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THE RECHARGEABILITY OF MANGANESE DIOXIDE IN ALKALINE ELECTROLYTE

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Abstract—Many attempts have been made to make the alkaline manganese dioxide–zinc cell rechargeable, but no systematic investigation of manganese dioxide types has been made to find out what properties favor rechargeability. Since it is impossible to study the huge matrix of parameters which face the investigator, it was decided to begin with the simplest task, namely a comparative testing of the International Common Samples provided by industry. The available samples differ greatly in physical properties, but they are very well defined analytically and much work has been done with these materials in many laboratories; experiments are therefore repeatable worldwide. The results point to the possibility that a low-cost rechargeable manganese dioxide–zinc battery can be designed with about 100–200 cycles in the capacity range of the present Ni–Cd battery. Designs of thin and bonded electrodes are much favored with regard to efficiency and current density.

1. INTRODUCTION

Primary alkaline manganese dioxide–zinc cells have captured a large segment of the portable power source market over the last ten years (364 million alkaline cells and 546 million Leclanché cells were sold in the USA in 1980). In applications where high currents and continuous drains are required, alkaline cells show a better service/cost ratio than carbon–zinc cells and have a superior shelf-life and low-temperature characteristics.

Historically, the alkaline cell is a "late-comer", it was introduced by industry in the 1960's, which is close to the 100-year anniversary of the Leclanché cell (1966). The literature about manganese dioxide was already voluminous at that time, but the significance of the use of Gamma-manganese dioxide, especially the electrolytically produced type was not clearly recognized until the studies performed by Brenet in the 1950 and 60's[1–4]. Of course, Vetter's thermodynamics of oxide electrodes[5] was new then, and the work of Washburg and Johnson[6] which considered manganese dioxide as a substance with ion-exchange properties was only appreciated much later when alkaline electrolytes instead of the ammonium chloride or zinc chloride solutions were used. The Pourbaix–Atlas[7] still contained a "reversible" electrode reaction leading to Mn(II), which was not reversible. The crystal structure of manganese dioxide modifications were well known to the mineralogists, but it was left to Bode and his coworkers[8] to study the chemical reduction of those types which were important in the primary cell production. The importance of mass transfer processes for the efficiency of electrodes was recognized in studies by Washburg since 1951 and confirmed by Huber[9] in 1960; that the presence of water in the lattice favors the movement of protons was stated by Brenet already in the 1955 paper[2] but it needed the studies of Era and coworkers[10] to make sure.

The amount of water in the lattice was considered to be important for the activity of the manganese dioxide in battery applications, therefore much work was devoted to it. Brenet[11] referred to it as "constitutional" water (liberated at high temperatures only). Sasaki and Kozawa[12] had similar ideas. The function of water in the lattice is still discussed today[13].

For the discharge of manganese dioxide in alkaline electrolytes the mechanism proposed by Kozawa and coworkers[14–16] is now widely adopted. This mechanism has strong support from technical performance data and offers the best explanations for the observed limited rechargeability of manganese dioxide. As Kozawa states repeatedly in his papers, the discharge behavior of manganese dioxide can not be satisfactorily explained by the thermodynamic treatment as a heterogeneous phase reaction, *eg* MnO_2 being converted to Mn_2O_3. Reactions which occur heterogeneously, like the reduction of HgO or of Ag_2O to the metal, result in a step-discharge, the equilibrium potential stays unchanged until *all* oxide is reduced. The MnO_2 discharge curve is sloping, indicating a homogeneous phase reaction. The potential changes continuously while protons originating from the water of the electrolyte are introduced into the ionic lattice of the manganese dioxide[15] according to the equation:

$$MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^- \qquad (1)$$

The electrode potential at any equilibrium state in the homogeneous phase may be determined by the ratio $[Mn^{3+}]$ to $[Mn^{4+}]$. The OH^- ion concentration in the lattice increases also. The ionic radius of the OH^- ion (1.53 A) is larger than that of the $O_2{}^{2-}$ (1.40 A) and Mn^{3+} (0.62 A) ions. The MnO_2 lattice expands and at a certain point of the discharge the mechanism changes. After that the discharge occurs in a heterogeneous phase reaction and follows the reaction:

$$MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^- \quad (2)$$

This second reaction step involves the dissolution of the $[Mn^{3+}]$ in the form of $[Mn(OH)_4]^-$, electroreduction on the graphite (admixed) to $[Mn(OH)_4]^-$ and precipitation of $Mn(OH)_2$ from it (second phase). In practical MnO_2–Zn cells this second step happens at a too-low voltage to contribute much to the service of the cell (under 0.9 V). There is much evidence for the second step: it is irreversible, it is accelerated by increase of temperature, higher KOH concentration and responds to complexing agents: proofs for a solution mechanism. The first, homogeneous phase reaction range is the rechargeable portion of the MnO_2 reduction process. Formally it is MnO_2 to $MnO_{1.5}$.

Detailed evidence for the described MnO_2–Reduction mechanism:

Bode, Schmier and Berndt[8] employed 0.5 molar hydrazine solution for a stepwise reduction at 70° C, took X-ray diagrams and measured the potentials. It was found that MnO_2 was reduced in homogeneous phase to $MnO_{1.6}$ forming an alpha-MnOOH (groutite) with a gamma structure. β-MnO_2 was only reduced homogeneously to $MnO_{1.96}$ or $MnO_{1.98}$.

Bell and Huber[17] found the homogeneous phase reduction only until $MnO_{1.7}$ was reached, a rhombic groutite structure. Below $MnO_{1.33}$ (formally Mn_3O_4) the presence of $Mn(OH)_2$ was found.

Gabano, Morignat and Laurent[18] measured the expansion of the unit cell volume during the homogeneous discharge to $MnO_{1.75}$ and computed the increase (in $Å^3$) to be $160 - 20x$ (x from MnO_x).

Boden, Venuto, Wisler and Wylie[19] studied the γ-MnO_2 discharge, confirmed the proton-mechanism but postulated an amorphous intermediate. The values representing an increasing internal resistance were plotted as a function of x in MnO_x and showed a rapid rise starting with $MnO_{1.6}$ and reaching the tenfold value of MnO_2 at $MnO_{1.4}$. Euler[20] studied the uneven discharge condition in technical electrodes and determined some patterns of discharge depending on the conductivity of the mix, the electrolyte penetration.

It should also be mentioned that none of the authors had at that time the benefit of the availability of International Common Samples of MnO_2. Each one had a different material to test. The "recuperation" of MnO_2-cathodes is related with the homogeneous phase discharge mechanism and indicates potential gradients under load conditions, an important factor in recharging MnO_2 electrodes which may have been locally discharged below the desired limit $MnO_{1.6}$.

The recharging of discharged manganese dioxide was also studied by Boden *et al.*[21] and they found that the first homogeneous step was reversible to MnO_2. Any Mn_3O_4 remained unchangeable. However, $Mn(OH)_2$ could then be reoxidized to Mn_3O_4. They found no evidence of MnOOH. but blamed high resistive films for the irreversible behavior. The reversible portion was written as:

$$MnO_2 + nH^+ + ne^- \rightarrow MnO_{2-n}(OH)_n \quad (3)$$

$$\text{or: } MnO_2 + nH_2O + ne^- \rightarrow MnO_{2-n}(OH)_n + nOH^- \quad (4)$$

The quantity of electricity withdrawn to the amount recharged was found to be almost equal *above* $MnO_{1.55}$. From $MnO_{1.46}$ on, the diffraction peaks of Mn_3O_4 were found. Electrodes discharged to $MnO_{1.29}$ show a rapid rise of the charge voltage and a large amount of Mn_3O_4.

Kang and Liang[22] investigated rechargeability in different concentrations of KOH. Table 1 shows the results.

These data show that the homogeneous phase discharge would be the only discharge possible in low-caustic solutions. The practical range of concentrations for MnO_2–Zn cells is 6–10 M potassium hydroxide because the anode capacity drops too low and passivation occurs easily.

Ohira and Ogawa[23] determined the cycle life as a function of the depth of discharge in 7 M KOH and recharged 140 per cent each cycle. They obtained 30 cycles at 30% DOD to -0.25 V *vs* HgO.

McBreen[24] used cyclic sweep voltametry for testing the rechargeability of manganese dioxide electrodes. He could clearly show the poor rechargeability of deep-discharged MnO_2.

2. MANGANESE DIOXIDE

The structure and morphology of manganese dioxide has been the subject of many researchers; unfortunately, seemingly minor variations can be very significant for the battery manufacturer. The chemical composition and the crystallographic type is usually well known but the treatments which the materials receive during the processing steps are often of great importance. For the use in alkaline cells the situation is much simplified because only electrolytically produced γ-MnO_2 can be commercially used. The term "γ-

Table 1. Limiting x-values in MnO_x on discharge and charge as a function of electrolyte concentration

Electrolyte concentration	x-Value of the discharged oxide at the end of discharge charge at -1.0 V *vs* HgO	x-value of the charged oxide at the end of charge to $+0.6$ V *vs* HgO
1 M KOH	1.51	1.93
2 M KOH	1.45	1.89
4 M KOH	1.35	1.78
6 M KOH	1.24	1.72
10 M KOH	1.14	1.65

MnO_2" is at the present time still a collective name for a series of phases characterized mainly by their diffraction patterns. Giovanoli, Maurer and Feitknecht[25] have classified gamma MnO_2 as intergrowth structures between ramsdellite and pyrolusite, which are members of the nsutite group. The basic unit cells are $[MnO_6]$-octahedra joined to alternating single-and double chains. Ruetschi *et al.*[26] have summarized the types of MnO_2 materials which must be considered important for batteries.

Burns *et al.*[27] and Giovanoli[28] have discussed the standpoint of the mineralogists. Generally it is agreed that γ-MnO_2 is reduced in homogeneous phase to MnOOH, forming groutite (alpha MnO_2). The build-up of it on the particle-surfaces is the rate determining process. It is understandable that the proton migration is reversible as long as the original γ-structure is maintained. Ion-exchange properties are also explained by the sieve like multi-chain structures. Alkali metals and also zinc can be incorporated. Delta-[24] and epsilon-[13] types of MnO_2 are also mentioned. However, it should be noted that the structural information on MnO_2–materials are usually derived from X-ray powder analysis data and, unfortunately, the better the crystal structure can be defined, the less useful is that MnO_2 material for batteries. Structural changes can also be effected by heating[16]. While the heating of γ-MnO_2 improved the performance of the cathodes in non-aqueous Li-cells, aqueous cells of the alkaline type seem not to respond favorably.

The production of electrolytic MnO_2 (EMD) consists of several main process lines: the grinding and dissolving of the ore (usually rhodochrosite with 39% Mn, 4% Fe and 5% SiO_2) in sulfuric acid, purifying the solution the solution and performing the electrolysis under very strict conditions. The electrolysis-product is then washed, ground to specifications, p_H-adjusted and finally dried and packaged.

Kozawa[16] and Takahashi[29] describe the process as used by the Mitsui Mining and Smelting Co. as an example.

The overall chemical reaction during electrolysis is:

$$MnSO_4 + 2H_2O \rightarrow MnO_2 + H_2SO_4 + H_2 \quad (5)$$

The temperature (88–98°C), concentration (0.5–1.2 mole/l $MnSO_4$ with 0.5–1.0 mole/l. H_2SO_4) and current density (0.7–1.2 A/dm^2) are carefully controlled. As electrodes serve Titanium-, lead-alloy and carbon electrodes. Post-electrolysis treatments vary considerably.

All of the present commercial battery companies use electrolytic MnO_2 (EMD) for alkaline cells. However, chemically prepared manganese dioxide (CMD) could be used if lower costs are decisive and some loss of performance is acceptable[30].

From the previous discussion it is now obvious that any meaningful testing of the rechargeability of MnO_2–types must be limited to well known materials. The International Common Samples available since 1973 are listed in the following Table 2. (Sample: 1 kg MnO_2)

Performance-testing of the I.C. Samples for alkaline cells was done by Tsuchida[31] and Sugimori[30], but the tests did not include rechargeability. A collection of physical properties was made by Kozawa[16, 32], it lists surface area, particle size distribution, resistance, chemical-and thermogravimetric analysis data.

3. EXPERIMENTAL

A preliminary experiment was made to find out if dimensional changes during charge and discharge of cathodes are reversible. For that test a cathode, 3 mm thick and 10 mm dia., was mounted in a steel cup (as confinement) and on a flat plate, contacted with slight pressure, but free to expand. The dimensional changes were measured with an electronic gauge and recorded.

Figure 1 shows the perpendicular expansion and contraction during the first few cycles of the disc-cathode. It is also clear to see that the confined electrode and the free electrode behaved very differently. Bulging and mechanical disintegration finished one of the experiments after four cycles, the other went on and seemed to reach equilibrium as far as its geometry was concerned. A gradual small loss of capacity was observed.

This experiment explains why cylindrical cells with sleeve-cathodes (like the LR-20, LR-14 and LR-16 alkaline MnO_2–Zn cells) can be recharged several times—until the zinc or the separator fails. Flat, unrestrained plate-cathodes disintegrate fast unless they have a binder incorporated. With the expansion and contraction we observe a simultaneous resistance increase and decrease, in spite of the fact that the cathode mixes contain 20 per cent graphite. Figure 2 shows the curves which Boden, Venuto *et al.*[19]

Table 2. International Common Samples of manganese dioxide, available from: The I.C. MnO_2 Sample Office, P.O.B. 6116, Cleveland, Ohio, 44101, USA. In Europe: K. Kordesch, T. U. Graz, Postfach 32, Graz, Austria, 8013

No. 1: Electrolytic MnO_2, Ti-anode process	Japan
No. 2: Electrolytic MnO_2, Pb-anode process	Japan
No. 3: Electrolytic MnO_2, Carbon anode	Japan
No. 4: Electrolytic MnO_2	La Pile Leclanché, France
No. 5: Chemically prepared MnO_2	Japan Metals and Chem. Co
No. 6: β-MnO_2 (by decomposition)	Regent grade MnO_2
No. 7: Natural ore MnO_2	Ghana Ore
No. 8: Chemically prepared MnO_2	Sedema, Belgium
No. 9: Electrolytic MnO_2 (coarse)	Kerr–McGee Corp., U.S.A.
No. 10: Electrolytic MnO_2 (regular)	Kerr–McGee Corp., U.S.A.
No. 11: Chemical MnO_2 (Chlorate Proc.)	Kerr–McGee Corp., U.S.A.
No. 12: Chemically prepared MnO_2	Sedema, Belgium, Faradizer M.
No. 13: Natural ore MnO_2	COMILOG

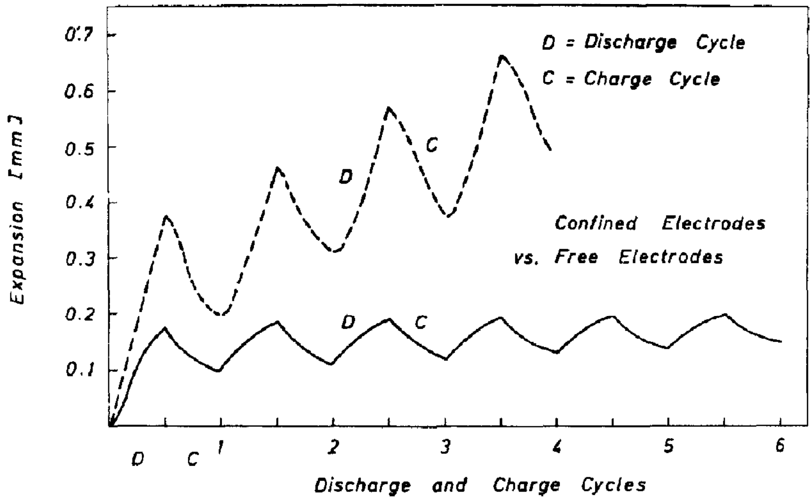

Fig. 1. The perpendicular expansion and contraction of 3 mm thick manganese dioxide–graphite discs during cycling.

obtained. During the cycling of our discs we decided to stop the discharge at approximately $MnO_{1.6}$ ($MnO_{1.5}$ corresponds to the 1 e^- equivalent or to 0.31 Ah per g MnO_2). The failure-mode is therefore not the build-up of an insulating layer, but a mechanical disintegration accompanied by a resistance increase.

In all following tests we wished to avoid the mechanical problems and a special test assembly was built which allowed a known pressure to be exerted on the cathode disc. In another preliminary experiment the pressure effect was determined, to be sure that the later test series were made under reasonable conditions. Table 3 shows the results of this study.

In all the tests reported in this paper the pressure was adjusted to 27 N/cm^2 by means of a screen over the cathode surface. The test cell used is described in

Table 3. Dependence of the number of cycles on the pressure exerted on the surface of the cathode. MnO_2-content: 79 %, Graphite mix

No. of cycles	P (N/cm^2)	P (kgf/cm^2)	Notes
20	1	0.1	MnO_2-Type: I.C. 2
40	27	2.7	Conc. KOH: 9 M
70	150	15	Current density: 10 mA/cm^2
90	500	50	
75	1000	100	Depth of D.: 35 %

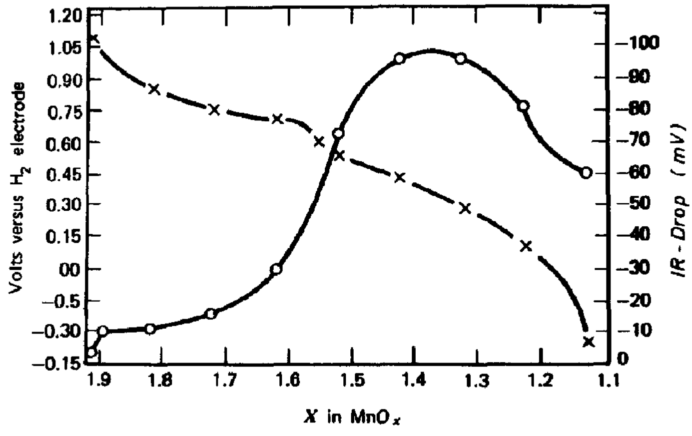

Fig. 2. The discharge of a manganese dioxide electrode electrode at 5 mA/cm^2 in 7 M KOH[19].

reference[33]. To make sure that mass-transport problems would not falsify the data, the thickness of the electrodes was reduced to 0.5 mm. The diameter of the disc remained 10 mm. The weight of one disc was about 0.1 g. The pressure used for molding the disk was 100 bar.

Description of the cycling tests

The samples were discharged for 60 min at a current density of 9.50 mA/cm^2 and then charged for 5 h potentiostatically at 1.70 V *vs* zinc (the voltage was controlled against HgO). The depth of discharge was fixed at 35 % of the 1 e^- capacity of the true MnO_2 content of the International Common Samples tested.

Dependence of the cycle number on the depth of discharge (DoD)

Within the "allowed" range of the 1 e^- equivalent discharge there is a strong relationship between the DoD and the number of charge- and discharge cycles. A logarithmic function was described by E. Voss (34) on the basis of a statistical approach, assuming that an electrode loses a certain amount of capacity each cycle. He applied this consideration to lead-acid batteries and in this case the decay was the loss of active material for various reasons, like shedding, sulfatation, etc.. The general equation is:

$$\log(\text{No. of cycles}) = A - B \cdot \text{DoD (in \%)} \qquad (6)$$

It turned out that this equation fitted our expectations well, for instance with A = 3 and B = 0.04 and 35 % DoD the cycle No. is 39. For 20 % DoD the cycle No. becomes 158. Since we did not wish to let the many tests which we planned run too long (for lack of time) and, on the other hand did not want to punish the cathodes unreasonably, we settled on the 35 % DoD for all I.C. Sample tests.

Figure 3 shows the results of depth of discharge studies on two types of MnO_2: the I.C. Sample No. 2 (EMD) and I.C. Sample No. 5 (CMD) are compared. The calculation above fits the I.C. No. 2.

Results of the I.C. Sample-cycling tests

The reproducibility was very high, when the characteristic "knee' of the envelope curve was considered as the cut-off point (1.0 V against Zn) the accuracy was ± one cycle. After that point the resistance of the cathode increased rapidly—so we did not go lower. It was also noted that the cycling led to the deposition of a material which was a poor conductor[21]. The source of lower manganese oxides out of the solution phase can be twofold: from local over-discharge, but also from overcharge. Oxidation to the VI-valent Mn (manganate) and disproportionation to Mn(II) and Mn(IV) appears very likely. If we picture parts of the MnO_2-particle surfaces getting coated and some particles loosing contact with the graphite by an intervening liquid layer (wetting) it is understandable that "active material" gets lost gradually (6). Such a model explains also the effect of pressure. The different I.C. Samples should give very different cycling results, that was expected; actually we eliminated the very inferior I.C. Samples No. 6, 7 and 13 after preliminary tests. I.C. Sample No. 12 is still undergoing tests.

However, what we did not expect was, that no correlation was found between the cycling data and the physical properties of the I.C. Samples. Table IV presents the obtained cycle numbers.

Figure 4 compares the primary capacity of the different I.C. Samples with the cycle numbers obtained. The capacity is given in per cent of the 1 e^- capacity to a cut-off voltage of 1.0 V *vs* Zn, at a current density of 9.5 mA/cm^2. They are arranged in decreasing weight-capacities and the corresponding cycle numbers are in the upper curve. There is also no correlation with resistance data, surface areas, particle-sizes, pore-diameters or any chemical analysis values[32]. The total water content data now exist for all I.C. Samples, but do not conform; may be they should be divided into specific temperature fractions.

The following Figs 5–13 show the cycling behaviour of the nine I.C. Samples listed in Table 4. The graphs are replicas of the recorded curves and go from right to

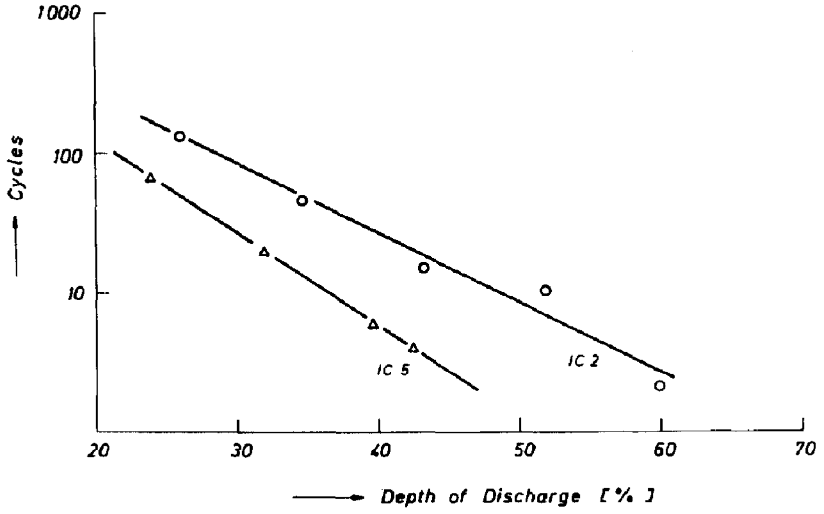

Fig. 3. The number of discharge–charge cycles as a function of the depth of discharge for I.C. No. 2 (EMD) and I.C. 5 (CMD).

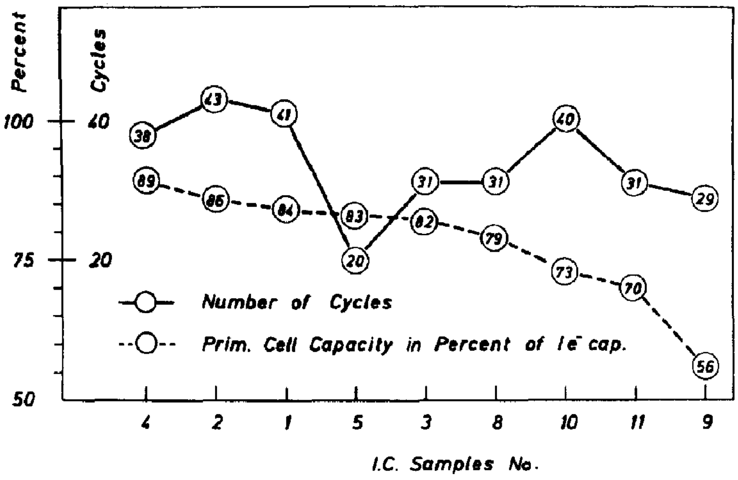

Fig. 4. Primary capacity *vs* cycling capability of I.C. Samples No. 5, 8 and 11 (CMD's) and No. 1, 2, 3, 4, 9 and 10 (EMD's).

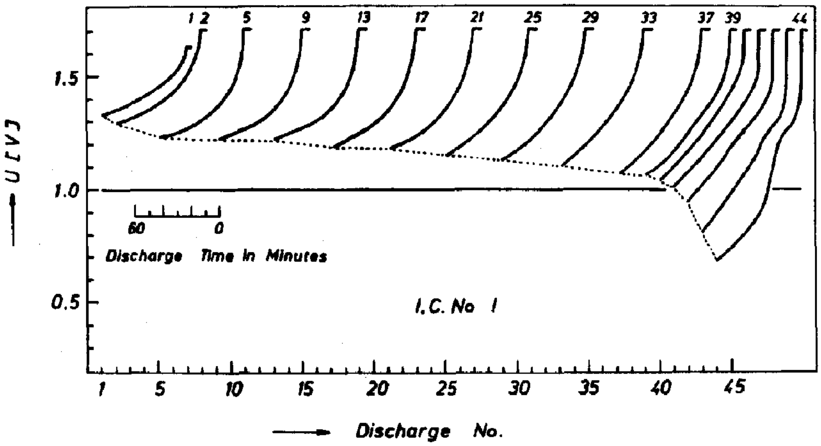

Fig. 5. Cycling behaviour of I.C. Sample No. 1, EMD, Ti-anode, Manufactured in Japan.

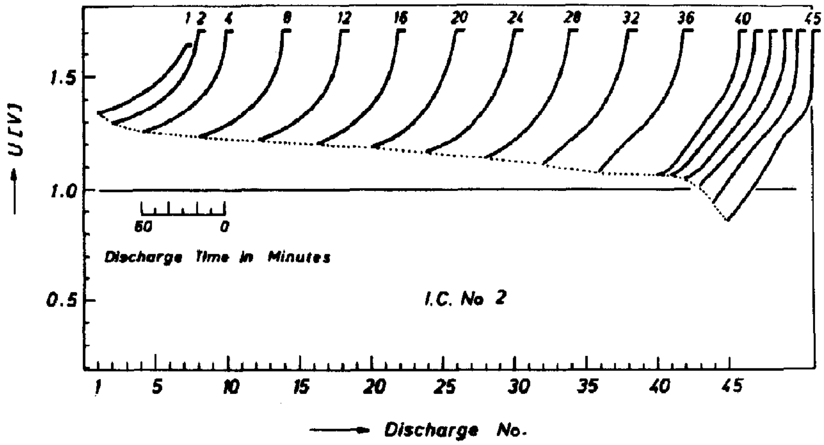

Fig. 6. Cycling behaviour of I.C. Sample No. 2, EMD, Pb-anode, Manufactured in Japan.

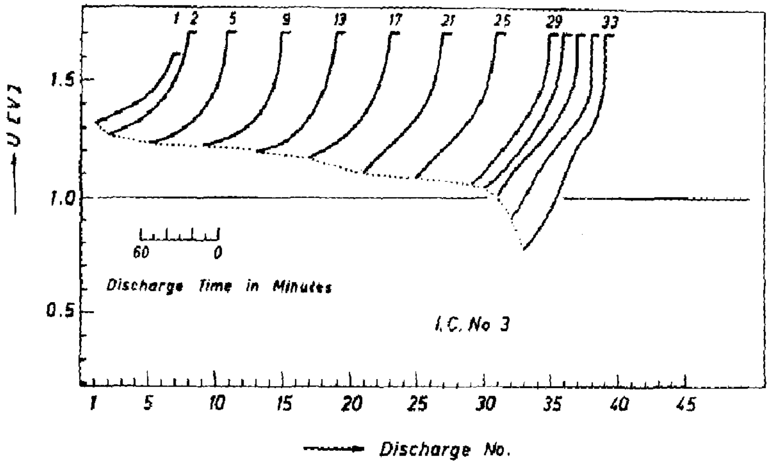

Fig. 7. Cycling behaviour of I.C. Sample No. 3, EMD, C-anode. Manufactured in Japan.

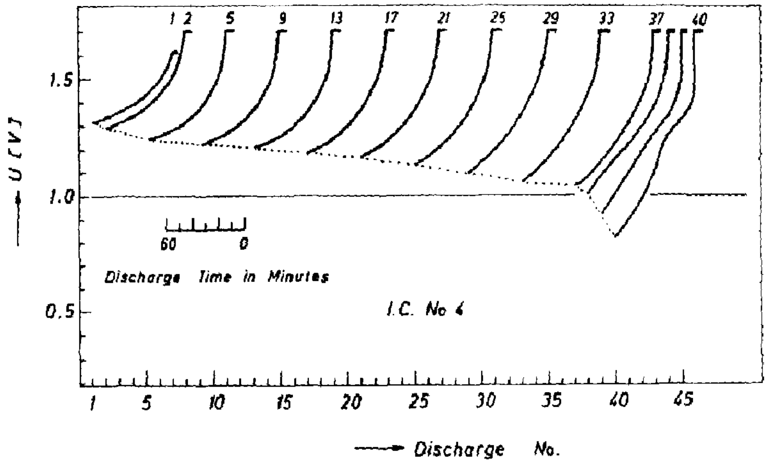

Fig. 8. Cycling behaviour of I.C. Sample No. 4, EMD, from LaPile Leclanché. Manufactured in France.

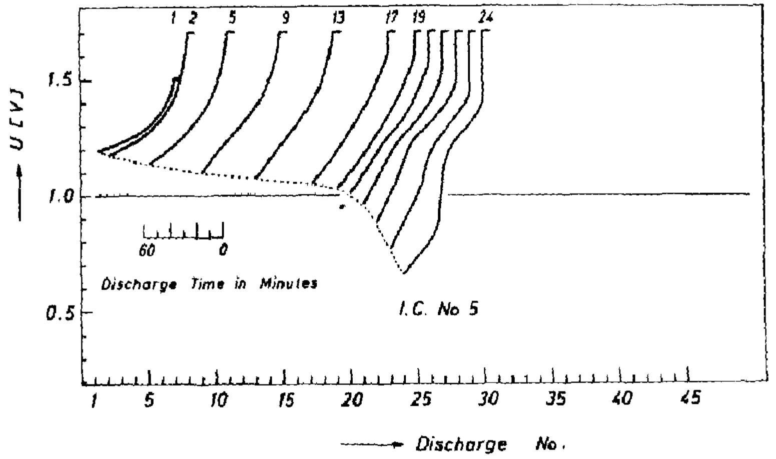

Fig. 9. Cycling behaviour of I.C. Sample No. 5, CMD, from Japan Metals and Chemicals Co.

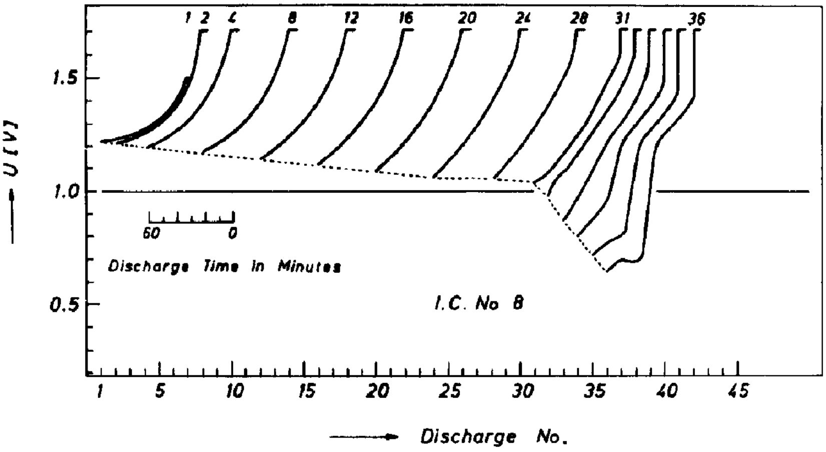

Fig. 10. Cycling behaviour of I.C. Sample No. 8, CMD, from Sedema, Belgium.

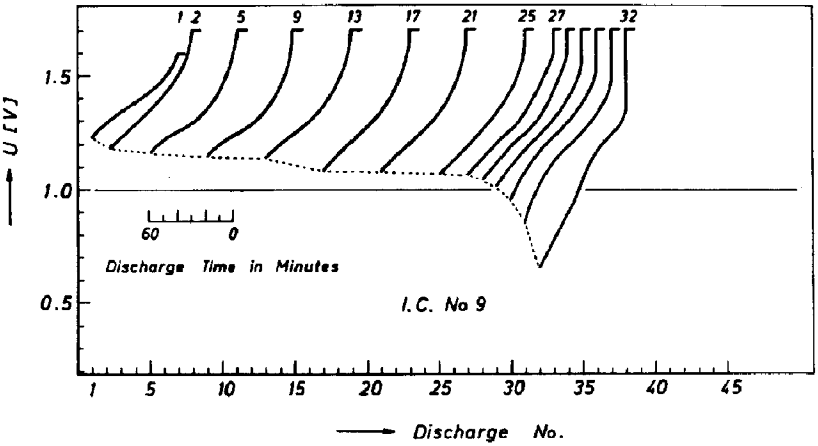

Fig. 11. Cycling behaviour of I.C. Sample No. 9, EMD, from Kerr–McGee Corp., U.S.A. (coarse material).

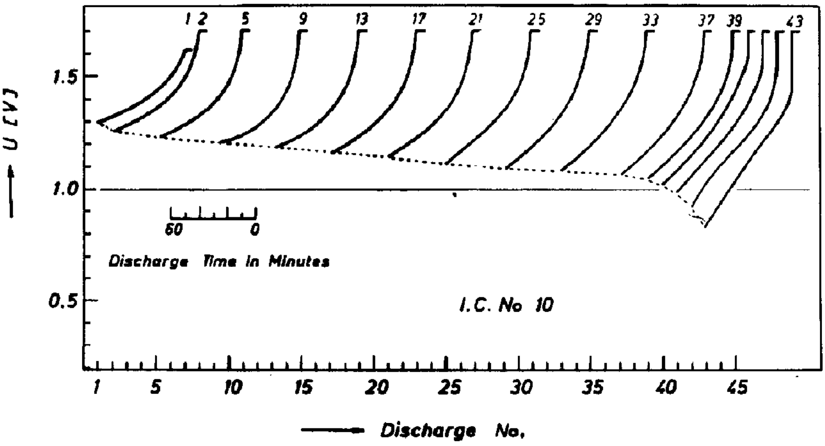

Fig. 12. Cycling behaviour of I.C. Sample No. 10, EMD, from Kerr–McGee Corp. U.S.A. (regular material).

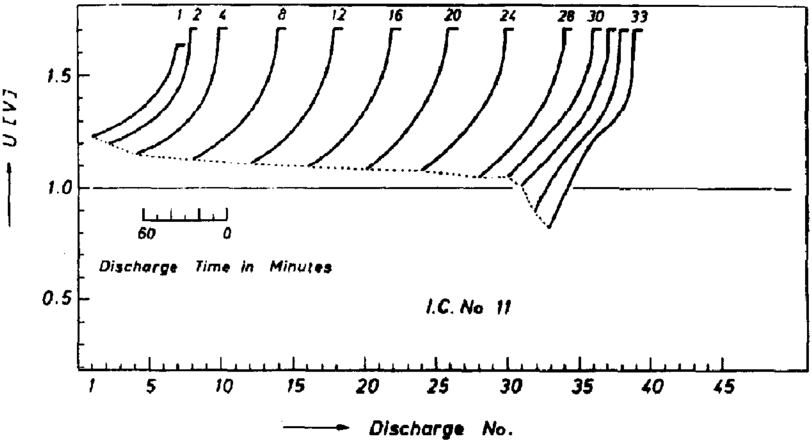

Fig. 13. Cycling behaviour of I.C. Sample No. 11, CMD, from Kerr-McGee Corp., U.S.A. (Chlorate processes).

Table 4. Cycle numbers obtained with the I.C. Samples

I.C. No.:	1	2	3	4	5	8	9	10	11	12
Cycles:	41	43	31	38	20	31	29	40	31	—

left, progressing to the right as cycle numbers increase.

Relating the results to complete cells

The authors have built actual rechargeable alkaline MnO_2–zinc cells in the LR-14 size with the best of the I.C. Samples. The manganese dioxide rechargeability was at least as good as reported, in many cases even better—pointing to higher internal pressures. Adopting the principle that commercial cells must be zinc-limited to be fool-proof against discharge beyond the 1 e^- limit, it is possible to redesign the cells with more MnO_2 than regular primary cells of the same size contain. This leads to depth of discharge ranges on the cathodic side between 15 and 25 per cent, which in turn leads to a cycle life of the MnO_2 electrode of 100–200 cycles—still with a competitive capacity per cycle.

The present attempts to construct a rechargeable alkaline MnO_2–Zn cell are finding more troubles on the zinc side than on the MnO_2-side of the cell[35]. A survey of the criteria for the "successful" rechargeable MnO_2–zinc cell is available[36].

4. FUTURE WORK

A low-cost manganese dioxide cell with a recharging capability is desirable from the raw material and energy saving standpoint. Such a cell need not be an inferior product, just the opposite: alkaline MnO_2 cells have a better shelf life than *eg* Ni–Cd cells, the power output can be tremendously increased by adopting the thin-electrode constructions of multi-cell battery stacks or the efficient design of spirally wound cells. There are commercial cells on the market which point in that direction, a 6 V camera battery and a sealed lead acid cell, to name two examples. The utilization of MnO_2 in our cylindrical cells is poor at high current densities. The low-temperature characteristics must be improved to compete with new non-aqueous systems[37].

As far as improvement in rechargeability of MnO_2 is concerned, the deposition methods for MnO_2[38] must be studied, the possibility of doping the lattice must be explored and all the empirical results of these efforts subjected to scientific confirmation with the modern and more powerful instrumentarium available today.

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