

Thermal analysis of active materials for the lead/acid battery

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Abstract

Leady oxide, basic lead sulfates and material from cured positive and negative plates have been characterized by differential scanning calorimetry and thermogravimetry. The free-lead content can be conveniently measured, and the thermal transitions show promise as indicators of phase composition.

Introduction

The aim of this paper is to report preliminary results of the thermal analysis of Barton-pot oxide and paste in positive and negative plates after curing. Differential scanning calorimetry (DSC) is sensitive to the phase composition of materials [1] and, hence, the technique holds promise for battery materials. The long-term objective is to develop thermal analysis as a possible quality control procedure for analysing and producing battery plates of consistent quality.

A comprehensive study of the phase composition of leady oxides has been published by Corino *et al.* [2]. In that investigation, it was shown that DSC can be used to determine the percentage of free lead in oxides prepared by various methods. The estimates of free lead from the latent heat of melting of lead measured by DSC correlated well with chemical and X-ray diffraction techniques [3]. Indeed, it was shown that the DSC method was free of some of the difficulties experienced in the other methods. It appears that the enthalpy of fusion of lead is not affected either by the particle size or by contact with lead oxide. At the practical level of battery-paste manufacture and curing, there still appears to be room for improvements in measuring and controlling the amount of free lead in the paste, and the phase composition during the various stages of battery-plate production [4].

Thermal analysis has also been applied to the study of lead dioxide in charged positive plates [5]. In that case, combined thermogravimetry and differential thermal analysis (DTA) was employed to determine the endotherms and mass losses associated with the high-temperature decomposition of α -PbO₂ and β -PbO₂ to PbO_x, then Pb₃O₄, and finally α -PbO. These observations suggested that thermal analysis may be a useful diagnostic tool for the mixtures of lead compounds that occur in the cured material of battery plates and, hence, the present project was undertaken.

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Method

Lead oxide samples were obtained from the Barton-pot process. Pure samples of the basic lead sulfates were obtained from Commonwealth Litharge and Red Lead (a division of Dulux Australia Ltd.). The cured positive and negative plate materials were produced via the normal manufacturing process, i.e., conditioning by heating for 24 h at 40 °C and 100% relative humidity, followed by 48 h at 60 °C in the dry state.

Polymer Laboratories PL-DSC and PL-STA (simultaneous thermal analysis) instruments were employed. The DSC was calibrated with 99.999% lead. Under the conditions of the experiments, with temperature scan rates of 5 to 10 °C min⁻¹, the error in temperature was ±0.5 °C and the enthalpy changes obtained by integrating the DSC peaks had an error of about ±5%.

Differential scanning calorimetry

Leady oxide

The DSC of a well-aged sample (two years after preparation) of leady oxide from the Barton-pot process is shown in Fig. 1. The free lead shows up clearly as a sharp endotherm commencing at 326.8 °C. The observed heat change per unit mass is Q , obtained by integration of the endothermic peak. Now, the total heat absorbed is $Qm = Q_{Pb}m_{Pb}$ where m is the total mass of sample, and m_{Pb} is the mass of free lead. The enthalpy of fusion of pure lead Q_{Pb} is known to be 23.1 mJ mg⁻¹ [6]. The percentage of free lead is $100m_{Pb}/m = 100Q/Q_{Pb}$. From the data of Fig. 1, a value of 6.1% free lead is found. This is lower than the normal range for battery oxides because of the gradual decrease of free lead with time in aged samples [2].

Tribasic lead sulfate

In Fig. 2, the DSC of a pure sample of tribasic lead sulfate is shown. The broad endotherm commencing at 190 °C is assigned to the loss of water from the

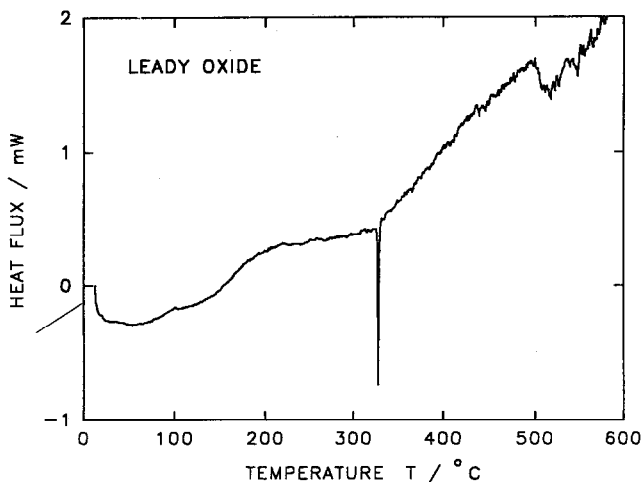


Fig. 1. Differential scanning calorimetry of an aged sample of leady oxide from the Barton-pot process. The 18.18 mg sample was run at 5 °C min⁻¹ in pure nitrogen. The sharp endotherm that commences at 326.8 °C is the melting of lead. The integrated heat change is 1.4 mJ mg⁻¹.

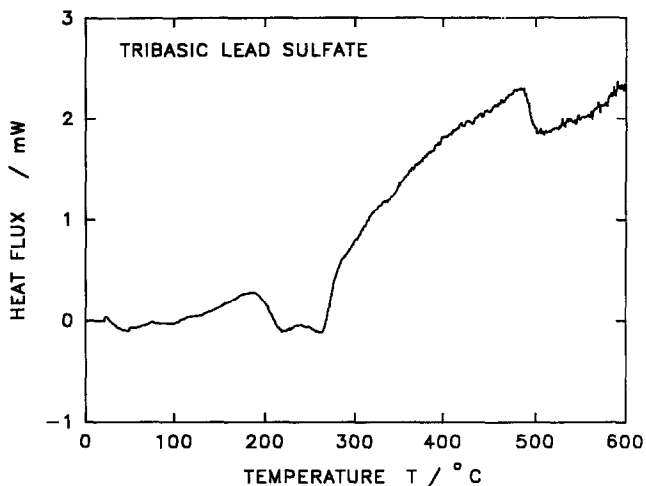


Fig. 2. Differential scanning calorimetry of tribasic lead sulfate. A 11.60 mg sample was scanned at $5\text{ }^{\circ}\text{C min}^{-1}$ in pure nitrogen. The endotherm that commences at $190\text{ }^{\circ}\text{C}$ has an integrated heat change of 41.7 mJ mg^{-1} .

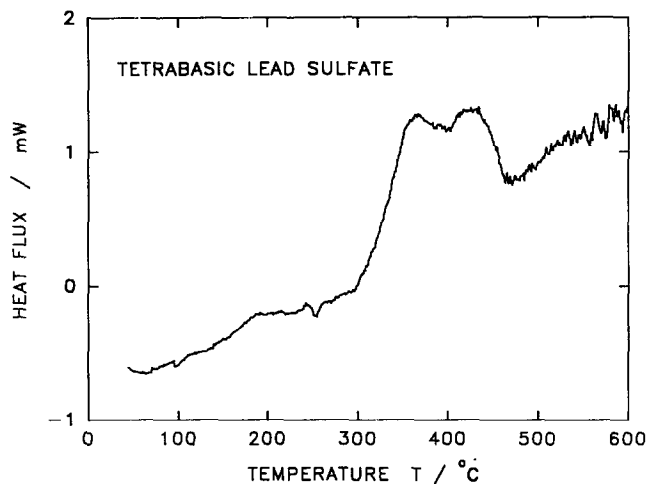


Fig. 3. Differential scanning calorimetry of tetrabasic lead surface. A 22.58 mg sample was scanned at $5\text{ }^{\circ}\text{C min}^{-1}$ in pure nitrogen. The small endotherm that commences at $246\text{ }^{\circ}\text{C}$ has a heat change of 0.4 mJ mg^{-1} . The large exotherm that commences at $294\text{ }^{\circ}\text{C}$ has a heat change of -53.6 mJ mg^{-1} .

$3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ crystals. The thermogravimetric (TG) data (see below) confirm that mass is lost in this temperature range.

Tetrabasic lead sulfate

The DSC for tetrabasic lead sulfate is given in Fig. 3. The small endotherm at $246\text{ }^{\circ}\text{C}$ may be due to the loss of some strongly adsorbed water. The large exotherm commencing at $294\text{ }^{\circ}\text{C}$ has a heat change of -53.6 mJ mg^{-1} , and this is assigned to

the decomposition into litharge and tribasic lead sulfate, namely:



At the end of the DSC scan to 600 °C, the sample had a very pale yellow colour. This indicates the presence of some β -PbO which is the stable form above 489 °C.

Negative-plate material after curing

Samples of cured positive and negative plate materials, that had been stored in air for about one week after curing, were tested by the DSC method. The curves are shown in Fig. 4. The negative-plate material was a dark-grey colour initially, due to the carbon black used in the paste formulation. After the DSC test, it was light brown with tinges of white (PbSO_4). A few metallic globules (Pb) smaller than 100 μm were visible under the microscope. The three DSC features are assigned as follows (the onset of each peak was used as its characteristic temperature):

- endotherm, 203 °C, 19.5 mJ mg^{-1} : water loss as for tribasic sulfate (see Fig. 2)
 - endotherm, 323 °C, 2.9 mJ mg^{-1} : free lead 12.6 wt.%
 - exotherm, 349 °C, -15.0 mJ mg^{-1} : oxidation of carbon and lignosulfonate additives
- The oxidant for the postulated oxidation processes would be PbO which would then form a little more free lead than was originally present.

Positive-plate material after curing

The material was very light-grey before the DSC run. Afterwards, it was a very pale yellow. Some very small black spots were visible under the microscope; these were probably minute globules of free lead. Thus:

- endotherm, 207 °C, 25.6 mJ mg^{-1} : water loss as for tribasic sulfate (see Fig. 2)
- endotherm, 324 °C, 0.7 mJ mg^{-1} : free lead 2.9 wt.%

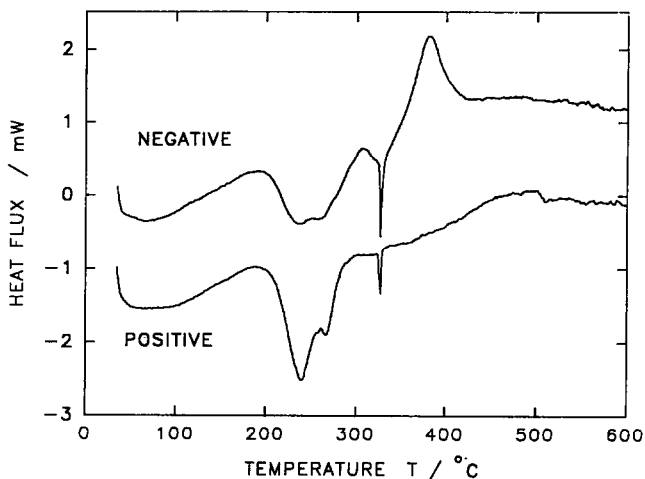


Fig. 4. Differential scanning calorimetry curves of negative (upper) and positive (lower) plate material after curing. The heat-flux curve for the positive-plate material has been displaced downwards by 1.0 mW in order to separate the two curves. Both samples were run at 5 °C min^{-1} in pure nitrogen. Negative: endotherm starting at 203 °C with heat of 19.5 mJ mg^{-1} ; endotherm starting at 323 °C with heat of 2.9 mJ mg^{-1} ; exotherm starting at 349 °C with heat of -15.0 mJ mg^{-1} . Positive: endotherm starting at 207 °C with heat of 25.6 mJ mg^{-1} ; endotherm starting at 324 °C with heat of 0.7 mJ mg^{-1} .

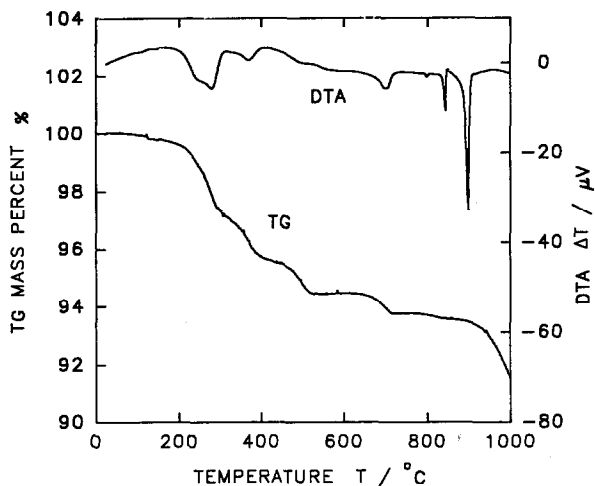


Fig. 5. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analysis of tribasic lead sulfate. A 22.19 mg sample was heated at $20\text{ }^{\circ}\text{C min}^{-1}$ under pure nitrogen. The upper DTA curve shows endotherms as down-going peaks. The TG curve gives the percentage loss of mass.

There is no sign of the exotherm at around $349\text{ }^{\circ}\text{C}$. This observation provides a clear difference from the negative-plate material.

In both the negative- and positive-plate materials, there are broad endotherms at approximately 200 to $260\text{ }^{\circ}\text{C}$. These are similar to the endotherm observed in the case of tribasic sulfate (see Fig. 2) and indicate that tribasic lead sulfate is present in both types of cured plate material. Pavlov [7] has shown that tetrabasic lead sulfate cannot be produced in negative plates due to the presence of lignosulfonates.

Thermogravimetry

A combined TG and differential thermal analysis (DTA) experiment was carried out using a reference sample of tribasic lead sulfate (Fig. 5). The endotherm at 170 to $300\text{ }^{\circ}\text{C}$ gives a mass loss of 2.63% . This endotherm corresponds quite well with the DSC endotherm that starts at $190\text{ }^{\circ}\text{C}$ as shown in Fig. 2. The calculated mass change for $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ losing one H_2O is -1.82% . The water content appears to be greater than the stoichiometric amount for one water molecule per formula unit. It is possible that the water loss includes strongly adsorbed water. Further mass losses occur before melting and evaporative losses are observed above $900\text{ }^{\circ}\text{C}$.

Conclusions

The preliminary results presented above show that thermal analysis is a promising method for characterizing cured plates. The free-lead content can be measured and the general shape of the DSC curve could be used to fingerprint the active material. In particular, the technique may indicate whether there are tribasic or tetrabasic lead sulfate phases present. Thus, the present results of the positive-plate material show

that there is no tetrabasic lead sulfate present because there is no exothermic peak in the 350 to 450 °C region.

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