 4 a & b) and that of powder (Fig. 4 c-e) and EMD deposited anode (Fig. 5) are presented. Scanning electron micrographs demonstrate that the basic fibrous structure is even realised in very small dimensions and consists of leaf-like layers (Fig. 4 a and b).

The variation of anode potential as a function of electrolysis time in a 250 A cell is represented in Fig. 6. In this figure, the i_R drop due to the growing thickness of EMD is also included which is proportional to the quantity of current put into the system. The rate of increase of anode potential is 0.003 V/hr. In such EMD cells, the possible anodic reactions are oxidation of Mn²⁺ and evolution of O₂ and Cl₂. The oxygen and chlorine evolution reactions are having overpotentials of ~ 400 mV on manganese dioxide coated electrode. In order to allow MnO₂ deposition reaction to take place with nearly theoretical efficiency in preference to oxygen or chlorine evolution reaction, advantage is to be taken of the property of oxygen overpotential on the anode and electrolysis conditions are to be adjusted to suit the requirement.

Table II: Treated titanium anode—Bench scale (Temperature 95-98°C)

Ex. No.	Experimental details for anode	Electrolyte	Current density (A/dm ²)	Mn ⁺⁺ concentration (M) (Average)	Acid concentration (M) (Average)	Voltage (V)		Energy (kWh/kg)	Duration (hrs)
						End.	Ave.		

TABLE II-A

1	Bare titanium	Chloride	1.40	0.80	0.41	5.30	4.42	3.03	144
2	Electrocleaning in alkali	Chloride	1.40	0.83	0.41	3.38	3.37	2.28	146
3	Treated titanium	Chloride	1.40	0.85	0.40	2.70	2.63	1.90	561
4	Treated titanium	Sulphate	1.46	1.02	0.40	2.40	2.60	1.50	720

TABLE II-B

1	Bare titanium	Sulphate [5]	1.41	0.85	0.42	—	3.03	1.87	312
2	Treated titanium	Sulphate	2.25	0.84	0.41	3.7	2.46	1.44	492

Table III: Treated titanium anode—Bench scale

Electrolysis Expt. No.	Current density* (A/dm ²)	Mn ⁺⁺ concentration (g/l) (Average)	H ₂ SO ₄ concentration (g/l) (Average)	Cell voltage (V) (Average)	Energy (kWh/kg)	Duration (hrs)
1	2.60	46.4	40.53	2.46	1.44	492
2	2.60	55.8	36.82	2.14	1.29	698
3	2.29	54.3	44.35	3.00	1.80	731
4	2.29	55.9	39.2	2.60	1.50	719

*Current density expressed to the solid plate

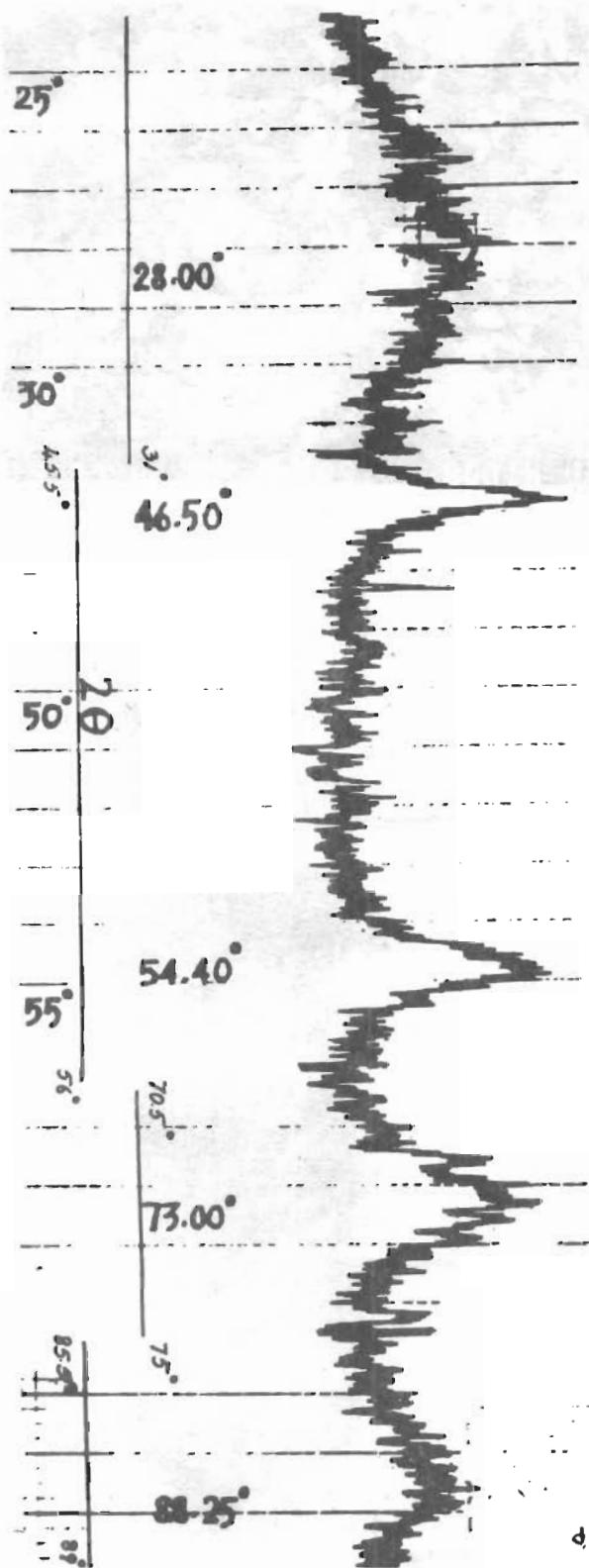


Fig.1 X-ray diffraction of EMD 250 A cell (Fe target, Mn filter)



Fig.2 Photograph of fibrous EMD chip

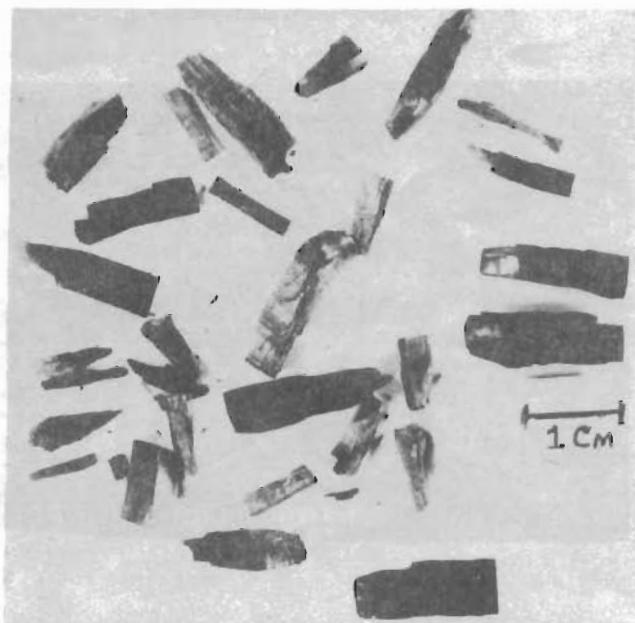


Fig.3 Needle-like particles in the crushed material

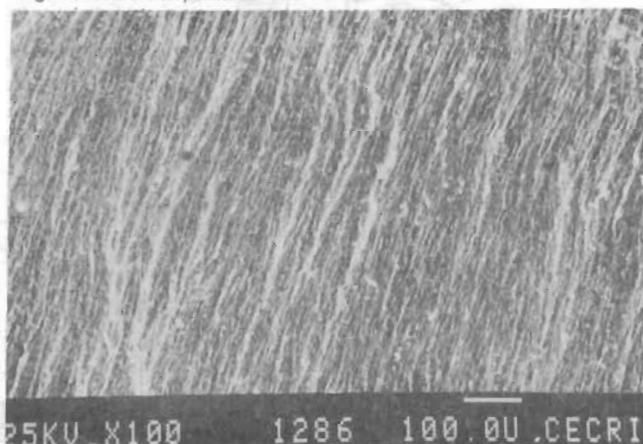
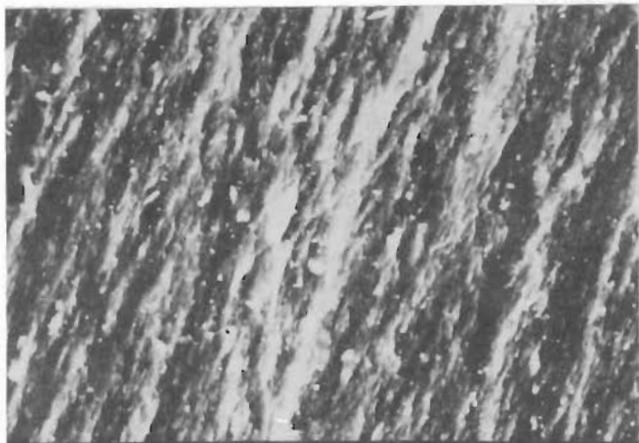


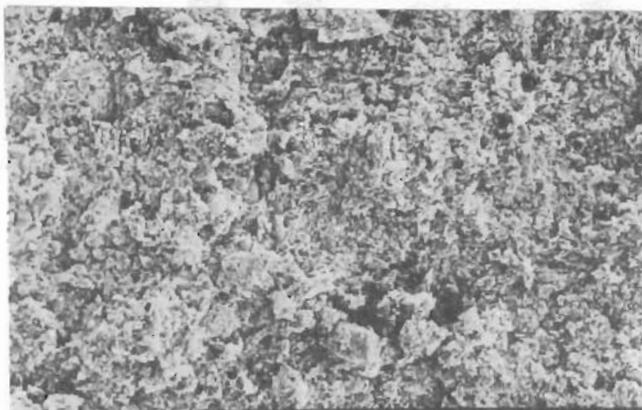
Fig.4 Scanning electron micrographs of: (a) & (b) crushed materials; (c)-(e) powder



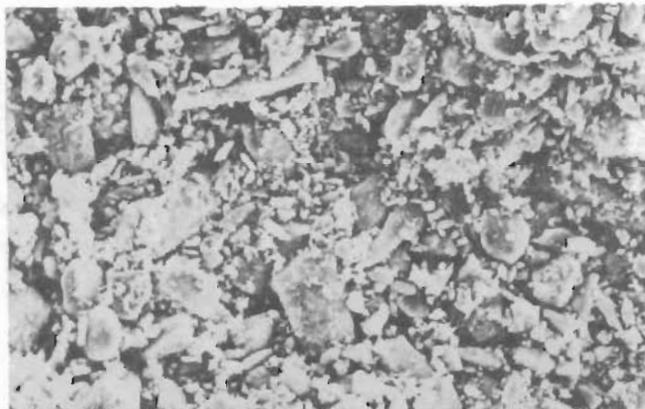
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5KV X1000 1287 10.0U CECRI



25KV X100 1289 100.0U CECRI



5KV X500 1288 10.0U CECRI

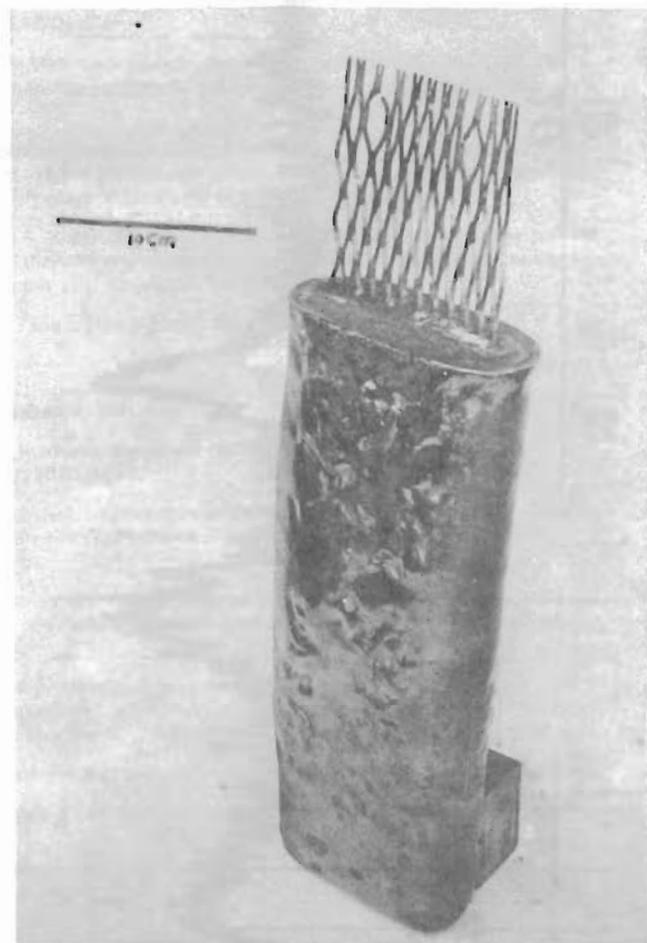


Fig.5 EMD deposited anode

Table IV: Treated titanium anode - Pilot plant

Manganese chloride concentration	= 0.95 - 0.71 M
Hydrochloric acid concentration	= 0.38 - 0.49 M
Anode current density	= 1.4 A/dm ²
Cathode current density	= 0.87 A/dm ²
Anodes	= Treated titanium
Cathodes	= Graphite plates

No.	Cell capacity per day of 24 hrs.	Duration of electrolysis (days)	Cell voltage (V)	DC Energy requirement for deposition (kWh/kg)	Temperature (°K)
1	(approx) 10 kg	32	2.29 - 3.50	2.11	363 - 368
2	(approx) 20 kg	17	2.58 - 3.42	1.85	368 - 371

Table V: Typical analysis of CECRI EMD employing chloride electrolyte

	Free Moisture %	MnO ₂ * %	Mn* %	x in MnO _x	Insoluble in HCl %	Fe %	Cu %	Pb %	SO ₄ %	Cl %	pH ⁽³⁾	Tapping density g/cc	Specific density g/cc	Surface area m ² /g	Activity ⁽⁴⁾
Titanium anode	1.80	91.75	59.44	1.98	...	0.036	Tr	Tr	5.2	2.49	4.43	54 ⁽¹⁾	4.08
Graphite anode	0.52	90.70	60.55	1.95	0.23	0.135	0.0032	0.0003	...	0.12	5.2	1.75	4.26	56 ⁽¹⁾ 0.71 ⁽²⁾	3.94
Limits specified in JIS	3.0 (max)	90 (min)	-	-	1 (max)	0.05 (max)	0.002 (max)	0.1 (max)	1.5 (max)						

Methods

Mn: Determined by Volhards method.

MnO₂: Determined by Na₂C₂O₄ method.

Free moisture: Determined by heating at 383°K for 2 hours in air.

Density: Using weighing bottle with benzene at ambient temperature.

* Based on dried sample at 383°K for 2 hours.

As pointed out, the main electrochemical reaction is the formation of EMD by the anodic oxidation of Mn²⁺ to Mn⁴⁺. If the applied c.d. is greater than the optimal value, the main competitive reaction would be oxygen evolution reaction. This leads to cover the substrate with a monolayer of oxygen, thereby facilitating passivation of the titanium substrate to set in. On further prolonged polarisation the various possibilities open are:

i) Oxidation to a higher oxidised state namely

Ti²⁺ → Ti³⁺ or Ti⁴⁺ (ii) recrystallisation of the substrate oxide layer and its further growth by diffusion of cations outwards or oxygen inwards or (iii) further growth of the layer. All these steps may occur at different stages of polarisation under appropriate conditions of electrolysis.

The five potential drops at this stage are pictorially depicted in Fig. 7 as:

- drop at titanium metal/titanium dioxide barrier layer
- drop through the thickness of the barrier layer
- drop through the thickness of the integral coating
- drop through the EMD deposit
- drop at the EMD deposit/electrolyte interface, the last being associated normally with the oxidation of Mn²⁺ to Mn⁴⁺.

During gradual substrate attack and its barrier film growth, (e) remains lower. If the barrier film is thick enough, the potential drop 'b' is the largest explaining lack of growth of EMD. This is illustrated in Fig. 8.

(1) Zinc-ion adsorption method.

(2) Air permeability method.

(3) Using 22% NH₄Cl + 10% ZnCl₂ solution of pH 5.4.(4) Determination by oxidation with ammoniacal hydrazine sulphate solution and expressed as a number/m²/g.**CONCLUSIONS**

Evidence has been presented to show the advantages of employing treated titanium in EMD preparation [6]. The characteristic features in adopting treated titanium as anode are:

- Longer life mainly contributed by efficient functioning of the anode and easy strippability of the deposited EMD.
- The adhesion of the deposited EMD is facilitated to the desired limit and at the same time any cracking or peeling off of the electrocrystallising manganese dioxide deposit by its electrodeposition stress is largely avoided.
- Homogeneous lava like product of uniform thickness (30 mm) and higher purity, free from substrate material like lead, graphite, carbon and its associated impurities.
- Purer electrolyte as a result of the absence of graphite and its impurities.
- Higher space-time yield, due to increased surface area of anode, higher anodic current density and higher current efficiency.
- Lower energy consumption resulting from low contact resistance by the avoidance of energy wasting barrier layer and dimensional stability.
- The usual disadvantages in adopting bare titanium as anode could largely be circumvented by special procedures.

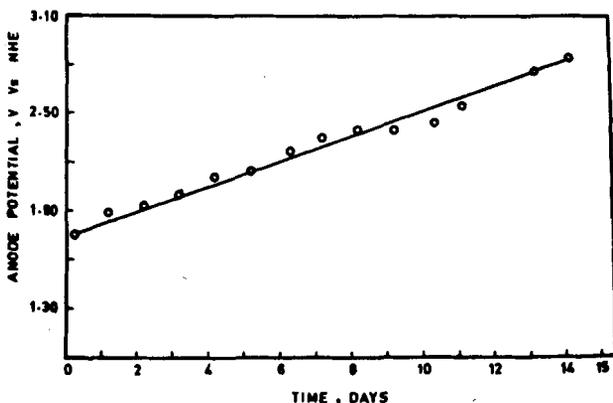


Fig.6 Anode potential V vs. time

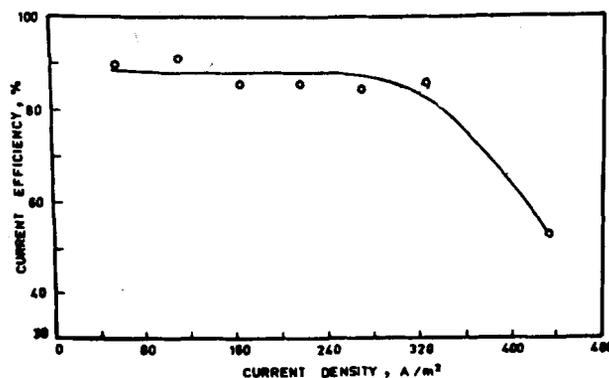


Fig.8 Current efficiency vs. current density

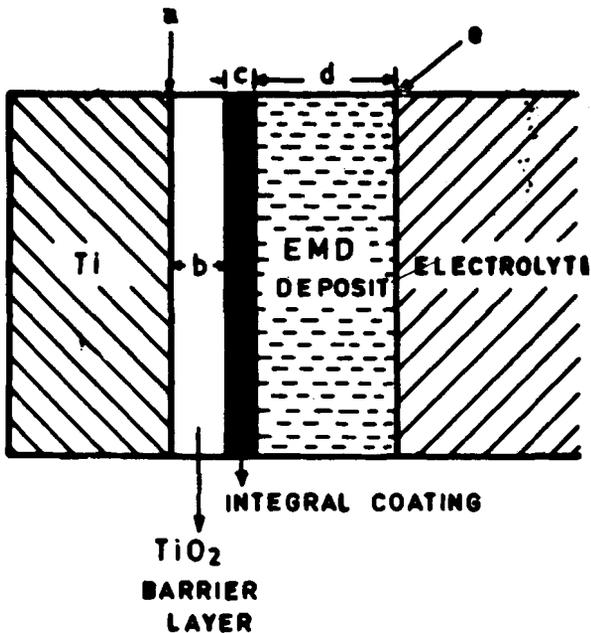


Fig. 7 Potential drops of anode

8. Avoidance of the use of expensive organic and inorganic chemical etchants like ethylene glycol, phosphoric acid, nitric acid, glacial acetic acid, hydrofluoric acid.
9. Production of EMD by using manganese salt solutions either alone or in admixture at various acid concentrations.
10. Permitting a higher acidity in the electrolyte and higher anode c.d. without getting the anode passivated.
11. A saving of DC electrical energy consumption.
12. Better mechanical strength, facilitating easy handling.

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