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Discharge performance of electrodeposited manganese dioxides in Leclanché cells

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Electrodeposited manganese dioxide is finding increasing use as the cathode in high performance Leclanché cells. In this study a number of commercial and pilot plant materials together with experimental variants were examined in Leclanché R.20 size cells and found to have widely different performances on a simulated motor discharge.

The initial X-ray diffraction diagrams of the manganese dioxides, viewed in order of decreasing discharge performance, show a gradual diminution of the γ phase peak and the emergence of a β phase peak. X-ray diffraction thus provides a means of recognizing a preferred electrodeposited manganese dioxide for the simulated motor discharge.

1. Introduction

Electrodeposited manganese dioxide [1–7] has found widespread use as the cathode in high performance Leclanché cells [8]. Japan, the U.S.A. and West Germany dominate world production with 34,400, 12,600 and 6,000 metric tons per annum respectively [9]. Japanese production has risen from approximately 2,500 tons in 1959 [10] to the present level, which reflects increasing use of electrodeposited manganese dioxide in Leclanché cells.

The manganese dioxide is deposited as a dense coherent plate of 0·6–3·0 cm thickness [8, 11] at a current density of 7–12 mA cm^{-2} [8] from a purified manganous sulphate/sulphuric acid electrolyte at a temperature of about 90°C [8, 11]. The various manufacturers can use different current densities, voltages, deposition times, plate thicknesses, temperatures, electrolyte compositions, prior electrolyte purification, anode material and cell design. There can also be differences in the finishing processes of stripping, washing, drying and grinding. The products from the various manufacturers may not therefore be identical.

The purpose of this paper is to compare the products of the major manufacturers in an R.20 size cell on one high-performance test. A major part of the work is concerned with examining the products and with subsidiary experiments, which have the object of identifying (a) possible reasons for the different performances observed and (b) characteristics by which a preferred product for the discharge conditions used may be recognized.

2. Experimental

2.1. *Materials*

Analyses of the 'as received' electrodeposited manganese dioxides are given in Table 1. Approximately 95% is accounted for in Table 1. In addition all electrodeposited manganese dioxides contain 3–4% of 'combined' water [12]. The remainder is largely derived from the manufacturing process; sulphate [8] from the deposition bath, sodium from a neutralization stage and lead [13] or carbon from the anode.

Analytical determinations were as follows; manganese by potentiometric titration with potassium permanganate [14], available (active)

Table 1. Analyses of electrodeposited manganese dioxides

Code no.	*x in* MnO_x	MnO_x*(%)*	*%*H_2O *lost at 110°C*
1	1·947	93·2	1·95
2	1·931	92·8	3·12
3	1·937	91·7	2·56
4	1·959	92·8	2·30
5	1·959	92·2	2·09
6	1·936	91·8	2·70
7	1·965	92·3	1·92
8	1·963	93·6	2·02
9	1·961	95·4	1·61
10	1·936	91·8	2·58
11	1·981	92·5	3·48
12	1·969	93·7	2·07

oxygen by the oxalate method [15] modified by addition of Fe^{3+} to prevent catalytic decomposition by $Mn^{2(+)}$ [16], hygroscopic moisture by heating at 110°C for three periods of 4 hours with intermediate weighing.

Materials 1 to 6 were obtained from major manufacturers in Japan, U.S.A. and West Germany.

Material 7 was from a pilot plant at The Ever Ready Co. (G.B.) Ltd.

Material 10 was from the Ever Ready pilot plant but deposition time was limited to 3 instead of the normal 14 days used for material 7.

Materials 11 and 12 were selected from normal Ever Ready pilot plant material on the basis of appearance differences which will be described later.

Materials 8 and 9 were material 1 after treatment at 90°C with a solution which contained 1M $MnSO_4$ and 0·2M H_2SO_4 for 50 and 100 hours respectively

2.2. *X-ray diffraction*

X-ray diffraction on the powders was carried out with (i) a Philips PW1010 diffraction generator/PW1050 goniometer connected to a recording unit and using FeKα radiation and a current of 10 mA at a potential of 28 kV, and (ii) a Crystalloblock 30 (Compagnie Generale de Radiologie, France) using Mokα radiation and a current of 10 mA at a potential of 50 kV. Similar features were noted by both although peak definition was better with arrangement (ii). Only results obtained with (ii) are presented here and these are from the Caudebec Laboratory of Compagnie Industrielle Des Piles Electriques.

Peak heights were measured in arbitrary units from the base line and no attempt made to correct for background. For γ and β phases the peaks close to d spacings of 4·0 Å and 3·1 Å were used respectively. Where no definite β peak existed the height was measured at 3·1 Å.

2.3. *Potential*

Each manganese dioxide was equilibrated at 25°C with 1·0 N KCl solution. The potential of the powder was measured with a platinum contact against a saturated calomel electrode using a Vibron electrometer (Electronic Instruments Ltd.) suitably backed off with an accurate D.C. source. The pH of the solution was measured with a Dynacap meter (W. G. Pye and Co. Ltd.) using a combined glass and reference electrode (W. G. Pye and Co. Ltd.). pH was then adjusted by small additions of acid or alkali and the equilibration and measurements repeated.

Potential was plotted against pH, a straight line drawn through the points [17] and the potential at pH 7 taken as characteristic.

2.4. *Microhardness*

The specimen was mounted in cold setting Araldite (Ciba Ltd.) and polished with a succession of silicon carbide papers and diamond pastes. The final polish was with a cloth impregnated with 1μ diamond paste. A GKN microhardness tester was used with a load of 100 g being applied to the specimen for 10 seconds through a square diamond pyramidal indentor. Microhardness was obtained from the average diagonal length of the indentation using standard tables.

2.5. *Cell manufacture*

Each R.20 size cell was made individually. 23·08 g of the 'as received' manganese dioxide was weighed into a 250 ml flask followed by weighed appropriate amounts of zinc oxide, ammonium chloride and acetylene black (P1042, VEB Stickstoffwerke Piesteritz) in that order. The flask was briefly shaken after addition of each component and finally for 10 minutes.

A known amount of zinc chloride solution (42·5% w/w) and then water was added to the flask from a burette so that the liquid fell onto the cathode mixture and not on the side of the flask. The first half of the liquid was added at a constant rate with gentle shaking to give even distribution. The rest was added drop by drop with energetic shaking every three drops until the whole mix consisted of small balls of 2–3 mm diameter.

After a final shaking of 10 minutes the whole of the cathode mix was transferred to an R.20 size zinc can having a suitable paper liner and bottom washer. The transfer was effected in approximately 20% lots with tamping after each. Care was taken to avoid contact between the mix and the zinc. The cell was finished with a centrally placed carbon rod, top washer and bitumen seal.

The importance of this procedure is that each cell was known to contain exactly the same amount of manganese dioxide, zinc chloride, zinc oxide, ammonium chloride and carbon black. There were slight differences in water content to allow cathode mixes of similar consistency to be produced from different manganese dioxides.

Two cells were made with each manganese dioxide.

2.6. *Cell discharge*

Cell discharge was commenced between 1 and 14 days after manufacture. Each cell was placed in a glass tube immersed in a water bath thermostatted at 20±1°C and discharged through 5 ohms for 2 hours every day. Cell voltage was recorded automatically (Speedomax H, Leeds and Northrup) to an endpoint of 1·1 volts. This discharge is considered representative of motor applications.

It is conventional to base discharge life on the time at which the cell first reaches the endpoint voltage. Such a procedure exaggerates differences due to the variable position of the preceding recuperation period relative to the endpoint time. This has been avoided by drawing a smooth curve through the lower voltage points of each discharge period and noting the time at which the smooth curve reaches the endpoint voltage.

The average number of coulombs delivered by the duplicate cells up to this time was obtained from the area under the 'sawtooth' curves and used to calculate the value of x in MnO_x at the endpoint.

Discharge efficiency was calculated on the basis that initial MnO_x to $MnO_{1\cdot5}$ constituted 100% efficiency.

3. Results and discussion

The discharge lives, x in MnO_x at the endpoint

Table 2. Discharge performance data and MnO_2 potentials

Code no.	*Discharge life (h)*	*x in MnO_x at endpoint*	*Discharge efficiency (%)*	*Potential vs. S.C.E. (V)*
1	12·7, 12·5	1·698	55·3	0·767
2	12·4, 12·4	1·690	55·9	0·781
3	13.7, 13·6	1·666	61·8	0·812
4	11·3, 11·3	1·741	47·5	0·755
5	11·4, 11·2	1·730	48·8	0·749
6	7·9, 7·6	1·789	33·7	0·704
7	9·7, 9·5	1·773	40·4	0·762
8	9·1, 8·4	1·803	34·8	0·695
9	6·5, 6·5	1·841	25·7	0·688
10	10·8, (8·6)	1·730	46·6	0·767
11	7·7, 7·4	1·830	30·1	0·758
12	11·9, 11·4	1·748	47·0	0·756

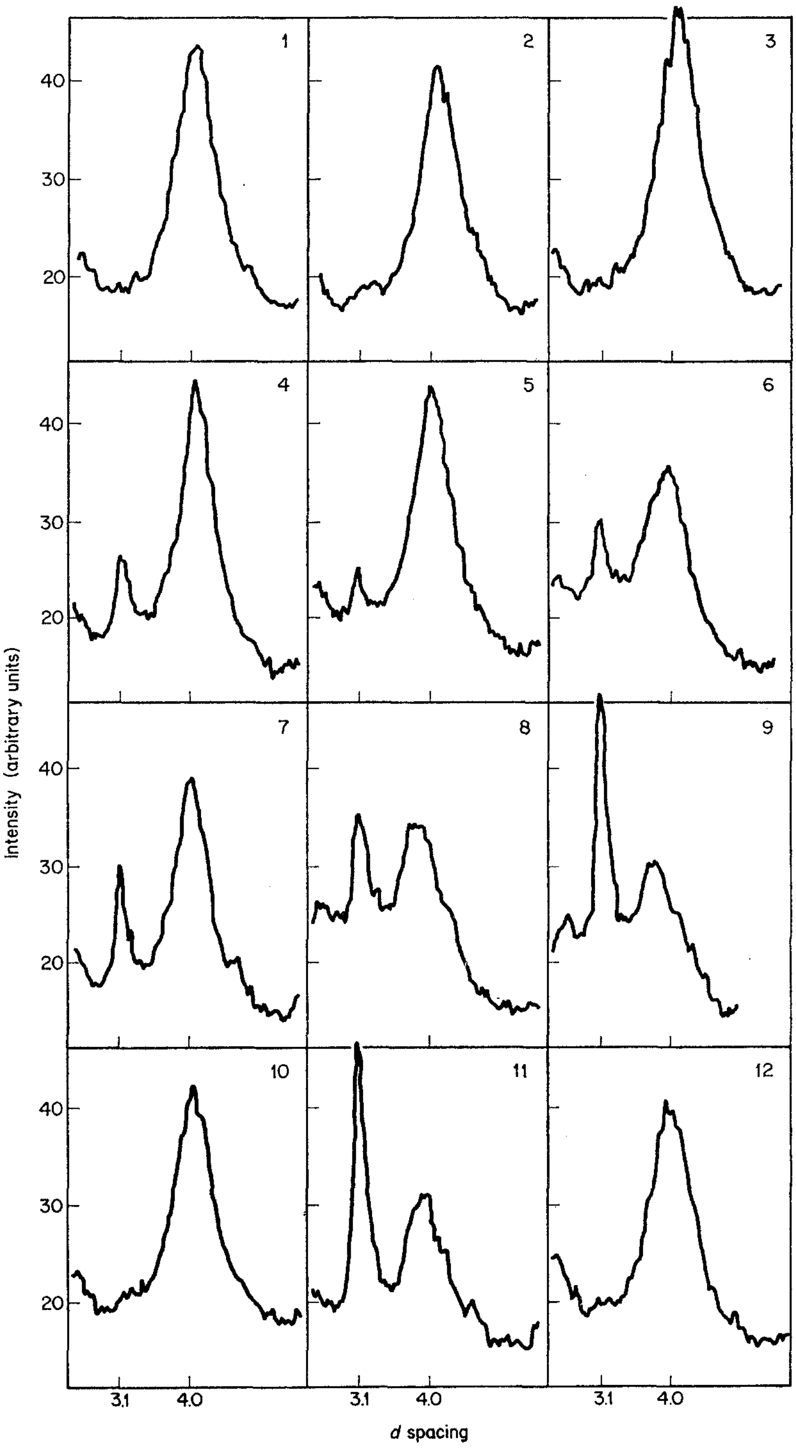

Fig. 1. X-ray diffraction. The number on each chart is the manganese dioxide code number.

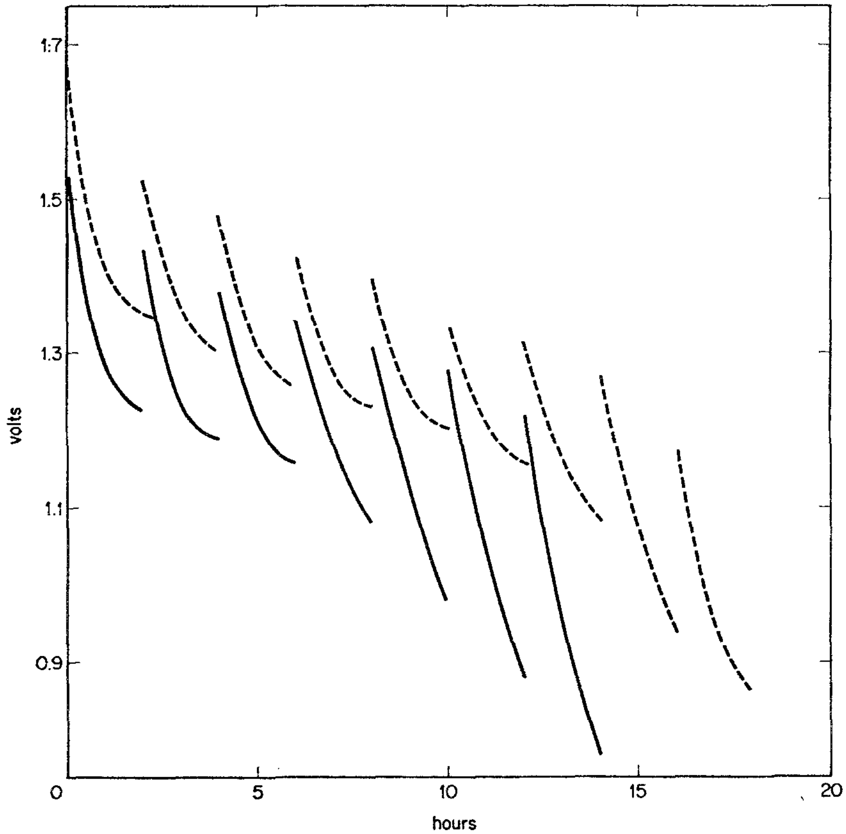

Fig. 2. Cell discharge curves.
--- Manganese dioxide no. 3
—— Manganese dioxide no. 6

voltage and discharge efficiencies given by the various manganese dioxides in R.20 size cells on the simulated motor discharge are shown in Table 2. The potentials found for the 'as received' manganese dioxides are also shown in Table 2. Relevant features of the X-ray diffraction are given in Fig. 1.

With the exception of material no. 10, the discharge lives of the duplicates agree well and demonstrate that the procedure of making individual cells is satisfactory.

There is a wide variation in the discharge lives obtained with commercially available materials (nos. 1 to 6). The discharge curves of the two extremes (nos. 3 and 6) are shown in Fig. 2. This is an important finding. The existence of such large differences in the battery activity of electrodeposited manganese dioxides has not been generally appreciated. These differences cannot be explained on the basis of chemical composition (Table 1). For example the extremes (nos. 3 and 6) have almost identical chemical composition.

Material from our pilot plant (no. 7) gave a low discharge life. Examination of the plated deposit revealed two types of manganese dioxide, one bright and faceted and the other dull (Fig. 3). Previous studies [1,4] have indicated that more than one form can be electro-deposited. Microhardness tests on a section through the plate showed that the dull material was soft and that the bright faceted material was hard (Fig. 4) As shown in Figs. 3 and 4 the two types of manganese dioxide occurred in sizeable patches which allowed an approximate manual separation to be made. The dull soft manganese dioxide (no. 11) gave a very poor discharge life (Table 2) while the hard bright manganese dioxide (no. 12) showed better discharge life than the normal unseparated product (no. 7).

X-ray diffraction (Fig. 1) shows that relative to the hard bright material (no. 12), the dull soft manganese dioxide (no. 11) has an enhanced β peak and a reduced γ peak. The commercial manganese dioxide with the poorest discharge performance (no. 6) also shows a definite β peak and a reduced γ peak compared to the other commercial products (nos. 1–5). The commercial manganese dioxides with the best discharge performances (nos. 1, 2 and 3) show strong γ peaks with almost no evidence of a β phase. The commercial manganese dioxides with intermediate discharge lives (nos. 4 and 5) show small but distinct β peaks.

This evidence suggests that the variation in discharge life of electrodeposited manganese dioxides is due to a varying proportion of a soft dull β containing phase. Manganese dioxide deposits at the electrolyte and not at the electrode interface [7]. On our pilot plant the β phase was usually found near to the electrode (Fig. 4) and hence had had a longer period in the electrolyte bath than the outer regions of the plate. It is therefore possible that the manganese dioxide is initially deposited as a hard bright γ phase but that at least some of this is transformed by the bath conditions to the soft β containing phase.

Two additional pieces of evidence support the preceding contention. Pilot plant material deposited for only 3 days (no. 10) instead of the normal 14 days (no. 7) shows only a suggestion of a β peak compared to the definite β peak in material no. 7. Material no. 1 which has no β peak developed an increasing β peak on heating in a solution of similar composition and at a similar temperature to that employed in deposition (nos. 8 and 9).

While prolonged time in the deposition bath at 90°C may be a necessary condition to produce β phase in the electrodeposit it is not sufficient. In laboratory experiments no β material was produced in runs extending to 25 days. Even attempts to simulate possible plant abnormalities by omitting stirring, using low and zero current densities for periods, passing current long after the theoretical exhaustion point of the manganous ion, and running with the deposit partially

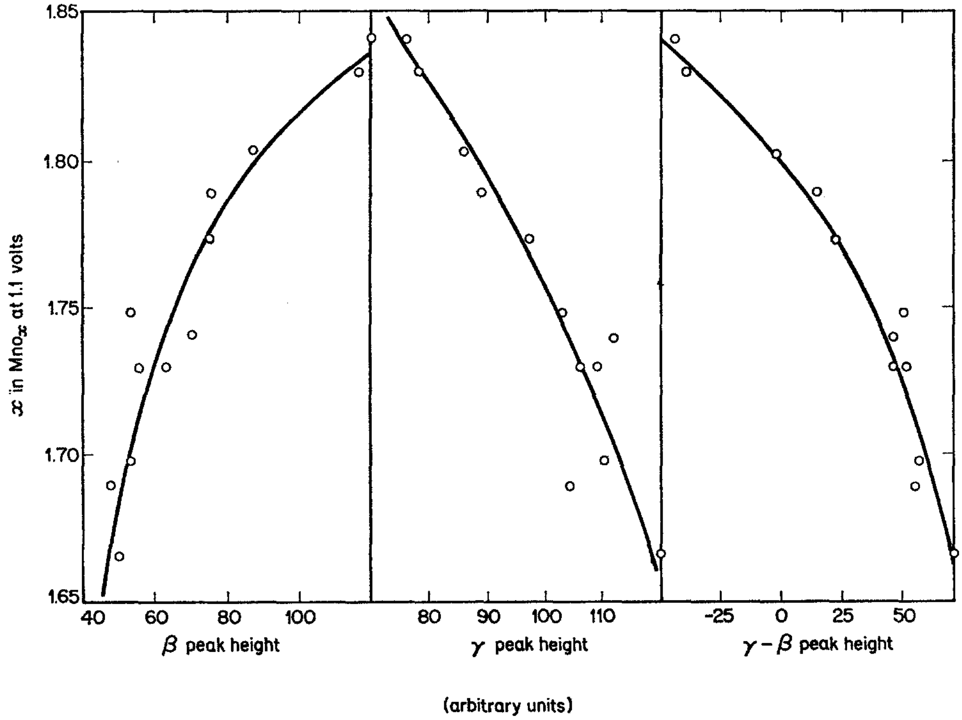

Fig. 5. x in MnO_x at voltage endpoint as a function of γ peak height, β peak height and γ–β peak height.

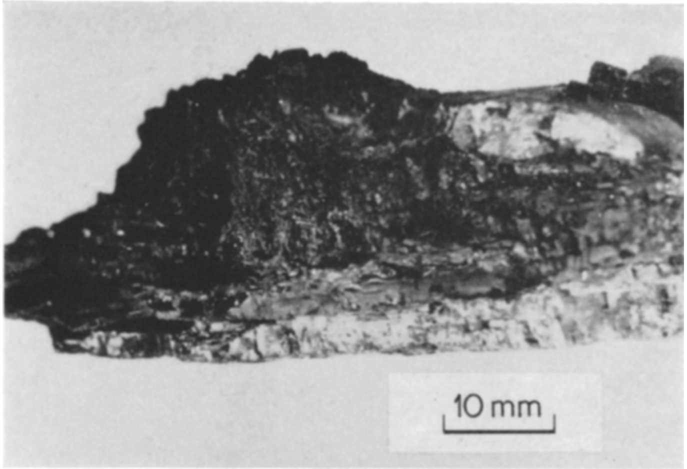

Fig. 3. Manganese dioxide plate.

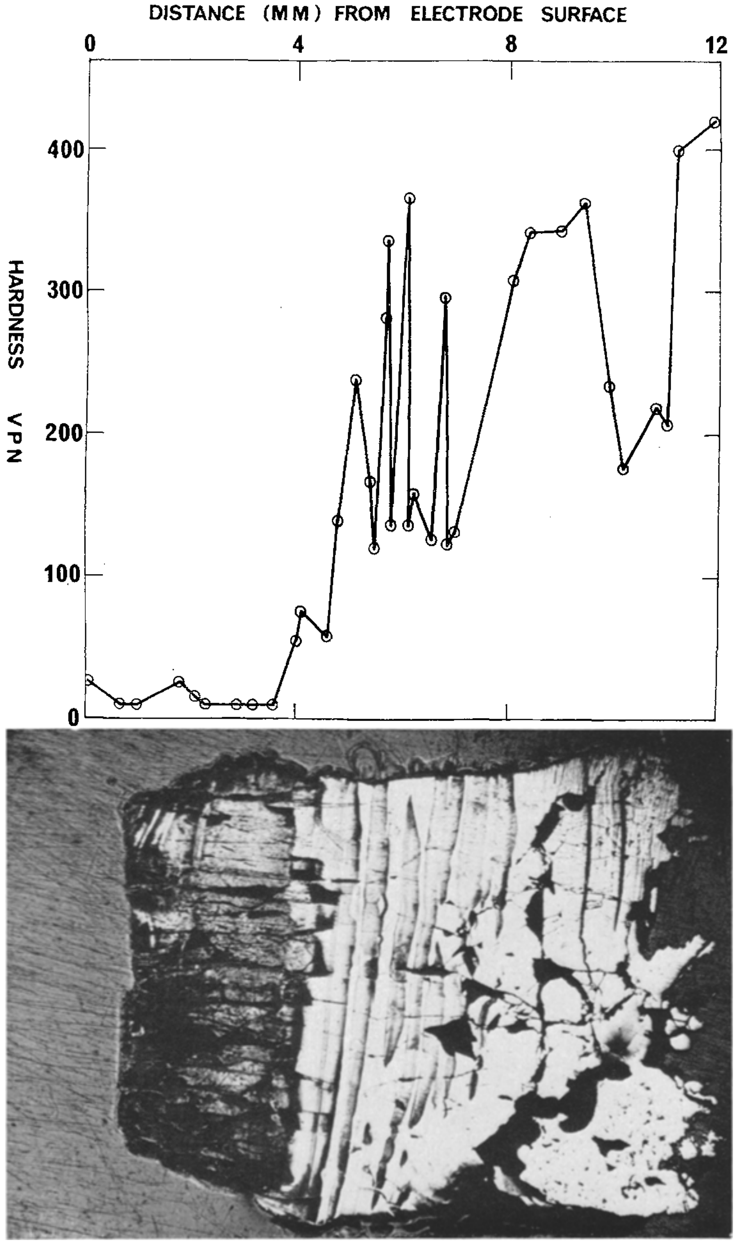

Fig. 4. Section through manganese dioxide plate and related microhardness.

separated from the electrode, failed to produce any β phase. The additional factor causing β phase which is present in some production plants thus remains unidentified.

A battery manufacturer needs to be able to recognize which of the offered manganese dioxides will give the best performance on the type of discharge under consideration. From the foregoing it is clear that for the discharge used in this work electrodeposited products with a strong γ peak and no β peak are preferred.

All possible correlations between γ peak height, β peak height and γ–β peak height and the three measures of discharge performance: life, efficiency, and x in MnO_x at the voltage endpoint have been attempted and five are shown in Figs. 5 and 6. The best correlation is between γ–β peak height and x in MnO_x at the endpoint and this correlation, considering the variety of products, is good.

Fig. 7 shows that some correlation between x in MnO_x at the endpoint and potential exists but is not as good as that found with the X-ray data.

Finally it must not be assumed that, because electrodeposited manganese dioxides with high values of γ–β peak height provide power to lower values of x in MnO_x in R.20 size cells on our simulated motor discharge, this will also be so for other discharge conditions and for other cell sizes. The converse could even be true. However it does seem that γ–β peak height may be a useful index of battery activity for the important closely related group of electrodeposited manganese dioxides. Only further work will show which discharge conditions require a high value of

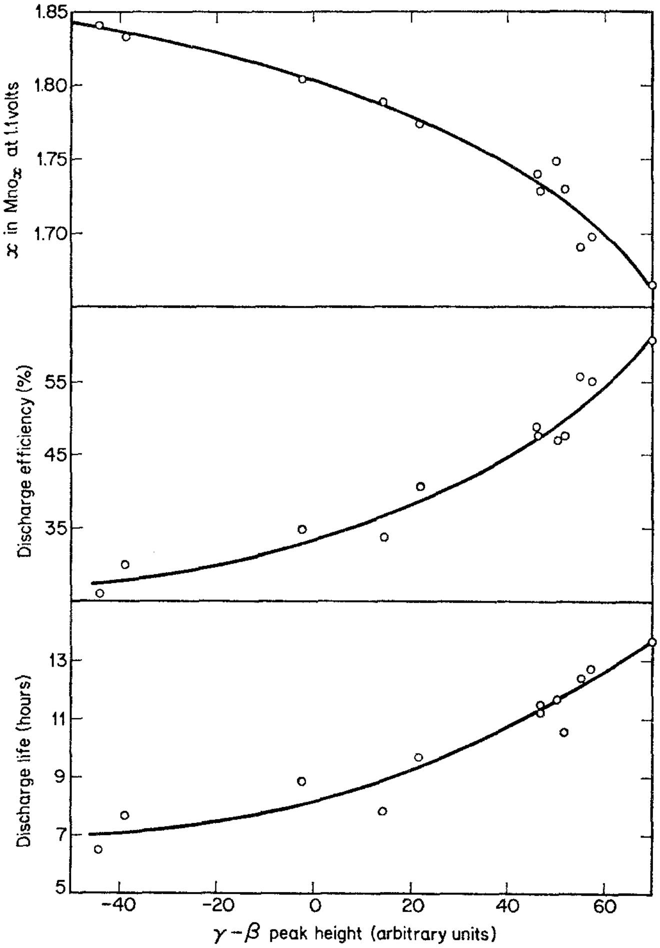

Fig. 6. x in MnO_x at voltage endpoint, discharge efficiency and discharge life as functions of γ–β peak height.

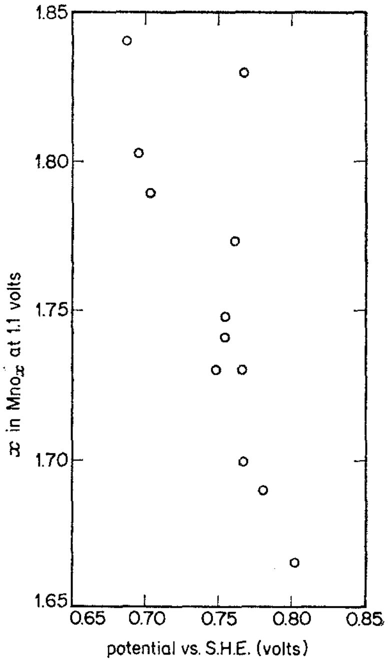

Fig. 7. Plot of x in MnO_x at endpoint vs. potential.

the index and which if any, a low value.

4. Conclusion

Electrodeposited manganese dioxides of commercial origin show considerable differences in performance when discharged through 5 ohms for 2 hours every day to 1·1 volts in Leclanché R.20 size cells. The poorer materials have lower γ peaks (d spacing 4·0 Å) and some β phase (d spacing 3·1 Å). Evidence is presented which suggests that the β phase arises by transformation of γ phase due to prolonged residence in the bath conditions and a further unidentified factor. The γ peak height at a d spacing of 4·0 Å minus the β peak height at a d spacing of 3·1 Å correlates well with the final value of x in MnO_x at 1·1 volts.

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