

Chemically activated manganese dioxide for dry batteries

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Abstract

The present investigation has enabled us to convert inactive β -manganese dioxide to high electrochemically active types by chemical processes. Natural and chemically prepared β -manganese dioxides were roasted at 1050 °C to form Mn_3O_4 . This compound was subjected to activation treatment using hydrochloric and sulfuric acid under various reaction conditions. The manganese dioxide so obtained was examined by X-ray diffraction, thermogravimetric, differential thermal and chemical analyses. The structure of the dioxide obtained was found to be greatly dependent on the origin of MnO_2 and type of acid used. Treatment with hydrochloric acid yield the so-called γ -variety while sulfuric acid tended to produce γ - or α - MnO_2 . In addition, waste manganese sulfate obtained as by-product from sulfuric acid digestion treatment was recycled and electrolytically oxidized to γ - MnO_2 . The discharge performance of the above-mentioned MnO_2 samples as battery cathodic active material was evaluated and compared with the ordinary battery grade.

Introduction

The production of MnO_2 of high electrochemical reactivity is one of greatest problems in the industrial production of cells of the Leclanché type, and indeed to all cells employing this material. Methods of activation of manganese dioxide include chemical, electrochemical and even physical processes.

Chemical activation methods are described in this work. Roasting manganese dioxide ores to lower oxides (Mn_2O_3 , Mn_3O_4) followed by digestion in different inorganic acids to obtain active manganese dioxide was carried out [1–16]. The influence of the acid concentration on the type and crystal structure of the produced oxide has been specified [4].

Fernandes *et al.* [17] reviewed the various physicochemical principles involved in the activation of natural manganese ore. Brenet and co-workers [18] and Ohzuku *et al.* [7] studied the kinetics of disproportion of the lower oxides in acid solution and they found that Mn^{2+} ions play a major role in the reaction rate.

The aim of the present work is to study the possibility of preparing active manganese dioxide local high-grade pyrolusites and inactive chemical grade β -type MnO_2 and evaluating the physicochemical and electrochemical characteristics of activated manganese dioxides in order to assess their suitability as active cathode material in dry cells.

Experimental

Material

Local MnO_2 ore (pyrolusite) of composition 91.2% MnO_2 (the amount of iron and silica are 0.16 and 0.7%, respectively) and chemical grade β -type with 95% MnO_2 (Merck) were used as starting materials.

TABLE 1

Classification of chemically activated MnO₂ samples

Samples	Classification
A	β -type local MnO ₂ ore
B	Chemical grade B-type MnO ₂ (Merck)
I	A roasted at 1050 °C
II	B roasted at 1050 °C
III	Product of digested roasted A in HCl
IV	Product of digested roasted B in HCl
V	Product of digested roasted A in H ₂ SO ₄
VI	Product of digested roasted B in H ₂ SO ₄

Samples were crushed and ground to 200 mesh size and then roasted in a thermostatically controlled muffle furnace at 1050 °C for 2 h to ensure the decomposition of MnO₂ to Mn₃O₄ [19]. The dissociated products were then cooled quickly. The roasted samples were digested with aqueous hydrochloric or sulfuric acid at 90 °C.

The reaction products were filtered, washed with water and then dried at 90 °C. The classification of the samples is shown in Table 1.

Identification of the samples

X-ray investigations (XRD) were performed with a Philips diffractometer (type pw 1051) with Fe K α radiation. Thermogravimetric (TGA) and differential thermal analyses (DTA) were carried out using a Netzch Geratebau simultaneous thermal analysis apparatus (STA 409, 6.223). Chemical analysis procedures applied in this investigation were those given by Vogel [20] and Brenet [21].

Production of electrolytic manganese dioxides

γ -MnO₂ was prepared electrolytically from manganese sulfate solution produced after the treatment of Mn₃O₄ with H₂SO₄ according to the procedure given in ref. 22.

Discharge characteristics of the different oxides tested were measured at a constant current of 20 mA/0.5 g mixture at room temperature. The polarization mixture consisted of 80% MnO₂ and 20% acetylene black. The solution was ZnCl₂ (330 g) + NH₄Cl (200 g) per litre at pH 4.2 using the technique adopted by Abdul Azim [23]. The potential versus saturated calomel electrode (SCE) was recorded as a function of time.

Results and discussion

Acid digestion of Mn₃O₄

Samples of the manganese dioxide, heated at 1050 °C, were treated by hydrochloric or sulfuric acid to obtain manganese dioxide. The basic reaction taking place in this process can be expressed as:



The optimum recovery of manganese dioxide is obtained when using 5 and 10% acid concentration at 2 and 5 h for hydrochloric and sulfuric acids, respectively, at 90 °C.

Chemical analysis

The results of the chemical analysis indicate that the leached samples have an O/Mn ratio of 1.90 ± 0.02 (non stoichiometric).

X-ray diffraction studies

The XRD patterns for the eight studied samples are shown in Fig. 1. All reflections characterized for samples A and B can be accounted for ASTM card of β - MnO_2 with sharp and intense lines.

Samples I and II give XRD patterns which are in good agreement with those obtained for cubic and tetragonal Mn_3O_4 , respectively.

The three strongest lines for samples III, IV and V are of γ - MnO_2 despite the slight variation in their relative intensity.

On the other hand, sample VI gives lines belonging to α - MnO_2 with maximum reflections around 2.39 Å.

From the above results it can be concluded that γ - MnO_2 seems to be formed from Mn_3O_4 (I and II) digested in hydrochloric acid, and from Mn_3O_4 (sample I) digested in H_2SO_4 .

On the other hand, during digestion of sample II in sulfuric acid, the disproportionation reaction may produce γ - MnO_2 as an intermediate reaction product and Mn^{2+} ions in solution [7, 24]. The proton-assisted rearrangement reaction in the presence of Mn^{2+} ions takes place to change γ - MnO_2 as intermediate to α - MnO_2 .

Thermogravimetric analyses

The difference in behaviour between the various MnO_2 modifications is reflected in the early part of the TGA curves, Fig. 2, and/or the temperature of transformation of MnO_2 to Mn_2O_3 and Mn_2O_3 to Mn_3O_4 . The difference in the initial part of the curve up to dehydration of MnO_2 may be attributed to varying amounts of water in MnO_2 (Table 2) which depends on its type, origin and conditions of preparation [25].

The MnO_2 prepared from the digestion of Mn_3O_4 in sulfuric acid possesses a higher water content. The existence of water-containing manganous and sulfate ions may affect the nucleation and/or irregular crystal growth of manganese dioxides leaving the structure with large tunnels containing water, anions or cations [26] and this may explain why MnO_2 prepared from acids containing the ions mentioned may contain excess amounts of water.

The TGA curves obtained from different samples investigated display different decomposition temperatures ($\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$) which depend on the crystal structure and origin of the samples.

Differential thermal analysis

The DTA behaviour of various MnO_2 samples is shown in Fig. 3. The first endothermic peak displayed in the range of 100 to 280 °C corresponds to a loss of water (hydration and structural) [27]. For the α - MnO_2 , the loss of water from this sample takes place in two successive stages. It may be expected that physically adsorbed water is lost in the first stage whereas chemically bound water is released in the second [28, 29]. The second endothermic peaks corresponding to the transformation of MnO_2 to Mn_2O_3 are shifted to higher temperatures in the order α - MnO_2 (510 °C) \rightarrow γ - MnO_2 (560 ± 10 °C) \rightarrow β - MnO_2 (610 °C). Further decomposition to Mn_3O_4 produces the third peak. The positions of these peaks varied according to the method of the preparation of the oxides [28].

Freeman *et al.* [30] have related the peak decomposition temperature of MnO_2 to Mn_2O_3 to their battery activity. According to their studies, a low peak decomposition

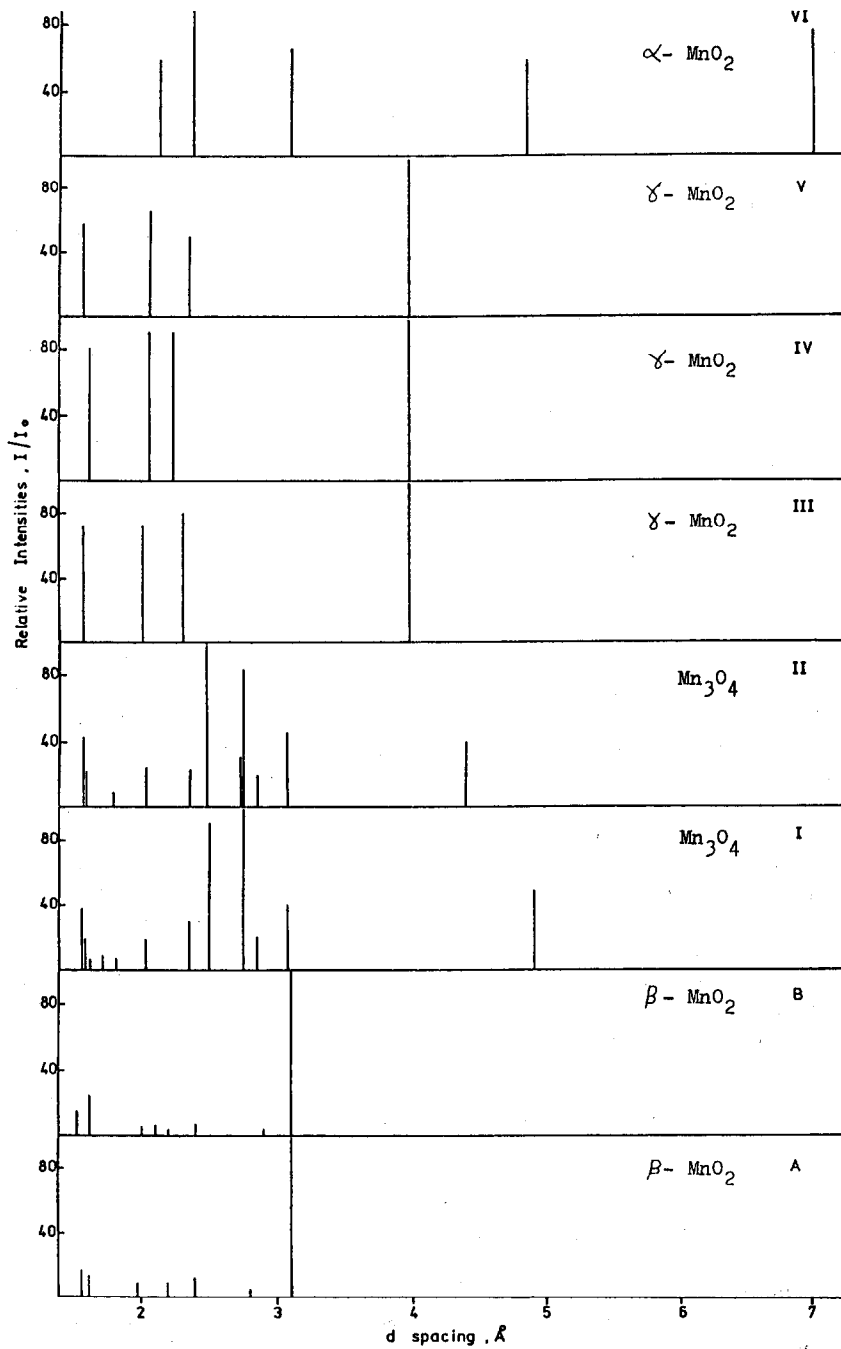


Fig. 1. X-ray diffraction patterns of the investigated samples.

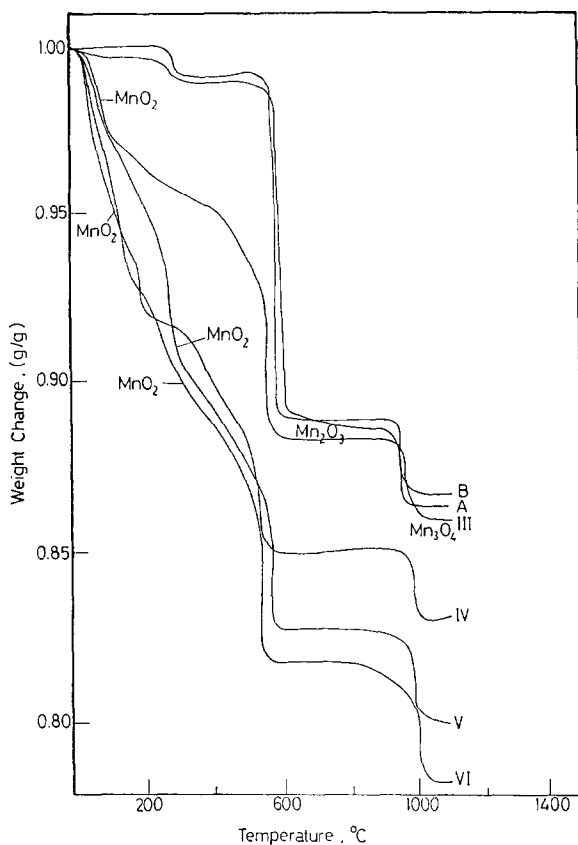


Fig. 2. Thermogravimetric analysis curves of the investigated MnO_2 samples.

TABLE 2

Water content of MnO_2 samples prepared with hydrochloric and sulfuric acids

Acid digestion	Water content	(%)
Hydrochloric acid	2.2 (III) ^a	6 (IV) ^a
Sulfuric acid	7.8 (V) ^a	9 (VI) ^a

^aSample no. in parentheses.

temperature indicates low thermal stability and, consequently, a weak Mn-O bond [29]. The smaller the bonding energy the higher is the electrode potential [1], since the acidic 'OH' groups in the active MnO_2 are directly linked with the Mn-O bond and influence the discharge capacity of the manganese dioxide [29].

Discharge characteristics

The activity of tested manganese dioxides is given in terms of the electrochemical reduction parameters for the different MnO_2 samples. The cathodic polarization curves for treated and untreated MnO_2 in $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ solution, pH 4.2, at 20 mA/0.5 g

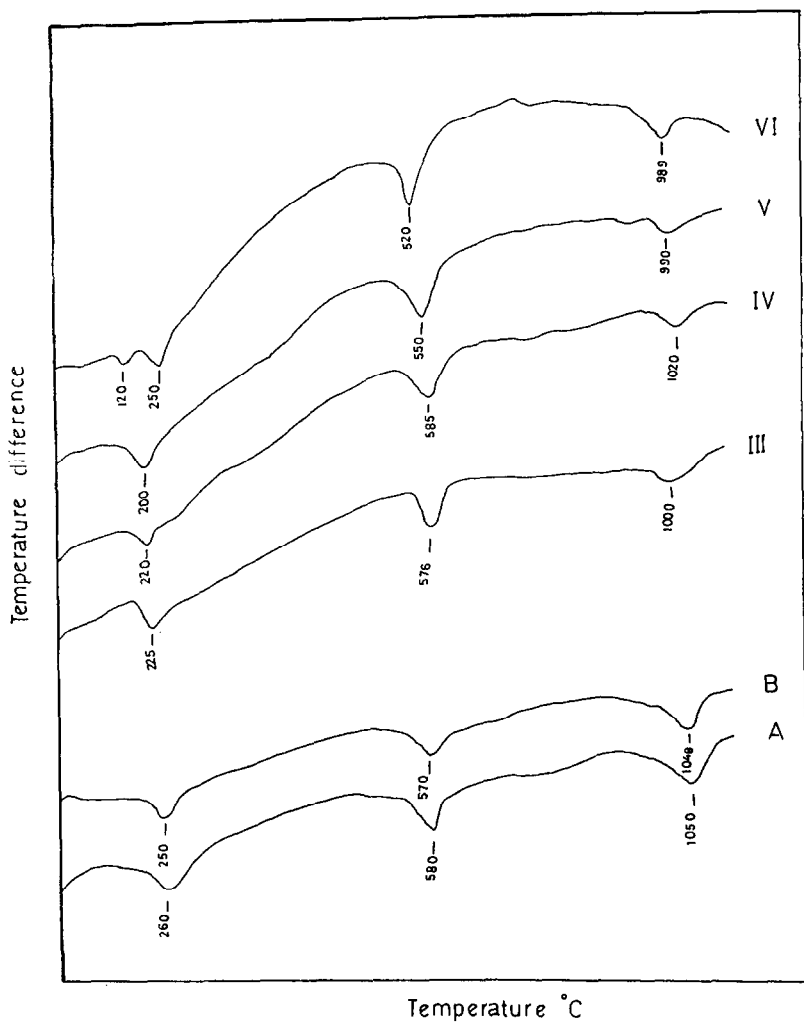


Fig. 3. Differential thermal analysis of the investigated MnO_2 samples.

of the mixture are shown in Figs. 4 and 5 together with those of ordinary battery grade (electrolytic and synthetic $\gamma\text{-MnO}_2$) and $\gamma\text{-MnO}_2$ produced by electrolysis of MnSO_4 , Fig. 6.

The discharge parameters for these samples are represented in Table 3, where T is the time corresponding to a one-electron discharge of MnO_2 .

For samples A and B, neither the open-circuit potential (OCP) values nor the capacity deduced from the quantity of electricity consumed during reduction indicates the presence of active MnO_2 .

The OCP values attained for the samples investigated decreases in the order of sample VI (672 mV) \rightarrow IV (660 mV) \rightarrow IV (648 mV) \rightarrow III (638 mV) \rightarrow A (455 mV) \rightarrow B (423 mV).

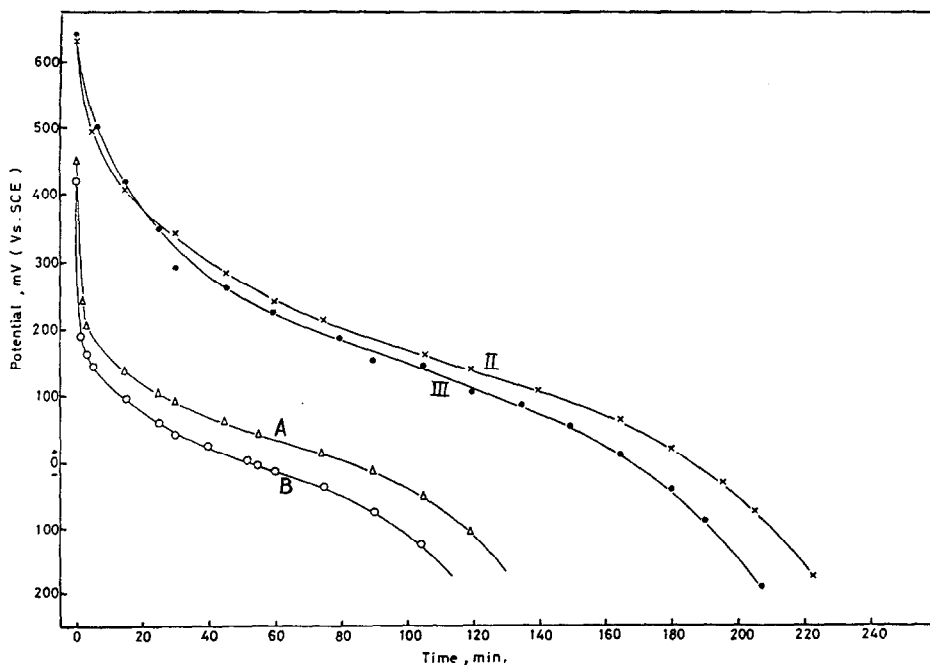


Fig. 4. Cathodic polarization curves of samples: (●) III; (×) IV; (Δ) A, and (○) B in $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ solution at 20 mA/0.5 g mixture.

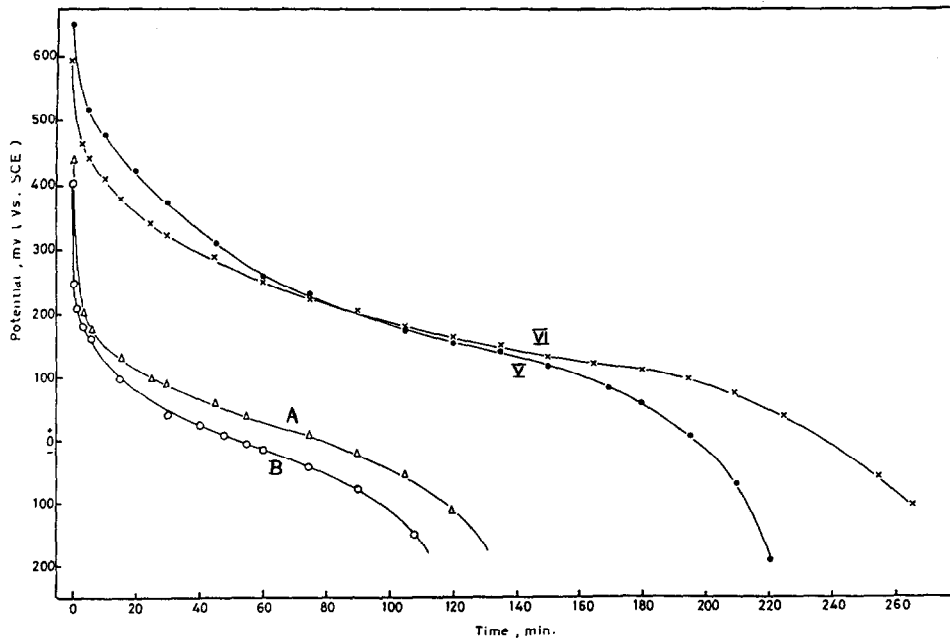


Fig. 5. Cathodic polarization curves of samples: (●) V; (×) VI; (Δ) A, and (○) B in $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ solution at 20 mA/0.5 g mixture.

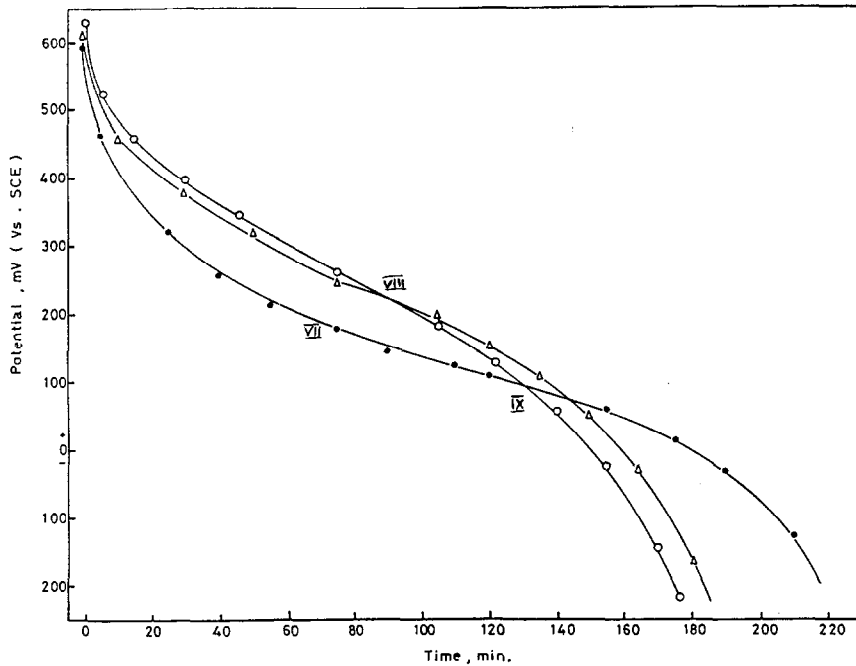
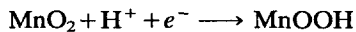


Fig. 6. Cathodic polarization curves of samples: (●) VII; (Δ) VIII, and (○) IX in $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ at 20 mA/0.5 g mixture.

They vary according to their crystal structure and preparation method. Samples III and IV (products of digest in hydrochloric acid) show remarkable increases in T values amounting to 110 ± 15 min with respect to the original samples, and correspond to ordinary battery-active MnO_2 .

On the other hand, samples V and VI (products of digestion in sulfuric acid) show better discharge performance with regard to the above samples where the highest values of T and closed-circuit potential (CCP) were achieved especially with $\alpha\text{-MnO}_2$ which performed better than all other samples with respect to all parameters (Table 3).

The cathodic reaction is controlled by the diffusibility of protons into the manganese dioxide crystals and the mobility of electrons according to the reaction:



The relation between the electrochemical activity of MnO_2 , water content and decomposition temperature of MnO_2 was established. Sasaki *et al.* [31] and Fukuda [32] observed a decrease in the discharge capacity with decreasing water content. Freeman [30] concluded that the low decomposition temperature of MnO_2 indicates low thermal stability and this reflects the strength of the Mn-O bond. The smaller the bonding energy the greater the possibility for the acidic 'OH' group, which is directly linked with the Mn-O bond, to provide a higher discharge capacity of MnO_2 .

Brenet [33] proposed an identical mechanism regardless of the type of manganese dioxide to take into consideration the formalism given by Balewski *et al.* [34] and this

TABLE 3
Discharge characteristics of investigated manganese dioxides

Sample	Method of preparation	Forms	Open-circuit potential (mV vs. SCE)	T (min)	Closed-circuit potential at end of discharge (mV vs. SCE)
A	Local MnO ₂ ore	β	455	85	-2
B	Chemical B-type MnO ₂	β	423	55	-1
III	Product of digested roasted A in HCl	γ	638	165	+8
IV	Product of digested roasted B in HCl	γ	648	180	+15
V	Product of digested roasted A in H ₂ SO ₄	γ	660	195	+10
VI	Product of digested roasted B in H ₂ SO ₄	α	672	233	+30
VII	Synthetic MnO ₂ from Belgium provided by the General Co. of Dry Batteries	γ	600	180	-1
VIII	EMD ^a from Germany provided by the General Co. of Dry Batteries	γ	617	165	-24
IX	γ-MnO ₂ from electrolysis of MnSO ₄	γ	604	155	-23

^aElectrochemically prepared MnO₂.

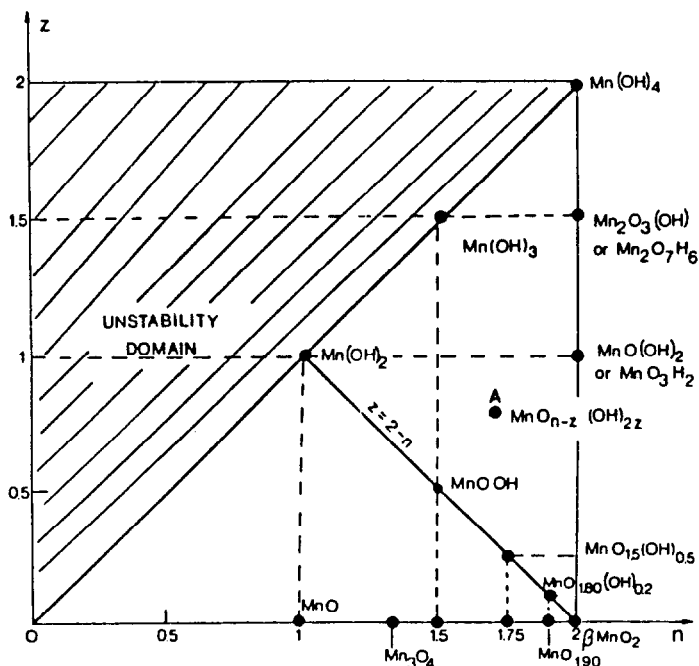


Fig. 7. Diagram of existing manganese oxides.

was subsequently redefined by Coeffier and Brenet [35]. The oxides of Mn [36] shown in Fig. 7 correspond to the formula given by Balewski *et al.* [34]:



Along the n -axis are shown the non-hydrated compounds MnO, Mn_3O_4 , Mn_2O_3 , $\beta\text{-MnO}_2$ for which $z=0$. In the case where $z=2-n$, we find the line on which are situated the compounds $\text{Mn}(\text{OH})_2$ and MnOOH , corresponding to $n=1$, $z=1$ and $n=1.5$, $z=0.5$, respectively.

On the graph there appear forbidden domains of existence since one should always respect the conditions:

$$z < n \quad (2)$$

On the diagonal corresponding to $z=2-n$, we find a compound that corresponds to the formula:



and if this compound contains molecular water we may write:



which is the formula given by Coeffier and Brenet [35].

This formula points up the existence of OH groups which confer the well-known ionic exchange properties of manganese dioxide that have been considered, in refs. 36–38.

Conclusions

Roasted natural and chemically inactive β - MnO_2 at 1050 °C gave cubic and tetragonal Mn_3O_4 , respectively.

Digestion with hydrochloric acid gave the γ -form of manganese dioxide while digestion with sulfuric acid gave γ - or α -manganese dioxides which possess high water contents and low decomposition temperatures. The electrochemical activities of the active manganese dioxides were characterized by a good depolarizing activity. The discharge capacity of samples digested in sulfuric acid are somewhat higher than those digested in hydrochloric acid.

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