

THERMAL DECOMPOSITION CHARACTERISTICS IN AIR AND THEIR RELATIONSHIP WITH ELECTROCHEMICAL ACTIVITY OF DIFFERENT POLYMORPHIC FORMS OF MnO_2

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ABSTRACT

Thermal decomposition characteristics of various synthetic MnO_2 samples were studied with the help of DTA and TG in air. Each crystalline modification group produced its own characteristic thermogram which could be distinguished from the thermogram of other modifications. However, there were a few instances of overlapping, because some samples were not truly homogeneous and contained one or more polymorphic forms as impurities. The results indicate that relationships exist between electrochemical activity and DTA peak temperature for the loss of initial molecular water on the one hand, and DTA peak temperature for the decomposition of MnO_2 to Mn_2O_3 , on the other hand. The amount of combined water determined by the difference in weight loss at 400 and 200°C was found to be related to the electrochemical activity or depolarizing capacity of the samples.

INTRODUCTION

The thermal decomposition characteristics of various polymorphic forms of manganese dioxide have been the subject of considerable investigation by various workers [1–10], mainly with a view to characterise or identify them and finally to select a suitable variety for use in dry cells. From a study of the differential thermal analysis (DTA) curves together with the X-ray powder diffraction data, these authors could identify the existence of at least four crystalline modifications of MnO_2 , namely, α , β , γ and δ - MnO_2 . Thermal decomposition of mineral ramsdellite is almost similar to that of γ - MnO_2 excepting the absence of an endothermic peak for the loss of combined water [8]. Brenet et al. [11] have characterised only three types of MnO_2 through thermogravimetric (TG) studies: (i) inactive pyrolusite including the α and β variety, (ii) chemically prepared γ - MnO_2 , and (iii) electrolytic γ - MnO_2 . The first attempt to screen battery-active MnO_2 with

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the help of thermal analysis was made by Fishburn and Dill [12] and subsequently, and with some success, by Regner et al. [13]. They observed that γ - MnO_2 samples with a characteristic DTA peak temperature range for the decomposition have a high depolarising capacity. Using carefully controlled inert (nitrogen or helium) and oxidising atmospheres, Freeman et al. [14] have shown that MnO_2 samples with lower DTG peak temperatures for decomposition to Mn_2O_3 have high battery activity. Kanungo [15] has shown that DTA peak temperatures for both water and oxygen loss from various crystalline modifications of MnO_2 are closely related to their catalytic activity for the oxidation of carbon monoxide.

The general conclusions drawn from the literature survey reveals that the thermal decomposition data of synthetic MnO_2 samples differ widely depending upon the method of preparation and, consequently, different authors give different interpretations of the results. This is because synthetic MnO_2 is rarely stoichiometric in nature and is usually a mixture of two or more oxides and oxyhydroxides of manganese. The purpose of the present paper is to search for common features of thermolysis among each group of MnO_2 and to relate them to depolarising capacity.

EXPERIMENTAL

Preparation of MnO_2 samples

The methods of preparation of different MnO_2 samples and their physico-chemical characteristics have been described in detail in a previous publication [16]. However, for the sake of ready reference the methods of preparation are briefly summarised here. The nature of the crystalline modification was identified with the help of X-ray powder diffraction patterns [16].

Sample 1. Oxidation of MnSO_4 by KMnO_4 .

Sample 2. Reduction of KMnO_4 by 6 M HCl.

Sample 3. Leaching of sample 2 in 3 M HNO_3 at 90°C .

Sample 4. Oxidation of $\text{Mn}(\text{NO}_3)_2$ by NaClO_3 in strong HNO_3 medium.

Sample 5. Oxidation of MnSO_4 by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1 M H_2SO_4 .

Sample 6. Oxidation of MnSO_4 by $\text{K}_2\text{S}_2\text{O}_8$ in 1 M H_2SO_4 .

Sample 7A. Electrolytic oxidation of MnSO_4 .

Sample 7B. Electrolytic oxidation of MnSO_4 .

Sample 8. Thermal decomposition of MnCO_3 in air at 400°C .

Sample 9. Sample 8 calcined at 750°C and leached in 3 M HNO_3 at 90°C .

Sample 10. Oxidation of $\text{Mn}(\text{OH})_2$ by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at pH 9.3

Sample 11. Leaching of MnOOH in 3 M HNO_3 at 90°C .

Sample 12. Thermal decomposition of $\text{Mn}(\text{NO}_3)_2$ at 150°C .

Sample 13. Oxidation of MnSO_4 by NaOCl in alkaline medium.

Sample 14. Sample 13 leached in 3 M HNO₃ at 90°C.

Sample 15. Commercial reagent grade MnO₂ from B.D.H. (India).

Sample 16. Reagent grade MnO₂ from Merck (Germany).

Thermal analysis

Thermal analysis of the samples was carried out in a MOM derivatograph (Budapest, Hungary) using a cylindrical platinum crucible. Calcined (1200°C) α -Al₂O₃ was used as a reference material. The samples were packed under nearly identical conditions, namely, using gentle tapping 6–7 times to fill $\frac{3}{4}$ of the crucible so that the tip of the thermocouple lay well within the samples. All the thermograms were taken in air and at a heating rate of 10°C min⁻¹ using the same DTA (1/10) sensitivity. However, TG sensitivity was varied from 200 to 500 mg depending upon the bulk density of the samples.

Depolarizing capacity

The depolarizing capacity of different MnO₂ samples was determined by discharging a pelleted mixture of 0.15 g sample and 0.015 g acetylene black in an electrolyte solution containing a mixture of 21% NH₄Cl and 27% ZnCl₂ (pH 4.1) at a constant current of 15 mA. The details of the method have been described in an earlier communication [17]. The time taken to reach an arbitrary voltage (0.6 V) was usually taken as the depolarizing capacity.

RESULTS

The thermolysis of MnO₂ in air up to 1100°C exhibits the following major effects: (1) loss of physisorbed water, (2) loss of chemically bound water or hydroxyl groups, (3) change of unstable phase to a stable phase (for example, γ -MnO₂ to β -MnO₂), (4) decomposition of MnO₂ to Mn₂O₃, and (5) decomposition of Mn₂O₃ to Mn₃O₄. The results of the thermal decomposition characteristics are presented later. The salient features of the TG and DTA curves are summarised in Table 1.

α -MnO₂. Figure 1 represents the DTA curves of different samples belonging to the α -modification. Sample 3 which is derived from a δ -MnO₂ sample (No.2) by acid-leaching, shows a much lower water content than its precursor, indicating that acid-leaching treatment results in the elimination of free (molecular) water, probably from the layer lattice of δ -MnO₂, to form a more compact tetragonal structure. Besides, the sharp exothermic peak at 520°C for sample 2 (cf. Fig. 4) is absent in sample 3. Instead, sample 3 exhibits only endothermic decomposition peaks at 600 and 925°C due to successive stages of oxygen loss. The DTA for sample 5 clearly indicates the

TABLE 1
Thermal decomposition characteristics of MnO₂ samples

Sample no.	Loss of physisorbed water		Loss of chemisorbed (or combined) water			
	DTA peak temperature (Endo) (°C)	Weight loss at 200°C (%)	DTA peak temperature (°C)		Weight loss at 400°C (%)	Difference in weight loss 400–200°C (%)
			1st peak (Endo)	2nd peak (Endo/Exo)		
<i>α-MnO₂</i>						
3	120	2.56			5.12	2.56
5	130	2.15		260(Exo) 345(Endo)	5.50	3.35
6	110	1.65	255	320(Exo)	4.12	2.47
8	180	2.08	245		3.71	1.63
<i>β-MnO₂</i>						
12	150		240			
15	120	1.01		240(Exo) 370(Endo)	2.01	1.00
16	160	0.80			1.51	0.71
<i>γ-MnO₂</i>						
4	170	3.01	270	325(Endo)	6.33	3.32
7A	150	2.88		330(Endo)	5.19	2.31
7B	160	1.50		330(Endo)	4.51	3.01
9	135	0.87	260	380(Endo)	3.90	3.03
11	145	1.44		330(Endo) 400(Exo)	2.87	1.43
14	170	1.71	285	380(Exo)	3.84	2.13
<i>δ-MnO₂</i>						
1	180	6.38	250		13.027	6.64
2	180	6.18			11.84	5.66
10	150	4.46	250	340(Exo)	9.82	5.36
13	210	5.05		390(Exo)	12.63	7.58

loss of two types of water at 130 and 345°C. But this is not much pronounced in sample 6 although two small endothermic effects at 110 and 255°C can be distinguished. This is followed by a sharp exothermic effect around 320°C possibly due to recrystallization through lattice rearrangement [18,19]. It is interesting to note that there is a close similarity between the

Decomposition of MnO ₂ to Mn ₂ O ₃				Decomposition of Mn ₂ O ₃ to Mn ₃ O ₄
DTA peak temperature (°C) (Endo/Exo)	Weight loss at 700°C (%)	Difference in weight loss (700–400°C) (%)	Oxygen loss calculated from free MnO ₂ content (%)	DTA peak temperature (Endo) (°C)
600(Endo)	11.26	6.14	7.95	925
560(Endo)	14.58	9.08	8.19	890
580(Endo)				
570(Endo)	10.29	6.17	7.53	910
640(Endo)				
570(Endo)	13.07	9.36	6.42	
650(Endo)				
640(Endo)	9.67	9.67	8.79	
660(Endo)	10.55	8.54	7.71	
690(Endo)	9.54	9.03	8.39	
580(Endo)	14.33	8.00	8.21	
590(Endo)	13.46	8.27	7.93	
585(Endo)	12.03	7.52	8.17	
640(Exo)				
600(Endo)	12.71	8.81	8.44	
600(Endo)	11.84	8.97	8.67	
590(Endo)	12.37	8.53	8.04	
590(Exo)	17.10	4.08	6.70	940
520(Exo)	14.67	2.83	6.53	940
540(Exo)	17.85	8.03	6.45	
660(Endo)				
515(Endo)	16.50	3.87	6.40	790
570(Exo)				

DTA traces of sample 6 and sample 10 (Fig. 4). As both these samples have been prepared by the persulphate oxidation method, although at different pH values, it may be possible that the two samples contain some common metastable centres which undergo exothermic rearrangement at 320–340°C to a more stable configuration.

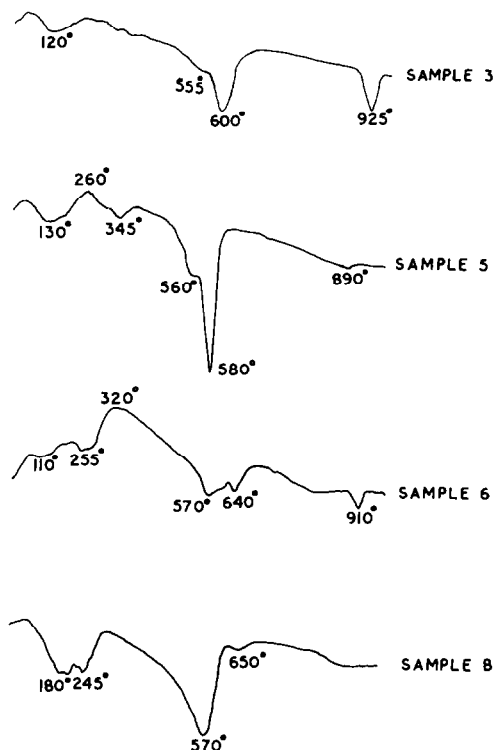


Fig. 1. DTA curves for the α - MnO_2 group of samples.

The endothermic effect due to decomposition of MnO_2 is a two-stage process for all three samples although their temperatures are different. Such a two-stage endothermic effect demonstrates that decomposition takes place in the heterogeneous phase. X-Ray diffraction patterns of these samples indicate the presence of a small quantity of γ - MnO_2 as impurity [16]. Since γ - MnO_2 decomposes at a lower temperature, a two-stage decomposition is therefore not unexpected. The thermal decomposition behaviour of sample 8 is somewhat different in as much as it is free from alkali metal content, although the X-ray diffraction pattern is closely similar to those of the α - MnO_2 group of samples.

β - MnO_2 . The DTA curves of the β - MnO_2 group of samples are shown in Fig. 2. The two minor initial endothermic peaks at 120 and 240°C for sample 12 do not show any corresponding weight loss in TG. While the occurrence of the former peak may be attributed to the transition of ferroelectric to paraelectric behaviour, which is observed characteristically in β - MnO_2 [20], the origin of the second peak is difficult to explain at this stage. Azim et al. [10] also found a small endothermic peak at 260°C for some β - MnO_2 samples which, however, showed a break in the TG curves at the same temperature. Probably the TG sensitivity in the present work was

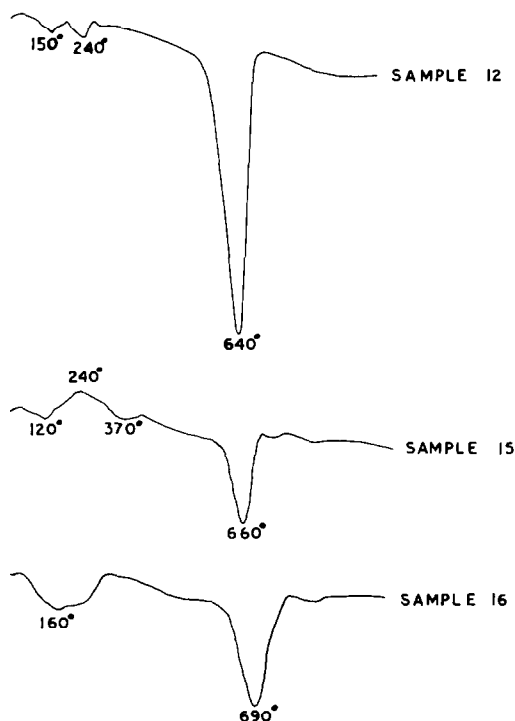


Fig. 2. DTA curves for the β - MnO_2 group of samples.

not enough to record this small change in weight. Bodas et al. [20] also did not observe any weight loss in the TG curve of β - MnO_2 up to 460°C . However, the rate of decomposition is very sharp for this sample reaching a maximum at 640°C . The weight loss at 700°C (9.67%) is higher than the calculated value of 8.78% obtained from the free MnO_2 content. This shows that a small quantity of weight loss of about 1% takes place before decomposition to Mn_2O_3 . Samples 15 and 16, however, do contain some water as shown in Table 1. Sample 15 shows a very minor endothermic peak at 370°C indicating the presence of some structural water also.

γ - MnO_2 . The thermal decomposition behaviour of this variety of MnO_2 is of considerable importance because of its high depolarising capacity in a dry cell. X-Ray powder diffraction data have indicated that samples 4, 7A, 7B, 9, 11 and 14 belong to the gamma variety [16]. Figure 3 shows two clear endothermic effects below 400°C for samples 7A, 7B, 9, 11 and 14 indicating the presence of at least two types of water. Lee et al. [21] have found three types of water in electrolytic γ - MnO_2 from a temperature program desorption (TPD) study. But the identification of three types of water from DTA has not yet been successful. In the present investigation only sample 4 exhibits three clear endothermic effects at 160, 270 and 325°C with corresponding changes in the slopes of the TG curves. The presence of a minor

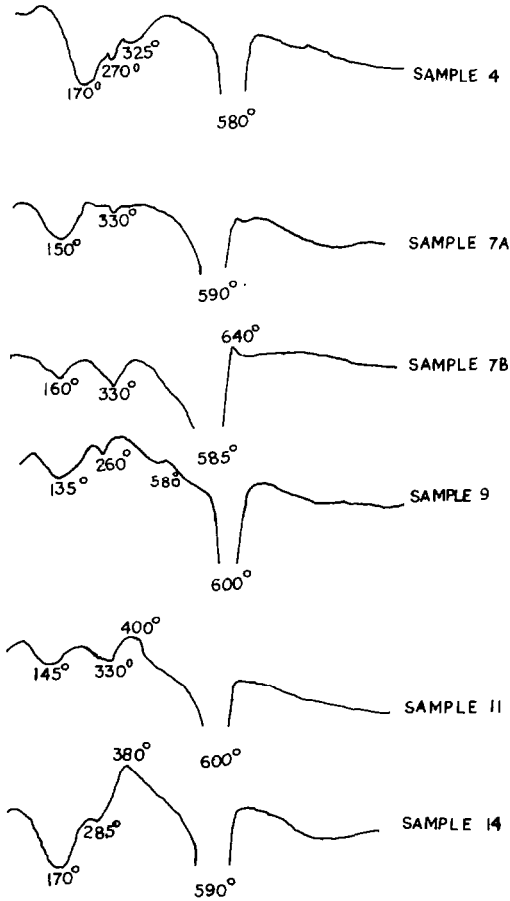


Fig. 3. DTA curves for the γ - MnO_2 group of samples.

exothermic effect around 400°C for samples 11 and 14 indicates a change from γ to β - MnO_2 structure [20,22]. Such an exothermic effect takes place at a lower temperature (340°C) for sample 7A, indicating the poor crystallinity of the sample. The peak temperature for decomposition of γ - MnO_2 to α - Mn_2O_3 varies from 580 to 600°C . Further decomposition to Mn_3O_4 is not observed even up to 1000°C as is evident from Fig. 3.

The difference in weight loss between 400 and 200°C (of Table 1) indicates that samples 4, 7B and 9 contain a considerable amount of combined water. Incidentally, these samples also show a high depolarizing capacity. The difference in weight loss between 700 and 400°C agrees well, within experimental error, with the theoretical amount of oxygen loss calculated from the free MnO_2 content, indicating that around 400°C complete loss of hydroxyl groups takes place. However, some of the samples take up oxygen from the air to replenish the oxygen vacancies created by dehydroxylation. As a result, the difference in weight loss (700 – 400°C) is a

little higher than that based on the calculated values.

δ - MnO_2 . Figure 4 illustrates the DTA curves of samples 1, 2, 10 and 13 belonging to the δ - MnO_2 group. Thermograms of all these samples show some interesting features. The samples are in hydrated form and their broad and diffuse X-ray powder diffraction patterns [16] indicate poor crystallinity. All the samples lose a considerable amount of water in the broad range of temperature (150–350°C) characterised by a wide and deep endothermic peak. Samples 10 and 13 show exothermic peaks at 340 and 390°C, respectively, possibly indicating partial rearrangement of the lattice due to simultaneous loss of both water and oxygen because of the labile nature of the Mn–O bond in the layer lattice of δ - MnO_2 [23]. This is supported by the small difference in weight loss at 700 and 400°C (Table 1) in comparison with other varieties for the decomposition to Mn_2O_3 . Since this variety of MnO_2 is non-equilibrium in nature, there is a tendency to recrystallise to a more stable form (α - MnO_2) immediately after the loss of water [18,22]. This aspect is well illustrated in the DTA curve of sample 10, which shows a broad exothermic peak at 340–350°C.

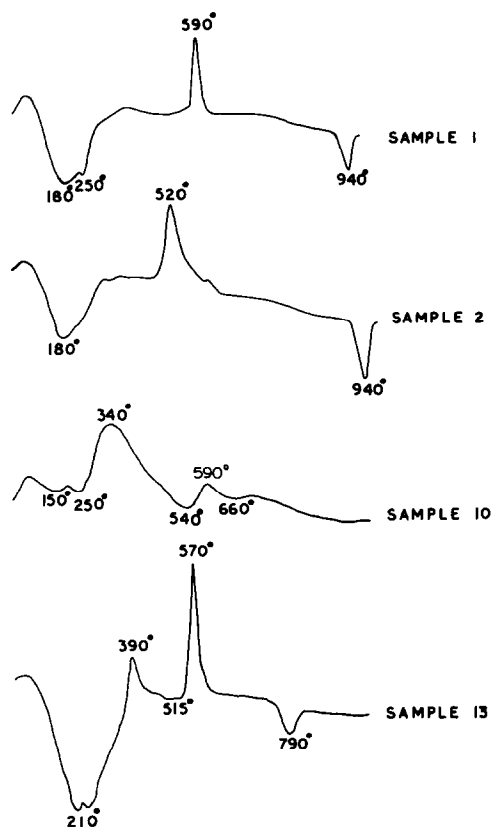


Fig. 4. DTA curves for the δ - MnO_2 group of samples.

The most interesting part of the DTA curves of samples 1, 3 and 13 is the presence of sharp exothermic peaks at 590, 520 and 570°C, respectively. The existence of such an exothermic peak in δ - MnO_2 has not been reported previously. However, Rhode [8] reported the presence of a similar exothermic effect at 515°C for a synthetic hydrous cryptomelane (α - MnO_2) containing 7.85% K_2O . Although the water content of the sample was not indicated, it is possible that Rhode confused his "cryptomelane" with hydrous δ - MnO_2 containing a high alkali content. When the temperature exceeds 500°C, the free alkali present in the samples reacts with lower oxides of manganese forming alkali manganate; this is a strong exothermic reaction and suppresses the endothermic effect at 500–600°C. However, the amount of free alkali is not sufficient to combine with all the lower oxides (Mn_2O_3) formed and, therefore, further decomposition of the latter to Mn_3O_4 takes place in the temperature range 800–900°C.

That the occurrence of an exothermic peak around 550°C is dependent upon the presence of free alkali content, i.e. alkali content which does not form part of the crystal structure, is further supported by the DTA curves of samples 3 and 14. In these samples free alkali was removed by leaching in dilute acid solution resulting in the disappearance of the exothermic peaks, although the samples, especially No.3, contain some combined alkali.

DISCUSSION

The performance of various types of MnO_2 as a depolarizer in Leclanché-type dry cells depends upon their physical and chemical properties which are determined by their origin and method of preparation. It is by now well-recognized that the water content is one of the key factors since it plays an important role in the discharge characteristics of MnO_2 [6,17]. The status of water in MnO_2 is determined by the magnitude of strength or energy by which the water is bound to MnO_2 . It is now generally agreed [21] that water present in MnO_2 can be classified as physically retained, sorbed and constitutional.

In the present investigation, the DTA curves indicate that the peak temperature for initial water loss lies, in almost all cases, above 110°C and in the case of sample 13 it is as high as 210°C. Such a high temperature for the loss of initial water indicates that adsorbed moisture is strongly bonded to the surface probably through hydrogen bonding as suggested by different authors (quoted in ref. 21). Therefore, the DTA peak temperature for initial water loss might give an indication of the strength of bonding of water not only on the surface but also on the subsurface layer. A plot of DTA peak temperature for initial moisture loss vs. the depolarising capacity of the samples (Fig. 5) shows that the depolarising activity is generally higher with those samples where the DTA peak temperature for initial water loss is

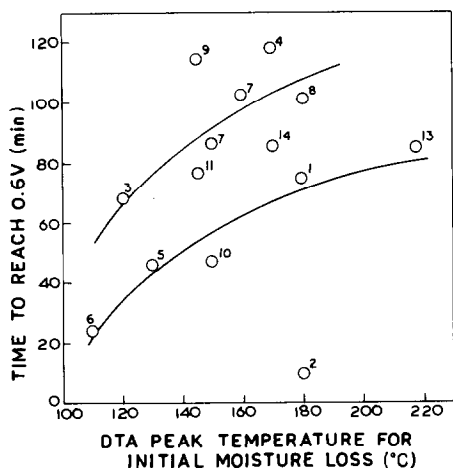


Fig. 5. Relationship between DTA peak temperature for initial moisture loss and depolarizing capacity of various MnO_2 samples. Superscripts denote the sample numbers.

higher. However, all the samples do not lie on a single curve: samples with high alkali content (α and δ - MnO_2) lie on a curve of lower activity. This is probably because alkali metal ions prevent the mobilisation of protons of the OH groups. Since the DTA peak temperatures for initial moisture loss from γ - MnO_2 samples lie within a small range, no well-defined correlation is observed for these samples.

The plot of DTA peak temperature for the decomposition of MnO_2 to Mn_2O_3 vs. depolarizing activity (Fig. 6) reveals some interesting features. While the activity shows an increasing trend with increase in peak tempera-

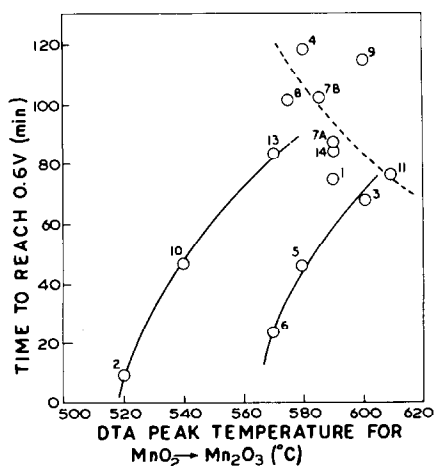


Fig. 6. Relationship between DTA peak temperature for conversion of MnO_2 to Mn_2O_3 and depolarizing capacity of various MnO_2 samples. Superscripts denote the sample numbers.

ture for α and δ - MnO_2 , the opposite behaviour is observed for γ - MnO_2 samples. In a non-stoichiometric compound like γ - MnO_2 , the removal of strongly bound OH groups is also accompanied by the loss of some lattice oxygen which leads to weakening and collapse of the structure. However, for α and δ - MnO_2 , combined water is not bound to the lattice as strongly as in γ - MnO_2 . Therefore, loss of water from these groups of MnO_2 samples does not weaken the lattice as in the case of γ - MnO_2 , and the DTA peak temperature remains practically unaffected by the water loss. Freeman et al. [14] observed that γ - MnO_2 samples of lower DTG peak temperature for the decomposition of MnO_2 to Mn_2O_3 are more active than those of higher peak temperature.

From the TG curves a distinction could be made between the initial loss of moisture and the loss of combined water. Since at 200°C all the physically adsorbed free water is lost and at 400°C both free and combined water are removed, the difference in weight loss at the two temperatures should give at least the order of magnitude of the amount of chemically bound water in MnO_2 samples. Figure 7 illustrates that this chemically bound water, as determined from TG curves, is related to the depolarizing capacity of the samples. It will be seen from the figure that the different groups of samples lie on three different curves. However, in each case the depolarizing capacity tends to increase with the increase in bound water content. The deviation observed for the α - MnO_2 group of samples (Nos. 3, 5 and 6) is probably due to the fact that most of the water in these samples occurs in the molecular state [16] and therefore does not take part in the electrochemical activity.

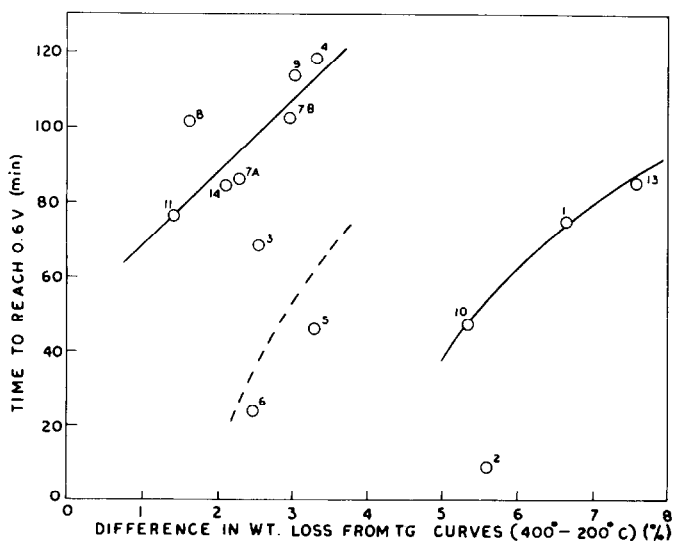


Fig. 7. Correlation between difference in weight loss at 400 and 200°C from TG curves and depolarizing capacity of MnO_2 samples. Superscripts denote the sample numbers.

The figure also indicates that a high water content, as in δ -MnO₂, is not beneficial for higher activity. It is the nature of occurrence of water which is more important, as is evident from the linear relationship for the γ -MnO₂ group of samples.

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