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ORGANIC DEPOLARISER BATTERIES

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

THIS IS AN INVENTION BY DR. PREM BEHARI MATHUR, NATCHI MUNIANDI AND REMASWAMY BALASUBRAMANIAN, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, (S. RLY.) INDIA, ALL INDIAN CITIZENS.

The followiug specification describes the nature of this Invention.

This invention relates to the improvement in or relating to the development of the magnesium-organic depolariser batteries.

Hitherto it has been the practice to use inorganic depolarisers as cathode materials in commercial primary as well as secondary battery systems.

Owing to the fact that reduction of the inorganic cathodic materials like manganese dioxide, lead dioxide is usually associated with one to three electrons transfer processes, the energy output per unit weight of these cathodic materials is considerably less than those of several organic compounds which involve the trasfer of large number of electrons say six to twelve during their electrochemical reduction. Extensive research and investigations during the past decade on the electrolytic reduction of organic materials have widely opened the scope of explotation of organic compounds as high energy density depolariser cathode materials in batteries. However, the development of a suitable commercial battery incorporating organic depolarisers calls for the exploration of a suitable composition of depolariser mix for obtaining high efficiency of reduction and low internal resistance, suitable separator materials to minimise the self discharge and leakage currents and thereby to increase shelf life, a suitable electrolyte composition and a suitable design of the cathode to provide high mechanical strength.

To these ends, the invention broadly consist in the development of a suitable cathode mix, the design of the negative electrode selection of suitable separator materials for primary and activated type of battery systems and lastly the assembly of the cells. The efficiency of the electrochemical reduction of the organic materials mata-dinitrobenzene has been improved by incorporating trace amounts of an oxide like copper oxide, nickel oxide, cobalt oxide manganese dioxide etc., in the cathode mix. Graphite powder or acetylene black or carbon black are used in the mix to improve the internal conductivity of the electrode systems. An organic gel like starch, cellulose, polyvinyl alcohol, carboxyl methyl cellulose agar etc., is used as binder material and cellophane paper and plastic fabric cloth are used as separator materials for primary cell while filter paper blotting paper and tissue paper are used for activated type cell. Magnesium alloy consisting of aluminium and zinc as trace impurities are used as anode material in the fabrication of batteries. Mixtures of salts consisting of perchlorate or bromide of divalent metals with additional agents are used as electrolyte. The electrolyte compositions is such as to achieve minimum corrosion of anode and efficient reduction of cathode.

The following typical examples are given to illustrate the invention :

Example 1

A representative cell of 250 AH capacity is fabricated for long duration continuous discharge over a period of 50 days. 250 to 300 gms. of m-dinitrobenzene are mixed with 100 to 175 gms. of acetylene black and a small quantity of oxide of a metal such as copper oxide, nickel oxide or MnO_2 and formed as plates of 21 cm x 12 cm size using an organic binder over a metallic wire mesh by applying pressure. The electrodes are wrapped with filter paper and cellophane paper separators. Magnesium plates of the same size and of 1.5 cm thickness were used as anodes. These anodes were placed in plastic fabric cloth bags such as terelyne or nylon. Four anodes and three cathodes were placed alternatively and the entire assembly is placed in a plastic container of 17 cm x 16 cm x 25 cm size. The electrode terminals which were coated with non-conducting plastic material were brought out to the lid of the container and soldered to two terminals marked positive and negative. A hole of diameter 3 mm to 5 mm was made at the centre of the lid. After filling the cell with the electrolyte solution containing magnesium perchlorate along with additional agents, the lid was sealed to the container. The cell was put on discharge at 210 mA rate and its discharge performance was noted continuously. Following are the typical data on the cell characteristic and its discharge behaviour.

Performance Characteristics of 250 AH Rated Capacity Cell

1. *Dimensions of cell*

   11 cm (l) x 16 cm (w) x 25 cm (h)
   Volume of cell=6.8 cubic decimeter
   Weight of cell=6 kg.
   Quantity of electrolyte solution=3 litres

2. *Performance characteristics* :

   Open circuit voltage=1.55 V
   Operational voltage=1.125 to 0.9 V
   Discharge current=210 mA
   Duration of discharge=50 days
   Drop in cell voltage after 50 days of discharge=0.225 V
   Ampere hour capacity per unit weight of cell=41.5 AH/kg.
   Ampere hour capacity per unit volume of cell=37 AH/lit,
   Material Efficiency of Active Cathode material=1 AH/g.

A low capacity (1 AH) cell using organic depolariser cathode and magnesium alloy anode is fabricated as described in example 1, except that tissue paper and filter paper or blotting paper are used as the separator materials around cathode in place of cellophane paper. This cell is operated as an Activated Cell. =The cell showed the time of activation less than two seconds for the rise of voltage to 1.25 V at 10.8 mA current drain which correspond to the 100 hours discharge.

The following are among the main advantages of the invention :

1. The use of specific composition of the cathode mix giving very high capacity per unit weight of active cathode material by bringing about its efficient reduction at different temperatures.

2. The special design of the cathode for obtaining good electrical performances like the constancy of the operating voltage between a working voltage of 1.15 to 0.9 V over 90% discharge capacity and over a long duration of discharge and high ampere hour capacity output per gram of the cathode mix.

3. The use of a suitable composition of electrolyte soultion which improves the efficiency of discharge of electrodes and minimise the chemical corrosion of magnesium anode.

(R. BHASKAR PAI)

PATENTS OFFICER

Council of Scientific and Industrial Research.

Dated this 20th day of February, 1970.

COMPLETE SPECIFICATION

ORGANIC DEPOLARISER BATTERIES

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES 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.

This invention relates to the improvements in or relating to the development of the organic depolariser cells or batteries.

Hitherto it has been the practice to use inorganic depolarisers as cathode materials in commercial primary as well as secondary battery systems.

Owing to the fact that reduction of the inorganic cathode materials like manganese dioxide, lead dioxide, is usually associated with one to three electrons transfer processes, the energy output per unit weight of these cathodic materials used to be considerably less than those of several organic compounds which involve the transfer of larger number of electrons, say six to twelve, during their electro-chemical reduction. Extensive research and investigations were conducted during the past decade on the electrolytic reduction of organic compounds which are high energy density depolariser materials for cathodes in batteries. However, a suitable commercial battery incorporating organic depolarisers has not appeared so far in the market as its development calls for the exploration of a suitable composition of depolariser mix for obtaining high efficiency of reduction and low internal resistance, suitable separator materials to minimise the self discharge and leakage currents and thereby to increase shelf life, a suitable electrolyte composition and a suitable design of the cathode to provide high mechanical strength.

We have developed an organic depolariser cell or battery which has an organic depolariser cathode consisting of a nitro or nitroso substituted organic compound such as dinitrobenzene, nitroso benzene coupled with an active metal or its alloy anode element like magnesium, zinc or aluminium.

According to the present invention, there is provided an organic depolariser cell or battery comprising an organic depolariser cathode, a magnesium, zinc or aluminium or their alloy as anode and magnesium perchlorate, lithium chromate or sodium or potassium hydroxide as electrolyte characterised in that the organic depolariser cathode consists of a mixture of nitro or nitroso substituted organic compound and a metal oxide applied on a conductive wire mesh and fixed thereon by an organic binder, the cathode being separated from the anode by a separator material.

The substituted organic compound may be metadinitrobenzene.

The metal oxide may be copper oxide, nickel oxide, iron oxide or vanadium oxide.

The organic binder may be starch, cellulose acetate, polyvinyl alcohol, carboxymethyl cellulose or agar agar.

The separator material may be cellophane paper, filter paper, nylon cloth or terelene cloth.

The cathode element is made by pressing the cathode mix over a conducting mesh cathode.

The cell is assembled by coupling organic depolariser cathode with magnesium or zinc or aluminium or their alloy anode using cellophane paper, filter paper, nylon cloth, terelene cloth as separator materials.

Solutions of individual electrolytes or a mixture of electrolytes like magnesium perchlorate, 5-25%, lithium chromate 0.5—5%, magnesium bromide 5-25% or sodium or potassium hydroxide 10-45% is used as electrolyte for the cell.

The invention thus includes within its scope the development of a suitable cathode mix, the design of the negative electrode, selection of suitable separator materials for primary and activated type of battery systems and lastly the assembly of the cells. The efficiency of the electrochemical reduction of the organic materials metadin nitrobenzene has been improved by incorporating trace amounts of an oxide or hydroxide like copper oxide, nickel oxide, cobalt oxide, manganese dioxide in the cathode mix. Graphite powder or acetylene black or carbon black are used in the mix to improve the internal conductivity of the electrode systems. An organic gel like starch, cellulose, polyvinylalcohol, carboxyl methyl cellulose, agar agar is used as binder material and cellophane paper and plastic fabric cloth are used as separator materials for primary cell, while filter paper, blotting paper and tissue paper are used for activated type cell. Magnesium alloy consisting of aluminium and zinc as trace impurities are used as anode material in the fabrication of batteries. Mixtures of salts consisting of perchlorate or bromide of divalent metals with additional agents are used as electrolyte. The electrolyte compositions is such as to achieve minimum corrosion of anode and efficient reduction of cathode.

The following typical examles are given to illustrate the invention :

Example 1

A representative cell of 250 AH capacity is fabricated for long duration continuous discharge over a period of 50 days. 250 to 300 gms. of m-dinitrobenzene mixed with 100 to 175 gms. of acetylene black and a small quantity of oxide of a metal such as copper oxide, nickel oxide or MnO_2 and formed as plates of 21 cm x 12 cm size using an organic binder over a metallic wire mesh by applying pressure. The electrodes are wrapped with filter paper and cellophane separators. Magnesium plates of the same size and of 1.5 cm thickness were used as anodes. These anodes were placed in plastic fabric cloth bags such as terelyne or nylon. Four anodes and three cathodes were placed alternatively and the entire assembly is placed in a plastic container of 17 cm x 16 cm x 25 cm size. The electrode terminals which were coated with non-conducting plastic material were brought out to the lid of the container and soldered to two terminals marked positive and negative. A hole of diameter 3 mm to 5 mm was made at the centre of the lid. After filling the cell with the electrolyte solution containing magnesium perchlorate along with additional agents like lithium chromate and ammonium chromate, the lid was sealed to the container. The cell was put on discharge at 210 mA rate and its discharge performance was noted continuously. Following are the typical data on the cell characteristics and its discharge behaviour.

Characteristics of 250 AH Rated Capacity Cell :

1. *Dimensions of cell*

   17 cm (l) x 16 cm (w) x 25 cm (h)

   Volume of cell=6.8 cubic decimeter

   Weight of cell=6 Kg

   Quantity of electrolytic solution=3 litres

2. *Performance characteristics* :

   Open circuit voltage =1.55 V

   Operational voltage =1.125 to 0.9 V

   Discharge current =210 mA

   Duration of discharge =50 days

   Drop in cell voltage after 50 days of discharge=0.225 V

   Ampere hour capacity/unit weight of cell=41.4 AH/Kg

   Ampere hour capacity/unit volume of cell=37 AH/lit

   Material Efficiency of active cathode material=0.8 to 1 AH/g

Example 2

A low 1 AH cell of the dimensions 4.8 x 2.3 x 2.5 cms using *organic depolariser cathode* and magnesium alloy anode is fabricated as described in example 1 except that the cell after assembly and activation with the electrolyte is completely sealed. Precautions of insulating the terminal leads were taken to avoid any short circuiting. The cell is discharged as sealed cell. The cell delivers 0.8 AH capacity between 1.1 to 1 V and at 100 mA current drain. The remaining capacity is obtained below 1 V at the same rate of discharge. The sealed cell did not show any rupture or deformation in the course of discharge.

The following are among the main advantages of the invention :

1. The use of specific composition of the cathode mix giving very high capacity per unit weight of active cathode material by bringing about its efficient reduction at different temperatures.

2. The special design of the cathode for obtaining good electrical performances like the constancy of the operating voltage between a working voltage of 1.15 to 0.9 V over 90% discharge capacity and over a long duration of discharge and high ampere hour capacity output per gram of the cathode mix.

3. The use of a suitable composition of electrolyte solution which improves the efficiency of discharge of electrodes and minimise the chemical corrosion of magnesium anode.

WE CLAIM :

1. An organic depolariser cell or battery comprising an organic depolariser cathode, a magnesium, zinc or aluminium or their alloy as anode and magnesium perchlorate, lithium chromate or sodium or potassium hydroxide as electrolyte characterised in that the organic depolariser cathode consists of a mixture of nitro or nitroso substituted organic compound and a metal oxide applied on a conductive wire mesh and fixed thereon by an organic binder, the cathode being separated from the anode by a separator material.

2. An organic depolariser cell as claimed in Claim 1 wherein the substituted organic compound is meta-dinitrobenzene.

3. An organic depolariser cell as claimed in Claim 1 wherein the metal oxide is copper oxide, nickel oxide, iron oxide or vanadium oxide.

4. An organic depolariser cell as claimed in Claim 1 wherein the organic binder is starch, cellulose acetate, polyvinyl alcohol, carboxymethyl cellulose or agar agar.

5. An organic depolariser cell as claimed in Claim 1 wherein the separator material is cellophane paper, filter paper, nylon cloth or terelene cloth.

6. An organic depolariser cell substantially as herein described.

(R. BHASKAR PAI)

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Council of Scientific and Industrial Research.

Dated this 3rd day of November, 1970.

Freeze Sales Corporation, Cal-20.