

Specification No. 106324, Application No. 106324, dated 25th July 1966. Complete specification left on 19th May 1967. (Application accepted 25th April 1968.)

Index at acceptance—14D2[LVIII(1)].

IMPROVEMENTS IN OR RELATING TO PRIMARY WET CELLS.

### PROVISIONAL SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFT MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

The following specification describes in the nature of this invention.

This is an invention by (1) PATTARAKALAM LUKA JOSEPH, (2) VENKATARAMAN BALASUBRAMANIAN, (3) GANGADHARAN JOTHINATHAN, (4) BALKUNJE ANANTHA SHENOI, all citizens of India and (5) MICHAEL ANGELO VINCENT DEVANATHAN, citizen of Ceylon, all of the Central Electrochemical Research Institute, Karaikudi-3, India.

The invention relates to improvements in or relating to primary wet cells.

Hitherto it has been proposed to use zinc anode, ammonium chloride, zinc chloride electrolyte and  $MnO_2/C$ —cathode for primary wet cells of the Leclanche type.

This is open to the objection that zinc gives lower ampere hour output than aluminium and zinc is a scarce material in our country as compared to aluminium. This factor suggests aluminium as a convenient and cheaper substitute to zinc in the Leclanche system. For the reason that zinc is an essentially imported raw material at present, it is desirable to replace the zinc chloride used in normal Leclanche system with a chemical more readily available in the country, such as manganese chloride.

The object of the invention is to obviate these disadvantages by using aluminium or aluminium based alloys in the form of sheet or cast or extruded rods or powder pressed and sintered in electrolytes containing manganese salts such as chlorides, sulphates, perchlorates, oxalates, acetates, nitrates with or without mercury compounds and with or without corrosion inhibitors.

To these ends the invention broadly consists in using aluminium or aluminium based alloys in suitable electrolytes with or without mercury salts and with or without corrosion inhibitors.

Typical corrosion inhibitors are alkyl pyridinium salts, alkyl quinolenium salts, tetra alkyl salts and their derivatives, soluble chromates.

The following typical examples are given to illustrate the invention.

#### EXAMPLE I

Aluminium	$MnSO_4$ solution Mercury Compound	$MnO_2$ C
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#### EXAMPLE II

Aluminium-zinc mercury alloy	$MnCl_2$ solution Alkyl pyridinium halide	$MnO_2$ C
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#### EXAMPLE III

Aluminium mercury alloy	Manganese chloride Tetra butyl ammonium chloride	$MnO_2$ C
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#### EXAMPLE IV

Aluminium	Manganese chloride borax Mercury compound	$MnO_2$ C
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The cells give open circuit voltages of 1.7 V and closed circuit voltages of 1.6 V under a load of 10 ohms. The cells can be discharged for three months under a load of 10 ohms to a cut off voltage of 75 V.

The following are the chief advantages of the invention:

1. Makes possible the use of aluminium in place of imported zinc.

2. For the same current output the weight of aluminium when used as anode would be 60 per cent. less than the weight of zinc when used as anode.

3. Gives higher open circuit and closed circuit voltages of the cell indicating the possibility of using smaller number of cells in place of the conventional Leclanche cells.

4. Makes possible the use of manganese salts which are indigenously available from the manganese ore deposits since zinc salts are not readily available in the country.

R. BHASKAR PAI

Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 15th day of July 1966.

### COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFT MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

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

This is an invention by (1) PATTARAKALAM LUKA JOSEPH, (2) VENKATARAMAN BALASUBRAMANIAN, (3) GANGADHARAN JOTHINATHAN, (4) BALKUNJE ANANTHA SHENOI, all citizens of India and (5) MICHAEL ANGELO VINCENT DEVANATHAN, citizen of Ceylon, all of the Central Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to improvements in or relating to primary wet cells.

Hitherto it has been proposed to use zinc anode, ammonium chloride electrolyte and sodium hydroxide as electrolytes and manganese dioxide carbon and air depolarised electrodes as cathodes.

This is open to the objection that zinc gives only 0.8 ampere hours per gram and that at present zinc is imported.

The object of the present invention is to obviate these disadvantages.

According to the present invention, the primary wet cell comprising an anode, electrolyte and cathode is characterised in that the anode consists of aluminium or aluminium based alloy in place of zinc and the

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electrolyte consists of manganese chloride or manganese sulphate with or without addition agents in place of ammonium chloride whereby the anode consumption is reduced by about 60 per cent. and the frequent change of electrolyte is avoided. Aluminium gives nearly 3 ampere hours per gram.

Thus, the primary wet cell may have an anode of aluminium or aluminium based alloy wherein the alloying elements are mercury (0.01 to 1 per cent.) or mercury (0.01 to 1 per cent.) and zinc (0.5 to 5 per cent.) or mercury (0.01 to 1 per cent.) and tin (0.01 to 2 per cent.).

The electrolyte may consist mainly of manganese salts of concentration 100 gms/litre to 600 gms/litre with or without mercury salt whose concentration ranges from 0.2 gm/litre to 5 gms/litre and with or without corrosion inhibitors such as alkali and ammonium chromate, EDTA, tetra alkyl ammonium salts and alkyl pyridinium salts in concentrations ranging from 0.1 gm/litre to 10 gm/litre.

The electrolyte may contain addition agents such as calcium chloride, magnesium chloride, sodium chloride, alkali pyrophosphates, borax and alkali citrates in concentrations ranging from 10 gm/litre to 50 gm/litre.

The cathode may consist of manganese dioxide and conducting carbon with or without binders such as carboxy methyl cellulose, polyvinyl alcohol, polyvinyl acetate solution, perspex solution or the electrolyte mentioned herein above.

The primary wet cell may employ a carbon rod with or without groove or thread along its length with the cathode mix packed around it or a porous carbon container in which the depolariser mixture is packed.

Thus, in the invented primary wet cell, aluminium and aluminium based alloys are used as anode. The electrolyte used in this invention constitutes mainly of manganese salts with or without mercury salts, addition agents and inhibitors. The cathode used in this invention consists of manganese dioxide with carbon or graphite powder with or without binding material.

Use is thus made of aluminium or aluminium based alloys such as aluminium-zinc alloy, aluminium-zinc-mercury alloy, aluminium-mercury alloy or aluminium-tin alloy, or aluminium-tin-mercury alloy, aluminium-indium alloy, aluminium-indium-mercury alloy in the form of sheet cast or extruded rod or powder pressed and sintered along with electrolyte and cathodes described below:

The electrolyte used in this invention consists mainly of manganese salts such as manganese chloride, manganese sulphate, manganese perchlorate and manganese acetate with or without mercury compounds and with or without corrosion inhibitors and addition agents.

The corrosion inhibitors are tetra alkyl ammonium salts, alkyl pyridinium halides and alkali or ammonium chromates.

The addition agents used are borax, EDTA, alkali pyrophosphates, ammonium chloride and alkali and alkaline earth chlorides.

In this invention, the cathode material used is manganese dioxide mixed with acetylene black or graphite powder with or without binding material. The binding material used are carboxy methyl cellulose, polyvinyl alcohol, perspex solution and manganese chloride solution.

Sac element is prepared by packing the above cathode material around a carbon or graphite rod. For better contact between the carbon rod and the cathode mix, the outside of the carbon rod is threaded uniformly to its whole length.

To these ends the invention broadly consists in using aluminium or aluminium based alloys in the electrolytes containing manganese salts with or without mercury salt, corrosion inhibitors or addition agents in conjunction with a cathode consisting of manganese dioxide and conducting carbon as depolariser.

The following examples are given to illustrate the invention:

#### EXAMPLE I

Aluminium (2S)	Manganese sulphate mercury compound	Manganese dioxide plus carbon
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Open circuit voltage 1.7 V. Closed circuit voltage with 10 ohms load 1.6 V.

#### EXAMPLE II

Aluminium (2S)	Manganese chloride mercury compound	Manganese dioxide plus carbon
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Open circuit voltage 1.75 V. Closed circuit voltage with 10 ohms load 1.6 V.

Works at a steady closed circuit voltage of 1.05 V for three months.

#### EXAMPLE III

Aluminium mercury alloy	Manganese chloride	Manganese dioxide plus carbon
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Open circuit voltage 1.8 V. Closed circuit voltage 1.6 V; with 10 ohms load gives a steady voltage of 1.15 V for three months.

#### EXAMPLE IV

Aluminium- mercury alloy	Manganese chloride	Manganese dioxide carbon plus binding materials (perspex solution or polyvinyl acetate solution)
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Open circuit voltage 1.65 V. Closed circuit voltage 1.55 V with 10 ohms load, gives a steady voltage of 1.05 V for 3 months.

#### EXAMPLE V

Aluminium-zinc mercury alloy	Manganese chloride	Manganese dioxide plus carbon
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Open circuit voltage 1.65 V. Closed circuit voltage 1.55 V at 10 ohms load. Efficiency 90 per cent.

#### EXAMPLE VI

Aluminium	Manganese chloride	Manganese dioxide plus carbon
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Open circuit voltage 1.5 V. Closed circuit voltage with 10 ohms load, 1.35 V. Works at a steady voltage of .95 V for 3 months.

#### EXAMPLE VII

Aluminium-tin- mercury alloy	Manganese chloride tetramethyl ammo- nium chloride	Manganese dioxide plus carbon
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Open circuit voltage 1.75 V. Closed circuit voltage 1.65 V. Efficiency 80 per cent.

#### EXAMPLE VIII

Aluminium-tin- alloy	Manganese chloride borax	Manganese dioxide plus carbon
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Open circuit voltage 1.75 V. Closed circuit voltage with 10 ohms load 1.65 V. Efficiency 85 per cent.

The concentration of manganese salt in solution ranges from 100 gms/litre to 600 gms/litre.

The concentration of mercury salt ranges from 0.5 gms/litre to 5 gms/litre.

The concentration of addition agents and inhibitor ranges from 2 gms/litre to 50 gms/litre.

The following are the main advantages of the invention:

1. Makes possible the use of aluminium in place of imported zinc.
2. About 60 per cent. reduction in the weight of the anode consumed for the same current output.
3. Gives higher open circuit and closed circuit voltages for the cell.
4. Makes possible the use of manganese salts for which abundant resources are available in India.

We claim:

1. A primary wet cell comprising an anode, electrolyte and cathode which is characterised in that the anode consists of aluminium or aluminium based alloy in place of zinc and the electrolyte consists of man-

manganese chloride or manganese sulphate with or without addition agents in place of ammonium chloride whereby the anode consumption is reduced by about 60 per cent. and the frequent change of electrolyte is avoided.

2. A primary wet cell as claimed in Claim 1 having an anode of aluminium or aluminium based alloy wherein the alloying elements are mercury (0.01 to 1 per cent.) or mercury (0.01 to 1 per cent.) and zinc (0.5 to 5 per cent.) or mercury (0.1 to 1 per cent.) and tin (0.1 to 2 per cent.)

3. A primary wet cell as claimed in Claims 1 and 2 wherein the electrolyte consists mainly of manganese salts of concentration 100 gms/litre to 600 gms/litre with or without mercury salt whose concentration ranges from 0.2 gm/litre to 5 gms/litre and with or without corrosion inhibitors such as alkali and ammonium chromate, EDTA, tetra alkyl ammonium salts and alkyl pyridinium salts in concentrations ranging from 0.1 gm/litre to 10 gm/litre.

4. A primary wet cell as claimed in Claims 1 to 3 wherein the electrolyte contains addition agents such as calcium chloride, magnesium chloride, sodium chloride, alkali pyrophosphates, borax and alkali citrates

in concentrations ranging from 10 gm/litre to 50 gm/litre.

5. A primary wet cell as claimed in Claims 1, 2, 3 and 4 wherein the cathode consists of manganese dioxide and conducting carbon with or without binders such as carboxy methyl cellulose, polyvinyl alcohol, polyvinyl acetate solution, perspex solution or the electrolyte mentioned in Claims 3 and 4.

6. A primary wet cell as claimed in Claims 1 to 5 using a carbon rod with or without groove or thread along its length with the cathode mix mentioned in Claim 5 packed around it or a porous carbon container in which the depolariser mixture mentioned in Claim 5 is packed.

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*Dated this 17th day of May 1967.*