

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) MANGANESE DIOXIDE FOR USE AS A CATHODE DEPOLARIZER AND A METHOD FOR PRODUCING SAID MANGANESE DIOXIDE



(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD., a corporation organized under the laws of Japan, of 1006, Oaza Kadoma, Kadoma-shi, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to manganese dioxide for use as a cathode depolarizer and to a method for producing such manganese dioxide.

Heretofore, electrolytic manganese dioxide has been produced by anodic oxidation using as electrolyte a manganese sulfate solution obtained by calcining rhodochrosite or natural ore and lixiviating and purifying the calcination product with sulfuric acid. The manganese dioxide obtained according to the said process is a powdery polycrystal of γ - MnO_2 and contains about 89 to 91% of effective oxygen.

Among the conventional manganese dioxides, β - MnO_2 has a high content of effective oxygen. This manganese dioxide, however, is not active as a depolarizer for cells. Further, the electrolytic manganese dioxide obtained according to the conventional process requires, at the time of production, a quantity of electricity of 2 Faradays per mole of manganese dioxide and, when used as a depolarizer for cells, 1 Faraday per mole of manganese dioxide, and the discharge utilization efficiency thereof is 35 to 65% when the quantity of electricity is 1 Faraday, though said ratio varies depending on the discharge rate. This is considered ascribable to the fact that the conventional electrolytic manganese dioxide is a powdery polycrystal, so that the crystal particles thereof are high in resistance

at the crystal interface. The discharge reaction of manganese dioxide is represented by the equation



This equation shows that the discharge is effected by solid phase diffusion of hydrogen ions. It is therefore considered that the higher the single crystallinity of the manganese dioxide, the quicker proceeds the reaction to make the utilization ratio higher.

Recently, the uses of dry cells have been broadened, and the development of high power cells usable for many purposes have been required. However, to increase the discharge capacity of cells by increasing the amount of depolarizing mixture is difficult since the cells are finite in volume and, in order to make the cells higher in capacity, it is necessary to develop a manganese dioxide which is higher in activity and greater in utilization efficiency.

A process for producing manganese dioxide having a new orientation has been proposed in which a manganese chloride electrolyte is used. This process is described and claimed in our specification No. 1,214,654. It has now been found that certain conditions for carrying out the process of the aforementioned specification lead to manganese dioxides which are particularly advantageous as cathode depolarizers. These manganese dioxides have a novel crystal structure, a high effective oxygen content, and a good discharge utilization efficiency. When they are used in cells, improved intermittent discharge characteristics are obtained.

According to a first aspect of the invention, there is provided a process for producing manganese dioxide by electrolytic deposition on

the anode of an electrolytic bath containing an electrolyte having a hydrochloric acid concentration of from 0.01 to 1.0 mol/l., a manganese chloride concentration of from 0.2 to 6.0 mol/l., and a temperature of 70° to 99°C, wherein a current density of 0.3 to 5.0 A/dm² is employed, the apparent current efficiency, as hereafter defined, being from 60 to 102%.

According to a second aspect of the invention, there is provided manganese dioxide having a) an X-ray diffraction pattern in which there is a peak of sharp intensity at $2\theta=28^\circ$ indicating an index of plane (110) of ramsdellite, b) an atomic ratio of oxygen to manganese of from 1.970 to 1.990 and c) 94 to 98.5% of effective oxygen.

According to a third aspect of the invention, there is provided a mixture of manganese dioxide as defined in the preceding paragraph and manganese dioxide having an orientated fibrous crystal structure, an atomic ratio of

oxygen to manganese of from 1.950 to 1.970, and from 90 to 94% of effective oxygen.

The invention also resides in cells using manganese dioxide as defined in either of the preceding paragraphs as a depolarizer.

Cells which use manganese dioxide as a cathode depolarizer include the Leclanché cell and primary and rechargeable cells which use caustic alkali as an electrolyte and zinc as an anode.

The manganese dioxides obtained according to the present invention are of the γ -form, but the physicochemical and electrochemical properties thereof are markedly different from those of γ -MnO₂ obtained by conventional processes. For convenience, therefore, they are referred to as γ_L -MnO₂ and γ_T -MnO₂, hereinafter. Table 1 shows a comparison in principal properties between the manganese dioxides according to the present invention and the conventional γ -MnO₂.

TABLE 1

Crystal form \ Properties	Effective oxygen (%)	Value of x of MnO _x	Characteristics
γ -MnO ₂	88 — 91.5	1.940 — 1.957	Powdery polycrystal.
γ_L -MnO ₂	90 — 94	1.950 — 1.970	Directional, similar in structure to fibres, and high in activity. Containing some amount of chlorine
γ_T -MnO ₂	94 — 98.5	1.970 — 1.990	Directional, and high in oxidation degree and utilization efficiency. Containing some amount of chlorine.

The process of the present invention is explained below.

The electrolysis conditions employed in the present invention are as follows:

Hydrochloric acid concentration	0.01 to 1.0 mole/l.	(I)	(1)
Manganese chloride concentration	0.2 to 6.0 mole/l.	(II)	
Bath temperature	70° to 99°C	(III)	
Current density	0.3 to 5.0 A/dm ²	(IV)	
Apparent current efficiency	60 to 102%	(V)	

By "apparent current efficiency" is meant

$\frac{B}{A} \times 100$ where A is the theoretical amount

of MnO₂ electrodeposited calculated from the electrolytic current in accordance with Faraday's law, and B is the amount of MnO₂ actually electrodeposited. In contrast, the true

current efficiency is $\frac{B}{A} \times P \times 100$, where A

and B are as above, and P is the purity of MnO₂ actually electrodeposited.

An apparent current efficiency of 108% corresponds to the true current efficiency of 100%. The apparent current efficiency takes into account the water content and the purities of manganese salt electrolyte and manganese dioxide.

The electrodes used should be resistant to hydrochloric acid. The anode is required to be higher in resistance to hydrochloric acid. The cathode and anode are graphite electrodes, in general. As the anode, platinum-plated titanium may also be used, though this is expensive.

In the above, when the conditions (I) to (IV) are decided, the condition (V) is automatically decided and, when the condition (V) is decided, the conditions (I) to (IV) are decided. By the combination of such conditions, γ_L -MnO₂ and γ_T -MnO₂ are obtained.

Among the above-mentioned conditions, the hydrochloric acid concentration is limited to 0.01 to 1.0 mol/l. for the reasons that it is difficult to restrict the said concentration to less than 0.01 mol/l. and that is is not economical from the industrial standpoint, and that the adoption of a concentration of more than 1.0 mol/l. is not desirable in view of the corrosion resistance of electrolytic apparatuses and equipments, though electrolysis is possible at said concentration.

If the manganese chloride (MnCl₂) concen-

tration becomes less than 0.2 mole/l., the current efficiency is greatly lowered to narrow the permissible electrolysis conditions. On the other hand, the adoption of a manganese chloride concentration of more than 6.0 mole/l. is not preferable since the utilization efficiency of ores is lowered where the preparation of manganese chloride solution has been effected according to a lixiviation method using an acid.

Even if the bath temperature is below 70°C, electrolysis can sufficiently be effected. However, the adoption of such a low bath temperature is not economical from the industrial standpoint, because the anode overvoltage becomes unnecessarily high, the current density is required to be considerably lowered, and the electrodeposition of manganese dioxide of low bulk density is brought about.

Even when the current density is less than 0.3 A/dm², electrolysis is possible. In this case, however, the productivity per cell becomes too low to bring about economical disadvantages. If the current density becomes more than 5.0A/dm², the consumption of electrodes becomes marked, the current efficiency is greatly lowered and the crystallinity of the resulting manganese dioxides becomes uneven.

The present invention is a process in which the aforesaid γ_L -MnO₂ and γ_T -MnO₂ are electrodeposited simultaneously. The electrolysis conditions adopted in the present invention are decided by the combination of the aforesaid conditions (1). Typical examples thereof are explained below with reference to the accompanying drawings.

Fig. 1 shows the relation between the current density, the bath temperature and the apparent current efficiency when the MnCl₂ concentration is 1.0 mole/l. and the HCl concentration is 0.4 N. The lines A and B are isocurrent efficiency lines showing that the apparent current efficiencies under said con-

ditions are 75% and 102%, respectively. Under the conditions in regions I, II and III which are sectioned by the lines A and B, there are obtained γ_L -MnO₂ or mixtures

of γ_L -MnO₂ and γ_T -MnO₂. Table 2 shows the proportions of γ_T -MnO₂ and γ_L -MnO₂ which are obtained under the conditions in said regions I, II and III.

TABLE 2

Region	I	II	III
γ_T -MnO ₂	More than 20	0 to 20	0
γ_L -MnO ₂	Less than 80	80 to 100	100
Apparent current efficiency	Less than 75	75 to 102	102 to 108

- 10 In Fig. 1, unevenness of the apparent current efficiency is in the range of $\pm 5\%$ in the case of the line A, and in the range of $\pm 2\%$ in the case of the line B. Factors resulting in such unevenness are differences in the kind of materials used in the electrodes, such as graphite and the like, and in the surface of the electrodes.

15 The isocurrent efficiency lines are not always straight lines, such as are shown in the drawing but sometimes are curved or broken lines depending on the conditions. For example, the lines are relatively straight when the acid concentration is in the range of 0.1 to 0.7 but are curved when the acid concentration is more than 0.7 N, and no straight lines can be attained when the manganese concentration is less than 0.5 mol/l. Factors which have the greatest influence on the

gradients of the isocurrent efficiency lines are the manganese concentration and the hydrochloric acid concentration. A general tendency is that the increase of manganese concentration and the decrease of hydrochloric acid concentration increases the gradients of the isocurrent efficiency lines, as shown in Fig. 2, whereas the decrease of manganese concentration and the increase of hydrochloric acid concentration decreases the gradients of the isocurrent efficiency lines. In Fig. 2, the electrolysis conditions are such that the hydrochloric acid concentration is 0.1 N and the manganese chloride concentration is 3.0 mol/l.

Typical examples, which show how the proportions of the resulting γ_L -MnO₂ and γ_T -MnO₂ vary depending on the electrolysis conditions, are set forth in Table 3.

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TABLE 3

MnCl ₂ (mole/l.)	HCl (N)	Bath tem- pera- ture (°C)	Current density (A/dm ²)	Apparent current efficiency (%)	γ _L -MnO ₂ /γ _T -MnO ₂
1.0	0.4	95	0.7	105	100/0
1.0	0.4	90	0.5	104	100/0
1.0	0.4	80	1.0	99	97/3
1.0	0.4	85	2.0	84	86/14
1.0	0.4	95	2.5	90	92/8
1.0	0.4	85	3.0	70	75/25
1.0	0.4	90	4.0	67	70/30
1.0	0.1	95	1.0	108	100/0
1.0	0.8	95	1.0	95	96/4
1.0	0.3	90	2.0	91	93/7
3.0	0.3	90	2.0	105	100/0
0.3	0.3	90	2.0	73	76/24
3.0	0.1	95	4.0	85	88/12
3.0	0.1	95	3.0	104	100/0

The properties of the manganese dioxides obtained under the conditions employed in the present invention are mentioned below.

5 Fig. 3a is a cross-section of manganese dioxide electrodeposited under the conditions in the aforesaid region of Figs. 1 and 2. Fig. 3b shows an enlarged cross-section of IIIb part in Fig. 3a. This manganese dioxide can be
10 easily divided into two layers at the portion 4. Fig. 4 shows X-ray diffraction patterns of this manganese dioxide, wherein the curve (1) is the diffraction pattern in the case where X-rays were applied from the direction 1
15 Fig. 3a, i.e. from the direction vertical to a flat graphite electrode 8; the curve (2) is the diffraction pattern in the case where X-rays were applied from the direction of 2 in Fig. 3a; the curve (3) is the diffraction
20 pattern in the case where X-rays were applied to the manganese dioxide at the portion 3 in Fig. 3 which had been ground to -325 mesh; and the curves (4), (5), (6) and (7) are diffraction patterns in the cases
25 where X-rays were applied to portions 4, 5, 6

and 7 in Figs. 3a and 3b which had been ground to -325 mesh. 6 In Fig. 3b means a mixture of portions 5 and 4.

The manganese dioxide showing the curves (1), (2) and (3) is γ_L-MnO₂, and the manganese dioxide showing the curves (4), (5), (6) and (7) is γ_T-MnO₂.

The curve (8) in Fig. 4 is the diffraction pattern of the conventional electrolytic γ-MnO₂ produced from manganese sulfate solution which had been ground to -325 mesh.

In the γ_T-MnO₂ of the curves (4), (5), (6) and (7), there is observed 1 to 4% of β-MnO₂, but most of the said manganese dioxide is γ_T-MnO₂ of high oxidation degree. In the conventional γ-MnO₂, the X-ray diffraction pattern of index of plane (110) of ramsdellite is low in intensity and broad, whereas in the γ_T-MnO₂, the said diffraction pattern is high in intensity and extremely sharp. γ-MnO₂ of high oxidation degree which shows such X-ray diffraction pattern has been entirely unknown hitherto.

The γ_L - MnO_2 , which has such new properties, electrodeposits with an apparent current efficiency of 102 to 108% by combining the aforesaid electrolysis conditions, and the γ_T - MnO_2 electrodeposits in the γ_L - MnO_2 when the apparent current efficiency is less than 102%. The electrolytic deposition mechanism of the γ_T - MnO_2 is not clear at present. However, when a $MnCl_2$ solution is electrolyzed, the anode overvoltage tends to increase under the conditions where the apparent current efficiency is less than 108%, and chlorine begins to generate at the anode when the apparent current efficiency becomes less than 102%. From this, it is considered that by the said chlorine at the generation stage at the anode or by chlorine gas or chlorine water, γ_L - MnO_2 which has once been electrodeposited is increased in oxidation degree without being injured in crystal form, with the result that such high oxidation degree manganese dioxide as γ_T - MnO_2 is obtained. Although it is considered that such oxidation reaction accompanies side reactions of forming minute amounts of lower oxides, MnO , Mn_2O_3 and Mn_3O_4 cannot be identified from X-ray diffraction patterns. In the γ_T - MnO_2 , however, there are observed unidentifiable X-ray diffraction lines (e.g. 44° , 49° , 56° , and 74°).

Using as a depolarizer each of a manganese dioxide mixture comprising γ_L - MnO_2 and γ_T - MnO_2 , which has been obtained under the conditions in the aforesaid region II, and γ - MnO_2 obtained according to a conventional process, UM-1 and UM-3 type (JIS) dry cells were prepared. These cells were compared with each other in discharge characteristics to obtain the results as shown in Figs. 5 to 7. In the drawings, the curve (a) represents the dry cell containing the mixture of γ_T - MnO_2 and γ_L - MnO_2 , the curve (a')

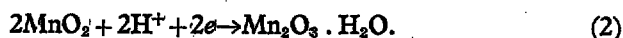
represents the dry cell containing the γ_T - MnO_2 , and the curve (b) represents the dry cell containing the conventional γ - MnO_2 , the curve (c) represents the dry cell containing the γ_L - MnO_2 .

Fig. 5 shows the 10 Ω continuous discharge curves of the UM-3 type dry cells at $20^\circ C$. As is clear from Fig. 5, the cell (a) according to the present invention is high in service voltage on the whole and excellent in efficiency.

Fig. 6 shows the 4 Ω intermittent (30 min./day, 6 days/week) discharge curves of the UM-3 type dry cells at $20^\circ C$, and Fig. 7 shows intermittent discharge curves of the UM-1 type dry cells under the said conditions. As is clear from Figs. 6 and 7, in the case of the cells (a) according to the present invention in which is used manganese dioxide, both the closed circuit voltage (C.C.V.) and the open circuit voltage (O.C.V.) recover the potentials when the closed circuit voltage becomes close to about 1.0 V to show characteristic discharge curves which have not been observed hitherto.

The reason why the cells of the present invention show such excellent discharge characteristics at the time of intermittent discharge has not been clarified yet, but is considered to be as follows:

When the closed circuit voltage is up to about 1.1 V, MnO_2 composed of γ_L - MnO_2 and γ_T - MnO_2 discharges according to a homogeneous reaction represented by the equation (2), like in the case of the conventional γ - MnO_2 , but when the closed circuit voltage becomes near to about 1.1 V, the MnO_2 brings about such a heterogeneous reaction as represented by the equation (3), so that both the open circuit and closed circuit voltages are recovered to greatly prolong the discharge duration time up to 0.85 V.



The reaction of the equation (3) can be substantiated by the fact that as the result of analysis, the amount of Mn^{2+} contained in the depolarizing mixture of the cell after completion of discharge was 4 to 10 times more than in the case of a conventional product, though the value somewhat varies depending on the discharge rate.

When only γ_L - MnO_2 is used as the depolarizer, both the utilization ratio and the duration time decrease by about 5 to 10% as shown by curves (c) in Figs. 5 to 7, and the recovery phenomenon of potential at the time of intermittent discharge is not so marked.

As mentioned above, the cell of the present invention which contains γ_T - MnO_2 as a depolarizer has a high capacity and is excel-

lent especially in intermittent discharge characteristics. This γ_T - MnO_2 , as mentioned before, is characterized in that it apparently has an orientation, is somewhat softer than γ_L - MnO_2 , has deep black color, has a peak indicating an index of plane (110) of ramsdellite in the X-ray diffraction pattern at 28° with a sharp intensity, has dull diffraction lines at 44° , 49° , 56° and 74° of 2θ , contains 94-98.5% of effective oxygen and x in MnO_x is 1.970-1.990.

WHAT WE CLAIM IS:—

1. A process for producing manganese dioxide by electrolytic deposition on the anode of an electrolytic bath containing an electrolyte having a hydrochloric acid concentration

The γ_L - MnO_2 , which has such new properties, electrodeposits with an apparent current efficiency of 102 to 108% by combining the aforesaid electrolysis conditions, and the γ_T - MnO_2 electrodeposits in the γ_L - MnO_2 when the apparent current efficiency is less than 102%. The electrolytic deposition mechanism of the γ_T - MnO_2 is not clear at present. However, when a $MnCl_2$ solution is electrolyzed, the anode overvoltage tends to increase under the conditions where the apparent current efficiency is less than 108%, and chlorine begins to generate at the anode when the apparent current efficiency becomes less than 102%. From this, it is considered that by the said chlorine at the generation stage at the anode or by chlorine gas or chlorine water, γ_L - MnO_2 which has once been electrodeposited is increased in oxidation degree without being injured in crystal form, with the result that such high oxidation degree manganese dioxide as γ_T - MnO_2 is obtained. Although it is considered that such oxidation reaction accompanies side reactions of forming minute amounts of lower oxides, MnO , Mn_2O_3 and Mn_3O_4 cannot be identified from X-ray diffraction patterns. In the γ_T - MnO_2 , however, there are observed unidentifiable X-ray diffraction lines (e.g. 44° , 49° , 56° , and 74°).

Using as a depolarizer each of a manganese dioxide mixture comprising γ_L - MnO_2 and γ_T - MnO_2 which has been obtained under the conditions in the aforesaid region II, and γ - MnO_2 obtained according to a conventional process, UM-1 and UM-3 type (JIS) dry cells were prepared. These cells were compared with each other in discharge characteristics to obtain the results as shown in Figs. 5 to 7. In the drawings, the curve (a) represents the dry cell containing the mixture of γ_T - MnO_2 and γ_L - MnO_2 , the curve (a')

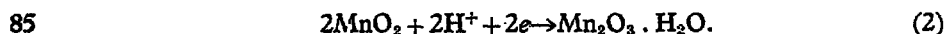
represents the dry cell containing the γ_T - MnO_2 , and the curve (b) represents the dry cell containing the conventional γ - MnO_2 , the curve (c) represents the dry cell containing the γ_L - MnO_2 .

Fig. 5 shows the 10 Ω continuous discharge curves of the UM-3 type dry cells at $20^\circ C$. As is clear from Fig. 5, the cell (a) according to the present invention is high in service voltage on the whole and excellent in efficiency.

Fig. 6 shows the 4 Ω intermittent (30 min./day, 6 days/week) discharge curves of the UM-3 type dry cells at $20^\circ C$, and Fig. 7 shows intermittent discharge curves of the UM-1 type dry cells under the said conditions. As is clear from Figs. 6 and 7, in the case of the cells (a) according to the present invention in which is used manganese dioxide, both the closed circuit voltage (C.C.V.) and the open circuit voltage (O.C.V.) recover the potentials when the closed circuit voltage becomes close to about 1.0 V to show characteristic discharge curves which have not been observed hitherto.

The reason why the cells of the present invention show such excellent discharge characteristics at the time of intermittent discharge has not been clarified yet, but is considered to be as follows:

When the closed circuit voltage is up to about 1.1 V, MnO_2 composed of γ_L - MnO_2 and γ_T - MnO_2 discharges according to a homogeneous reaction represented by the equation (2), like in the case of the conventional γ - MnO_2 , but when the closed circuit voltage becomes near to about 1.1 V, the MnO_2 brings about such a heterogeneous reaction as represented by the equation (3), so that both the open circuit and closed circuit voltages are recovered to greatly prolong the discharge duration time up to 0.85 V.



The reaction of the equation (3) can be substantiated by the fact that as the result of analysis, the amount of Mn^{2+} contained in the depolarizing mixture of the cell after completion of discharge was 4 to 10 times more than in the case of a conventional product, though the value somewhat varies depending on the discharge rate.

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of from 0.01 to 1.0 mol/l., a manganese chloride concentration of from 0.2 to 6.0 mol/l., and a temperature of 70° to 99°C, wherein a current density of 0.3 to 5.0 A/dm² is employed, the apparent current efficiency, as hereinbefore defined, being from 60 to 102%.

2. Manganese dioxide having a) an X-ray diffraction pattern in which there is a peak of sharp intensity at $2\theta=28^\circ$ indicating an index of plane (110) of ramsdellite, b) an atomic ratio of oxygen to manganese of from 1.970 to 1.990 and c) 94 to 98.5% of effective oxygen.

3. A mixture of manganese dioxide as claimed in claim 2 and manganese dioxide having an oriented fibrous crystal structure, an atomic ratio of oxygen to manganese of from 1.950 to 1.970, and from 90 to 94% of effective oxygen.

4. A cell containing manganese dioxide as claimed in claim 2 as a depolarizer.

5. A cell containing a mixture of manganese dioxide as claimed in claim 3 as a depolarizer.

6. A process for producing manganese

dioxide as claimed in claim 1, substantially as hereinbefore described with reference to Figs. 1 and 2 of the accompanying drawings.

7. Manganese dioxide as claimed in claim 2, substantially as hereinbefore described with reference to and as illustrated in Figs. 3a, 3b and 4 of the accompanying drawings.

8. A mixture of manganese dioxides as claimed in claim 3, substantially as hereinbefore described with reference to and as illustrated in Figs. 3a, 3b and 4 of the accompanying drawings.

9. A cell as claimed in claim 4, substantially as hereinbefore described with reference to Figs. 5 to 7 of the accompanying drawings.

10. A cell as claimed in claim 5, substantially as hereinbefore described with reference to Figs. 5 to 7 of the accompanying drawings.

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