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**"AN IMPROVED PROCESS FOR THE PREPARATION OF MANGANESE  
DIOXIDE COATED TITANIUM ANODES FOR USE IN THE PRODUCTION  
OF ELECTROLYTIC MANGANESE DIOXIDE".**

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under the Registration of Societies Act (Act XXI of 1860).**

**The following specification particularly describes and ascertains the  
nature of this invention and the manner in which it is to be performed :-**

**PRICE : TWO RUPEES**

161980

This is an invention by Veeraraghava Aravamuthan, of III B/3, VSSC Housing Colony, St. Xavier's College Post, Pallithura, Trivandrum-6, Chathangat Cherroolil Gopalakrishnan, of Kerala Minerals and Metal Ltd., Quilon, Rengachari Srinivasan, Srinivasa Iyer Visvanathan, Sillanatham Chockalinga Reddiar Chockalingam, Savari Kulandaisamy and Jeevanandham Praphakar Rethinaraj of the Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India, all Indian nationals and relate to a process for the preparation of manganese dioxide ~~using~~ <sup>for use</sup> coated titanium anodes <sup>in the production of electrolytic manganese dioxide</sup>. This is used as an effective cathodic depolariser in dry cell industry.

Hitherto it has been proposed to produce manganese dioxide by electrodeposition from an aqueous solution containing sulphuric acid in the range 0.2 - 0.5 and manganese sulphate 0.5 - 1.0 M using lead or lead based alloys or graphite as anode. Such deposited manganese dioxide, usually to a thickness of 2.5 cm on the anode is harvested by stripping suitably. Platinum and platinum plated titanium electrodes have been tried as alternative to graphite, lead or lead based alloy anodes.

This is open to the following objections namely:

It has been found (1) to be impossible to obtain the resultant electrolytic manganese dioxide product free from harmful contamination (containing at least a small quantity of the impurity) of substrate material of lead or lead alloy anodes. Even traces of lead is established to be a deleterious impurity in electrolytic grade manganese dioxide, especially for use in dry cells;

161980

(ii) to be extremely difficult to avoid the loss of substrate anode material particularly graphite, as the deposited electrolytic manganese dioxide is tenaciously adhering onto the anode surface, the adhesion increasing more, with successive removal and deposition of electrolytic manganese dioxide, with increase in acid concentration and anode current density;

(iii) to be difficult to avoid the breakage of graphite under the said conditions, while harvesting the electrolytic manganese dioxide deposits, necessitating periodical replacement, thereby increasing the manufacturing cost of resultant electrolytic manganese dioxide.

The cost of production of electrolytic manganese dioxide using platinum or platinum plated anodes is prohibitive.

Alternatively, electrolysis of manganese chloride (1 M to 0.64 M) - hydrochloric acid (0-0.7M) has been adopted using platinum plated titanium or highly corrosion-resistant graphite electrodes with some success. Such a procedure has resulted in the production of electrolytic grade manganese dioxide of greater purity and more useful crystalline structure associated with physical, chemical, catalytic and electro-chemical properties. With proper graphite anodes, in addition to said favourable features of the manganese dioxide, the consumption of graphite anode has been established to be very low in comparison with the conventional sulphate electrolysis.

161980

Recently, 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 electrolytic manganese dioxide deposit, but this procedure simultaneously paved the way for new difficulties to creep in during post-operative steps of the electrolysis such as passivation of anode, poor adherence of the deposit, loss of mechanical strength, as described hereunder at appropriate places, culminating in frequent stoppage of the electrolytic cell etc.

More recently, it has been found that utilisation of expanded titanium metal anode solves the above problems to a large extent and found to be better than sand-blasted anode.

The drawbacks connected with hitherto known processes are that:

- (i) It is difficult to increase the anode current density greater than  $1.4 \text{ A/dm}^2$  (based on solid plate area) at 41 g/l sulphuric acid concentration,
- (ii) It is difficult to increase the acidity greater than 14 g/l for a higher current density of  $1.80 \text{ A/dm}^2$  (based on solid plate area) in prolonged electrolysis without passivation and enhanced electrical energy consumption and
- (iii) It is difficult to avoid the frequent removal of anode from the cell and pre-treatment of the same and loss of titanium metal.

161980

The main object of this invention, inter alia, is to obviate these disadvantages:

This invention provides an improved process for the preparation of manganese dioxide coated titanium anodes for use in the preparation of electrolytic manganese dioxide.

The following pretreatment procedures have been adopted in the order given below:

- i) expansion of the metal sheet
- ii) cleaning in caustic soda by chemical/electrochemical or both
- iii) coating of manganese dioxide by chemical/electrochemical or both using manganese salt like nitrate.

The method adopted here consists in (i) treating titanium metal by suitable methods for expansion.

- (i) cleaning the expanded metal in caustic soda by chemical/electrochemical or both and
- (ii) coating of manganese dioxide by chemical method using manganese salt like nitrate.

The process makes use of titanium sheet-soft medium grade-suitable for expansion and chemicals of LR grade.

The anode material used is to be expanded suitably so as to have an increase in the exposed area in the range of 40-75% preferably 25%.

Such an expanded material is cleaned cathodically at a current density between 2.79 to 5.6 A/dm<sup>2</sup> in alkali of 4-4.5 M (sodium hydroxide) for about an hour employing suitable anode, the

161980

temperature range being 25-35°C. Alternatively chemically/electrochemically cleaned in fused sodium hydroxide or sodium nitrate and or sodium nitrite for 1 to several minutes.

Subsequently the treated electrode is quickly coated with manganese dioxide using a concentrated manganese nitrate solution by thermal method, the conditions being:

1. Temperature 200-350°C
2. 1-5 times coating
3. Every time the coating being dried for 5 minutes to 1/2 hr.

Accordingly this invention provides a process for the preparation of manganese dioxide coated titanium anode for use in the production of electrolyte manganese dioxide which comprises expanding the titanium used as anode suitably to increase the exposed area <sup>in the range 9/10 - 75%</sup> cleaning the expanded anode by ~~chemical and/or electrochemical method using~~ <sup>treating with</sup> an alkali salt and coating the cleaned anode ~~by a chemical method and/or electrochemical method~~ with a manganese salt solution.

According to a feature of the invention the electrochemical method for cleaning the anode consists in treating the same cathodically with a solution of sodium hydroxide at a current density of 2.79 to 5.6 A/dm<sup>2</sup> at a temperature range of 25-35°C for a period of about 1/2 an hour to one hour.

According to another feature of the invention the alkali salt used is 1-4.5 M of sodium hydroxide.

161980

According to a still another feature of the invention the coating of the cleansed anode is effected by treatment in a concentrated manganese nitrate solution at 200°C to 300°C 1-5 times.

According to a further feature of the invention the cleansing operation of the anode is preferably carried out in an electrolytic bath comprising 1.1M aqueous sodium hydroxide at a current density of 3.23 A/dm<sup>2</sup> and a temperature of 30°C for a period of 30 minutes and the coating thereon is carried out in a thermal chemical process by treatment with a solution of 900 g/l (5.2M) manganese nitrate at a temperature range of 200°-220°C.

The titanium metal is expanded suitably so as to increase the exposed area in the range of 10-75%. Such an expanded titanium electrode is cleaned in fused sodium hydroxide (or fused sodium nitrate and/or sodium nitrite for 1 to several minutes) or employed as a cathode in an electrolytic cell containing aqueous 1-4.5 M of sodium hydroxide using a suitable anode such as mild steel, nickel coated mild steel and cathodically cleaned at 2.79 - 5.6 A/dm<sup>2</sup> for half an hour to one hour, the temperature being 25-35°C. The treated electrode is to be quickly coated with manganese dioxide using a concentrated manganese nitrate solution. The process of coating and subsequent decomposition to obtain the manganese dioxide deposit in the temperature to 200-350°C is done for 1 to 5 times, every time the coating being dried for 5 minutes to half an hour.

161980

The electrode so treated is employed as an anode in the deposition of manganese dioxide from manganese salt solutions for 100-700 hours.

Employment of expanded, pretreated and manganese dioxide coated titanium anode (TSMD) prepared by the process described in this Specification results in uninterrupted electrolysis for a prolonged duration with lower energy consumption. This procedure also avoids the use of costly organic and inorganic chemical etchants like phosphoric acid, nitric acid, glacial acetic acid, hydrofluoric acid, ethylene glycol.

A considerable concentration of cations like  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Na^{+}$ ,  $NH_4^{+}$  either alone or jointly may be allowed to be present in the electrolyte without affecting appreciably the crystalline structure of electrolytic manganese dioxide.

As a result of this invention, we have found that homogeneous, very pure, thick (thickness being approximately 30 mm) deposit of electrolytic manganese dioxide can be produced under high current densities, with a low energy consumption and without the occurrence of passivation by using the TSMD anode. By this procedure, the adhesion of the deposited electrolytic manganese dioxide is facilitated to the desired limit thereby increasing the life of the anode and at the same time any cracking or peeling off of the electrocrystallising electrolytic manganese dioxide deposit by its electrodeposition stress is largely avoided.



161980

AC heating could be adopted (using a low voltage, high amperage transformer and graphite rods/plates as electrodes) in place of (a) conventional steam heating using suitable coils, which avoids the possible contamination of the electrolyte and EMD deposit with the material of construction of the coil, 1periodical cleaning and maintaining the steam coil (for effective heat transfer) and (b) silica cased immersion heaters thereby avoiding the breakage of costly silica sheaths due to the salt crystallisation at the electrolyte level and avoiding leakage of high voltage (230V) a.c. passing through the cell.

Overall ~~Energy~~<sup>energy</sup> consumption is reduced in the process by effecting modifications in various steps/stages, like anode preparation, preservation of heat of the electrolyte.

The efficacy of the process could be appreciated from the examples of Tables IA, IB, IIA & IIB.

THE I (EXPANDED TITRATION) - BRIN SOLN.  
(TEMPERATURE 95-98°C)

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Ex. Experimental NO. details for	Electrolyte	Current density $A/cm^2$	$Mn^{++}$ concentration (M)	Acid concentration (M)	Volage (V)	Reay WH/Kg	Duration	Remarks								
			Max	Min	Ave	Max	Min	Ave	Max							
1. Untreated	Chloride	1.4	0.9	0.57	0.8	0.53	0.34	0.41	7.8 <sup>a</sup>	2.2	7.2	-	2.97 <sup>a</sup>	292	at the end of 226 hrs.	
2. Cathodically treated in sodium hydroxide solution	Chloride	1.4	0.9	0.79	0.83	0.48	0.35	0.41	3.66	2.55	3.3	3.37	2.28	146	bet the end of 144 hrs.	
3. TSD	Chloride	1.4	0.96	0.77	0.85	0.51	0.34	0.40	2.76	2.30	2.70	2.63	1.64 <sup>a</sup> 1.9 <sup>a</sup>	561	C-at the end of 561 hrs.	
4. TSD	<del>Chloride</del> Sulfate	1.46	1.26	0.88	1.02	0.45	0.35	0.40	0.40	3.3	2.3	2.4	2.6	1.5 <sup>a</sup> 1.5 <sup>a</sup>	720	bet the end of 720 hrs.

THE -B

1. Untreated	Sulfate	1.41	-	-	0.85	0.44	0.39	0.42	3.75	2.42	-	3.03	1.87	312	* Literature reference
2. TSD	Sulfate	2.25	1.00	0.62	0.84	0.40	0.24	0.41	3.7	1.8	3.7	2.46	1.44	492	

### TABLE II A

AMMONIUM FLUOROBORATE, RESEARCH NITRILE PROCESS (USING TMD ANDE) - EACH SCALE

Electro-lysis	Current density A/cm <sup>2</sup>	Mn++ concentration g/l	H <sub>2</sub> O <sub>2</sub> Max	Mn Min	Ave	Initial Ave	Cell voltage V	Energy kwh/kg	Duration hrs.		
1	2	3	4	5	6	7					
1.	2.68 (24.2 A/F) 69.8	34.2	46.4	48	23.5	40.53	1.87	3.61	2.46	1.44	492
2.	2.68 (24.2 A/F) 76.3	39.5	55.8	46.4	25.34	36.82	1.89	2.70	2.14	1.29	698
3.	2.68 (24.2 A/F) 70.9	42.0	54.3	48	31.5	44.35	1.70	3.1	3.00	1.80	731
4.	2.29 (21.3 A/F) 69.6	44.1	59.9	44.5	33.8	39.23	2.50	2.46	2.60	1.50	719

Current density expressed to the solid state.

161980

TABLE II B-CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE PROCESS USING TSD ACIDE

Manganese chloride concentration = 0.95 M-0.71 M  
 Hydrochloric acid concentration = 0.38 M - 9.49 M  
 Anode current density = 1.4 A/cm<sup>2</sup>  
 Cathode current density = 0.87 A/cm<sup>2</sup>  
 Cathodes = Graphite plates

Expt. No.	Cell capacity per day of 24 hrs.	Duration of Electrolysis days	C.V. V	D.C. Energy requirement for deposition kWh/kg	Temperature °C	Vapor suppress or Energy kWh/kg BOD	Remarks
1	(approx.) 10 kg.	32	2.29-3.5	2.11	90.85	-	28 <sup>1</sup> 1. Using silica coated inert in heater x-ray diffraction d values 4.00, 2.45, 2.11, 1.66, 1.39.
2	(approx.) 20 kg.	17	2.58-3.42	1.85	95.98	YES	10.6 <sup>2</sup> 2. Using a low voltage high average transformer and graphite electrodes along with vapor suppressor

TABLE II C    **161980**

INFLUENCE OF ADDITION OF CATIONS AS CHLORIDES

(Bench Scale Experiments)

Experimental conditions : Same as in Table II B

Example No.	Cations added	Concentration g/l as chloride	x-ray data
1.	Ba <sup>++</sup>	10	d=3.9, 2.41, 2.11, 1.62 (Diffused gamma)
2.	Ba <sup>++</sup> & Ca <sup>++</sup>	10 & 30	d=4.06, 2.37, 2.14, 1.65
3.	NH <sup>+</sup> 4	5	d=2.41, 2.11, 1.63
4.	Na <sup>+</sup>	5	d=2.41, 2.11, 1.63, 1.39

The treated electrode is coated with manganese dioxide using a concentrated manganese nitrate solution by thermal method the coating being repeated for 1-5 times and dried for 5 minutes to 1/2 hour each time, in the temperature range 180-350°C, preferably 200-220°C.

A higher acid concentration for example sulphuric acid of approximately 40 g/l and higher anode current density of 1.2 - 1.6 times, preferably 1.4 times can also be used.

The anode functions efficiently with easy strippability of the deposited EMD from the anode and has a long life.

The method provides for a saving of 15-20% in the D.C. electrical energy consumption.

The following are the main advantages of the invention:

1. Production of electrolytic manganese dioxide by Using manganese salt solutions like manganese sulphate, chloride, nitrate, either alone or in admixture at various acid concentrations,
2. Tolerance of cations like  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  with special reference to chloride electrolyte.
3. Employment of valve metal like titanium as an anode for continuous electrolysis on prolonged duration after simple and effective pretreatment procedures, namely
  - (i) expansion of the metal sheet
  - (ii) cleaning in caustic soda by chemical/electrochemical or both
  - (iii) coating manganese dioxide by chemical/electrochemical or both using manganese salt, like nitrate avoiding the sand/shot blasting method and costly chemicals like noble metal salts, inorganic and organic and noble metals like platinum.
4. minimum metal requirement having mechanical strength and geometry suitable for the purpose.
5. economical size of the anode material, in conformity with the optimum dimensions of a standard commercial sized sheet and cell tank and mechanical characteristics of the anode.
6. bringing down the capital investment by using titanium as anode by this procedure comparable to that of graphite and which also incidentally results in recovering a more valuable scrap.
7. the preparation of a homogeneous electrolytic manganese

dioxide of greater purity free from substrate materials like lead, graphite, carbon.

8. efficient functioning of the anode and easy strippability of the deposited EMD from the anode resulting in longer life.
9. permitting a higher acidity in the electrolyte to the extent of approximately 3 times and higher anode current density in the range of 1.4 to 1.6 times (without getting the anode passivated), of the hitherto known conditions.
10. achieving higher "space-time yield" by applying higher anodic current density.
11. a saving of 15-20% in the DC electrical energy consumption in the preparation of electrolytic manganese dioxide at higher acid concentration and current density as claimed in 9 above.
12. utilisation of TSMD anode facilitates the adhesion of the manganese dioxide deposit to the desired limit, thereby leading to the mechanisation at the stage of harvesting the deposit.

The apparatus used consists of adoption of ac heating (using a low voltage, high amperage transformer and graphite rods/plates as electrodes) in place of (a) conventional steam heating using suitable coils, which avoids the possible contamination of the electrolyte and EMD deposit with the material of construction of the coil, periodical cleaning and maintaining the steam coil (for effective heat transfer) and (b) silica cased immersion (electrical) heaters thereby avoiding the breakage of costly silica sheaths due to the salt crystallisation at the electrolyte level and avoiding leakage of high voltage (230V) a.c. passing through the cell.

We claim:

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1. An improved process for the preparation of manganese dioxide coated titanium anodes for use in the production of electrolytic manganese dioxide which comprises expanding ~~the~~ <sup>sheet</sup> titanium used as anode suitably to increase the surface area, <sup>in the range of 7-10 to 75%</sup> cleaning the expanded anode by ~~chemical and/or electrochemical method~~ <sup>treating with</sup> using an alkali salt solution and coating the cleaned anode by ~~a chemical and/or electrochemical method~~ with a manganese salt solution.
2. An improved process as claimed in claim 1 wherein the cleaning of the anode consists in treating the anode cathodically with a solution of sodium hydroxide at a current density of 2.79 to 5.6 A/dm<sup>2</sup> and at a temperature range of 25-35°C for a period 1/2 an hour to about an hour.
3. An improved process as claimed in claims 1 & 2 wherein the alkali salt solution used is 4-4.5 M of sodium hydroxide.
4. An improved process as claimed in claim 1, 2, & 3 wherein the coating of the cleaned anode is effected by treatment with concentrated manganese nitrate solution.
5. An improved process as claimed in claims 1, 2, 3 & 4 wherein the coating of the cleaned anode is carried out between 200-300°C.
6. An improved process as claimed in claim 5 wherein the coating is done repeatedly 4 to 5 times.



**161980**

7. An improved process as claimed in any of the preceding claims wherein the cleaning of the anode is carried out in an electrolytic bath comprising 1.1M aqueous sodium hydroxide at a current density of 3.23 A/dm<sup>2</sup> and a temperature of 30°C for a period of 30 minutes and the coating thereon is carried out by treatment with a solution of 900 g/l (5.2M) manganese nitrate at a temperature range of 200°-220°C.

8. An improved process for the preparation of manganese dioxide coated titanium anodes for use in the production of electrolytic manganese dioxide substantially as herein described.

Dated this 27th day of June 1985.

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