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We, DURACELL INC., of Berkshire Corporate Park, Bethel, Connecticut 06801, United States of America, being the applicant in respect of Application No. 49971/93, state the following: -

1. The person nominated for the grant of the patent has entitlement from the actual inventors by assignment.

2. The person nominated for the grant of the patent has entitlement from the applicants of the applications listed in the declaration under Article 8 of the PCT by assignment.

3. The basic applications listed in the declaration under Article 8 of the PCT are the first applications made in a Convention country in respect of the invention.

For and on behalf of
DURACELL INC.

(Signature)

MARCH 24, 1995

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(56) Prior Art Documents
US 653791
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(57) Claim

1. A process for manufacture of gamma manganese dioxide comprising the steps of:

a) reacting $MnSO_4$ and $Na_2S_2O_8$ in a solution to produce a reaction product mixture comprising a precipitate of gamma MnO_2 comprised of particles characterised by filament-like protrusions radiating outwardly from the surface of said particles;

b) removing the gamma MnO_2 precipitate from said reaction product mixture; and

c) drying said precipitate.

9. A hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of electrolytic manganese dioxide (EMD), wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

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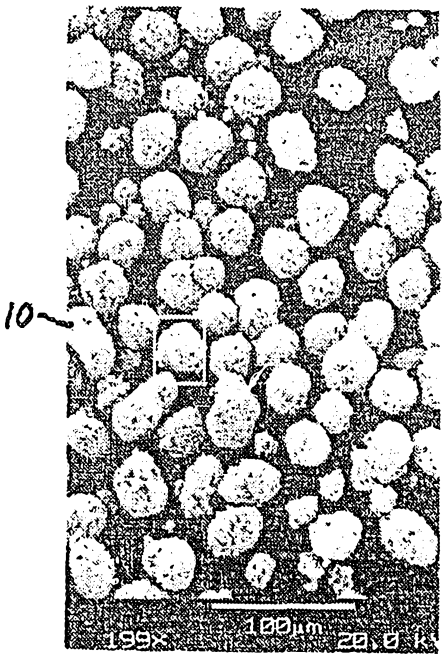

(57) Abstract

The invention relates to the manufacture of manganese dioxide by a chemical process. The resulting manganese dioxide product takes the form of particles characterized by filament-like protrusions jutting out from its surface. The manganese dioxide particles having such surface features can be manufactured by reacting manganese sulfate with sodium peroxodisulfate in an aqueous solution. The process can be controlled to yield high density manganese dioxide. The manganese dioxide formed in the process can be deposited directly onto the surface of electrolytic manganese dioxide (EMD). The manganese dioxide product is particularly suitable for use as a cathode active material in electrochemical cells.

PROCESS FOR PRODUCING MANGANESE DIOXIDE

The invention relates to a process for production of manganese dioxide, particularly for use as a cathode active material in electrochemical cells.

Manganese dioxide is commonly employed as a cathode active material in commercial batteries. Such manganese dioxide has been derived from naturally occurring manganese dioxide (NMD) and synthetically produced manganese dioxide which includes electrolytic manganese dioxide (EMD) and chemical manganese dioxide (CMD). NMD has a high impurity content and cannot be employed in alkaline or lithium cells.

EMD is typically manufactured by direct electrolysis of manganese sulfate and sulfuric acid. It's high purity and high density make gamma manganese dioxide desirable for use as a cathode active material in alkaline and lithium cells.

According to a first aspect of the invention, there is provided a process for manufacture of gamma manganese dioxide comprising the steps of:

a) reacting $MnSO_4$ and $Na_2S_2O_8$ in a solution to produce a reaction product mixture comprising a precipitate of gamma MnO_2 comprised of particles characterised by filament-like protrusions radiating outwardly from the surface of said particles;

b) removing the gamma MnO_2 precipitate from said reaction product mixture; and

c) drying said precipitate.

According to a second aspect of the invention, there is provided a hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of electrolytic manganese dioxide (EMD), wherein said gamma MnO_2 material has filament-like protrusions

radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

According to a third aspect of the invention, there is provided a hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of carbon material selected from the group consisting of graphite and carbon black, wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

According to a fourth aspect of the invention, there is provided a hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of another material wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

According to a fifth aspect of the invention, there is provided an electrochemical cell having MnO_2 cathode active material in said cell, characterised in that at least 95% of said MnO_2 material comprises gamma MnO_2 particles wherein said gamma MnO_2 particles have filament-like protrusions radiating outwardly from the surface of said particles, said filament-like protrusions being visible at a magnification of between 200 and 2,000 times actual size.

According to a sixth aspect of the invention, there is provided an electrochemical cell having MnO_2 cathode active material in said cell, characterised by said electrochemical cell having an anode comprising lithium, and further characterised by said MnO_2 material comprising gamma MnO_2 particles having filament-like protrusions

radiating outwardly from the surface of said particles, said filament-like protrusions being visible at a magnification of between about 200 and 2,000 times actual size.

According to a seventh aspect of the invention, there is provided a hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of electrolytic manganese dioxide (EMD), wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 9,850 times actual size.

The features of the product of the invention will be better appreciated with reference to the following figures:

Fig. 1A is an electron photomicrograph showing the MnO_2 particles from the process of the invention carried out at slow rate of heating of reactants.

Fig. 1B is an electron photomicrograph of the particles in Fig. 1A enlarged to show the filament-like surface protrusions.

Fig. 2A is an electron photomicrograph showing smaller sized MnO_2 particles from the process of the invention carried out at fast rate of heating of the reactants.

Fig. 2B is an electron photomicrograph of the particles in Fig. 2A enlarged to show the filament-like surface protrusions.

Fig. 3A is an electron photomicrograph of EMD particles (prior art).

Fig. 3B is an electron photomicrograph of the EMD particles in Fig. 3A enlarged to show the characteristically irregular particle shape and smooth surface structure.

Fig. 4A is an electron photomicrograph of EMD particles coated with MnO_2 produced by the process of the invention (P-CMD).

Fig. 4B is an electron photomicrograph of coated EMD particles in Fig. 4A enlarged to show the filament-like surface protrusions.

Fig. 5A is an electron photomicrograph of prior art chemical manganese dioxide (CMD) particles.

Fig. 5B is an electron photomicrograph of the particles in Fig. 5A enlarged to show surface features.

Fig. 6A is a graphical plot of the voltage profile (voltage versus service hours) in an alkaline AA cell at 3.9 ohm constant load, comparing performance of the P-CMD with conventional EMD.

Fig. 6B is a graphical plot of the voltage profile (voltage versus milli amp-hour per gram MnO_2) in a flooded alkaline cell at 0.3 milli-amp/cm^2 current drain rate, comparing performance of the P-CMD with conventional EMD.

Fig. 7A is a graphical plot of the voltage profile (voltage versus milli amp-hour per gram MnO_2) in a lithium cell at 0.17 milli-amp/cm^2 current drain rate comparing performance of P-CMD with conventional EMD.

Fig. 7B is a graphical plot of the voltage profile (voltage versus milli amp-hour per gram MnO_2) in a lithium cell at 1.0 milli-amp/cm^2 current drain rate, comparing performance of P-CMD with conventional EMD.

Fig. 8A is a graphical plot of the voltage profile (voltage versus milli amp-hour per gram MnO_2) in a lithium cell at 0.17 milli-amp/cm^2 current drain rate, comparing performance of P-CMD with conventional CMD (WSLi).

Fig. 8B is a graphical plot of the voltage profile (voltage versus milli amp-hour per gram MnO_2) in a lithium cell at 1.0 milli-amp/cm^2 current drain rate, comparing performance of the MnO_2 product of the invention (P-CMD) with conventional CMD (WSLi).

The present invention involves a process for production of battery grade chemical manganese dioxide (CMD). P-CMD when used in electrochemical cells, particularly alkaline and lithium cells, provides these cells with higher capacity and energy density per gram than are obtainable from the same cells employing electrolytic manganese dioxide (EMD). The process of the invention allows for greater control of properties such as density, surface area and particle size than is possible with present processes for the manufacture of conventional forms of EMD or CMD. The process of the invention therefore allows for production of high purity CMD which can be made to have properties more nearly optimal for a given electrochemical cell type. The high density of our MnO_2 product is comparable to

that obtained from electrolytic manganese dioxide (EMD), yet the surface area of each MnO_2 particle is greater than that obtained from conventional EMD and CMD processes. The high useful surface area of each particle allows for better performance, particularly in lithium cells containing MnO_2. By "useful" surface area we refer to the surface area which is accessible to the electrolyte.

The process of the invention for production of battery grade manganese dioxide is carried out principally by reacting an aqueous solution of manganese sulfate with sodium peroxodisulfate.

The reaction may be represented as follows:

$$MnSO_4 + Na_2S_2O_8 + 2H_2O = MnO_2 + Na_2SO_4 + 2H_2SO_4 \quad (I)$$

When an aqueous solution of manganese sulfate ($MnSO_4$) is reacted with sodium peroxodisulfate ($Na_2S_2O_8$), a gamma crystal structure of MnO_2 is directly obtainable as a reaction product in the form of a precipitate. The MnO_2 precipitate tends to form spherical particles having filament-like protrusions emanating outwardly from each particle surface and are substantially uniformly distributed over the particle surface. The term "filament-like" as used herein shall be construed as including thin, elongated, protruding structures such as but not limited to filaments, hairs, needles and fibers. The "filament-like" protrusions are characterized by a length to width ratio between about 2:1 and 20:1, typically between about 3:1 and 10:1, wherein the width and length refer to those portions of the protrusions which are visible from the particle surface. The average length of the "filament-like" protrusions is typically between 0.3 to 1 micron and the average width is typically between 0.1 to 0.3 micron. These dimensions are measurable at a magnification of about 40,000 times actual size. The "filament-like" protrusions result in high surface area of the MnO_2 particle. The MnO_2

particles of the invention as above described may be referred to in the specification drawings and claims as P-CMD.

Unlike the well known Sedema process as disclosed in U.S patent 2,956,860, the present invention permits the average particle size and density of the MnO_2 product to be altered by regulating the rate of the above reaction (I). This can be accomplished by simply controlling the amount or rate of heat supplied to the reaction. Unlike the Sedema process the present reaction does not require a catalytic MnO_2 substrate for receiving the MnO_2 product. In fact no catalyst is required and the MnO_2 product forms into dense, discrete particles without the need of a substrate material. However, it has been discovered that the reaction mixture can be seeded with almost any nonreactive solid material including metals and such material will act as a substrate for the P-CMD. That is, the MnO_2 reaction product will precipitate directly on the solid material.

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It has been discovered that the above reaction mixture can be seeded with particles of electrolytic manganese dioxide (EMD) and the MnO_2 reaction product will deposit directly on the EMD. This results in a very high density hybrid gamma MnO_2 whose outer surface comprises a P-CMD coating having filament-like protrusions and high surface area, while the overall particle shape and interior structure is that characteristic of EMD. This hybrid form of MnO_2 can advantageously be used as cathode active material in electrochemical cells, particularly alkaline or lithium cells. It is especially attractive for use in lithium cells, since the exposure of the EMD particles to H_2SO_4 during the reaction of the invention, leaches out small amounts of sodium that is trapped within the EMD particles. This r ces the amount of sodium impurity in the P-CMD product, w h is particularly advantageous if it is to be used as

cathode active material in lithium cells. It has also been discovered that the reaction mixture can advantageously be seeded with graphite or carbon black particles. In such case the MnO_2 reaction product will deposit directly onto the surface of these particles to form a hybrid particulate material which may also be used as cathode active material in electrochemical cells.

The above reaction (I) may typically be carried out in a temperature range between about 30 and 100° C, preferably between 70 and 90° C. The reaction (I) is preferably carried out in a temperature range between about 70° C and 80° C when the intended use of the P-CMD is as a cathode active material in an alkaline cell, and between about 80 and 90° C when the intended use is as a cathode active material in a lithium cell. (For end application of the P-CMD in alkaline cells it is preferable to keep the final temperature below 85° C in order to obtain a gamma MnO_2 product with higher running voltage and capacity than EMD.) After the reaction is complete, the MnO_2 precipitate is collected and rinsed with distilled water until it has a pH of 7. It may then be dried at room temperature if its intended use is as a cathode active material in an alkaline cell. Alternatively, it may be dried at elevated temperature for more thorough drying, if its intended use is as cathode active material in a lithium cell. The resulting dry gamma MnO_2 has a high purity and low sodium content of less than about 500 ppm. The dry P-CMD contains at least 95% gamma MnO_2 in particulate form. (No other crystalline forms of MnO_2 have been detected in the dry P-CMD of the invention, but 95% is the limit of resolution of the x-ray diffraction analysis employed for MnO_2.) Every MnO_2 particle made by the process of the invention, when observed between 200 and 2000 times actual size, appears to have filament-like protrusions radiating outwardly from the particle surface and these protrusions appear to be uniformly distributed around the

particle surface. The P-CMD so produced may subsequently be heat treated in conventional manner to convert it to a gamma-beta variety, if desired. This treatment is preferred if the end use of the MnO_2 is as cathode active material in lithium cells. The heat treatment is well known, a suitable heat treatment process being disclosed in U.S. patent 4,921,689.

It has been determined that various properties of the MnO_2 product can be altered and controlled by controlling the rate at which the reaction mixture is heated. In general a denser P-CMD is obtained if the reaction is carried out at a slower rate, e.g., if the reaction temperature is increased at a slower rate. In a slower reaction individual particles of MnO_2 have time to grow to form larger, more compact particles. In a faster reaction, e.g. produced by faster increase of the reaction temperature, the individual particles of the P-CMD do not have sufficient time to grow to form larger particles. Therefore the individual particles are smaller and less compact. They have a fluffier appearance and lower average density than particles obtained from a slower rate of heating.

A sufficiently slow reaction rate to provide a P-CMD product bulk density of about 15 to 32 g/in^3 (0.9 and 2 g/cm^3) SAD (Scott Apparent Density) is obtained if the aqueous reaction mixture of $MnSO_4$ and $Na_2S_2O_8$ is maintained at an initial temperature of about 50° C for about 18 hours and then slowly increased at nearly constant rate for between about 5 and 10 hours until a final temperature of between about 70 to 90° C is obtained. The reaction mix may then be left to stand for about 1 hour at this final reaction temperature, to obtain a maximum yield, typically about 70% of the stoichiometric amount of $MnSO_4$ converted to P-CMD. In this manner battery grade P-CMD can be obtained having densities comparable to or even higher than the density of electrolytic manganese dioxide (EMD) which typically is at a

level of about 25 to 28 g/in^3 (1.5 to 1.7 g/cm^3) SAD (Scott Apparent Density). In general a bulk density of the P-CMD between about 15 and 32 g/in^3 (0.9 and 2 g/cm^3) can be achieved by heating the aqueous solution of $MnSO_4$ and $Na_2S_2O_8$ from an initial temperature between about 40° C and 70° C for a period during reaction at an average rate of less than about 7° C per hour for at least 5 hours, typically between about 1° C per hour and 7° C per hour for at least 5 hours.

A sufficiently fast reaction rate to achieve a P-CMD product bulk density of between about 8 to 15 g/cm^3 (0.5 to 0.9 g/cm^3) (Scott Apparent Density) is obtained if the aqueous reaction mixture of $MnSO_4$ and $Na_2S_2O_8$ is heated at about constant rate from room temperature so that a final temperature of between 70 and 90° C is achieved in about one to two hours. The reaction mixture may be left to stand for about one hour at this final temperature, to obtain a maximum yield, typically about 70% of the stoichiometric amount of manganese in $MnSO_4$ converted to MnO_2. In general a bulk density of the MnO_2 product between about 8 g/in^3 and 15 g/in^3 (0.5 and 0.9 g/cm^3) can be achieved by heating the aqueous solution of $MnSO_4$ and $Na_2S_2O_8$ from an initial temperature between about 30° C and 100° C for a period during reaction at an average rate greater than 7° C per hour for less than about 5 hours, typically between about 7° C and 20° C per hour for less than about 5 hours.

It has been determined that the stoichiometric yield of MnO_2 can be dramatically increased to about 95% by slowly adding a suitable alkaline base slowly to the reaction mixture. As the reaction proceeds the base reacts with the H_2SO_4 as it forms, thereby improving the reaction kinetics and ultimate yield of MnO_2. A preferred base is Li_2CO_3. Alternative bases can be employed to react with the H_2SO_4 to produce the same increase in yield of MnO_2. Such compounds include Na_2CO_3, LiOH, NaOH and MgO.

For ultimate use of the MnO_2 product in lithium cells it would be preferred to add compounds such as Li_2CO_3 and LiOH to the reaction mixture to increase yield. For ultimate use of the MnO_2 product in alkaline cells it would be preferred to add Na_2CO_3 or NaOH to the reaction mixture. If such compounds are added, they should be added slowly to the reaction mixture to prevent the pH of the mixture from abruptly increasing to a pH greater than about 3.

The MnO_2 reaction product of the invention takes the form of discrete particles having a spherical shape and gamma crystalline structure. The particle size of the P-CMD can also be controlled by varying the rate at which the reaction mixture is heated. If the reaction mixture is heated to produce a constant rate of increase in temperature then the MnO_2 particle size distribution will be uniform, that is, there will not be much variance in the diameter of individual MnO_2 particles. If the reaction mixture is slowly heated at constant rate, e.g., of between about 1° C and 7° C for at least 5 hours, the MnO_2 product will take the form of relatively large uniform spherical particles as above mentioned. If the reaction mixture is rapidly heated at a fast constant rate, e.g., between about 7° C per hour and 20° C per hour for less than about 5 hours, the P-CMD product will tend to take the form of relatively small spherical particles. If the reaction mixture is initially heated at a slow constant rate of temperature increase and later at a fast constant rate of temperature increase, the reaction product will contain a distribution of both large and small MnO_2 particles.

The following examples illustrate the method of preparation of battery grade MnO_2 by the the process of the invention. All parts are parts by weight unless specified otherwise.

Example 1:

High density gamma MnO_2 is prepared by the process of the invention as follows:

120 g of $MnSO_4$ H_2O is dissolved in 1800 ml of distilled water. Then, stoichiometric amount of $Na_2S_2O_8$ (169 g) is added to the clear pinkish solution to form a reactant solution. While stirring, the temperature of the solution is raised over a period of about 2 hours from room temperature (20° C) to 50° C and is maintained at a temperature of 50° C overnight (about 18 hrs) while continually stirring. This enhances the nucleation process. The reaction proceeds according to reaction (I) above referenced. The clear pinkish solution slowly turns brown and then eventually turns a black color as more MnO_2 is precipitated. After the 18 hour period the solution is heated from about 50° C to produce a constant rate of temperature increase of about 25° C per hour for about 1 hour to a temperature of about 75° C and is maintained at 75° C for about 3 hours. The solution is then heated at constant rate of about 10° C per hour for about 1 hour to a temperature of 85° C and maintained at 85° C for 1 hour. The solution is again heated at a constant rate 30° C per hour for about 1/2 hour to a temperature of about 100° C and maintained at 100° C for about 1 1/2 hours at which time the run is ended. The pH of the solution at the end of the run is less than 0.5. The solution is then cooled to room temperature (20° C) in about one hour. The solution is filtered and the solid MnO_2 is continually rinsed with distilled water until the filtrate stream has a neutral pH of about 7. The resulting black powder is dried at 100° C to drive off surface water. The overall yield of P-CMD is 41 g or 67% of theoretical yield.

The resulting product is battery grade MnO_2 at least 95% of which is verified by x-ray diffraction to be of the gamma crystalline structure. (No other type MnO_2 crystalline structure was detected, the 95% threshold being the limit of resolution of the x-ray diffraction analysis.) The P-CMD product has a high

bulk density of about 23 g/in^3 (1.4 g/cm^3) SAD (Scott Apparent Density). An electron photomicrograph representative of this MnO_2 product is shown in Figs. 1A and 1B. The uniform spherical structure of the P-CMD particles (e.g. particle 10) is shown in Fig. 1A taken at 199X magnification. The filament-like (e.g. hair-like) protrusions 15 emanating from the surface of each spherical particle are clearly visible in Fig. 1B, which shows an individual particle at 2,030X magnification. By comparison the electron photomicrographs of the commercial battery grade CMD (WSLi) particles are shown in Figs. 5A and 5B, which are taken at 202X and 2060X magnification, respectively. (The WSLi brand of CMD is available from Sedema, a division of Sedacem, S.A., Terte, Belgium.) It is clear from Figs. 5A and 5B that representative particles 70 do not exhibit filament-like protrusions characteristic of the MnO_2 product of the invention (Figs 1A and 1B).

Example 2:

Lower density gamma MnO_2 is prepared by the process of the invention as follows:

The P-CMD is made in a similar manner as described in example 1, except that rate of heating is faster leading to smaller size and less dense particles. Specifically, the same method of preparation and conditions as in example 1 are employed except the reactant solution is heated from 50° C to 100° C at rate of about about 17° C per hour for a period of less than 5 hours, namely about 3 hours. Figures 2A and 2B are electron photomicrographs of the resulting MnO_2 product. The product sample represented in Figs. 2A and 2B had a bulk density of about 8.7 g/in^3 (0.53 g/cm^3) (Scott Apparent Density) and is at least 95% gamma MnO_2.

The filament-like (e.g. hair-like) surface protrusions 20 and 25 of the individual particles may be seen in Figs. 2A and 2B, respectively. The P-CMD particles as described in this example

may be used as cathode active material in electrochemical cells, particularly alkaline and lithium cells. If intended for use in lithium cells the gamma MnO_2 may be heated at a temperature between about 300-400° C, typically for about 6 hours at 350° C or 32 hours at 300° C to convert the gamma MnO_2 to gamma-beta crystalline structure and to evaporate any residual moisture entrapped within the MnO_2 particles.

Example 3:

P-CMD is produced in a manner similar to that described in Example 1 except that Li_2CO_3 is added to the reaction mixture in order to increase the yield of MnO_2. 583 g of $MnSO_4$ H_2O is first dissolved in 8 liter of distilled water in a 12 liter round bottom flask. Then stoichiometric amount of $Na_2S_2O_8$ (822 g) is added to the slightly pinkish solution. The solution is heated at a constant slow rate for 6 hours from room temperature (20° C) to 55 °C. Then 23 g of Li_2CO_3 is then slowly added and the solution is maintained at a temperature of about 55° C for 18 hours while continually mixing. An additional 69 g of Li_2CO_3 is added after the 18 hour period and the solution is heated at a constant rate of about 6° C per hour for about 2.5 hours up to a temperature of 70° C. Another 36 g of Li_2CO_3 is then added and the solution is heated at a constant rate of about 5° C per nour for 2 hours up to a temperature of about 80° C. The solution is then heated at a reduced constant rate of about 3.3° C per hour for 3 more hours up to a temperature of 90° C. The solution temperature is held for about 18 hours and then cooled in about 1 hour to room temperature (20° C). P-CMD is recovered and dried in the manner described in example 1. The yield of MnO_2 is 270 g or 90% of the theoretical yield. At least 95% of the MnO_2 product is verified by x-ray diffraction to be gamma MnO_2. The bulk density of the P-CMD is measured as 20 g/in^3 (1.2 cm^3) (Scott Apparent Density). This P-CMD product can be heat treated as in Example 1 whereupon it becomes particularly

suitable for use as a cathode active material in lithium cells.

Example 4:

This example demonstrates the use of EMD particles as a substrate for the precipitation of MnO_2 made in accordance with the invention.

120 g of $MnSO_4$ H_2O is dissolved in 1.6 liter of distilled water in a 2 liter beaker by stirring. 120 g of $Na_2S_2O_8$ and 20 g of EMD (from Kerr-McGee) are then added to the slightly pinkish clear solution.

The heating regimen is as follows. The whole mixture is fir heated from room temperature (20° C) to 55° C in about 2 hours and held at this temperature for 18 hours while continually mixing. The whole mixture is then heated slowly at constant rate for about 5.5 hours to a temperature of 75° C. Then the whole mixture is heated for another hour at constant rate to a temperature of 100° C. Thereupon the mixture is cooled to room temperature (20° C) in about 1 hour.

The hybrid MnO_2 product is rinsed with distilled water until neutral. Then it is filtered and dried at 100° C to remove surface water. The total yield of hybrid MnO_2 product is 60 g and its bulk density is 24 g/in^3 (1.5 g/cm^3) (Scott Apparent Density). The hybrid MnO_2 product contains about 67 wt% of the deposited gamma MnO_2 and 33 wt% EMD.

The MnO_2 product consists of gamma MnO_2 deposited uniformly over the surface of the individual EMD particles to form a hybrid MnO_2 product. Each particle of the hybrid MnO_2 product retains the overall irregular shape of the EMD particle, but exhibits a surface formed of uniformly distributed filament-like protrusions characteristic of the gamma MnO_2 made in accordance with the process of the invention. Representative electron photomicrographs of the hybrid MnO_2 particles are shown in Figs. 4A and 4B. By way of comparison Figs. 3A and 3B are electron photomicrographs of the EMD particles. These figures clearly

show the irregular shape and smooth surface of each EMD particle. Fig. 4A shows the overall shape of each hybrid particle, e.g., particle 60 (at a magnification of 450 times actual), as resembling the shape of the EMD particles, e.g. particle 50 (Fig 3A). However, as may be seen from Fig. 4B, the surface features of each hybrid MnO_2 particle exhibit filament-like protrusions, e.g. protrusions 65, emanating from and uniformly covering the surface of each hybrid particle. This is the result of the deposition of the gamma MnO_2 of the present process onto the EMD particles. An advantage of this hybrid is that it has higher surface area than EMD, but yet also has high bulk density. It is also cheaper to manufacture than an equivalent weight of gamma MnO_2 produced by the process of the invention. The hybrid MnO_2 so produced can be used as cathode active material in electrochemical cells. If heat treated before application, e.g. as in Example 1, it can be employed as cathode active material in lithium cells.

Example 5:

This example demonstrates the preparation of high density P-CMD specifically for use as cathode active material in alkaline cells.

583 g of $MnSO_4$ H_2O are dissolved in 8000 ml of distilled water contained in a 12 liter round bottom flask. Then, stoichiometric amount of $Na_2S_2O_8$ (822 g) is added to the clear pinkish solution. The solution is heated from room temperature (20° C) to 50° C in about 2 hours. The solution is then slowly heated from 50° C to 65° C over a period of eight hours and maintained at a temperature of 65° C for 18 hours while continually stirring. The reaction proceeds according to reaction (I) above referenced. The clear pinkish solution slowly turns to a brown and then eventually black color as more MnO_2 is deposited. Following the 18 hour period the solution is then finally heated slowly at about a constant rate from 65° C

to 80° C over a period of eight hours. The solution is cooled to room temperature (20° C) in about 1 hour. The gamma MnO_2 product is recovered by filtering the final solution and continually rinsing with distilled water until the filtrate has a neutral pH of about 7. The resulting black powder is dried as in the preceeding examples to drive off surface water. The resulting product is battery grade MnO_2 which is verified by x-ray diffraction to be of the gamma crystalline structure. The MnO_2 product has a high bulk density of about 28 g/in^3 (1.7 g/cm^3) SAD (Scott Apparent Density). (For usage in an alkaline cell, the MnO_2 product of the invention preferably should exhibit a high SAD, preferably of at least 25 g/in^3 (1.5 g/cm^3) which in turn has been found to result in a high load voltage and capacity.)

Performance Tests:

Example 6:

The P-CMD product of the invention (P-CMD) is evaluated for its electrochemical performance in an AA cell. The performace of the P-CMD as cathode active material in an alkaline AA cell is shown in figure 6A and compared to conventional EMD cathode active material (from Kerr-McGee Corp.) for the same type cell. It is clear that P-CMD exhibits a slightly higher running voltage and a greater capacity (amp-hrs) than obtainable for the same cell using EMD as cathode material. The P-CMD product is believed to be the first CMD that exhibits better performance in alkaline cells than EMD.

Example 7:

P-CMD is evaluated for its performance in a flooded alkaline cell. This cell utilizes conventional zinc anode and KOH electrolyte and paper separator as employed in commercial alkaline cells. The flooded cell is in the shape of a disk of same diameter as that of a Duracell AA cell. The flooded cell is cathode limited, thus excess electrolyte (1.5 g) and excess zinc (5.6 g) are used in order to evaluate the intrinsic

performance of the MnO_2 product (0.17 g) as cathode active material. The flooded cell is fabricated by first pouring a mixture of MnO_2 powder, graphite and KOH (60 wt% MnO_2, 34.5 wt% graphite and 5.5 wt% KOH) into the bottom of an empty AA size nickel coated stainless steel can which is open at one end and closed at the other. The MnO_2 powder is then compacted into a disk-like shape. A paper separator is then placed on top of the MnO_2 disk. The separator is then filled with the KOH electrolyte and the remaining volume of the can then filled with a zinc slurry. The open end of the can is covered with a stainless steel cap. The cap is in electrical contact with the zinc slurry through a nail penetrating from the cap into the slurry.

Two flooded cells are made as above described, but with one containing P-CMD as cathode material and the other containing conventional battery grade EMD (from Kerr-McGee Co.) as cathode material. The performance of the two cells are compared at a current drain rate of 0.3 milli-amp/cm^2 and the results shown in Figure 6B. It may be seen from the voltage profiles reported in Figure 6B that the performance of the flooded alkaline cell utilizing P-CMD is superior to that employing the EMD.

Example 8:

The P-CMD product obtained by the process described in example 3 is heated at about 350° C for about six hours to convert the gamma MnO_2 to a gamma-beta phase.

A coin shaped cell is fabricated utilizing a cathode active material prepared by mixing MnO_2, graphite and polytetrafluoroethylene binder in a weight ratio of 6:3:1. The cathode mixture is compacted by press molding it onto a stainless steel mesh and spot welding it onto a steel case which forms the positive electrode. The positive electrode containing the cathode material is immersed in a conventional lithium salt electrolyte composed of lithium hexafluorophosphate ($LiPF_6$) dissolved in propylene carbonate and dimethoxyethane organic

solvents. Other conventional lithium salt electrolytes such as lithium perchlorate and organic solvents such as propylene carbonate, ethylene carbonate, dimethoxyethane and mixtures thereof can also be used. Excess amount of lithium is employed for the negative electrode. The negative electrode is formed by press molding a lithium foil onto a stainless steel mesh which in turn is spot welded to a steel case. A separator composed of a non-woven cloth is applied over the lithium foil. The positive electrode is assembled over the negative electrode with the separator therebetween. The assembly is performed in an argon filled dry chamber. The entire assembly is filled with the liquid electrolyte and then sealed by crimping the edge of the cell.

Two lithium coin-shaped cells made in the above manner are discharged down to 1.2 volts with current drain rates of 0.17 and 1 milliamp/cm^2, respectively. The resulting voltage profiles for these cells using P-CMD are shown in figures 7A and 7B for drain rates at 0.17 and 1 milliamp/cm^2, respectively. Each figure also shows comparative voltage profiles obtained for a like cell at same current drain rates, but instead using conventional EMD cathode active material (from Kerr-McGee Corp.) which is heat treated and press molded for use in the lithium cell. As may be seen from the figures, P-CMD exhibits a greater capacity (milliamp-hr/g) than the EMD. The capacity improvement of the P-CMD over that of EMD at current drain rates of 0.17 and 1 milliamp/cm^2 are about 20% and 28%, respectively. The P-CMD, thus, shows performance improvement over EMD in lithium cells, particularly at the higher current rates.

Example 9:

The same tests are performed as in example 8 using the coin-shaped lithium cells assembled, as above described, except that the performance of the P-CMD is compared to that of CMD. The

CMD chosen is a commercially available CMD from Sedema intended for specific use in lithium cells.

Two coin-shaped lithium cells are prepared as in example 8 but with one cell containing Sedema CMD and the other containing the P-CMD as cathode active material. The voltage profiles for these two cells are given at current drain rates of 0.17 and 1.0 milliamp/cm^2 as illustrated in figures 8A and 8B, respectively. As can be seen from these figures, the P-CMD has significantly greater capacity (milliamp-hr/g) than the Sedema CMD at the current drain rates tested.

Although the present invention has been described with reference to specific embodiments, it should be recognized that variations are possible within the scope of the invention. Therefore, the invention is not intended to be limited to specific embodiments, but rather is defined by the claims and equivalents thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for manufacture of gamma manganese dioxide comprising the steps of:

a) reacting $MnSO_4$ and $Na_2S_2O_8$ in a solution to produce a reaction product mixture comprising a precipitate of gamma MnO_2 comprised of particles characterised by filament-like protrusions radiating outwardly from the surface of said particles;

b) removing the gamma MnO_2 precipitate from said reaction product mixture; and

c) drying said precipitate.

2. The process of claim 1 wherein the filament-like protrusions are visible at a magnification between about 200 and 2,000 times actual size.

3. The process of claim 1 or 2 wherein the solution is characterised by an aqueous solution and said aqueous solution during step a) is heated to a temperature between about 30° C and 100° C.

4. The process of claim 3 and further characterised by bringing the temperature of said aqueous solution to between 40 and 70° C and then raising the temperature thereof during a period of at least 5 hours at an average rate of less than 7° C per hour, whereby the bulk density of the resulting gamma MnO_2 will be between 15 and 32 g/in^3 (0.9 and 2 g/cm^3).

5. The process of claim 3 and further characterised by bringing the temperature of said aqueous solution to between 30 and 100° C and then raising the temperature thereof during a period of less than 5 hours at an average rate of greater than 7° C per hour, whereby the bulk density of the resulting gamma MnO_2 will be between 8 and 15 g/in^3 (0.5 and 0.9 g/cm^3).

6. The process of any one of claims 1 to 5 further comprising adding a compound reactive with H_2SO_4 to said solution during or prior to step a) to increase the yield of MnO_2, wherein said compound is selected from the group consisting of Li_2CO_3, Na_2CO_3, LiOH, NaOH and MgO.

7. The process of any one of claims 1 to 6 further comprising adding carbon particles to said solution during or prior to step a), wherein the carbon particles are selected from the group consisting of graphite and carbon black and wherein the MnO_2 precipitate deposits on the surface of the carbon particles.

8. The process of anyone of claims 1 to 7 further comprising adding electrolytic MnO_2 (EMD) particles to said solution during or prior to step a), wherein the MnO_2 precipitate deposits on the surface of the EMD particles.

9. A hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of electrolytic manganese dioxide (EMD), wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

10. A hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of carbon material selected from the group consisting of graphite and carbon black, wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

11. A hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of another material wherein said gamma MnO_2 material has filament-like protrusions

radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 2,000 times actual size.

12. An electrochemical cell having MnO_2 cathode active material in said cell, characterised in that at least 95% of said MnO_2 material comprises gamma MnO_2 particles wherein said gamma MnO_2 particles have filament-like protrusions radiating outwardly from the surface of said particles, said filament-like protrusions being visible at a magnification of between 200 and 2,000 times actual size.

13. An electrochemical cell having MnO_2 cathode active material in said cell, characterised by said electrochemical cell having an anode comprising lithium, and further characterised by said MnO_2 material comprising gamma MnO_2 particles having filament-like protrusions radiating outwardly from the surface of said particles, said filament-like protrusions being visible at a magnification of between about 200 and 2,000 times actual size.

14. The electrochemical cell of claim 13 wherein the gamma MnO_2 particles comprise at least 95% of said MnO_2 material.

15 The electrochemical cell of claim 13 or 14 characterised by the filament-like protrusions being substantially uniformly distributed over the surface of said particles and the filament-like protrusions having a length to width ratio between about 2:1 and 20:1.

16. A hybrid MnO_2 material comprising gamma MnO_2 deposited on the surface of electrolytic manganese dioxide (EMD), wherein said gamma MnO_2 material has filament-like protrusions radiating outwardly from its surface, said protrusions being visible at a magnification between about 200 and 9,850 times actual size.

17. A process for the manufacture of gamma manganese dioxide, substantially as herein described with reference to any one of the Examples or any one of Figs. 1A, 1B, 2A, 2B, 4A, 4B, 5A, 5B, 6A, 6B, 7A, 7B, 8A and 8B but excluding any comparative examples therein.

18. A hybrid MnO_2 material, substantially as herein described with reference to any one of the Examples or any one of Figs. 1A, 1B, 2A, 2B, 4A, 4B, 5A, 5B, 6A, 6B, 7A, 7B, 8A or 8B but excluding any comparative examples therein.

DATED this 1st day of November, 1995

DURACELL INC

Attorney: RUTH M. CLARKSON
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

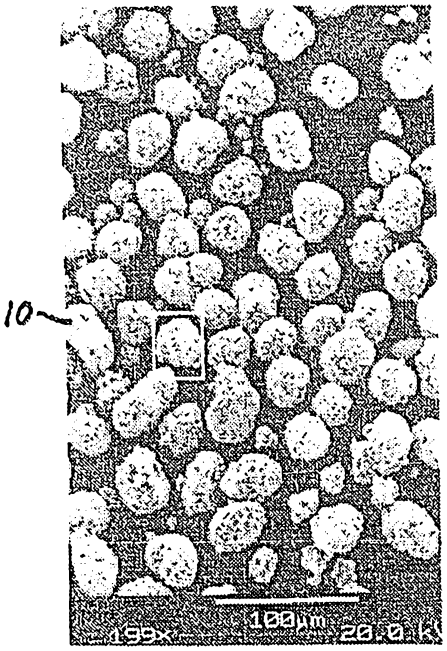


FIG. 1A

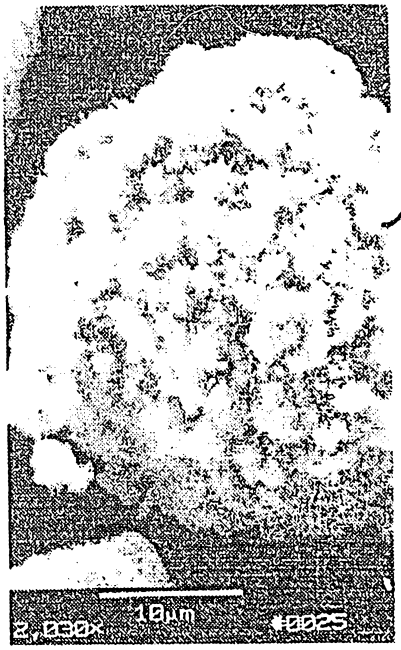


FIG. 1B

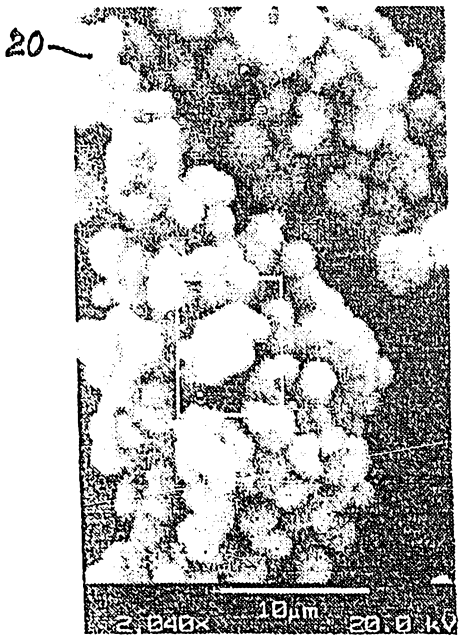


FIG. 2A

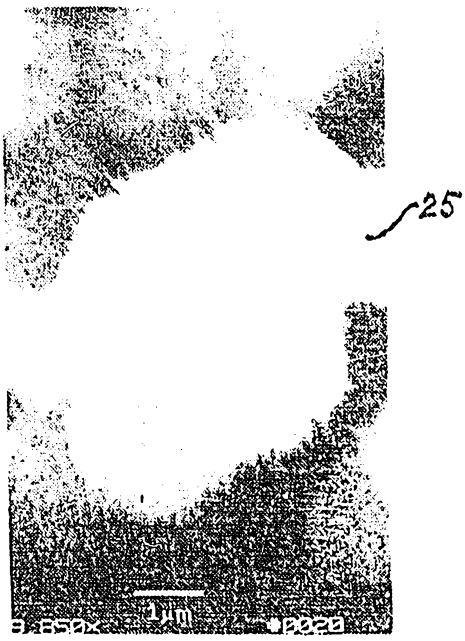


FIG. 2B

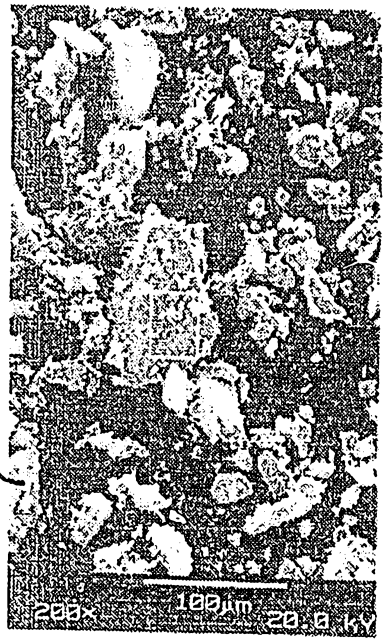


FIG.3A

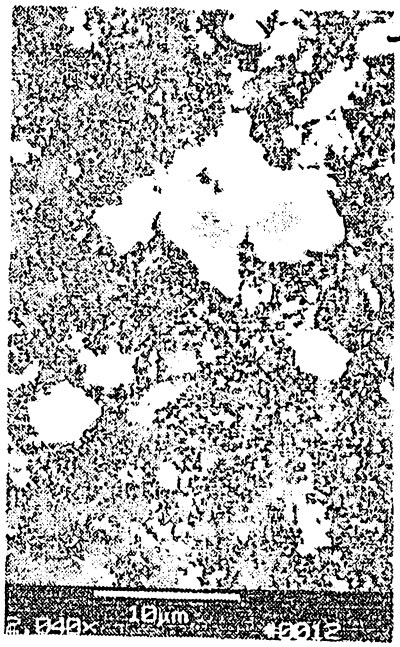


FIG.3B

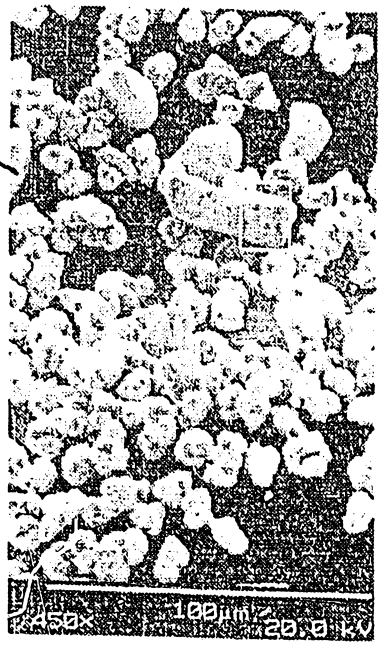


FIG.4A

FIG.4B

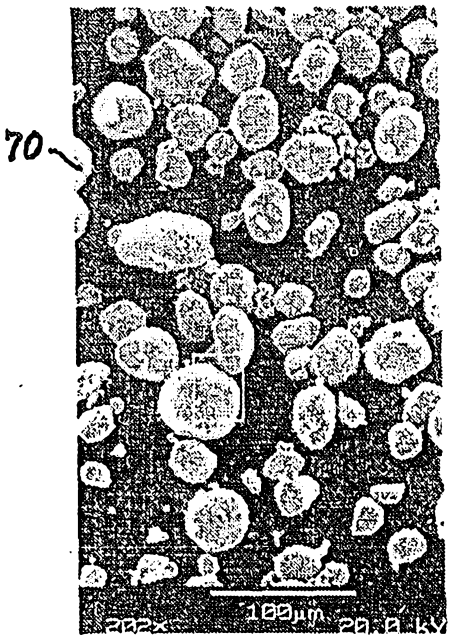


FIG. 5A

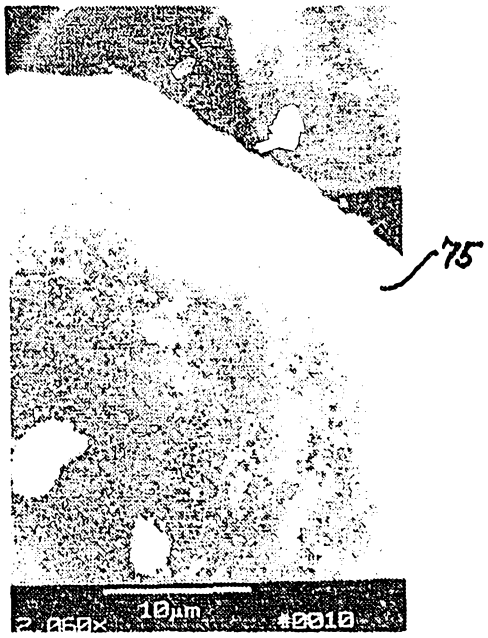


FIG. 5B

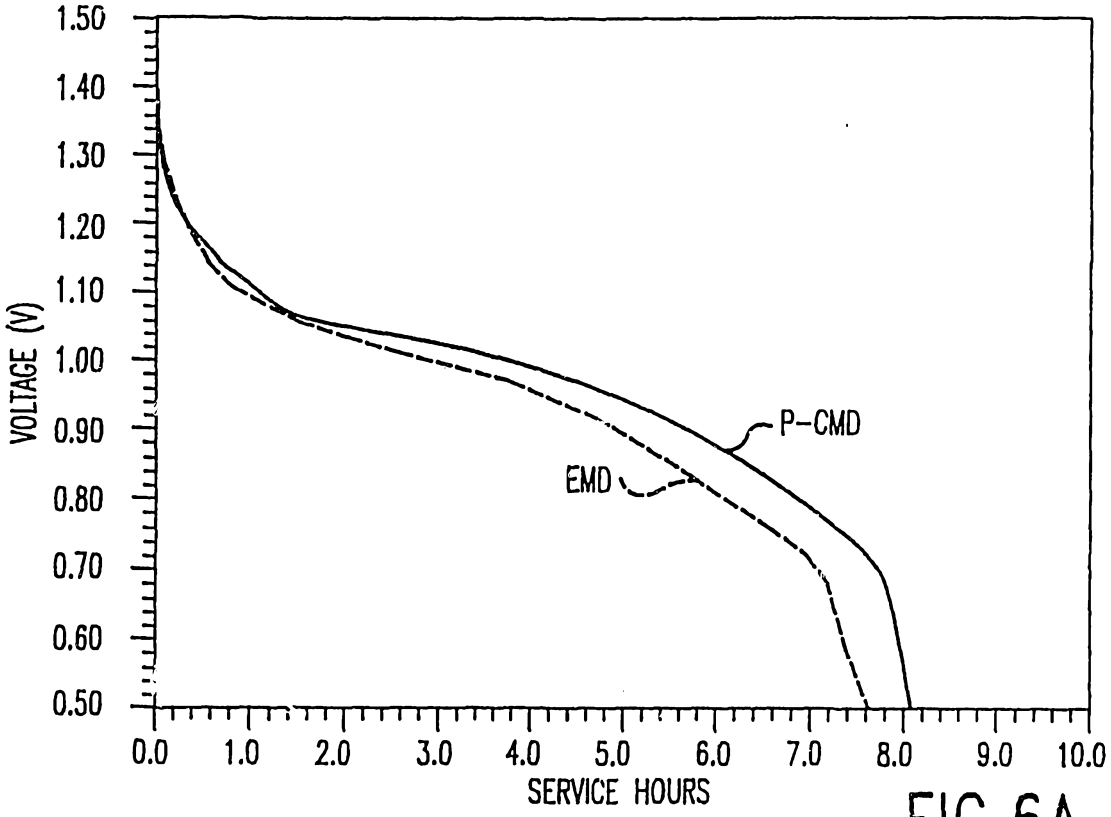

1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
VOLTAGE (V)
P-CMD
EMD
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
SERVICE HOURS

FIG.6A

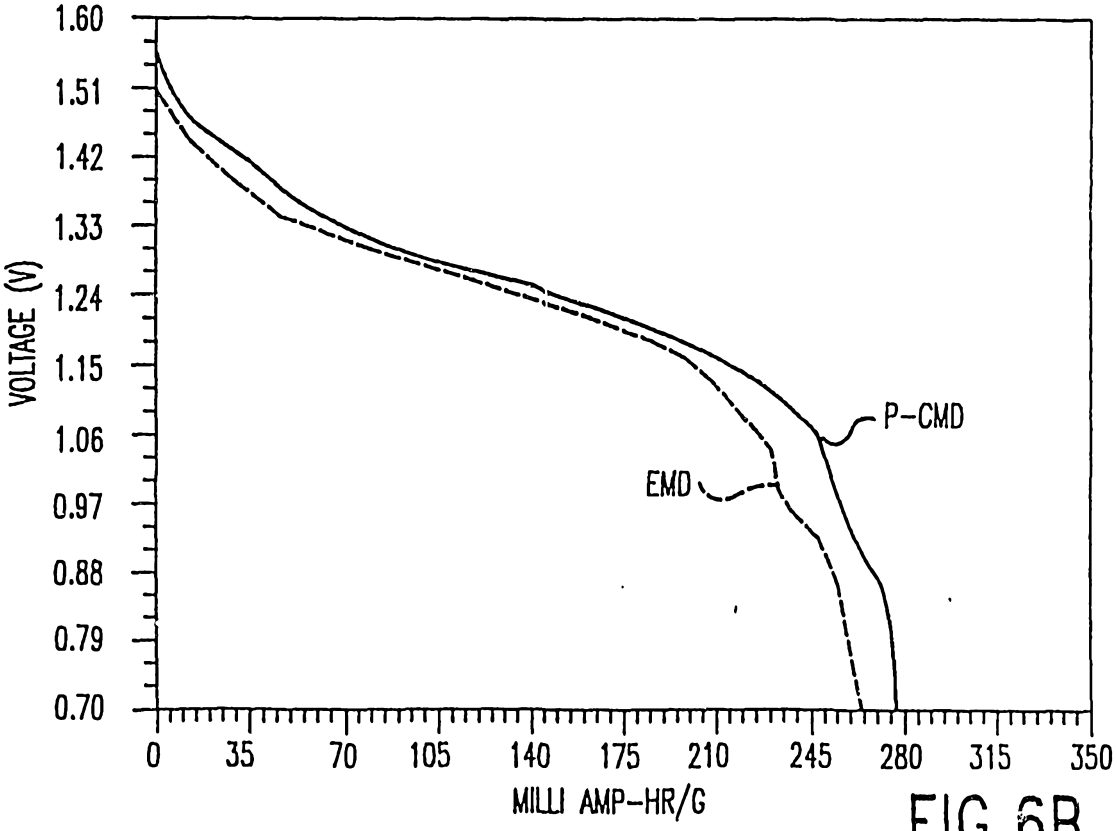
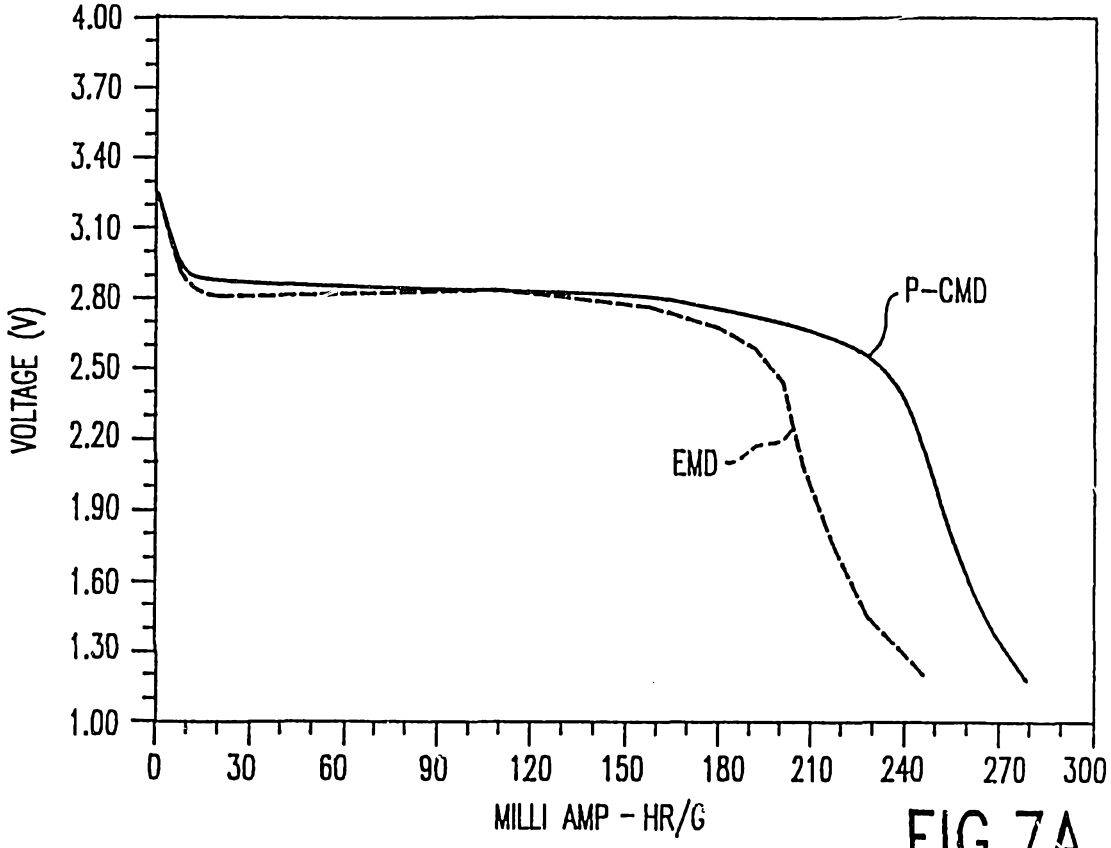

1.60
1.51
1.42
1.33
1.24
1.15
1.06
0.97
0.88
0.79
0.70
VOLTAGE (V)
P-CMD
EMD
0
35
70
105
140
175
210
245
280
315
350
MILLI AMP-HR/G

FIG.6B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3.70
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3.10
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1.30
1.00
VOLTAGE (V)
P-CMD
EMD
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30
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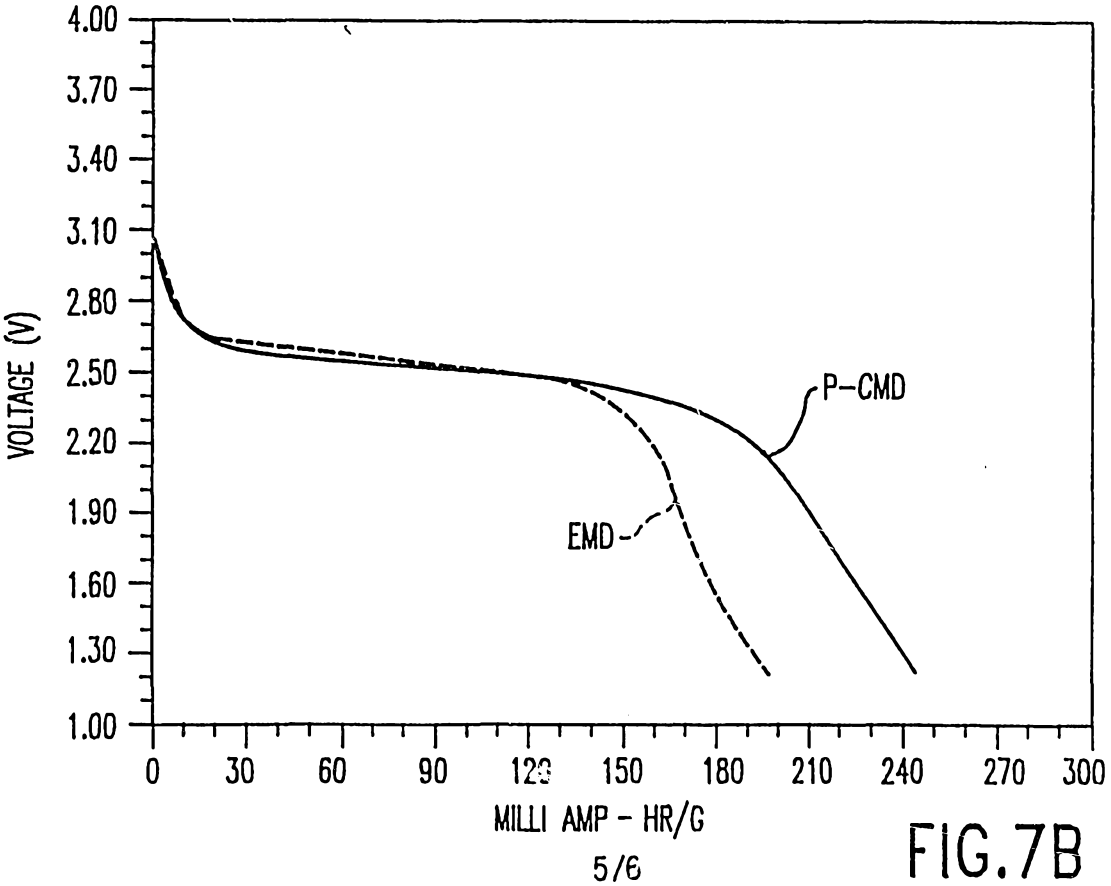
90
120
150
180
210
240
270
300
MILLI AMP - HR/G

FIG.7A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1.00
VOLTAGE (V)
P-CMD
EMD
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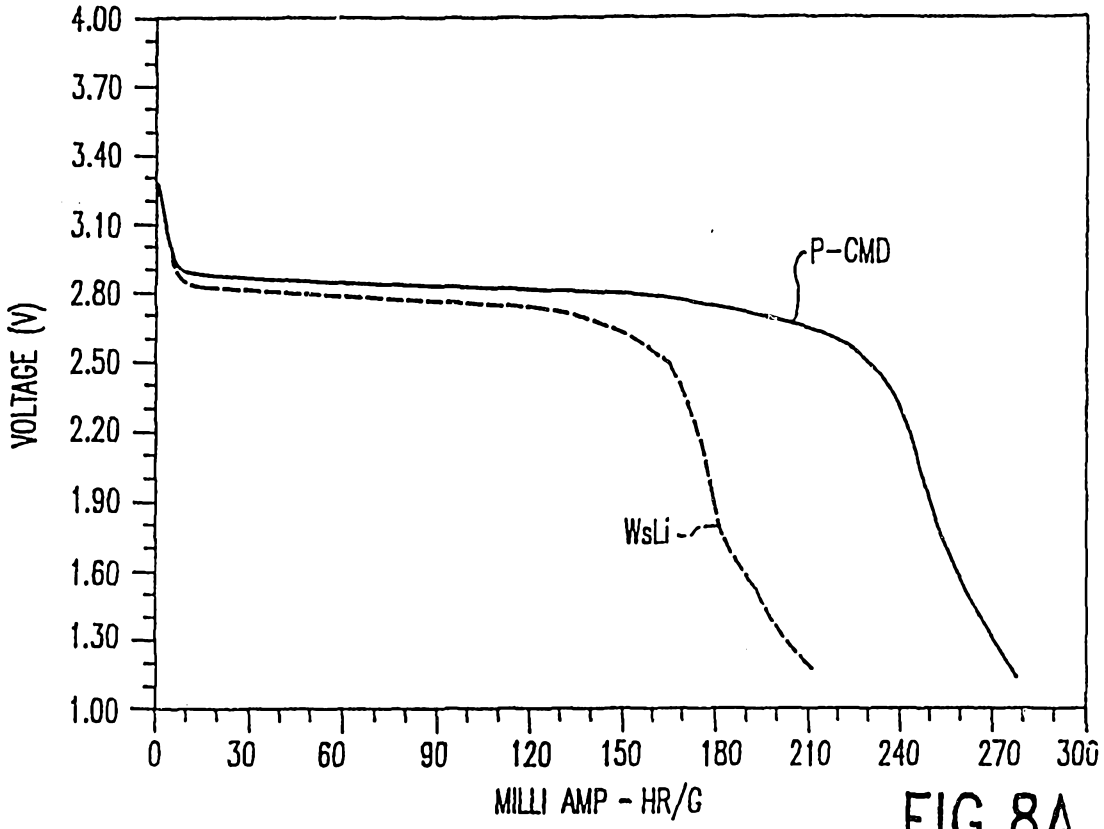
MILLI AMP - HR/G

FIG.7B


4.00
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1.60
1.30
1.00
VOLTAGE (V)
P-CMD
WsLi
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30
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90
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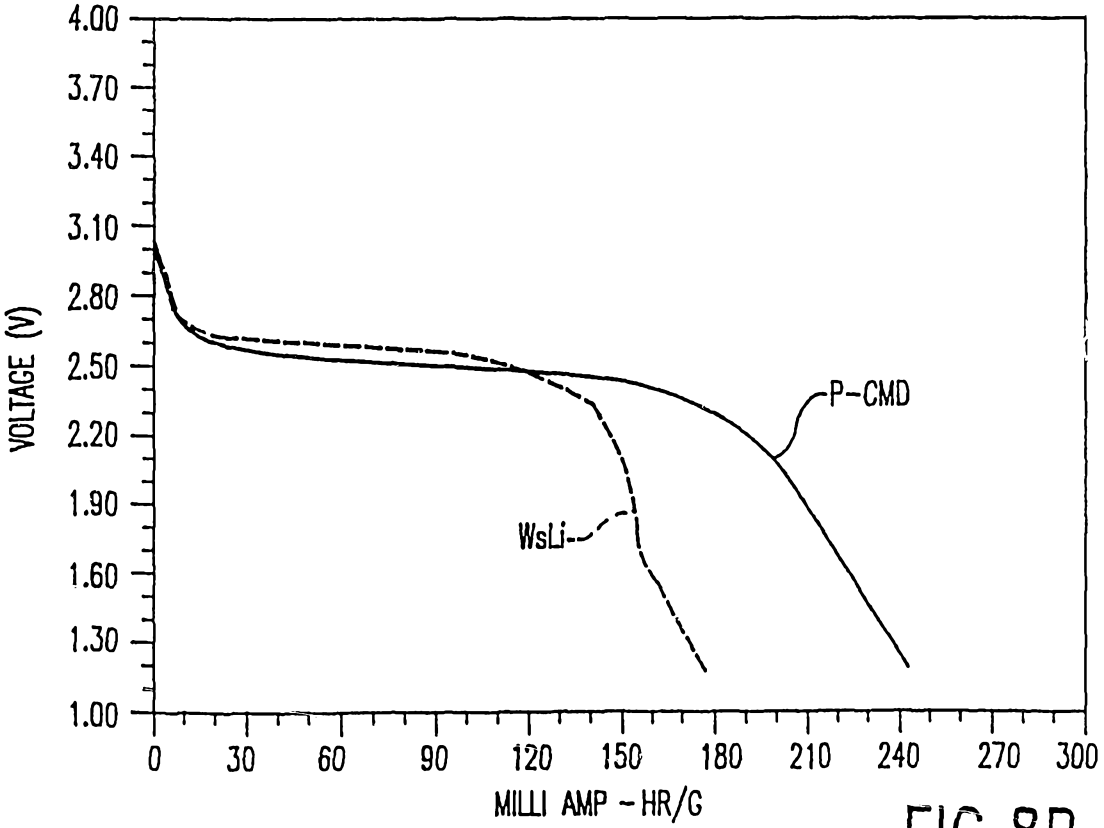
MILLI AMP - HR/G

FIG.8A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2.20
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1.30
1.00
VOLTAGE (V)
P-CMD
WsLi
0
30
60
90
120
150
180
210
240
270
300
MILLI AMP - HR/G

FIG.8B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07333

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01G 45/02
US CL :423/50,605;429/224
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/50, 605; 429/224

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

S-Battery and Cathode and reacting and manganese sulfate and mixture and sodium peroxodisulfate and solution and precipitate.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A 2,956,860 (Welsh) 18 October 1960	1-16
A	US,A 4,277,360 (Mellors et al) 07 July 1981	1-16
A	US,A 4,959,282 (Dahn et al) 25 September 1990	1-16
A	US,A 5,069,988 (Tomantschger et al) 03 December 1991	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
20 OCTOBER 1993	12 NOV 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer for THOMPSON, W.J.
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-3818

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