Government of India, The Patent Office, 214, Acharya Jagadish Bose Road, Calcutta-17. Complete Specification No.129511. Application and Provisional Specification filed on 8th December 1970. Complete Specification filed on 4th October 1971. Acceptance advertised on 21st April 1973.

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IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF MERCURIC OXIDE ELECTRODES FOR USE IN ALKALINE MERCURIC OXIDE CELLS.

Council of Scientific and Industrial Research, Rafi Marg, New Delhi 1, India, an Indian registered body incorporated under the Registration of Societies Act(Act XXI of 1860).

The following specification describes the nature of this invention:

This is an invention by Srinivasam Sarangapani, Senior Scientific Assistant, Dr.Nityanandan John Paul, Scientist, Shri Srinivasam Venkatesan, Senior Scientific Assistant, and Dr. Narayanan Ramasamy, Senior Scientific Assistant and Shri Veerarghavan Aravamuthan, Scientist, all Indian Citizens working in the Central Electrochemical Research Institute, Karaikudi 3 (Tamil Nadu).

Price: TWO RUPEES.

129511

This invention relates to improvements in or relating to the preparation of mercuric oxide electrodes for use in alkaline mercuric oxide cells.

Hitherto it has been proposed to make the mercuric oxide plate electrodes using a i) metal matrix which has been electroplated (Patent No.98157), ii) mix comprising of mercuric oxide made conducting by the use of carbon or graphite or acetylene black in right proportions (Patent No.116490), iii) a binder of known quantity and composition so as to make it adherent to the matrix (Patent No. 116490), and iv) by means of pasting and pressing and other after treatments. It is known in literature that foreign metals like Pd, Co, Ag, Ni and Mg are included in anode plates and cathodes for various purposes.

This is open to the objection that when the cells are cut open at various levels of discharge, the mercury metal from the reduction of the cathode blocks, upto a certain extent, are retained in the pores of the block in the form of finely dispersed droplets and beyond certain state of discharge, they tend to trickle down the electrode and collect at the bottom of the cell, thus endangering a short circuit between electrodes and causing the cell to come to its life's end suddenly. Just like the sludge in the secondary battery, this is a possible cause for sudden failurexx among healthy cells which otherwise would have lived for some more time.

The object of this invention is to obviate these disadvantages by careful planning of the design and pattern of the electrode, whereby some mercury could be held on to it as amalgam in 'tailed' condition. This can accommodate only very low percentage of the total amount of mercury. On the other hand, by manipulating the binder composition, (non-wetting type) quantity and the pressure, the plate thickness (therefore as a result porosity) could be controlled. This also could not accommodate all the mercury metal in the pores of the plate. It has therefore been found that if the mercury could be held in the cathode block in the form of amalgam (very similar to the matrix being amalgamated very heavily and accounting for housing large quantity of mercury in 'tail'), this danger of shorting between electrodes could be averted.

To these ends, the invention broadly consists in making mercuric oxide electrodes using certain metal powders with the mix with the purpose of amalgamating the mercury which otherwise would be trickled and collected and would have caused shorting problem. The metal powders incorporated in the mercuric oxide mix is, in no way, interferring with the expected performance characteristics of the electrode which normally consists of only mercuric oxide and acetylene black; the metal powder incorporated must be so chosen that it can easily form amalgam or 'tailing' with mercury; the metal powder incorporated dispenses with the use of acetylene black so far used which is a bulky material thereby resulting in the formation of very thin slim cathode blocks which may add to capacity/unit volume; the metal powder in this case being good conductors themselves serve the function of the acetylene black meant for the purpose. To this intent, the metals best suited are in the group iron, cobalt, nickel, silver, copper and gold.

The following typical examples are given to illustrate the invention:

EXAMPLE 1

The mercuric oxide electrode is prepared in the following manner:

A metal matrix electrode (Patent No.98157) which has been electroplated is packed with the mercuric oxide mix of the composition

(A) Silver	Mercuric oxide (200 mesh)	50-80%	by weight
	Metal A power (-40 +80 mesh)	50-19%	-do-
	Acetylene black	0-1%	-do-

using a binder of known quantity and composition so as to make it adherent to the matrix (Patent No.116490) by means of pasting, pressing and other after-treatments. This electrode used in conjunction with a zinc electrode forms a mercuric oxide cell, the discharge characteristics of which are compared with a cell incorporating mercuric oxide electrode in which no metal power has been added.

EXAMPLE 2

A mercuric oxide electrode fabricated using another metal powder (Metal B) without acetylene black is prepared with the following composition:

(B) Nickel	Mercuric oxide (200 mesh)	50%	by weight
	Metal B (-40 +80 mesh) Powder	50%	-do-
	Acetylene black	nil	

using the same binder and technique as indicated in Example 1. The

performance characteristics of this electrode in conjunction with zinc anode in alkaline electrolyte are compared with the mercuric oxide electrode in which no metal powder is incorporated. The polarisation studies are as follows:

Current density mA/cm^2	Electrode using metal A (in v.)	Electrode using metal B (in v.)	Electrode using no metal
5	1.36	1.36	1.26
10	1.34	1.34	1.23
20	1.29	1.29	0.98
30	1.26	1.24	...

It is found that the performance characteristics of the electrode are not affected by the inclusion of metal powder in the cathode block.

The following are the main advantages of the invention:

1. The purpose of using certain metal powders in the mix of the mercuric oxide electrode which is used in alkaline mercuric oxide cells is to form amalgam with the mercury that is collected in the electrode during partial or complete discharge which otherwise would have trickled down and caused shorting.

2. The metal powder included in mercuric oxide plate formation is in no way interferring with the expected performance characteristics of the electrode which normally consists of only mercuric oxide and acetylene black.

3. The metal powder incorporated is so chosen that it can easily form amalgam or 'tailing' with mercury.

4. The metal powder incorporated dispenses with the use of acetylene black so far used which is a bulky material thereby leading to formation of very thin, slim cathode blocks which may have high capacity/unit volume.

5. The metal powders in this case being good conductors themselves serve the function of the acetylene black meant for the purpose.

[redacted]

Dated this 30th day of November, 1970.

PATENTS OFFICER,
Council of Scientific & Industrial Research.

INDIAN PATENTS AND DESIGNS ACT 1911

COMPLETE SPECIFICATION

Section 4

IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF MERCURIC OXIDE ELECTRODES FOR USE IN ALKALINE MERCURIC OXIDE CELLS

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi 1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

129511(A)

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

2. This is an invention by Srinivasan Sarangapani, Senior Scientific Assistant, Dr. Nityanandan John Paul, Scientist, Shri Srinivasan, Venkatesan, Senior Scientific Assistant, Dr. Narayanan Ramasamy, Senior Scientific Assistant And Shri Veeraraghavan Aravamutham, Scientist, all working in the Central Electrochemical Research Institute, Karaikudi 3 (Tamil Nadu) and all Indian Citizens.

3. This invention relates to improvements in or relating to the preparation of mercuric oxide electrodes for use in alkaline mercuric oxide cells.

4. Hitherto it has been proposed to make the mercuric oxide plate electrodes using a i) metal matrix which has been electroplated (Indian Patent No.98157), ii) mix comprising mercuric oxide made conducting by the use of 5 carbon or graphite or acetylene black in right proportion (Indian Patent No.116490),iii) a binder of known quantity and composition so as to make it adherent to the matrix (Indian Patent No.116490) and iv) by means of pasting and pressing and other after treatments. It is known in literature that foreign metals like Pd, Co, Ag, Ni and Hg are included in anode plates and cathodes for various purposes.

5. This is open to the objection that when the cells are examined at various levels of discharge, the mercury metal formed by the reduction of the cathode blocks, upto a certain extent of discharge, are retained in the pores of the block in the form of finely dispersed dreplets and beyond certain stage of discharge, they tend to trickle down the electrode and collect at the bottom of the cell, thus endangering a short circuit between electrode and causing the cell to come to its life's end suddenly. Just like the sludge in the secondary battery, this is a possible cause for sudden failure among healthy cells which otherwise would have lived for some more time.

6. The object of this invention is to obviate these disadvantages by careful planning of the design and pattern of the electrode whereby some mercury could be held on the the electrode as amalgam in 'tailed' condition. This can accommodate only very low percentage of the total

amount of mercury. On the other hand, by manipulating the binder composition, (non-wetting type), quantity and the pressure, the plate thickness (therefore as a result porosity) could be controlled. This also could not accommodate all the mercury metal in the pores of the plate. It has, therefore, been found that if the mercury could be held in the cathode block in the form of amalgam (very similar to the matrix being amalgamated very heavily and accounting for housing large quantity of mercury in 'tail'), this danger of shrting between electrodes could be averted.

According to the present invention, there is provided a process for making cathodes for mercuric oxide cells by pasting a depolariser mix of mercuric oxide and a binder such as carboxy methyl cellulose, polyvinyl alcohol or perspex solution on to a matrix electrode characterised in that metal powders such as iron, cobalt, nickel, copper, silver, gold are incorporated with the mix.

The depolariser mix is compacted by applying pressures of the order of 5 to 50 tons to attain a thickness of 1 to 3 mm.

Metal powder of particle size ranging from -40 to +300 mesh is used.

Acetylene black is added to the depolariser mixture of mercuric oxide and metal powder.

The particle size of the depolarizer mercuric oxide lies between -100 to +300 mesh, preferably of 200 mesh size and the particle size of the metal powder lies between -40 and +300, preferably +180 mesh size.

The metal powders before adding to depolarizer are given a suitable pre-treatment such as a dip in 5% ammonium chloride or 10% hydrochloric acid for five minutes or annealed in air oven under inert atmosphere.

A pressure of 5-50 tons is applied, preferably 35 tons, for compacting the depolariser mixture and the binders.

7. Thus, mercuric oxide electrodes are made using certain metal powders with the mix with the purpose of amalgamating the mercury which otherwise would be trickled and collected and would have caused shorting problem. The metal powders incorporated in the mercuric oxide mix is, in no way, interferring with the expected performance characteristics of the electrode which normally consists of only mercuric oxide and acetylene black; the metal powder incorporated is so chosen that it can easily form amalgam or 'tailing' with mercury; the metal powder incorporated dispenses with the use of acetylene black so far used which is a bulky material thereby resulting in the formation of very thin, slim cathode blocks which may add to capacity/ unit volume; the metal powders are given a pre-treatment to remove the inherent oxide film and being good conductors themselves serve the function of the acetylene black meant for the purpose. The pre-treatment, for example, consists in treating the metal powders in dilute acid or a suitable solvent to remove the oxide or the stabilizer film. To this intent, the metals best suited are in the group iron, cobalt,

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nickel, silver, copper and gold.

8. It is shown in literature that foreign metals like Pd, Cu, Ag, Ni and Hg are included in anode plates and cathodes for various purposes. But it is not so far reported in connection with mercuric oxide electrode mix depolarisers. The addition of metal powder does not interfere with this expected performance characteristics of the electrode; the addition of metal powder thus retains the structure and the dimensions of the electrode; it also holds the mercury in the electrode structure and prevents from flowing down, thereby prevents shorting between electrodes; the thickness of the electrode is reduced to some extent in comparison with the use of acetylene black, when employed in such a way that the total capacity is not affected; the metal powder in this case being good conductors themselves serve the function of the acetylene black meant for the purpose.

9. The mercuric oxide electrode is made of a depolariser mix of mercuric oxide, metal powders with or without acetylene black mixed into a paste with a binder and pasted on to a matrix electrode- wherein the addition of metal powder to the depolariser mix because of its amalgamating property retains the liquid mercury and prevents shorting between electrodes and also retains the dimension and geometry of the elec trode and because of its highly conducting property replaces acetylene black thereby facilitating the preparation of thinner electrodes which as a consequence leads to a higher ampere hour capacity/unit volume.

EXAMPLE 1

The mercuric oxide electrode is prepared in the following manner:

A metal matrix electrode (Indian Patent No.98157) which has been electroplated is packed with the mercuric oxide mix of the composition:

Mercuric oxide (200 mesh size)	50-80% by weight
Nickel powder (-40 - +80 mesh)	50-19% by weight
Acetylene black	0-1% by weight

using a binder of known quantity and composition so as to make it adherent to the matrix (Indian Patent No.116490) by means of pasting, pressing and other after-treatments. This electrode used in conjunction with a zinc electrode forms a mercuric oxide cell, the discharge characteristics of which are compared with a cell incorporating mercuric oxide electrode in which no metal power has been added.

EXAMPLE 2

A mercuric oxide electrode fabricated using another metal powder (Metal B) without acetylene black is prepared with the following composition:

Mercuric oxide (200 mesh size)	50% by weight
Silver powder (-40 - +80 mesh)	50% by weight
Acetylene black	nil

using the same binder and technique as indicated in Example 1. The performance characteristics of this electrode in conjunction with zinc anode in alkaline electrolyte are compared with the mercuric oxide electrode in which no metal powder is incorporated. The polarization studies as as follows:

Current density mA/cm^2	Electrode using metal A (in v.)	Electrode using metal B (in v.)	Electrode using no metal powder
5	1.36	1.36	1.26
10	1.34	1.34	1.23
20	1.29	1.29	0.98
30	1.26	1.24	..

It is found that the performance characteristics of the electrode are not affected by the inclusion of metal powder in the cathode block.

11. The mercury that is formed during discharge does not trickle down but held in the structure of the electrode as amalgam. Hence the shorting between electrodes is avoided and the electrodes also maintain their structure and dimensions. The metal powders are conductors and therefore they replace partially or completely the acetylene black which has been used hitherto. Such replacement results in the preparation of very thin electrode blocks because the bulky acetylene black is replaced by highly conducting metal powders. The formation of thin electrode enables the preparation of batteries with more capacity/unit volume. This also disposes with the acetylene black which is being imported now.

12. The inclusion of metal powders in cathode depolariser mix enables the preparation of highly conducting, structurally and dimensionally stable, very slim electrodes, leading to the advantages that a battery having higher capacity per unit volume, free from shorting trouble due to the flowing down of mercury can be fabricated.

WE CLAIM

1. A process for making cathodes for mercuric oxide cells by pasting a depolariser mix of mercuric oxide and a binder such as carboxy methyl cellulose, polyvinyl alcohol or perspex solution on to a matrix electrode characterised in that metal powders such as iron, cobalt, nickel, copper, silver, gold are incorporated with the mix.

2. A process as claimed in Claim 1 wherein the depolariser mix is compacted by applying pressures of the order of 5 to 50 tons to attain a thickness of 1 to 3 mm.

3. A process as claimed in Claim 1 or 2 wherein metal powder of particle size ranging from -40 to +300 mesh is used.

4. A process as claimed in any of the preceding claims wherein acetylene black is added to the depolariser mixture of mercuric oxide and metal powder.

5. A process as claimed in any of the preceding claims wherein the particle size of the depolarizer mercuric oxide lies between -100 to +300 mesh, preferably of 200 mesh size and the particle size of the metal powder lies between -40 and +300, preferably +180 mesh size.

6. A process as claimed in any of the preceding claims wherein the metal powders before adding to depolarizer are given a suitable pretreatment such as a dip in 5% ammonium chloride or 10% hydrochloric acid for five minutes or annealed in air oven under inert atmosphere.

7. A process as claimed in any of the preceding claims wherein a pressure of 5-50 tons is applied, preferably 35 tons, for compacting the depolariser mixture and the binders.

8. A process for making cathodes for mercuric oxide cells substantially as hereinbefore described.

Dated this 1st day of October 1971.

R. Bhaskar Rao

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