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THE EFFECT OF SAMPLING CONDITIONS ON THE THERMAL DECOMPOSITION OF ELECTROLYTIC MANGANESE DIOXIDE

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Abstract

The effect of sampling conditions on the decomposition of electrolytic manganese dioxide using thermal methods is reported. Significant differences were observed in the mechanism of the decomposition by simply changing the reaction environment from a closed pan to an open pan configuration. The purge gas atmosphere was also observed to influence the decomposition mechanism. As a product of the decomposition is oxygen, the change in the mechanism observed between the experimental conditions may be explained in terms of the ease of removal of oxygen from the reaction site.

Keywords: DSC, electrolytic manganese dioxide, TG

Introduction

The characterisation of solid-state decomposition reactions using thermal techniques is complex as experimental parameters such as sample size and shape can strongly influence the measured temperatures of the decomposition processes as well as the mechanism of decomposition [1]. The thermochemistry of manganese dioxide (MnO_2) is a case in point where the decomposition temperatures are known to be a function of experimental conditions, such as the purge gas atmosphere [2–4], the crystal structure [5, 6] and the origin of the specimen [2–7].

The decomposition process of MnO_2 results in the reduction of the manganese(IV) ion where the final product produced on heating to 1500°C is manganese(II) oxide (MnO). In a typical thermogravimetry experiment, mass loss is observed through a series of decomposition steps until the final product is obtained [2]:

$$MnO_2 \ {}^{I}\ Mn_2O_3 \ {}^{II}\ Mn_3O_4 \ {}^{III}\ MnO \qquad (1)$$

Step I is usually observed between 450–550°C, Step II around 950°C and Step III around 1300°C. Considerable variance in the temperature of decomposition for each of these steps has been observed. The variance can be attributed to the dy-

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namic nature of the experiment, the rate of removal of oxygen from the reaction site and physical factors such as particle size, crystallite size, porosity and crystal structure [2–7]. As each reduction step requires the removal of oxygen as the degradation product, the rate and temperature of the decomposition is strongly dependent on the rate of removal of oxygen and therefore the partial pressure of oxygen in the purge gas atmosphere. If the partial pressure of oxygen is increased, the temperature, at which Step I occurs, increases to a maximum of approximately 680°C [4]. Under reducing conditions using a hydrogen–nitrogen purge gas mix (1:3), the reduction has been reported to be as low as 300°C for the transformation described by Step I with the complete reduction to MnO by 450°C [6].

The source and, therefore, the physical characteristics such as porosity, crystallite size and phase morphology of the MnO_2 phase has also been observed to influence the decomposition temperature [2, 5, 6]. Additionally, the mechanism of decomposition has been observed to vary with low oxygen partial pressure or inert atmospheres producing Mn_5O_8 as an intermediate phase prior to the completion of Step I [4, 8]. As a range of decomposition processes and temperatures has been observed in the literature, a study to investigate, simply, the experimental conditions under which MnO_2 decomposes was implemented. This paper reports the preliminary results of the study of the decomposition of a specimen of electrolytically synthesised -MnO_2 (EMD) under varying experimental conditions.

Experimental

EMD was supplied by Delta EMD Australia Pty Limited. The specimen was determined to be -manganese dioxide by X-ray diffraction (XRD) analysis. Although the specimen was used in the ‘as received’ state in all experiments, as EMD is a heterogeneous product in terms of its morphology, particle size and water content, prior to sampling the specimen was shaken on a SPEX Industries mixer for 5 min to obtain a representative sample for each experiment.

Differential scanning calorimetric (DSC) experiments were carried out on a TA Instruments MDSC 2920. Samples of 5.0, 10.0 or 20.0 (0.05) mg were placed in aluminium pans with an internal diameter of 6 mm and a lip height of 1.5 mm. The pans were then either used in the ‘open pan’ configuration or a lid was placed on the pan and crimped to produce the ‘closed pan’ configuration. In order to prevent excessive build up of evolved gases in the closed pan configuration, a pinhole was made in each lid. The pans were then placed in the sample chamber of the DSC with an appropriate reference pan and heated at a rate of 5°C min^{-1}. The typical experiment used a nitrogen purge (100 mL min^{-1}) on 20.0 0.05 mg in an open pan configuration. Additional sampling environments included a static air environment where the cell was flushed with air prior to loading a sample contained in an open pan and a platinum crucible (internal diameter 6 mm, lip height 3.5 mm) was used to demonstrate the inert nature of the aluminium pans. Calibration was carried out by melting pure metals in closed aluminium pans. The temperature was calibrated using indium, lead and zinc as the calibration standards. The cell constant was determined from the melting enthalpy of indium.

Thermogravimetric (TG) analysis was carried out using a TA Instruments SDT 2960. Sample preparation was similar to that of DSC analysis with 20 0.05 mg of the sample placed in the platinum crucible. Samples were heated at 5°C min^{-1} from ambient temperature to 1200°C with a constant flow of nitrogen at 130 mL min^{-1}.

XRD was carried out on a Siemens Kristalloflex X-ray diffractometer using CuK radiation. The diffractometer was fitted with a high temperature stage. The EMD was dispersed in acetone and then pipetted onto the platinum heating strip to produce an even film of EMD. The sample compartment was then purged with nitrogen. The temperature was raised at 5°C min^{-1} to the desired temperature. Once the sample had been acclimatised for 10 min, the XRD pattern was collected between 2 =16 and 70° using a step of 0.02° with an accumulation time of 1.5 s per step under dry nitrogen purge. It should be noted that in addition to the manganese oxide, the diffraction pattern for the platinum substrate was also present with three characteristic peaks at 2 =40, 46 and 67°.

Results and discussion

The effect of testing environment on the decomposition processes of EMD is clearly observed in Fig. 1. Four sample conditions are displayed; open and closed pan configuration using aluminium pans under a constant nitrogen purge, open platinum pan under a constant nitrogen purge and the open pan configuration in static air. For both the open and closed aluminium pan sampling configurations under nitrogen purge, a complex series of four decomposition peaks are identifiable in the temperature range 400 to 600°C (Table 1). Although, all four decomposition steps

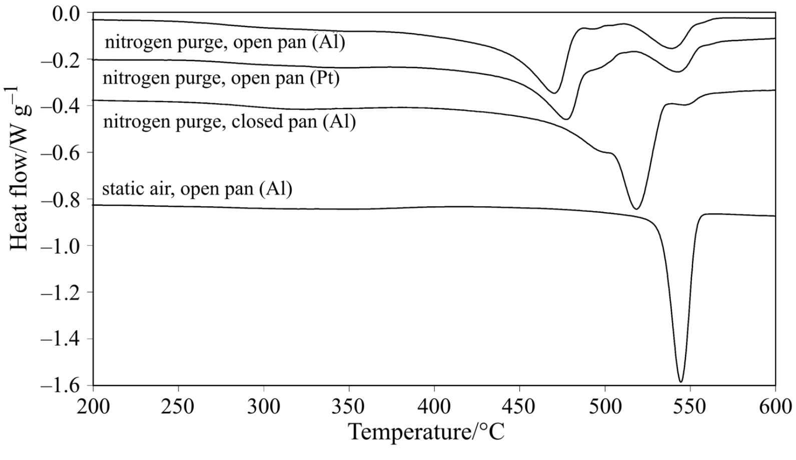

Fig. 1 DSC curves of the thermal decomposition of EMD in static air and under nitrogen purge in open and closed aluminium pan and configuration and open platinum pan configurations

Table 1 Peak temperatures (°C) for the thermal decomposition of MnO_2. Unless otherwise stated, the specimen was tested as 20.0 0.05 mg

Testing conditions	Peak 1	Peak 2	Peak 3	Peak 4
1. Effect of atmosphere in DSC				
Nitrogen purge, open Al pan	473	496	508	542
Nitrogen purge, open Pt pan	479	498	–	545
Nitrogen purge, closed Al pan	–	502	519	548
Static air, open Al pan	–	–	–	546
2. Sample size in DSC				
5.0 mg, nitrogen purge, open Al pan	463	491	–	530
10.0 mg, nitrogen purge, open Al pan	467	495	–	536
20.0 mg, nitrogen purge, open Al pan	472	494	509	542
3. Thermogravimetric analysis				
Nitrogen purge, open Pt pan	482	–	–	539

may be observed in the shape of the curves for the open pan configuration, the decomposition process is characterised by the predominance of the two steps at 473 and 542°C. A similar trace is observed in the open platinum pan where the peaks are observed at 479 and 545°C. For the closed pan configuration the predominant steps are at 502 (shoulder) and 519°C, although a small peak is also observed at 548°C. In the open pan, static air environment, only one decomposition step can be easily identified at 546°C. These significant differences are produced by the sampling conditions.

As a number of decomposition peaks were observed, to aid identification of the intermediates, XRD as a function of the temperature was carried out in an ‘open’ configuration under a nitrogen purge (Fig. 2). The ‘as received’ EMD was observed to be in the -MnO_2 phase, as represented by the characteristic peak at 2 =22°, and was

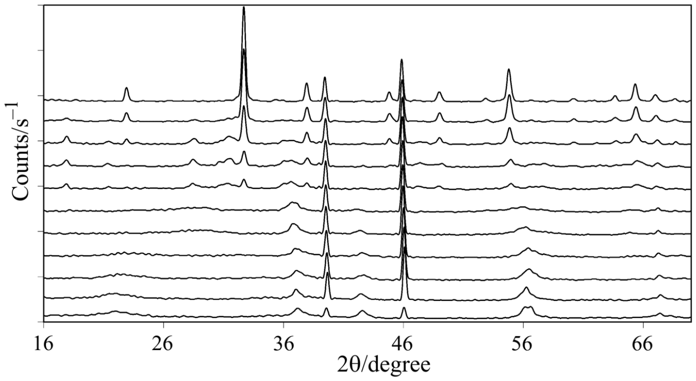

Fig. 2 XRD patterns for EMD at the following temperatures listed from bottom to top: as received at room temperature, 100, 200, 300, 400, 425, 450, 475, 500, 550

observed to be present up to 300°C. The shape of the -MnO_2 peak at 2 =22° is, however, affected by the increase in temperature as a change in the peak shape and a shift in position to approximately 2 =23.4° is observed. These observations can be attributed to the loss of bound water from the -MnO_2 structure [2, 9, 10]. In the 400 and 425°C XRD patterns a broad weak peak at 2 =29° was observed which correlates with the transformation of the - to the -MnO_2 phase [5]. The broad nature of the peak at 2 =29° indicates the presence of a significant degree of disorder in the phase in addition to small crystallite size. At 600°C, on completion of Step I (Reaction 1), only the single phase of Mn_2O_3 was observed in the XRD data. During the decomposition step, however, the partial reduction of MnO_2 to the intermediate phase Mn_5O_8 was identified, based on the peaks observed at 2 =18, 21.6, 28.6 and 31.7°. Mn_5O_8 was observed first at 425°C, in significant proportions between 450 and 500°C, and was still present in reduced amounts at 550°C. The Mn_2O_3 phase was also observed between 450 and 550°C. The first major peak in the DSC curve at 473°C for the open pan configuration under nitrogen, therefore, corresponds to the decomposition of MnO_2 to Mn_5O_8 and Mn_2O_3. A possible stoichiometry for the reaction is:

$$7MnO_2 \quad Mn_5O_8+Mn_2O_3+1.5O_2 \tag{2}$$

As the peak at 2 =22° had been replaced by a broad peak around 2 =29° by 400°C, it is likely that the transformation of Reaction 2 is occurring from the phase rather than the phase. The disappearance of the Mn_5O_8 phase by 600°C in the XRD data indicates that the second of the two major peaks in the DSC at 542°C, in the open pan configuration under nitrogen purge, corresponds to the decomposition of Mn_5O_8 to Mn_2O_3.

$$2Mn_5O_8 \quad 5\,Mn_2O_3+0.5O_2 \tag{3}$$

Although not shown in Fig. 2, further heating in the diffractometer showed the Step II decomposition of Mn_2O_3 to Mn_3O_4 in the 800°C diffraction pattern. Completion of the reaction occurred by 900°C as only Mn_3O_4 was present in the diffraction pattern. The stoichiometry of this reaction is likely to be:

$$3Mn_2O_3 \quad 2\,Mn_3O_4+0.5O_2 \tag{4}$$

The characterisation of the decomposition of MnO_2 was also carried out by TG analysis (Fig. 3). The mechanism for decomposition observed correlates well with the decomposition processes observed in the DSC in both the open aluminium and open platinum pans. The mass losses for the step at 482 and 539°C are 6.4 and 1.4%, respectively. The calculated mass losses for decomposition Reactions 2 and 3 are 7.9 and 2.0%, respectively. The variance observed between the experimental and calculated values indicates the possibility of deviance from these reaction stoichiometries. The mass loss for the step at 744°C was observed to be 3.8%. This reaction appears at a lower temperature than observed in the X-ray diffraction experiments, but is likely to follow the scheme given by Reaction 4 as the product of decomposition recovered at 900°C was observed to be Mn_3O_4 based on crystallographic analysis. The calculated mass loss for Reaction 4 is 3.4%, correlating well with the measured mass loss for the step.

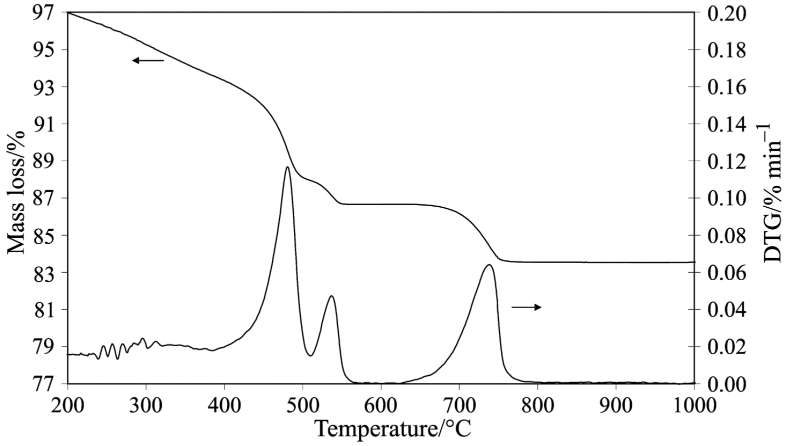

Fig. 3 TG and DTG curves for the decomposition of MnO_2 under nitrogen atmosphere in an open platinum pan configuration

XRD analysis of the intermediate products of decomposition for the closed pan environment was not carried out. The mechanism for the decomposition is therefore speculative, but a similar process may occur as multiple decomposition peaks are observed and Mn_2O_3 is observed as the final product at 600°C. As the DSC peaks are at intermediate temperatures relative to the open pan configuration, the initial step resulting in the formation of Mn_5O_8 (as well as Mn_2O_3) is possibly delayed by a reduced rate of removal of oxygen from the sample environment. It is, however, possible that a different mechanism is at work as the shoulder (502°C) and the major peak (519°C) are observed as small peaks in the open pan configuration. Additionally, a third peak is observed at 548°C which most closely corresponds to the peak in the open pan configuration under nitrogen purge identified as the transformation from Mn_5O_8 to Mn_2O_3. As the peak at 548°C is not one of the significant processes for the closed pan configuration, the mechanism for the reduction may be different.

In the closed pan configuration, the sample is in intimate contact with the aluminium. As aluminium is a reactive metal that is only passivated by a thin oxide layer, the intimate contact of the aluminium with the sample may be the origin of the differences in the mechanism where the aluminium may be acting as a reducing agent changing the mechanism of the decomposition. In order to eliminate the influence of the aluminium pans in the decomposition of MnO_2, an open pan experiment was carried out in a platinum crucible (Fig. 1). It is apparent that the decomposition mechanism is similar to that of the open aluminium pan even though the peak temperatures are shifted to slightly higher temperatures (Table 1). Although the latter experiment was carried out in a similar purge of nitrogen, the purge is not likely to be as effective as the clearance above the platinum crucible, between the crucible and the ceiling of the cell, was less than 1 mm relative to approximately 3 mm for the aluminium pans. Since decomposition products are not removed as swiftly a delay is expected and indeed evident in the temperature at which the decomposition processes occur.

The shift to higher temperatures based on the slow removal of oxygen from the reaction crucible can be demonstrated by varying the mass of the sample. The effect of sample size on the position of the decomposition peaks is shown in Fig. 4. It is apparent that the larger the sample size the higher the peak temperature of the decomposition step (Table 1). The observed higher temperatures of decomposition may be attributed to the larger sample size which is likely to inhibit the removal of decomposition products. The higher peak temperatures observed in the platinum pan configuration is, therefore, considered to be due to the delayed removal of oxygen from the reaction site.

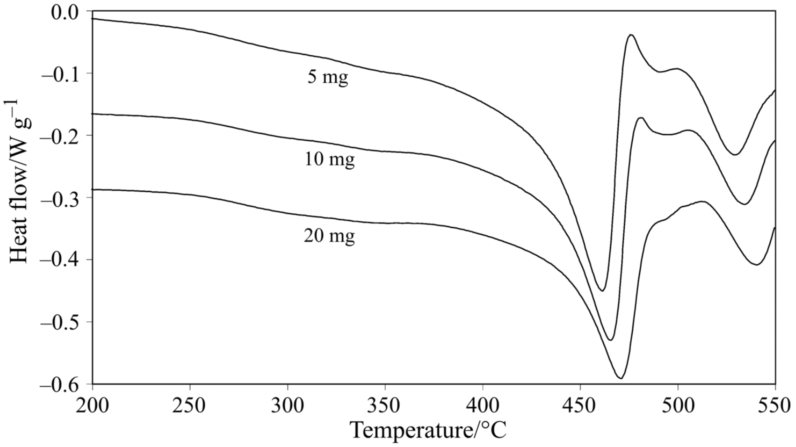

Fig. 4 DSC curves of the thermal decomposition of EMD in an open aluminium pan configuration as a function of the sample mass

The comparison of the DSC curves for the decomposition of MnO_2 in open platinum and aluminium pans, both under a nitrogen purge, and the TG curve, also under nitrogen purge, indicates that the aluminium does not influence the reaction mechanism in a significant way. The shift in the position of the decomposition peaks in the closed pan configurations is, therefore, most likely to be associated with the inhibition of the removal of oxygen. In order to confirm the influence of a high partial pressure of oxygen on the mechanism of decomposition of the EMD specimen used in this study, the decomposition was also carried out in a static air environment (Fig. 1). In the air environment, all the lower temperature decomposition peaks corresponding to intermediate steps are suppressed reducing the decomposition step to a single step at 546°C. The reduction of the process to a single step reflects the influence of high concentrations of reaction products on the decomposition mechanism. Although not confirmed by independent data, the shift in the peaks in the closed pan configuration is, therefore, most likely to be associated with the inhibition of the transformation due to the slow removal of oxygen from the reaction medium. As a nitrogen purge was used in the closed pan configuration, an excess of oxygen was not available for the complete suppression of the transformation to intermediates prior to the final decomposition to Mn_2O_3 at 600°C.

Conclusions

The influence of parameters such as crystal size, structure, atmosphere and specimen origin on the temperatures of processes involved in the decomposition of manganese dioxide has been well documented. This study has also demonstrated the sensitivity to some of these parameters. The significant differences observed in the mechanism of the thermal decomposition of EMD by simply changing the pan configuration reinforces the necessity for care in the application of thermal methods to materials characterisation. Where care is taken, however, reproducible results are obtained allowing the use of thermal analysis in the characterisation of subtle morphological differences between samples.

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