

PATENT SPECIFICATION

(11)

1 557 754

13

1 557 754

(21) Application No. 8356/78 (22) Filed 2 Mar 1978

(44) Complete Specification Published 12 Dec 1979

(51) INT CL² H01M 4/50 6/06

(52) Index at Acceptance
H1B 450 606 614 614A

(72) Inventors: FRANK LAURENCE TYE
JOHN EDWARD ANDREW SHAW
ANDRZEJ KRYSZTOF AGOPSOWICZ

(19)



(54) IMPROVEMENTS IN DRY ELECTRIC CELLS

(71) We, EVER READY COMPANY (HOLDINGS) LIMITED, a British Company of Ever Ready House, 1255 High Road, Whetstone, London, N20 0EJ, 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:-

5 The present invention relates to dry electric cells of the Leclanché type.

Cathode mixes for dry cells of the Leclanché type usually contain manganese dioxide, zinc oxide, carbon black, zinc chloride, ammonium chloride and sometimes graphite. The best cell capacities are achieved by using chemically or electrolytically manufactured manganese dioxides. Such manganese dioxides usually have an γ or ρ crystal structure and usually contain about 90% MnO_2 .

10 Naturally occurring manganese dioxides can also be used in cathode mixes for Leclanché cells because they are much cheaper although they give somewhat poorer cell capacities. The naturally occurring ores which are generally preferred for use in cathode mixes for such cells also have the γ or ρ crystal structure and after appropriate refining generally contain up to 82% MnO_2 . Deposits of this type of ore are scarce and in some cases nearing exhaustion.

The most common naturally occurring type of manganese ore is pyrolusite in which the manganese dioxide has a β -crystal structure (β - MnO_2). Although grades of pyrolusite containing up to 92% MnO_2 are available, the pyrolusite ores are generally known to give very poor results when used in cathode mixes for cells of the Leclanché type.

The superior capacity of cells containing γ and ρ crystalline manganese dioxides has been ascribed to the fact that they undergo electrochemical reduction in the homogeneous phase down to a composition represented by $\text{MnO}_{1.5}$.

The overall cell reaction is



In contrast, in cells containing β - MnO_2 , the electrochemical reduction proceeds in the heterogeneous phase. In such cells, the overall cell reaction predominantly is $\text{MnO}_2 + \text{Zn} + 4\text{NH}_4\text{Cl} + \text{Zn Cl}_2 \rightarrow \text{Mn Cl}_2 + 2\text{Zn}(\text{NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O}$ which results in consumption of the electrolyte salts NH_4Cl and ZnCl_2 in the cell. The working life of cells of this type is thus limited by the exhaustion of these electrolyte salts.

30 We have now found that in certain circumstances high capacity cells in which the manganese dioxide in the cathode mix is all or predominantly β - MnO_2 can be obtained.

Accordingly, the present invention provides a dry electric cell of the Leclanché type having a cathode mix which includes (i) MnO_2 having a β -crystal structure, and (ii) either hetaerolite ($\text{ZnO.Mn}_2\text{O}_3$) or materials which enable hetaerolite to be generated *in situ* at a sufficiently rapid rate so that it constitutes the major discharge product even at moderate to high rates of discharge.

In this specification the terms "moderate" and "high" rates of discharge are used to mean discharge rates for Leclanché cells of the order given in the International Electrotechnical Commission's (IEC) publication No. 86-2 (Primary Batteries) for a given size of battery as suitable for application in "portable lighting", "transistor radios" and "pocket calculators".

40 We have found that β - MnO_2 can be utilised efficiently in dry electric cells provided that hetaerolite is the discharge product of the cell. Under typical discharge conditions hetaerolite does not appear to nucleate spontaneously when untreated β - MnO_2 ore is used alone. However, if hetaerolite nuclei are provided by appropriate pretreatment of the

45

14
2

1,557,754

2

β -MnO₂ ore, or by addition of hetaerolite to the cathode mix, or by addition to the cathode mix of a manganese dioxide which produces hetaerolite spontaneously as a result of discharge, the main overall discharge product formed in the cell will be hetaerolite. The result of the pretreatment of the ore or the use of the additives which include or generate hetaerolite at a sufficiently rapid rate is that the β -MnO₂ is reduced with high efficiency in the cell. Furthermore, when the main discharge product is hetaerolite, little or no ammonium chloride or zinc chloride are consumed when the cell is in operation. Thus less ammonium chloride and more manganese dioxide can therefore be included in the cell to improve its capacity.

The β -MnO₂ is preferably obtained as a naturally-occurring ore such as pyrolusite. Preferably 40 - 100% of the total weight of the MnO₂ in the cathode mix of the cell of the present invention is β -MnO₂.

Synthetically prepared hetaerolite is an example of a type of hetaerolite which can be added to the cathode mix as a separate ingredient. An alternative source of hetaerolite is β -MnO₂ containing ore pretreated in the presence of zinc or a compound of zinc so as to produce some hetaerolite phase in the ore.

Alternatively, the hetaerolite phase can be generated *in situ* in the cathode mix by incorporating in the cathode mix materials which enable hetaerolite to be formed at a sufficiently rapid rate so that it constitutes the major discharge product even at moderate to high rates of discharge when the cell is discharged. Examples of such materials are certain types of chemically precipitated manganese dioxides which, in the presence of zinc of a zinc compound, are capable of generating hetaerolite. Manganese dioxide precipitated by the action of bleaching powder on manganous chloride solution and an acid washed precipitated manganese dioxide obtained as a by-product of saccharin manufacture are found to be particularly effective for this purpose. In a preferred embodiment of the cell of the present invention up to 60% by weight of the MnO₂ in the cathode mix is such a chemically precipitated MnO₂.

It has been found that in the cells of the present invention optimum efficiency can be obtained even though an amount of ammonium chloride which is smaller than the amount usually found necessary in corresponding cells containing γ and ρ manganese dioxides is used. Therefore, cathode mixes can contain a greater proportion of manganese dioxides and this results in the cells having excellent capacities.

The invention also provides a battery including one or more cells according to the present invention.

The following Examples illustrate the invention.

Example 1. Pretreatment of β -MnO₂ to produce hetaerolite

A solution was prepared by mixing equal volumes of aqueous zinc chloride solution (S.G. 1.45) and water. The solution was then saturated at 25°C with respect to ammonium chloride and zinc oxide. To 100 ml of this solution were added:

92% grade β -MnO ₂ ore of Moroccan origin.	50g.
Hydrated manganous chloride MnCl ₂ ·4H ₂ O	3.25g
Zinc oxide	3g
Ammonium chloride	4g

The slurry was stirred for 4 days at temperatures in the range 80° - 90°C. The solids were then filtered off, washed and dried. X-Ray diffraction analysis of the resultant treated ore showed, in addition to the phases originally present in the ore, a trace of hetaerolite ZnO·Mn₂O₃.

Two separate cathode mixes were prepared using treated and untreated ore according to the formulation:

Manganese dioxide (treated or untreated)	23.08g
Zinc oxide	0.25g
Ammonium chloride	11.36g
Acetylene black	3.55g
Zinc chloride solution (S.G. 1.45)	7.47g
Water	4.25g

Two paper lined R20 sized cells containing 48.1 g cathode mix per cell were made. Each cell was subjected to a discharge test through a 5 ohm resistance for 30 minutes per day, 7 days per week at 20°C. The discharge curves and the open circuit voltages measured immediately before each discharge cycle are plotted in Figure 1 as curve *a* for untreated ore and curve *b* for treated ore. It can be seen that the cell which had been made with the

untreated ore give a steeply falling discharge curve. Its on load voltage fell below 0.75v. after 8.5 hours total discharge. On the other hand the cell which had been made with treated ore gave a flatter discharge curve and sustained an on load voltage above 0.75v for 21.5 hours of discharge.

5 After discharge the cells were opened, the discharged cathode mixes extracted and subjected to X-ray diffraction analysis. No hetaerolite could be detected in the mix made with untreated ore while a strong diffraction pattern corresponding to hetaerolite was recorded on the mix made with treated ore.

10 *Example 2. Addition of Hetaerolite*

A cell made with 92% β - MnO_2 ore gave a discharge life of 58 hours when subjected by a discharge test through a 40 ohm resistance 4 hours per day, 7 days per week at 20°C to an end point of 0.9v. The discharge curve and open circuit voltage for this cell are shown on Figure 2 as curve c. A similar cell in which a 4: 1 mixture of 92% β - MnO_2 ore and laboratory synthesised hetaerolite was substituted for the manganese dioxide gave 203 hours discharge life on the same discharge test. The discharge curve and open circuit voltage for this cell are shown in Figure 2 as curve d.

20 *Example 3. Addition of Chemically Precipitated Manganese Dioxide*

A cathode mix of the following composition was prepared:

25	92% β - MnO_2 manganese dioxide ore	22.42g	
	Chemically prepared 5 - manganese dioxide (generates hetaerolite on discharge of cell)		25
	Zinc oxide	5.61g	
	Ammonium chloride	0.3g	
30	Acetylene black	5.96g	
	Zinc chloride solution (S.G. 1.45)	3.55g	30
	Water	8.45g	
		4.08g	

35 An R20 cell was made with 48.1g of the above mix. When subjected to a 5 ohm., 30 min. per day, 7 days per week at 20°C discharge test it gave a life of 26.4 hours down to the 0.75v end point. The corresponding discharge curve is shown on Figure 1 as curve e. A calculation showed that the improvement was not due only to the inherent capacity contributed by the chemically precipitated manganese dioxide. A synergistic effect had occurred whereby a high discharge efficiency was obtained from the β - MnO_2 .

40 *Example 4. Addition of Commercial Battery Grade Chemically Prepared Manganese Dioxide*

45 A cathode mix of the following composition was prepared:

45	84 % grade β - MnO_2 manganese ore	14.01g	45
	Synthetic Managanese Dioxide, trade name Faradiser (generates hetaerolite on discharge of cell) (see U.S. Patent No. 2758012)		
50	Zinc oxide	14.01g	50
	Ammonium chloride	0.3 g	
	Acetylene black	5.96g	
55	Zinc chloride solution (as.f. 1.45)	3.55g	
	Water	8.45g	55
		4.08g	

60 A cell containing 48.1g of the above mix gave a life of 24.4 hours when subjected to a discharge test through a 5 ohm. resistance for 30 min per day, 7 days per week, down to a 0.75v endpoint. The discharge curve which was obtained is shown on Figure 1 as curve f. The present invention thus enables one to use sources of manganese dioxide previously considered unsuitable for use in cathode mixes and to achieve greater cell and battery capacities using natural ore than has been possible in the past.

65 WHAT WE CLAIM IS:-



15

3

1,557,754

3

untreated ore give a steeply falling discharge curve. Its on load voltage fell below 0.75v. after 8.5 hours total discharge. On the other hand the cell which had been made with treated ore gave a flatter discharge curve and sustained an on load voltage above 0.75v for 21.5 hours of discharge.

5 After discharge the cells were opened, the discharged cathode mixes extracted and subjected to X-ray diffraction analysis. No hetaerolite could be detected in the mix made with untreated ore while a strong diffraction pattern corresponding to hetaerolite was recorded on the mix made with treated ore. 5

10 *Example 2. Addition of Hetaerolite* 10

A cell made with 92% β -MnO₂ ore gave a discharge life of 58 hours when subjected by a discharge test through a 40 ohm resistance 4 hours per day, 7 days per week at 20°C to an end point of 0.9v. The discharge curve and open circuit voltage for this cell are shown on Figure 2 as curve c. A similar cell in which a 4: 1 mixture of 92% β -MnO₂ ore and laboratory synthesised hetaerolite was substituted for the manganese dioxide gave 203 hours discharge life on the same discharge test. The discharge curve and open circuit voltage for this cell are shown in Figure 2 as curve d. 15

20 *Example 3. Addition of Chemically Precipitated Manganese Dioxide* 20

A cathode mix of the following composition was prepared:

25	92% β -MnO ₂ manganese dioxide ore	22.42g	25
	Chemically prepared 5 - manganese dioxide (generates hetaerolite on discharge of cell)	5.61g	
	Zinc oxide	0.3g	
	Ammonium chloride	5.96g	
30	Acetylene black	3.55g	30
	Zinc chloride solution (S.G. 1.45)	8.45g	
	Water	4.08g	

35 An R20 cell was made with 48.1g of the above mix. When subjected to a 5 ohm., 30 min. per day, 7 days per week at 20°C discharge test it gave a life of 26.4 hours down to the 0.75v end point. The corresponding discharge curve is shown on Figure 1 as curve e. A calculation showed that the improvement was not due only to the inherent capacity contributed by the chemically precipitated manganese dioxide. A synergistic effect had occurred whereby a high discharge efficiency was obtained from the β -MnO₂. 40

Example 4. Addition of Commercial Battery Grade Chemically Prepared Manganese Dioxide

45 A cathode mix of the following composition was prepared: 45

50	84 % grade β -MnO ₂ manganese ore	14.01g	50
	Synthetic Managanese Dioxide, trade name Faradiser (generates hetaerolite on discharge of cell) (see U.S. Patent No. 2758012)	14.01g	
	Zinc oxide	0.3 g	
	Ammonium chloride	5.96g	
	Acetylene black	3.55g	
55	Zinc chloride solution (as.f. 1.45)	8.45g	55
	Water	4.08g	

60 A cell containing 48.1g of the ab. mix gave a life of 24.4 hours when subjected to a discharge test through a 5 ohm. resistance for 30 min per day, 7 days per week, down to a 0.75v endpoint. The discharge curve which was obtained is shown on Figure 1 as curve f. 60

The present invention thus enables one to use sources of manganese dioxide previously considered unsuitable for use in cathode mixes and to achieve greater cell and battery capacities using natural ore than has been possible in the past.

65 WHAT WE CLAIM IS:- 65

16
4



1,557,754

4

1. A dry electric cell of the Leclanché type having a cathode mix which includes (i) MnO_2 having a β -crystal structure, and (ii) either hetaerolite ($\text{ZnO.Mn}_2\text{O}_3$) or materials which enable hetaerolite to be generated *in situ* at a sufficiently rapid rate so that it constitutes the major discharge product even at moderate to high rates of discharge.
2. An electric cell according to Claim 1 in which hetaerolite has been added as a separate ingredient to the cathode mix.
3. An electric cell according to Claim 1 in which the materials which enable hetaerolite to be generated *in situ* are chemically precipitated MnO_2 and zinc or a zinc compound.
4. An electric cell according to Claim 1, wherein the β - MnO_2 is one which has been subjected to a chemical or thermal pre-treatment in the presence of zinc or a compound of zinc so as to produce some hetaerolite therein.
5. An electric cell according to any one of the preceding claims, wherein the β - MnO_2 is obtained from a naturally-occurring ore.
6. An electric cell according to Claim 5, wherein the naturally-occurring ore is pyrolusite.
7. An electric cell according to any one of the preceding claims, wherein up to 60% by weight of the MnO_2 is chemically precipitated manganese dioxide.
8. A dry electric cell according to Claim 1 substantially as described in any one of the foregoing Examples.
9. A battery including one or more cells, each of which cells is as claimed in any one of the preceding claims.

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27 Chancery Lane,
London, WC2A 1NT.

Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1979.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.