

A SCREENING METHOD FOR ASSESSING THE BATTERY ACTIVITY OF MANGANESE DIOXIDES

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ABSTRACT

A resistance technique involving dynamic environments of product gas, oxygen, at supra-atmospheric pressures has been used to study the decomposition of manganese dioxide to its lower oxide. It has the advantages of good reproducibility, small peak band widths and close control of the oxygen environment pressures. (Being a surface as opposed to bulk measuring technique the method offers few advantages over TG as a screening method for comparing different types of manganese dioxide.)

INTRODUCTION

Recently in these laboratories a correlation between the battery activity of manganese dioxide samples and temperatures of decomposition to the lower oxide, $\text{MnO}_2 \rightarrow \alpha\text{Mn}_2\text{O}_3$ was established¹. The lower the temperature for the decomposition the more electrochemically active the dioxide appears to be. Derivative thermograms were obtained under carefully chosen conditions. These included a dynamic environment of product gas oxygen at atmospheric pressure which improved resolution significantly for reasons excellently described by Garn². The purpose of the present work was to establish whether resolution could be further improved by the use of supra-atmospheric pressures of oxygen. Since such an environment would require extensive modifications to an existing TG system³, a simple technique, incorporating a high pressure facility, based on the abrupt change in electrical resistance accompanying the transition to the lower oxide^{4,5} has been developed.

$\alpha\text{Mn}_2\text{O}_3$ has room temperature resistivities 10^2 – 10^5 times and activation energies for conduction 3–5 times greater than manganese dioxide (depending on the grade). Thus the expected form of the resistivity/temperature curve and its derivative through the $\text{MnO}_2/\text{Mn}_2\text{O}_3$ phase transition is as shown in Fig. 1.

EXPERIMENTAL

Materials

Compositional details of five of the manganese dioxides scrutinized and designated R1, R2, R5, R20 and R30 appeared in a previous publication¹.

R1 is an ore of Ghanian origin and ρ -phase, R2 a commercially electrodeposited

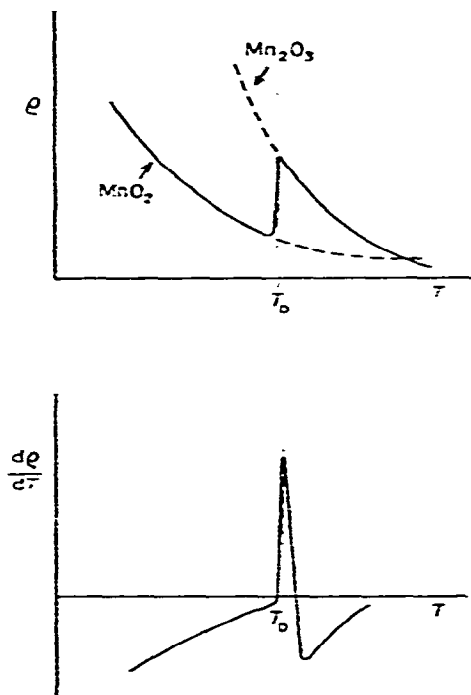


Fig. 1. Expected resistivity, ρ and $d\rho/dT$ temperature plots at the decomposition temperature for the reaction $\text{MnO}_2 \rightarrow \alpha\text{Mn}_2\text{O}_3$.

γ -phase, R5 a Botswana ore comprising a mixture of β - and ρ -phases, R20 a β -phase ore of Moroccan origin and R30 a similar ore but of Caucasian origin. Additionally a synthetic β -phase material prepared from manganous nitrate according to Covington et al.⁶ including a final heating stage in a slow stream of oxygen was investigated. All samples were powders with at least 80% passing through B.S.S.* 200. Weighed specimens were loaded into a cylinder, described later in text, and compressed between the electrodes at a load of approximately 30 lb.

Apparatus

Figure 2 depicts the resistance bomb together with pressure transducers, valves and flow meter. Manganese dioxide specimens were positioned in the lower part of a long Pyrex or quartz cylinder, 7 mm in diameter, between two spring-loaded platinum electrodes. The glass cylinder was bedded into a nickel/chrome/iron alloy block (Inconel 600) to reduce temperature gradients in the vicinity of the specimen, and enclosed in bomb casing of the same alloy. A tube furnace surrounded the lower half of the bomb and its temperature was regulated by a solid state controller (Solid State Controls Thermic Type T/C). This was programmed by synchronous motors providing for linear increases in temperature over the range 25–700°C at fixed rates of 1.8, 3 or 6.8°C/min. The top of the pressure casing was water-cooled to prevent damage to the compression spring mechanism and 'O' ring pressure seals.

*B.S.S. refers to British Standard Sieve.

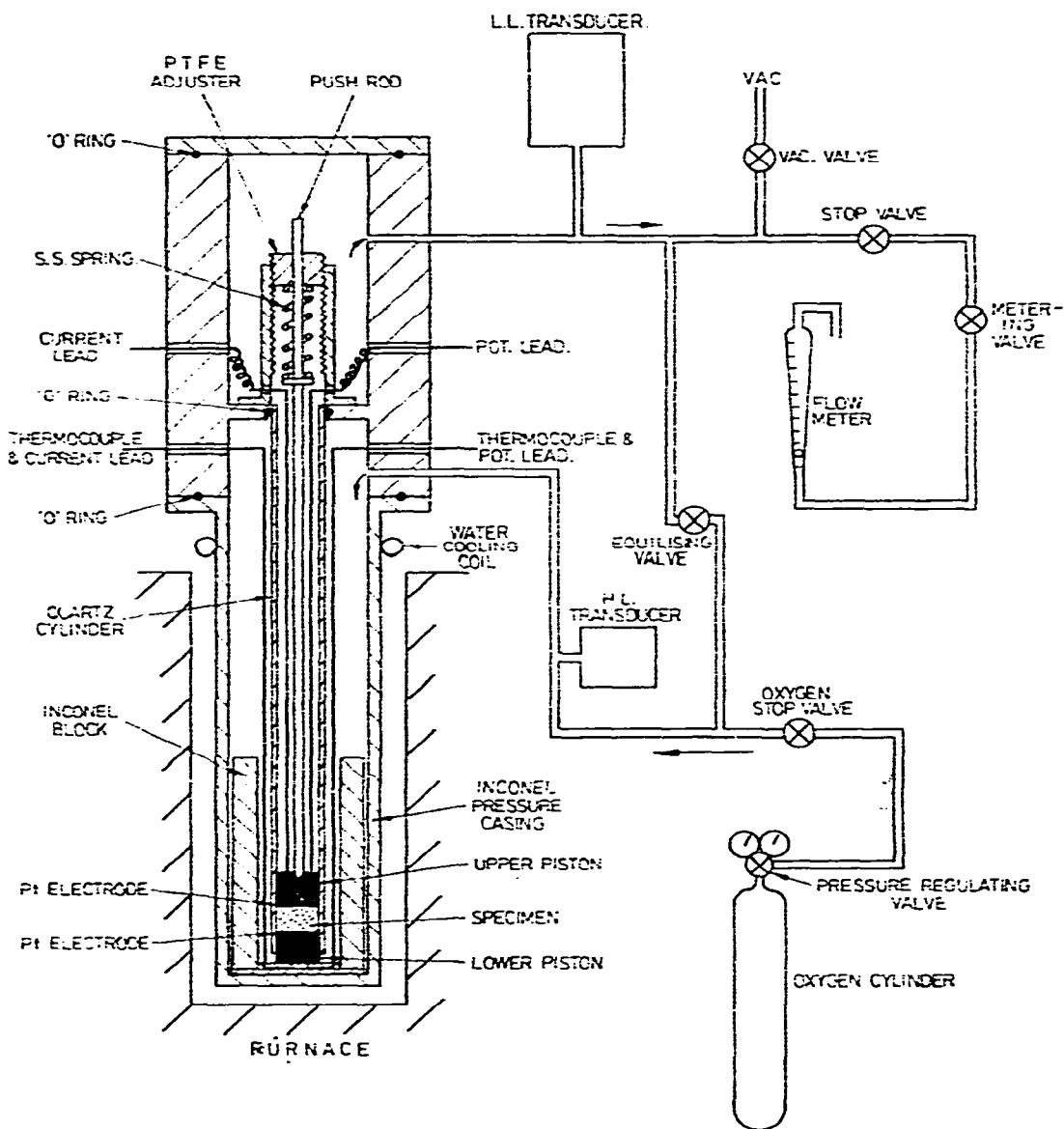


Fig. 2. Resistance bomb.

Oxygen gas was passed through the bomb having first been preheated by contact with the pressure casing wall. Flow-rates and pressures (up to 150 psi) were controlled via needle valves and a pressure-reducing valve. Rates of flow were measured by a "Meterate" meter (Glass Precision Eng. Ltd.) and inlet/outlet pressures by Ether transducers (Type BP1). Entry and exit port pressure differences, necessary to provide the requisite rate of flow, were always less than 0.3 psi. The specimen temperature sensor was a chromel/alumel thermocouple welded to the lower platinum electrode and connected through an ice junction to the X amplifier of an X-Y recorder (Bryans Type 2100).

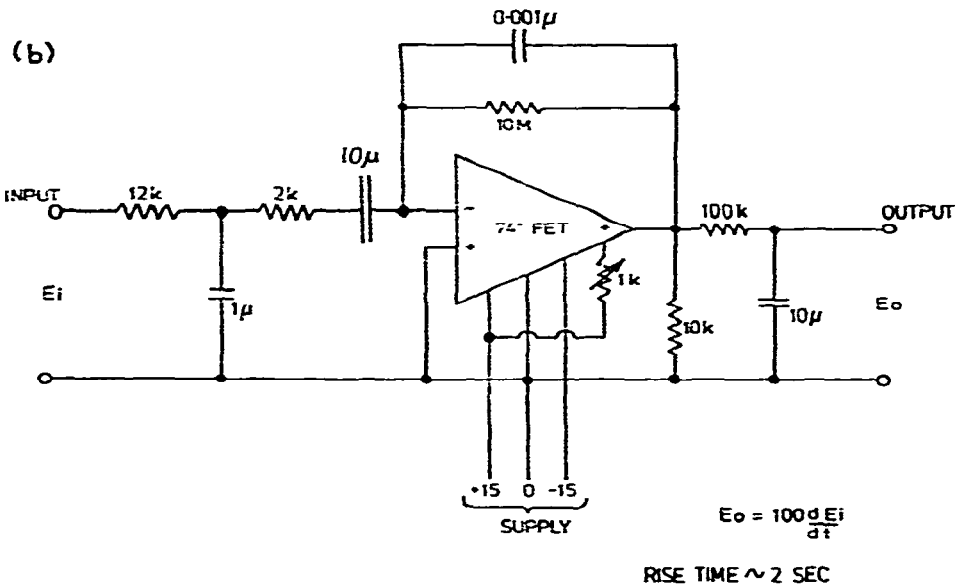
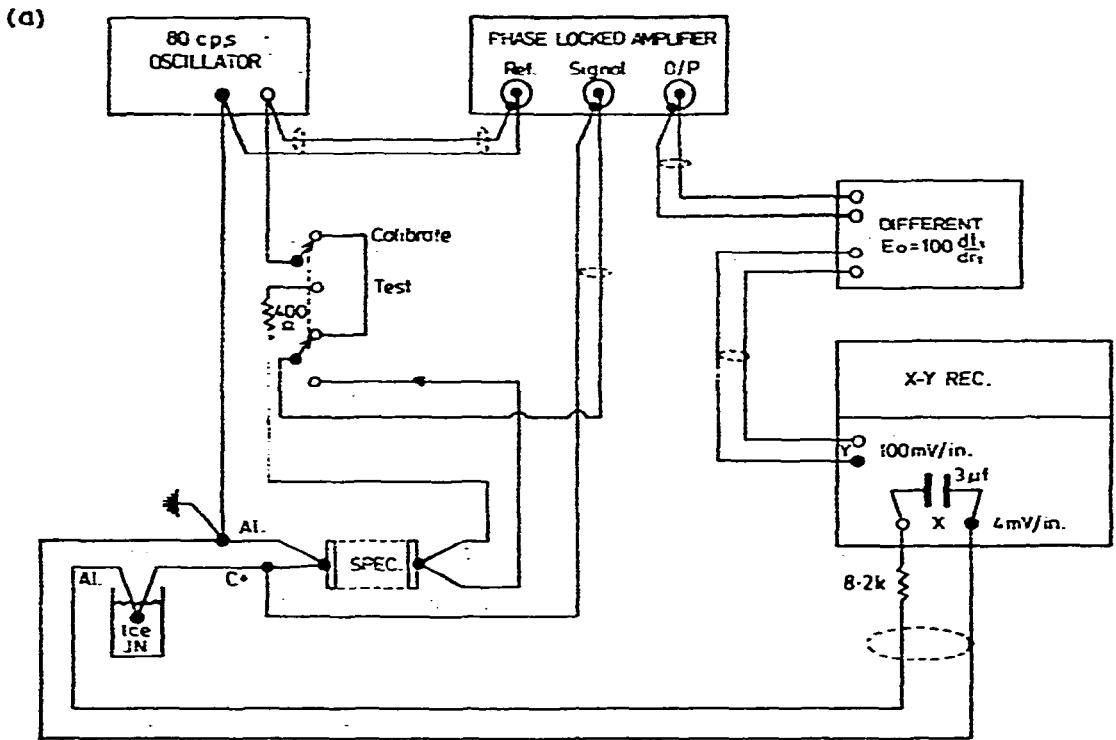


Fig. 3. (a) Resistance/temperature monitoring system. (b) Differentiator circuit.

The AC system used to monitor the electrical resistance of specimens had separate current and potential leads to eliminate lead resistance and is shown in Fig. 3a. The energising source was an oscillator (Levell Type TG 200M) set to 100 mV amplitude (RMS sine), 80 cps and the potential developed across the specimen was measured by a phase-locked amplifier (Brookdeal Type 401). The DC output from this instrument was either recorded directly on the Y axis of the X-Y plotter or more usually electronically differentiated, (Fig. 3b), first. Use of an AC measuring system permitted the thermocouple leads to double as potential/current leads—the AC signal for resistance monitoring, the DC component for temperature measurement after suitable filtering.

The temperature axis of the X-Y plotter was calibrated before each run to a full scale movement of 40 mV. The bomb was evacuated for 5 min before admitting oxygen at the required pressure with the pressure-equalising valve open. Flow-rate was adjusted to the required value, and the equalising valve closed. After 30 min the specimen was heated at constant rate, further adjustments to pressure and flow-rate being made during the run as necessary. Up to temperatures of 200°C the specimen resistance was plotted on the recorder, its sensitivity being adjusted to suit the grade of manganese dioxide. The time derivative of the resistance was then recorded.

RESULTS AND DISCUSSION

Figure 4 is a trace obtained for the electrodeposited sample R2 at 60 psi oxygen pressure, 4 ml/min rate of flow and 6.8°C/min rate of heating for a specimen of mass 0.5 g. The sharp 'decomposition' peak at ~600°C is easily distinguished. Table 1 summarizes the effects of variations of sample mass, rate of flow oxygen and rate of heating on peak temperatures, T_D , and peak widths. The 'decomposition' peak amplitudes are narrowest when the mass of the sample is small, rates of flow of oxygen appreciable and heating rates low. Temperature inhomogeneities within the oxide bed are lessened by the use of smaller samples as are diffusion restrictions to the product gas and desorbing water vapour. The removal of water, a diluent to the oxygen atmosphere, from the oxide compacts is more easily achieved at higher flow-rates and this also sharpens the 'decomposition' peaks. The heating-rate affected the 'decomposition' peak temperature as well as its amplitude, a lower heating-rate producing a lower apparent T_D and a narrower peak amplitude. The former effect is attributed to a smaller lag in temperature between sample and sensor and the latter to improved temperature homogeneity in the sample as the rate of temperature rise decreased. Increases in environmental oxygen gas pressures produce increases in T_D as would be expected for a reversible or partially reversible decomposition, and little change in peak widths except for R1, Table 2.

Practical considerations such as duration of experiments, signal-to-noise ratio of the resistance monitoring system and the tendency to remove part of the specimen by the flushing action of the oxygen dictate a compromise in conditions for good resolution of resistance peaks. Standard conditions chosen were as follows: sample

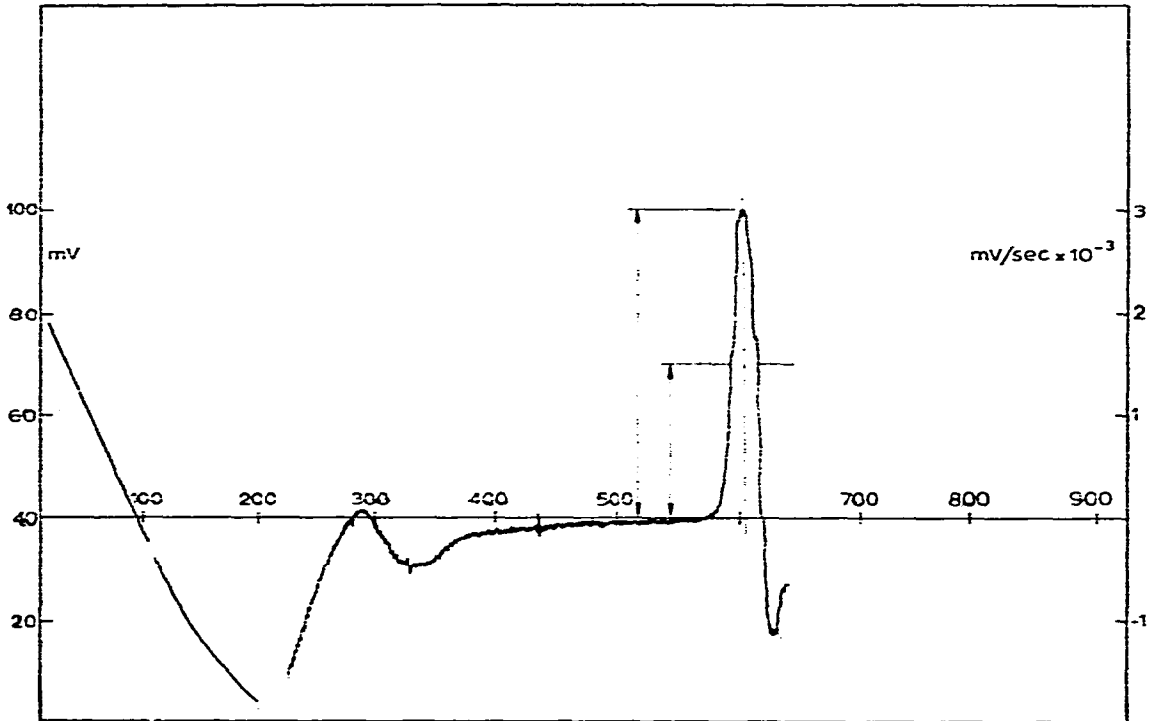


Fig. 4. Resistance and derivative trace for the electrodeposited sample.

TABLE I

DECOMPOSITION PEAK TEMPERATURE AND WIDTH AS A FUNCTION OF SAMPLE SIZE, OXYGEN FLOW-RATE AND HEATING-RATE FOR R2

Oxygen pressure 60 psi abs.

Sample size (g)	Flow-rate (ml/min)	Heating-rate ($^{\circ}\text{C}/\text{min}$)	T_D ($^{\circ}\text{C}$)	Decomposition peak width ($^{\circ}\text{C}$)
0.75	4	6.8	604	23
0.50	4	6.8	604	20
0.25	4	6.8	600	15
0.12	4	6.8	598	11
0.5	0	6.8	600	22
0.5	4	6.8	604	20
0.5	10	6.8	602	19
0.5	28	6.8	602	12
0.5	4	1.8	586	9
0.5	4	3	590	13
0.5	4	6.8	604	20

TABLE 2

EFFECT OF ENVIRONMENTAL OXYGEN GAS PRESSURES ON 'DECOMPOSITION' PEAK TEMPERATURES AND WIDTHS

Sample mass 0.2 ± 0.05 g and flow-rate 5 ± 1 ml/min.

Sample type	Pressure of oxygen (psi abs.)	T_D ($^{\circ}C$)	Decomposition peak width ($^{\circ}C$)
R2	20	573	11
	40	587	10
	60	594	9
	80	602	10
	100	607	9
	120	610	9
	140	612	10
R1	20	607	33
	60	634	27
	100	645	21
R20	20	653	26
	60	675	25
	100	686	24
R30	20	678	21
	60	703	18

TABLE 3

COMPARISON OF 'DECOMPOSITION' PEAK WIDTHS, AND TEMPERATURES UNDER STANDARDIZED CONDITIONS USING THIS METHOD AND DTG

Sample	DTG temp.	Peak width	Present technique	
			Temp.	Width.
R2	619	21	594	9
R1	662	28	634	27
R5	704, 678	66	647, 605	—
R20	700	48	675	25
R30	722	32	703	18

mass 0.2 ± 0.05 g, flow-rate 5 ± 1 ml of oxygen/min, heating-rate $3^{\circ}C/min$, oxygen pressure 60 psi. Peak temperatures could be located with an accuracy of $\pm 1^{\circ}C$ and although the reproducibility has not been tested so extensively as in the earlier work¹ it appears improved at $\pm 2^{\circ}C$. With the exception of the Ghana ore all peak amplitudes were considerably less than in the standardized screening tests¹ (Table 3). T_D values for the dioxides decomposing under identical conditions were in the same order as found TG study. It is to be expected that the lower the crystallinity of the sample the easier and earlier decomposition will be⁷ and this is reflected in the order

$\gamma < \rho < \beta$ (Fig. 5). The synthetic β material decomposed earlier than the β ores but its X-ray diffraction pattern indicated poorer crystallinity.

Decomposition temperatures were lower than reported in the TG investigation although the values quoted in Table 3 are not strictly comparable in that the TG temperatures refer to atmospheric pressure whereas in this technique to 60 psia of oxygen. At atmospheric pressure 'decomposition' temperatures were 50–60°C lower but the siting of thermocouples is different in the two studies and much closer to the sample in this apparatus. Additionally it cannot be assumed that the peaks of the derivatives coincide with TG or DTA peak locations for identical specimen temperatures. The resistance measurements reflect the state of crystallite surface layers rather than bulk processes and resistance is not a linear function of oxygen loss. In view of Drucker and Huttner's⁸ suggestion, that oxygen is initially desorbed from manganese dioxide forming surface skins of lower oxide through which subsequent escape of oxygen is slow and the detection of such surfaces on thermally pretreated electro-

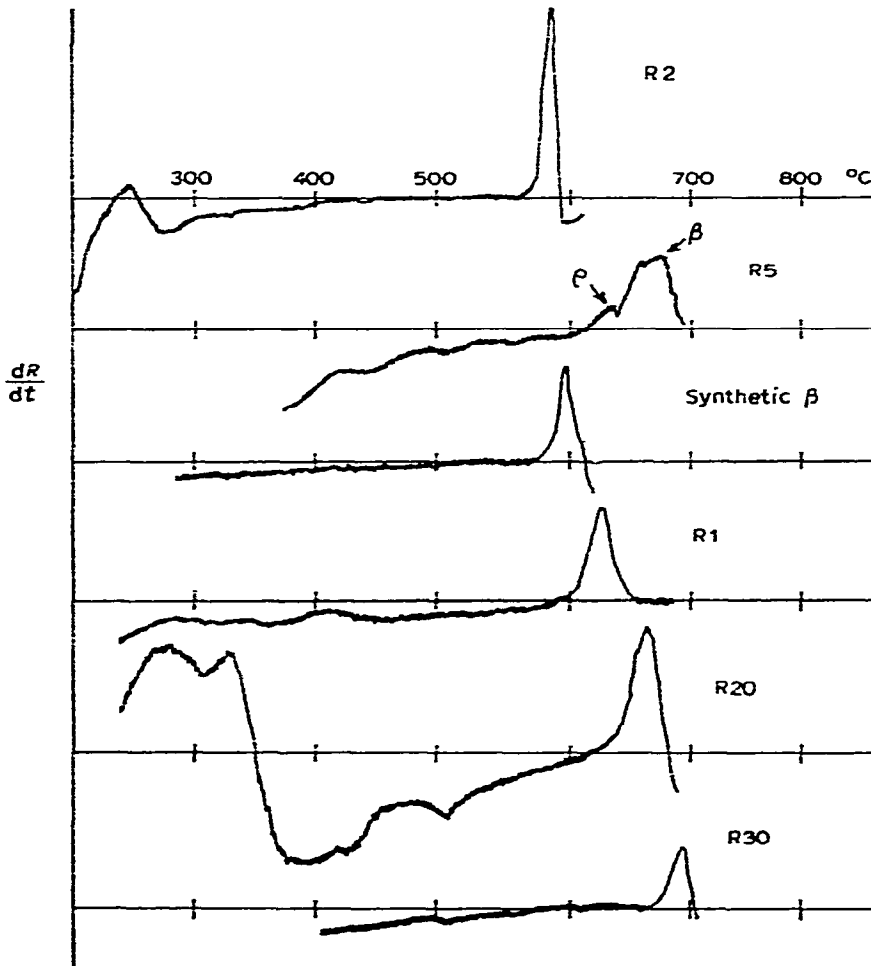


Fig. 5. Comparison of 'decomposition' traces.

deposited samples still essentially present as the dioxide⁹, it is perhaps surprising that 'decomposition' behaviour from the two screening tests is similar.

Some resistance derivative traces (Fig. 5) have characteristic shapes below decomposition temperatures. The small peak at 250°C for the electrodeposited sample was independent of oxygen pressure but was shifted to significantly lower temperatures by increasing the oxygen flow-rate or decreasing the heating-rate. This peak is probably the result of desorption of water which is known to occur at these temperatures¹⁰ and influences the semiconductor properties of the dioxide⁹.

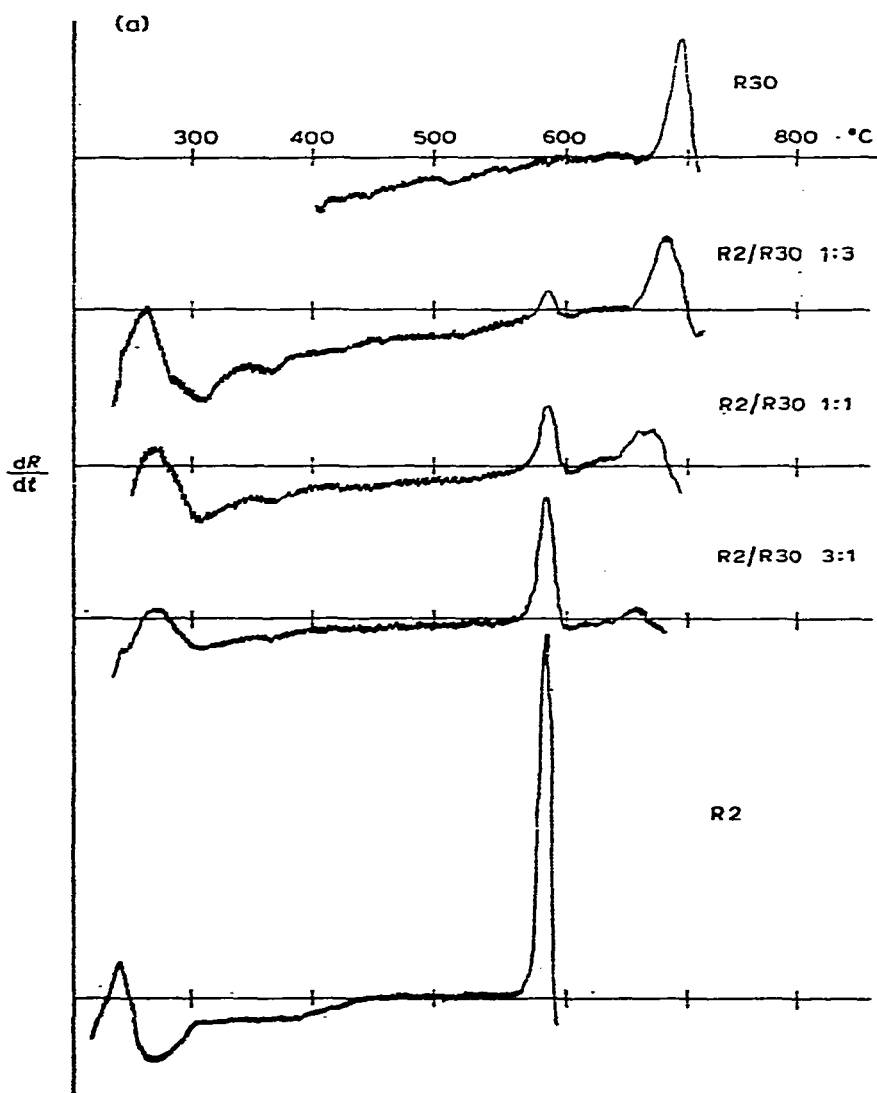


Fig. 6 (a).

Fig. 6. Derivative resistances for mixtures. (a) Electrodeposited-Caucasian ore; (b) electrodeposited-synthetic β .

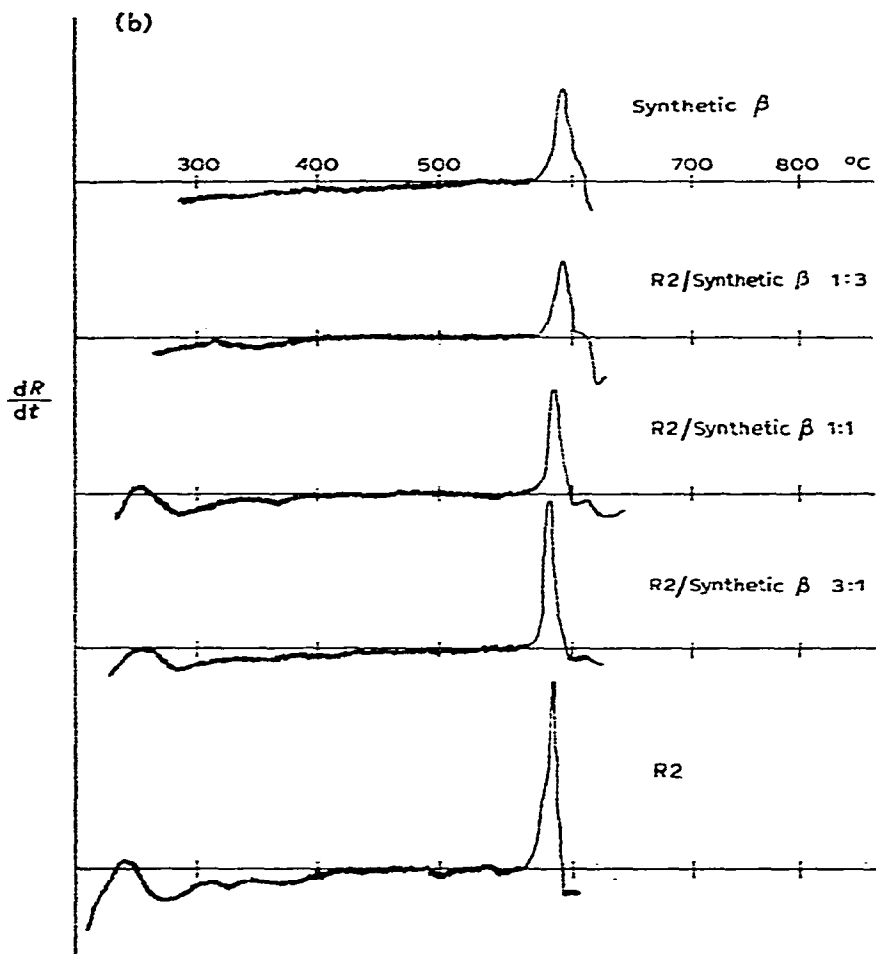


Fig. 6 (b).

The partial pressure of the product vapour will be lowered by the flushing action of higher oxygen gas flows or reduced heating-rates leading to the observed effects. The behaviour of the Moroccan ore at $\sim 300^\circ\text{C}$ is not clear since no significant weight-change is observed at these temperatures. The peak was independent of oxygen pressure and appeared to be irreversible. It could be due to the desorption of trace impurities but was not investigated further.

Derivative resistivity traces for mixtures (Fig. 6) show that a clear indication of constituent components could be made provided that individual decomposition temperatures differed by more than 10°C . Although two peaks are evident as expected for the electrodeposited-Caucasian ore mixture, the decomposition temperature of the ore component was progressively lowered in the presence of increasing amounts of the γ -phase material. The presence of $\alpha\text{Mn}_2\text{O}_3$ in equal proportions to the electrodeposited sample also depressed the peak. No such effect has been observed with TG and only a small shift discernible in DTA¹¹ suggesting that this effect is mainly

confined to the crystallite surface. The Mn_2O_3 formed via the decomposition of the less thermally stable component in a mixture apparently induces a slight surface catalytic effect on the more thermally stable component. The two crystalline components in R5 produce two peaks in the derivative resistance trace as expected (Fig. 5).

The relative amounts of phases could not be estimated in a proportional manner from peak areas as appears possible with TG and DTA¹¹.

Linear $\log P_{O_2}$ vs. $1/T_D$ relationships were obtained for the samples (Fig. 7). However, calculated enthalpy and entropy changes (Table 4) based on the premise of reversibility are up to twice those values reported for direct measurements of equilibrium oxygen pressures for decomposition although considerable differences in the

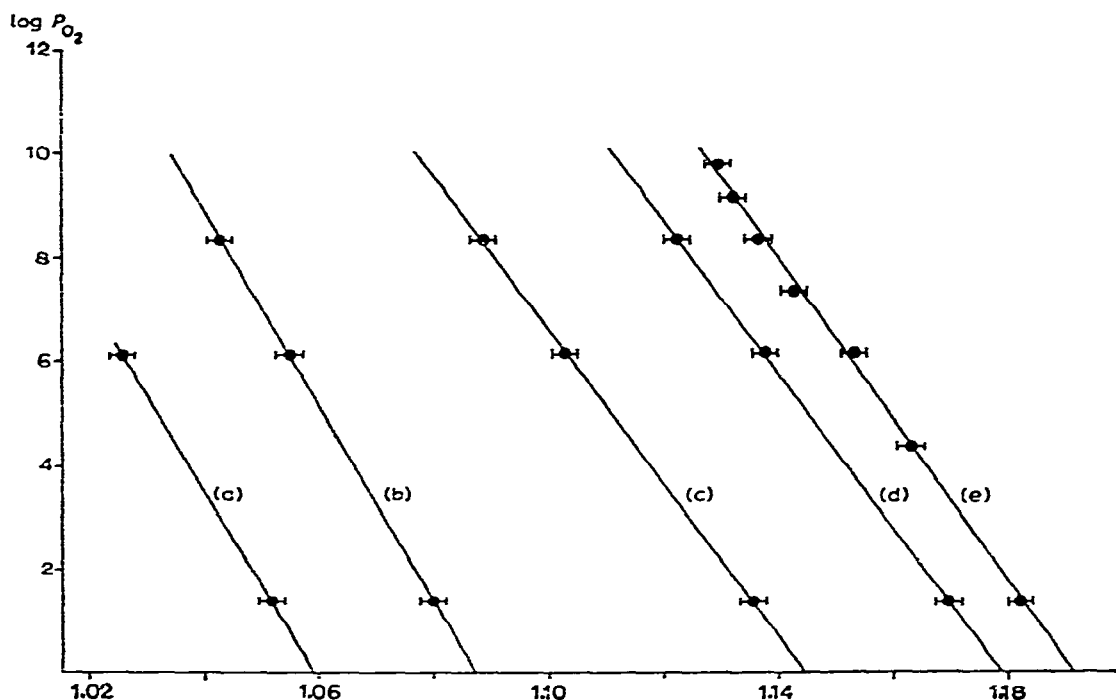


Fig. 7. $\log P_{O_2}$ vs. $1/T_D$ plots. (a) Caucasian ore; (b) Moroccan ore; (c) Ghana ore; (d) synthetic β ; (e) electrodeposited samples.

TABLE 4

ENTHALPY AND ENTROPY CHANGES FOR THE DECOMPOSITION

Type of material	Enthalpy change (kcal/mole)	Entropy change (kcal/mole K)
Electrodeposited R2	71	83
Synthetic β	68	80
Ghana ore R1	66	75
Moroccan ore R20	86	93

equilibrium pressures measured at the same temperatures are apparent with other workers^{8,12-14}. The enthalpy values substantiate the view that the temperatures at the maximum rate of change of resistance in this dynamic method do not reflect true equilibrium points. A recent thermogravimetric study¹⁵ in the pressure range 15-600 psi of oxygen found an even higher enthalpy change for the process of 90 kcal/mole with the same reservations regarding interpretation. The lack of thermodynamic significance does not detract from the usefulness of the technique as a screening procedure.

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