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THERMOCHEMICAL AND MORPHOLOGICAL ASPECTS OF THE THERMAL DECOMPOSITION OF LEAD DIOXIDE

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ABSTRACT

The thermal decomposition of a range of PbO_2 samples prepared by different techniques has been studied using thermogravimetric analysis, differential thermal analysis, X-ray diffraction and scanning electron microscopy. The effects of preparation technique, material crystallinity, particle size and morphology, gas atmosphere and heating rate were studied.

A range of decomposition sequences were found from which it was concluded that no definite decomposition sequences exist for either α-PbO_2 or β-PbO_2.

Morphologically it was not found possible to study the nucleation and growth of the intermediate oxides formed.

INTRODUCTION

In the lead/acid cell the main reaction of interest is:-

$$\underset{(Pos.)}{PbO_2(s)} + \underset{(Neg.)}{Pb(s)} + 2H_2SO_4\,(aq) \underset{recharge}{\xrightarrow{discharge}} 2PbSO_4(s) + 2H_2O(l)$$

As the performance of the cell is dependent on the cycling characteristics of the PbO_2 positive active material it can be seen that a thorough understanding of the chemical and physical changes that occur during cycling is necessary.

After initial formation the positive active material typically has a composition of:- 70% orthorhombic α-PbO_2, 15% tetragonal β-PbO_2 and 15% amorphous PbO_2, however after approximately 50 deep cycles (at 60% depth of discharge) the composition has changed to:- 95% β-PbO_2 and 5% amorphous PbO_2. It is believed that the conversion of α-PbO_2 to β-PbO_2 is achieved as follows.

$$\alpha\text{-}PbO_2 \xrightarrow{discharge} PbSO_4 \xrightarrow{recharge} \beta\text{-}PbO_2$$

It is known that the polymorphs of PbO_2 are converted to $PbSO_4$ by different mechanisms. Mark (1) has shown that on α-PbO_2 electrodes continuous films of $PbSO_4$ are formed isolating the underlying PbO_2, whereas individual crystals of

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$PbSO_4$ are formed on β-PbO_2. Unfortunately the nucleation and growth of $PbSO_4$ crystals is very difficult to study in an acid environment, however the thermal decomposition of PbO_2 to PbO involves a similar nucleation and growth process, where various PbO_x compounds are formed on the surface of the PbO_2. The nucleation sites for the PbO_x compounds are thought to be the same as those for the $PbSO_4$.

There have been a large number of studies on the thermal decomposition of PbO_2, Holtermann (2) found two intermediate oxides in the decomposition sequence.

$$PbO_2 \xrightarrow{370^\circ C} Pb_7O_{11} \xrightarrow{460^\circ C} Pb_3O_4 \xrightarrow{550^\circ C} PbO$$

whereas Anderson et al (3) found three

$$PbO_2 \xrightarrow{293^\circ C} Pb_{12}O_{19} \xrightarrow{351^\circ C} Pb_{12}O_{17} \xrightarrow{374^\circ C} Pb_3O_4 \xrightarrow{606^\circ C} PbO$$

Later Butler and Copp (4) found that $Pb_{12}O_{19}$ and $Pb_{12}O_{17}$ did not have fixed compositions and should in fact be designated α-PbO_x $(1.5 < x < 1.6)$ and β-PbO_x $(1.33 < x < 1.5)$ respectively. Bussiere et al (5) found that particle surface areas played a major role in the decomposition process, there being distinct decomposition sequences for low and high surface area materials for both α- and β-PbO_2. Sorrell (6) studied the oxidation of PbO and identified two intermediate oxides as being $PbO_{1.44}$ and $PbO_{1.57}$.

The purpose of this investigation was to determine the effects of preparation technique, decomposition rate and atmosphere on the decomposition sequence and particle morphology of a number of different samples of α- and β-PbO_2.

2. EXPERIMENTAL

2.1 Materials - Preparation Details

(a) Chemically prepared α-PbO_2

A mixture of ammonium persulphate (125g) and water (125ml) plus saturated ammonium acetate solution (500 ml) was added to a solution of lead acetate (190g) plus 28% aqueous ammonia (150 ml). This mixture was stirred for 24 hrs. the resulting precipitate being filtered and washed. The overall reaction is

$$4NH_4OH + Pb(CH_3COO)_2.3H_2O + (NH_4)_2S_2O_8 \longrightarrow \alpha\text{-}PbO_2 + 2(NH_4)_2SO_4 + 2NH_4(CH_3COO) + H_2O$$

(b) Electrodeposited α-PbO_2

A saturated solution of orthorhombic PbO dissolved in 5M NaOH (aq) was prepared from which α-PbO_2 was electrodeposited onto a platinum anode at a current density of 10mA cm^{-2}.

(c) Formed β-PbO_2

Formed positive active material was taken from a battery plate that had received 60 deep cycles (80% depth of discharge).

(d) Chemically prepared β-PbO_2

β-PbO_2 prepared by boiling Pb_3O_4 ($2PbO.PbO_2$) in nitric acid.

$$Pb_3O_4 + HNO_3(aq) \longrightarrow \beta\text{-}PbO_2 + 2Pb(NO_3)_2(aq) + 2H_2O$$

(e) 'Analar' β-PbO_2

Sample obtained from British Drug Houses, preparation details unknown.

2.2 Characterization of Materials

All samples were characterized using a Philips 1710 horizontal stepping X-ray diffractometer. Cu Kα radiation was used and the samples were scanned between 10 and 70 degrees 2θ at 2^{o} min^{-1}.

Powder morphologies were studied using a Jeol JSM 35 scanning electron microscope.

2.3 Thermal Analysis Techniques

(a) Thermogravimetric Studies

A. C.I. Electronics 'Robal' electromagnetic balance was used in conjunction with a 'Nichrome' wound furnace which was controlled by a 'Newtronics' temperature controller. All the decomposition reactions were carried out at heating rates from $1^{o}C$ min^{-1} up to $20^{o}C$ min^{-1} starting at $20^{o}C$ and finishing at $700^{o}C$. Samples were decomposed under both air and nitrogen gas atmosphere at flow rates up to 250 ml min^{-1}.

(b) Differential Thermal Analysis

A 'Stanton-Redcroft' DTA-674 thermal analyser was used in conjunction with a DAPS data analyser. Decompositions were carried out in both air and nitrogen at a heating rate of $10^{o}C$ min^{-1}.

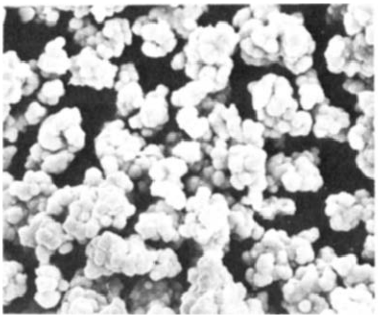


Figure 1 x 2200

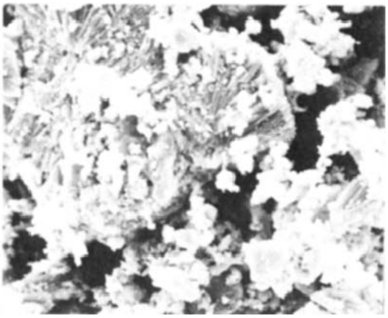


Figure 2 x 1000

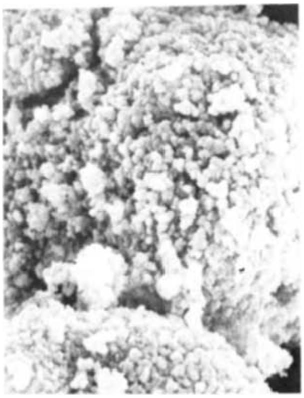


Figure 3 x 2200

Figure 4 x 2200

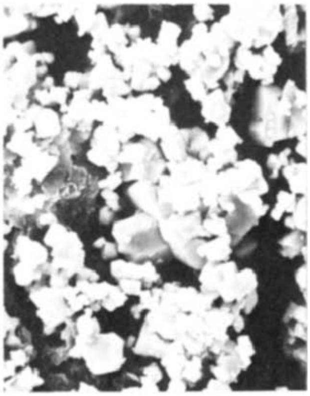


Figure 5 x 2200

3. RESULTS AND DISCUSSION

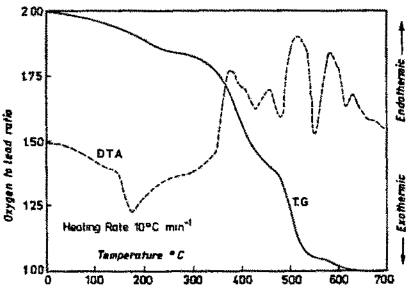
3.1 Materials

X-ray diffraction analysis showed that both samples of α-PbO_2 had low crystallinity while all the β-PbO_2 samples were highly crystalline. Figures 1 to 5 show representative micrographs of the various oxides used, these show that a large variation in particle morphology was achieved.

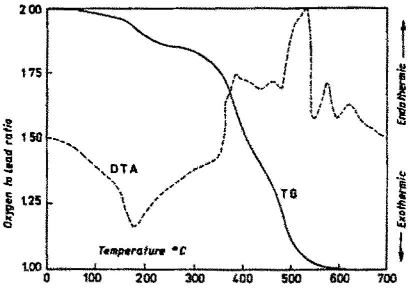
3.2 T.G. and D.T.A. Results

Figure 6 shows the T.G. and D.T.A. data for the thermal decomposition of chemically prepared α-PbO_2 in A) air and B) nitrogen at a heating rate of 10^oC min^{-1}. The decomposition in both gas atmospheres is characterized by an initial broad exothermic peak accompanied by a small weight loss, followed subsequently by a multistage endothermic decomposition during which a number of inflexions occur in the weight loss curve which is indicative of the formation of a number of intermediate oxides. It can be seen that the effect of the nitrogen atmosphere is to suppress some of the endothermic reactions.

Figure 7 shows the effect of heating rate on the thermal decomposition characteristics. At low heating rates the inflexions are very distinct however increasing the heating rate 'smooths' the weight loss curve out which implies decreased thermal stability of the intermediate oxides with high heating rates.



A) Thermal decomposition of chemically prepared α PbO$_2$ in air



B) Thermal decomposition of chemically prepared α PbO$_2$ in nitrogen

Figure 6

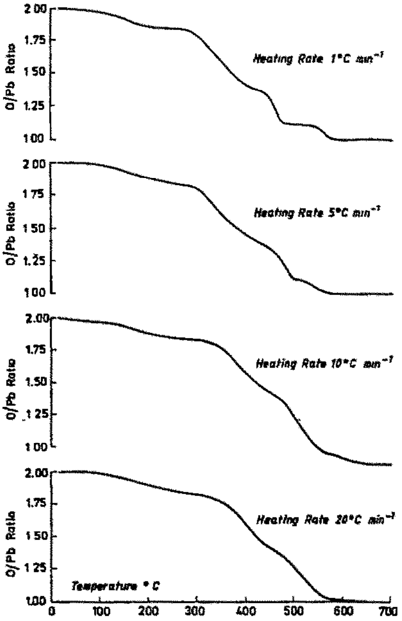
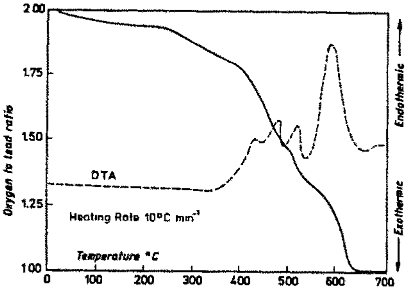
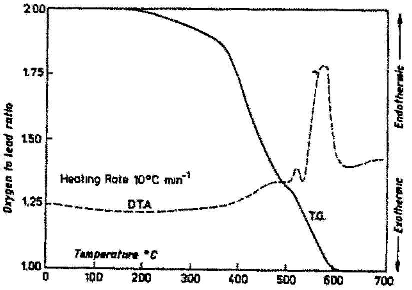


Figure 7

Figures 8 to 11 show the decomposition data for the other oxide samples. Electrodeposited α-PbO$_2$ (Figure 8) shows no initial exothermic decomposition but a small weight loss is seen, which implies the loss of adsorbed or 'trapped' water. The thermal decomposition of electroformed β-PbO$_2$ (Figure 9) is very similar in nature to that of chemically prepared α-PbO$_2$ (Figure 6), the main differences being that the former material is less thermally stable having fully decomposed by 550°C. Chemically prepared β-PbO$_2$ (Figure 10) also shows an initial endothermic reaction and weight loss, however for this material the important characteristic is the very large final endothermic peak which is accompanied by a weight loss from O/Pb ~ 1.33 down to 1.0. A nitrogen atmosphere appears to have little effect on the decomposition mechanism. Figure 11 shows that 'Analar' β-PbO$_2$ is thermally stable up to 350°C after which it undergoes a rapid succession of small decompositions, implying the production of thermally unstable intermediate oxides, followed by a final large decomposition giving a large weight loss.

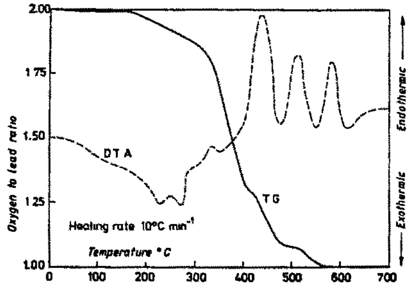


A) Thermal decomposition of electrodeposited α PbO_2 in air

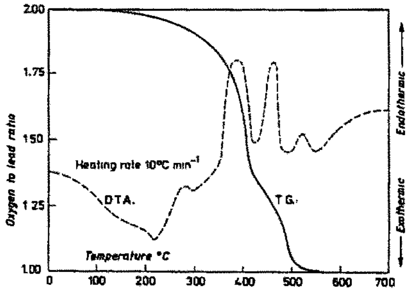


B) Thermal decomposition of electrodeposited α PbO_2 in nitrogen

Figure 8



A) Thermal decomposition of formed β-PbO_2 in air



B) Thermal decomposition of formed β-PbO_2 in nitrogen

Figure 9

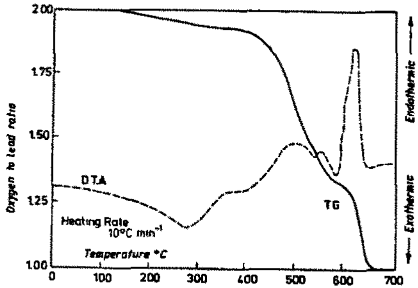
3.3 X-ray Diffraction Analysis

X-ray diffraction analysis of the intermediate products of decomposition gave the following decomposition sequences for the various oxides:-

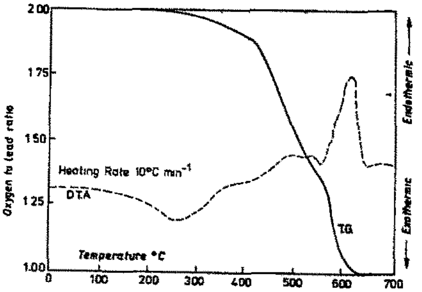
Chemically prepared α-PbO_2

20°-220°C $\alpha\text{-PbO}_2\text{(OH)} \longrightarrow \alpha\text{-PbO}_2$
220°-425°C $\alpha\text{-PbO}_2 \longrightarrow \alpha\text{-PbO}_x$
425°-480°C $\alpha\text{-PbO}_x \longrightarrow \text{PbO}_{1.44}$
480°-550°C $\text{PbO}_{1.44} \longrightarrow \text{Pb}_3\text{O}_4$ + tetragonal PbO
550°-610°C Pb_3O_4 + tet. PbO $\longrightarrow$ tetragonal PbO
610°C Tetragonal PbO $\longrightarrow$ Orthorhombic PbO

This sequence compares favourably to that found by Simon et al (7) for the same material, the major difference being that they found that α-PbO_x decomposed to a mixture of β-PbO_x and Pb_3O_4. It is thought that this material contained sufficient adsorbed water and probably hydroxyl ions to give rise to a O/Pb ratio of 2:1, however on initial heating O_2 and H_2O are given off until α-PbO_2 is stabilised at a O/Pb ratio of 1.88 to 1. Rapid heating rates prevent slow crystal lattice reorganisations from occurring, thus fewer of the intermediate non-stoichiometric oxides are seen, in particular the Pb_3O_4 phase. Evidence from the decompositions in nitrogen atmospheres suggests that an oxygen partial pressure is required to stabilize Pb_3O_4, without this all the intermediate oxide phases decompose directly to PbO

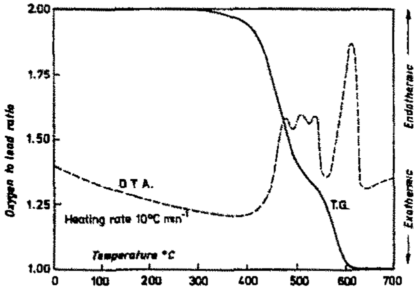


A) Thermal decomposition of chemically prepared β PbO_2 in air

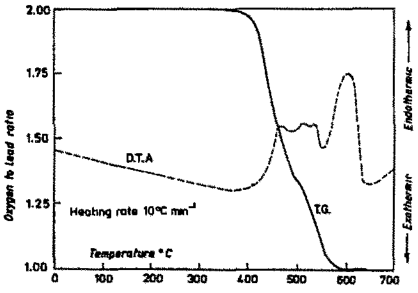


B) Thermal decomposition of chemically prepared β PbO_2 in nitrogen

Figure 10



A) Thermal decomposition of 'Analar' β-PbO_2 in air



B) Thermal decomposition of 'Analar' β-PbO_2 in nitrogen

Figure 11

Electrodeposited α-PbO_2

20°-350°C	α-PbO_2 thermally stable
350°-450°C	α-$PbO_2 \longrightarrow$ α-PbO_x
450°-485°C	α-$PbO_x \longrightarrow PbO_{1.44} + Pb_3O_4$
485°-530°C	$PbO_{1.44} + Pb_3O_4 \longrightarrow Pb_3O_4$
530°-660°C	$Pb_3O_4 \longrightarrow$ tetragonal PbO
>660°C	tetragonal PbO $\longrightarrow$ orthorhombic PbO

This material has no attached hydroxyl groups, the small initial weight loss on heating is thought to be due to the loss of 'trapped' water in the material lattice. Very heavy mechanical grinding of this material eradicates this reaction and also improves the crystallinity of the material. For this form of α-PbO_2 the most stable intermediate oxide appears to be Pb_3O_4, it is seen even in a nitrogen atmosphere and is stable up to 550°C.

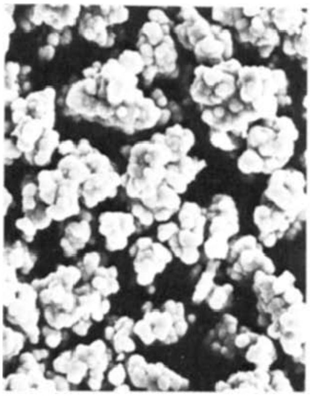


Figure 12 x 2000

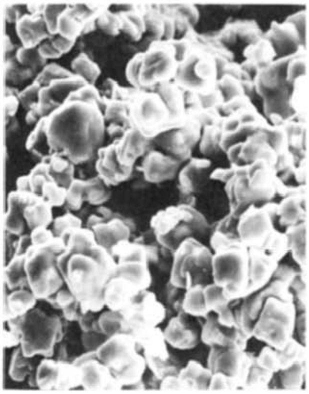


Figure 13 x 2500

Figure 14 x 400

Electroformed β-PbO_2

20°-300°C	β-$PbO_2(OH)$ + amorphous $PbO_2(OH) \longrightarrow \beta$-$PbO_2$ + amorphous PbO_2
300°-370°C	β-PbO_2 + amorphous $PbO_2 \longrightarrow \beta$-$PbO_2$ (ordered)
370°-475°C	β-$PbO_2 \longrightarrow PbO_{1.44}$
475°-535°C	$PbO_{1.44} \longrightarrow Pb_3O_4$ + tetragonal PbO
535°-610°C	Pb_3O_4 + tet. PbO $\longrightarrow$ tetragonal PbO
>610°C	tetragonal PbO $\longrightarrow$ orthorhombic PbO

The exothermic peak seen at 175°C was the result of reordering of the PbO_2 lattice with the evolution of H_2O and O_2. As mentioned earlier formed PbO_2 contains amorphous material, as decomposition proceeds this material becomes ordered giving rise to the reaction peak between 300° and 370°C. The ordered β-PbO_2 decomposes directly to $PbO_{1.44}$ in both air and nitrogen then forms a mixture of Pb_3O_4 and red PbO (in air) or decomposes directly to red PbO (in nitrogen).

Chemically prepared $\beta\text{-PbO}_2$

20°-225°C	$\beta\text{-PbO}_2\text{(OH)} \longrightarrow \beta\text{-PbO}_2$
225°-540°C	$\beta\text{-PbO}_2 \longrightarrow \text{Pb}_3\text{O}_4 + \alpha\text{-PbO}_x$ (trace)
540°-580°C	$\text{Pb}_3\text{O}_4 + \alpha\text{-PbO}_x \longrightarrow \text{Pb}_3\text{O}_4$
580°-640°C	$\text{Pb}_3\text{O}_4 \longrightarrow$ tetragonal PbO
>640°C	tetragonal PbO → orthorhombic PbO

This material decomposes with the production of only one major intermediate oxide, (in both air and nitrogen), Pb_3O_4. There appears to be a small loss of O_2 and H_2O initially, with this reaction being slightly suppressed in the nitrogen atmosphere.

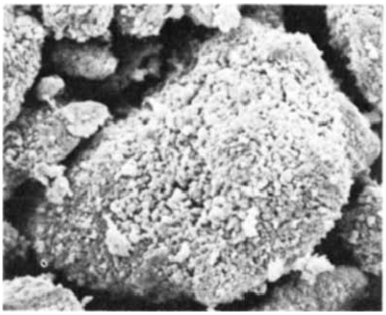


Figure 15 x 2000

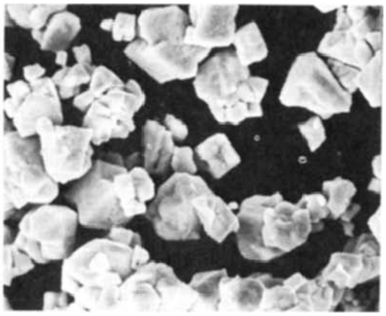


Figure 16 x 2000

'Analar' $\beta\text{-PbO}_2$

20°-400°C	$\beta\text{-PbO}_2$ thermally stable
400°-490°C	$\beta\text{-PbO}_2 \longrightarrow \beta\text{-PbO}_2 + \alpha\text{-PbO}_x$ (trace)
490°-530°C	$\beta\text{-PbO}_2 + \alpha\text{-PbO}_x \longrightarrow \text{PbO}_{1.55}$
530°-570°C	$\text{PbO}_{1.55} \longrightarrow \text{Pb}_3\text{O}_4$
570°-635°C	$\text{Pb}_3\text{O}_4 \longrightarrow$ tetragonal PbO
>635°C	tetragonal PbO → orthorhombic PbO

'Analar' $\beta\text{-PbO}_2$ is thermally stable up to a temperature of 400°C, between 400° and 570°C it undergoes a rapid series of decompositions producing thermally unstable intermediate oxides until the composition for Pb_3O_4 is reached. The effect of nitrogen is to suppress the early reactions and shift the final decomposition to a lower temperature.

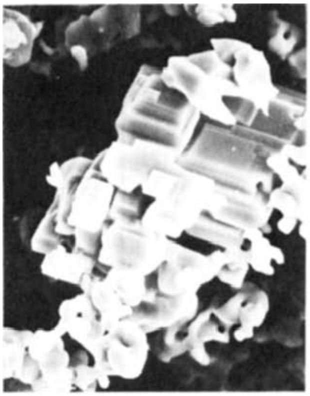


Figure 17 x 2000

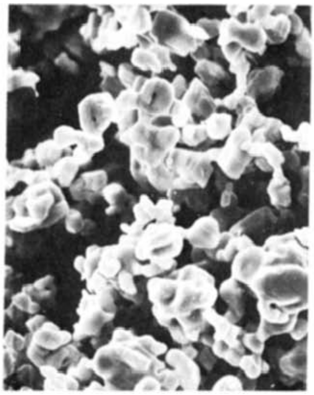


Figure 18 x 2000

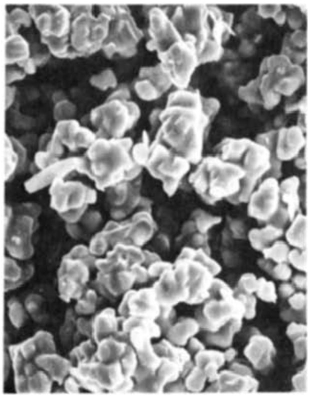


Figure 19 x 2000

3.4 Morphological Aspects of Decomposition

Figures 12 and 13 show chemically prepared α-PbO_2 decomposed up to 540° and 700°C respectively. The material in Figure 12 is unchanged from the start material whereas the material in Figure 13 shows large amounts of particle coarsening and sintering leading to a material of much reduced surface area. Figure 14 shows electrodeposited α-PbO_2 decomposed up to 700°C. At this temperature the oxide particles are still virtually unchanged, with the 'block like' morphology persisting. The electroformed β-PbO_2 decomposed up to 700°C (Figure 15) shows little gross morphological change, there has been some surface recrystallization but the large oxide particles still retain their characteristic 'cauliflower' morphology. The chemically prepared β-PbO_2 (Figure 16) decomposed up to 540°C, shows only minor morphological change, some surface recrystallization has occurred leading to the 'rounding' of the sharp angular edges. The effects of heating rate on the decomposition of 'Analar' β-PbO_2 up to 700°C are seen in Figures 17 to 19. At slow heating rates (1°C min^{-1}) (Figure 17), extensive recrystallization occurred with massive faceted crystallites being formed. At 5°C min^{-1} (Figure 18) there is extensive sintering and coarsening whereas at 10°C min^{-1} (Figure 19) there is only a small amount of sintering occurring.

4. CONCLUSIONS

The results of this study have shown that there are not distinct decomposition sequences for both α-PbO_2 and β-PbO_2. It would appear that decomposition route is dependent on preparation technique, crystallinity and particle morphology.

The intermediate phases α-PbO_x, $PbO_{1.57}$ and $PbO_{1.44}$ have all been identified by X-Ray diffraction while no evidence for β-PbO_x was obtained. The appearance of α-PbO_x in most of the decomposition sequences suggests that this compound does not have a fixed stoichiometry but one that apparently varies between $PbO_{1.65}$ and $PbO_{1.44}$.

The effect of a nitrogen atmosphere on the decomposition process is to suppress the formation of intermediate oxides. An increase in heating rate has similar effects to that of a nitrogen atmosphere. It would therefore appear that the crystallization processes for the formation of the intermediate oxides are slow, time being required for complete stabilization.

Morphologically it has proved impossible to follow the nucleation and growth of any of the intermediate oxides on the PbO_2 samples studied. All the materials proved remarkably stable up to temperatures of about 500°C above which they underwent coarsening and sintering processes, which is not unexpected for these materials which have a melting point of 897°C. The fact that no mechanical disruption is seen prior to this is surprising as these materials undergo large crystalline volume changes on decomposition.

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