

PEAKS[®]: A PC-BASED METHOD FOR QUANTITATIVE X-RAY DIFFRACTION PHASE ANALYSIS OF LEAD-ACID BATTERY MATERIALS

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Summary

A computer program, PEAKS[®], has been written to provide a quantitative determination of the relative amounts of up to 11 crystalline phases commonly found in samples of lead-acid battery materials. The necessary observed data are the heights (or areas) of a set of pre-selected X-ray powder diffraction peaks collected with Cu K α radiation. The program is designed for use on an IBM (or compatible) personal computer and has been written in the "C" language to facilitate data input and output and to simplify user interaction with the software. The method is rapid, accurate, and does not require an expert knowledge of either diffraction or crystallography. The amount of amorphous material present in the sample may also be determined by the addition of a known proportion of an internal standard material (CeO₂).

Introduction

The manufacture of lead-acid batteries and their subsequent charge-discharge operation involves a daunting array of complex chemical and electrochemical processes. As in any other chemical process/system, identification of the reactant and product phases and precise estimates of their relative abundances are of considerable importance for quality control, trouble-shooting, and research and development. Nevertheless, not all of the reactions taking place during battery production and service are well understood, and many are not accurately monitored either *in* or *ex situ*.

The most commonly used method for phase identification and quantification is X-ray powder diffraction (XRD). Such studies of the lead oxide/lead sulphate system are, however, complicated by difficulties associated with the poor crystallinity of some of the phases, strong X-ray absorption, and severe diffraction peak overlap [1]. Furthermore, many lead-acid battery and lead chemical companies do not have direct access to XRD

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equipment, and they may also lack the necessary in-house expertise to interpret the results obtained therefrom.

Over the past 10 years, we have developed a wide range of XRD analysis methods and associated software, with various levels of sophistication, to fulfil the on-going analytical requirements of our lead-acid battery research programme [1 - 8]. In addition, many companies have submitted lead-acid battery materials to our laboratories for XRD analysis: (i) after having experienced problems with their manufacturing process; (ii) when requiring characterization of their starting materials, paste formulation, cured and/or formed plates; (iii) when a need has arisen to monitor product quality and/or performance after sale.

During the course of this work, it became clear that battery and lead chemical companies would be well served by ready access to a globally applicable method for the routine analysis of battery materials in-house. The method should: (i) not require substantial equipment purchase; (ii) be rapid, yet sufficiently accurate; (iii) not require an advanced knowledge of diffraction or crystallography. This paper describes the development of just such an analytical XRD system, named PEAKS[®], and provides examples of its application to several problems in the lead-acid battery industry. The software has already been received with enthusiasm by a number of battery companies world-wide.

What is PEAKS[®] ?

PEAKS[®] is a free-standing (personal) computer program that uses XRD data to provide a quantitative estimate of the relative amounts of one or more of 11 phases in the crystalline state that are commonly found in samples of lead-acid battery materials. These 11 phases are listed below under the stage of battery production where they are most often encountered, along with the short designations used, henceforth, for some in the text.

Precursor leady oxide

Pb	free lead
α -PbO	litharge (tetragonal)
β -PbO	massicot (orthorhombic)
Pb ₃ O ₄	minium (red lead)

Paste-mixing/curing

PbSO ₄	anglesite	OBS
PbO·PbSO ₄	monobasic lead sulphate	1BS
3PbO·PbSO ₄ ·H ₂ O	tribasic lead sulphate	3BS
4PbO·PbSO ₄	tetrabasic lead sulphate	4BS
2PbCO ₃ ·Pb(OH) ₂	hydrocerussite	HC

Plate formation/cycling:

α -PbO ₂	(orthorhombic)
β -PbO ₂	plattnerite (tetragonal)

In a recent development, the amount of amorphous or poorly crystalline material present in the sample may be determined along with the abundance of the crystalline components by the addition of a known amount of CeO₂ as an internal standard.

What is needed to use PEAKS®?

PEAKS® is designed to work on an IBM personal computer (XT, AT, PS/2, or compatible) with a minimum configuration of: (i) MS/PC-DOS 2.0; (ii) one 5.25 in. floppy disk drive; (iii) 256K RAM. A printer, although not necessary, is recommended so that a hard-copy of the results can be obtained. The data may also be stored on a disk for printing later, or for further manipulation. Use of a hard disk and/or floating point co-processor will speed analyses, but is not essential.

The data used by PEAKS® consist of the observed/measured intensities (on any arbitrary scale) of a pre-selected set of 20 diffraction peaks in an X-ray pattern of the sample to be analysed. If in-house X-ray equipment is not available, the required diffraction pattern can usually be obtained (for a nominal charge) from the Physics, Chemistry, or Geology Departments of most Universities, or from any other research organization that operates standard equipment for materials characterization.

The diffraction peak-intensity information can be obtained either by direct reading from the diffraction chart paper itself, or from a list of peak heights/areas* printed automatically by diffractometer peak-search routines (if available). The diffraction pattern should be collected with Cu K α X-rays (wavelength = 1.5418 Å), and should cover the angular range 7 - 57° 2 θ to ensure that all of the required 20 peaks are measured. Other wavelength X-rays can be used, if necessary, but the diffraction peak positions must then be recast in terms of the corresponding positions obtained with Cu K α in order to provide appropriate data for PEAKS®. (Note that the peak intensities should also be amended slightly if this procedure is used.)

How does PEAKS® work?

Every crystalline material produces a unique set of diffraction peaks, the intensity and position of which is characteristic of that particular phase. The diffraction pattern obtained from a mixture of several phases will

*The intensity of a diffraction peak is most accurately provided by its area, but the more easily measured peak height value is equally valid if the individual phases have similar crystallite sizes and therefore similar peak widths [9, 10].

be a superimposition of the diffraction patterns from each of the individual component phases. Inspection of the total diffraction pattern permits the identity of the component (crystalline) phases to be determined*. Furthermore, for a given component, the intensity of the diffraction pattern is proportional to the amount of that phase present, and, hence, the total pattern obtained from the mixture can also be used to obtain information about the relative abundance of this component.

Unfortunately, a particular weight of a given phase does not necessarily produce a diffraction pattern of the same intensity as that produced from the same weight of another phase. The differences in intrinsic (absolute) pattern intensity must be incorporated into a set of so-called normalization constants, which are then used to convert the diffraction peak heights into weight percentages [1, 3].

For each component phase in a mixture, PEAKS[®] takes the average height (or area) of up to three preselected diffraction peaks as a measure of the intensity of the entire pattern of each component. The use of more than one peak from each phase minimizes the possible effects of certain systematic errors (such as "preferred orientation" and "extinction" [9, 10]) in the sample. Background corrections are automatically applied to the peak intensities, and overlaps between diffraction peaks are taken into account by using stored values of their relative intensities. PEAKS[®] then uses the predetermined normalization constants to convert the average peak intensities into the corresponding relative weight fractions of each component**.

It is noted here that measurement by XRD of the amount of metallic (free) lead in an otherwise non-metallic sample is notoriously difficult, primarily because of the shielding effects of layers of oxide/sulphate material that tend to accumulate on, and in, the lead particle surfaces [6]. Thus, separate determination of the free lead content (*e.g.*, by a wet-chemical technique such as EDTA titration or acetic acid digestion [6]) is strongly recommended. If an independent lead value is available, PEAKS[®] ignores the lead peaks in the diffraction pattern, takes the entered value as fixed, and adjusts the contents of the other phases accordingly.

For more detailed investigations requiring an estimate of the amount of amorphous material, the sample can be spiked with a known weight of well-crystallized CeO₂ (*e.g.*, a sample fired at 1200 °C). In this case, PEAKS[®] references the intensities of the lead-phase diffraction peaks to the intensities of the CeO₂ internal standard peaks (through the normalization constants), to obtain absolute, rather than relative, weight percentages of the other crystalline components in the mixture.

*A compilation of the diffraction patterns for most of the 11 phases that can be analysed by PEAKS[®] has been published previously [3], and the remainder may be found in the publications of the Joint Committee for Powder Diffraction Standards (JCPDS), International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, Pennsylvania 19081-2389, U.S.A.

**For further details of the methodology of phase analysis of battery systems by diffraction methods, see refs. 1 - 4, 6 - 8.

Steps for obtaining a phase analysis with PEAKS®

(i) Collecting a diffraction pattern

Cu K α radiation should be used, otherwise the 2θ angles of the diffraction peaks listed during operation of PEAKS® will not be appropriate. Diffraction data should be collected over the angular range $7 - 57^\circ 2\theta$, with the pattern appearing either in analog (chart or graph paper) or in numerical (as peak positions and intensities) form. Details of sample-preparation and data-collection procedures are provided in several standard XRD texts [9, 10] and in the Users' Manual supplied with the PEAKS® program.

(ii) Annotation of the pattern

It is recommended that the diffraction pattern be inspected prior to the analysis in order to identify which lead phases are present in the sample (*i.e.*, whether the unique set of diffraction peaks for each individual phase is visible at the appropriate diffraction angles), and to ascertain the presence, or otherwise, of any foreign (*i.e.*, non-lead) phases. This step can also be valuable in the detection and treatment of shoulder peaks that appear in some samples (see below). Compilations of the standard diffraction patterns of the relevant lead phases have been published* and are also available in the PEAKS® Users' Manual.

(iii) Loading and running the program

The PEAKS® software is supplied on a 5.25 in. (or, if requested, a 3.5 in.) floppy disk and can be executed immediately by typing "PEAKS" on the keyboard of the computer. A title-page is then displayed, and the user is requested to provide a file name for storage of the final results together with a title for the particular analysis. The next piece of information required is the free-lead content of the sample, if available. The data-entry screen is then displayed; this is where all 20 of the required diffraction-peak intensities are entered into the program.

The first two items of information that must be provided are the observed values of the background at two specified points in the pattern. These values, along with all of the diffraction peak intensities to follow, are taken from the X-ray powder diffraction pattern. The background and peak heights can be measured directly off the pattern with a ruler and entered as millimetres, inches, or any other unit. Alternatively, a table of peak heights/areas (in counts) may have been produced by the X-ray diffractometer during recording of the pattern; these values can also be entered for analysis by PEAKS®.

After each background or peak-intensity value is entered from the keyboard, PEAKS® moves a highlight to the next data-entry field on the screen. These fields appear as a line of text giving a particular diffraction angle and the phase to which the peak at this position is assigned. In all, a

*See footnote on p. 318.

total of 20 peak intensities must be entered (some may be zero) to allow for the presence of some, or all, of the 11 possible lead phases in the sample. Mistakes made while entering the peak intensities can be easily corrected by moving the highlight up or down the list, as needed, using the <Up-Arrow> and <Down-Arrow> keys. If PEAKS[®] asks a question that is not understood, help messages can be accessed by pressing the <F1> key.

After entering the peak-intensity values, the results of the analysis are automatically displayed in tabular form on the screen and options are presented that allow the results to be sent to the printer or a normal ASCII disk file. The latter may be read into a word-processing or spreadsheet program.

Pitfalls

There are two potential problems for the unwary user of PEAKS[®]. The first involves the determination of the free-lead content, discussed above, and the second relates to shoulder peaks. The program automatically allows for completely overlapping peaks, but is unable to judge how much of the height of a particular shoulder peak is due to the presence of its larger neighbour. Only a few of the diffraction peaks used by PEAKS[®] are so affected, but in these circumstances, it is desirable to have the diffraction pattern annotated prior to the analysis so that partitioning of the intensity can be made by eye. Further details are provided in the PEAKS[®] Users' Manual.

How well can PEAKS[®] perform?

Table 1 provides examples of the quality of the results that can be obtained with PEAKS[®] when due care is taken with sample preparation

TABLE 1

Demonstration of the accuracy of PEAKS[®] in determining the phase composition (wt.%) of synthetic mixtures simulating formed/cycled and cured positive plates

Phase	As weighed	From PEAKS [®]
1. Positive plate		
β -PbO ₂	74.8	72.7
PbSO ₄	25.2	27.3
2. Cured plate		
α -PbO	62.5	59.6
4BS	29.2	32.6
3BS	5.3	5.4
1BS	2.4	1.9
HC	0.7	0.5

and diffractometer alignment; details of these procedures can be found in standard XRD texts [9, 10], and in the PEAKS[®] Users' Manual. In the first test case, the phase composition of a partially discharged positive plate was synthesized by weighing out quantities of AR-grade β -PbO₂ and PbSO₄ in the ratio 3:1. For the second test, pure forms of five phases were combined in proportions roughly equivalent to the composition that would result from the curing of a pasted plate under high temperature and high humidity conditions (*i.e.*, one containing 4BS as the dominant basic lead sulphate).

The results shown in Table 1 demonstrate that the phase analyses provided by PEAKS[®] closely approximate the as-weighed compositions of each sample. The maximum absolute error is 3.4 wt.% for the 29.2 wt.% of 4BS in the cured-plate example. In general, the overall error is of the order of 10% (relative) for some of the more difficult cases (*e.g.*, PbSO₄ in the presence of red lead; free lead in any sample), but is generally better than this for other phases. The accuracy of the determination will be degraded if:

- (i) the material used for the analysis is not representative of the bulk specimen;
- (ii) the samples have not been homogenized by adequate grinding;
- (iii) the surface of the sample in the X-ray holder is not flat;
- (iv) the component phases have markedly different particle sizes (this can be corrected by further grinding);
- (v) the components are prone to preferred orientation.

Further details of potential problems in phase-analysis methods are provided elsewhere [1, 9, 10].

General examples of PEAKS[®] applications

Leady oxides

The diffraction pattern obtained from a sample of leady oxide from a Barton pot is shown in Fig. 1; the results of the corresponding PEAKS[®] analysis are given in Table 2. In Fig. 1 and other diffraction patterns to follow, the positions of the diffraction peaks from each phase are separately shown as rows of tick marks below the diffraction profile. The free-lead content of this sample was determined by wet-chemical methods as 14.5 wt.%, so the abundance of this phase was fixed at this value in the analysis. The PEAKS[®] data reveal that the leady oxide consists principally of α -PbO together with a smaller quantity of β -PbO (and Pb).

The results of similar PEAKS[®] analyses of leady oxides can be used to provide accurate information about: (i) the degree of oxidation of the Pb; (ii) the ratio of α -PbO to β -PbO; (iii) the amount of Pb₃O₄ present. For example, in Fig. 2 the β -PbO content of Barton-pot leady oxide is shown to be critically dependent on the reaction temperature; the β -PbO content rises sharply near the transformation temperature of α -PbO to β -PbO, so that careful control of the reaction must be exercised if the generally accepted [11] optimum β -PbO content of around 15 wt.% is to be achieved.

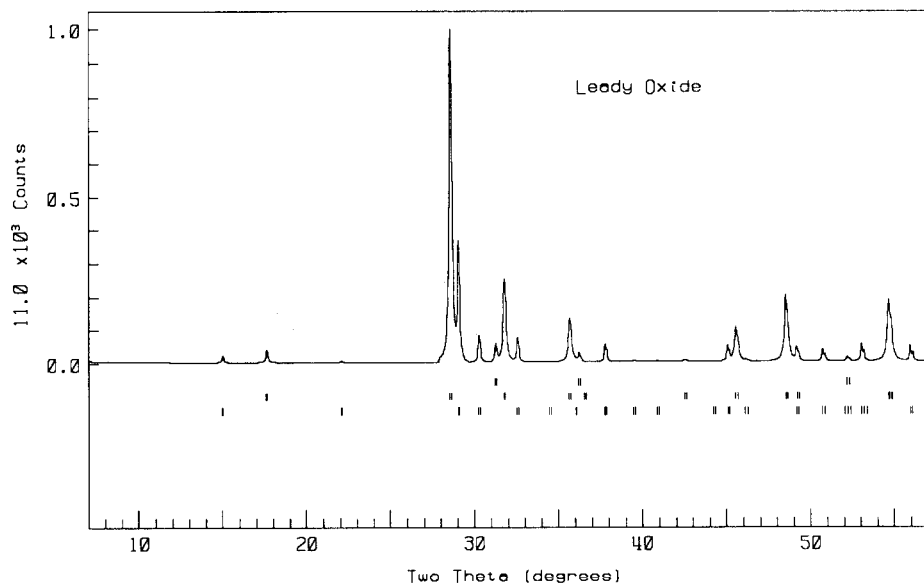


Fig. 1. Cu K α XRD pattern for leady oxide (PEAKS[®] data given in Table 2). Rows of vertical tick marks below the pattern correspond to positions of all diffraction peaks, in descending order, arising from Pb, α -PbO, and β -PbO.

TABLE 2
PEAKS[®] analyses of battery materials

Phase	wt.% ($\pm 10\%$ rel.)
Leady oxide	
Pb	14
α -PbO	61
β -PbO	25
Cured plate	
Pb	3
α -PbO	32
β -PbO	1
4BS	41
3BS	15
1BS	7
HC	1
Cycled positive plate	
α -PbO ₂	6
β -PbO ₂	81
PbSO ₄	13
Amorphous content of PbSO₄	
CeO ₂	29
PbSO ₄	71
Amorphous	nil

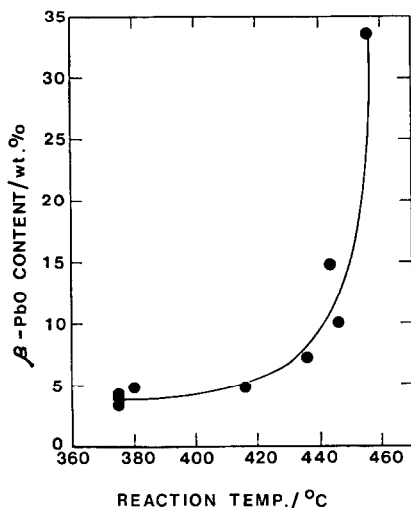


Fig. 2. Proportion (wt.%) of β -PbO determined by PEAKS[®] for a Barton-pot leady oxide as a function of reaction temperature.

Cured plates

Table 2 gives the results of a PEAKS[®] analysis undertaken on a plate using the above leady oxide (Fig. 1) and cured under conditions of high temperature and high relative humidity; Figure 3 shows the corresponding XRD pattern. The dominant basic sulphate of lead formed under these conditions is 4BS, but the analysis also shows that there is some 3BS present, together with substantial residual unreacted α -PbO and minor amounts of 1BS and Pb. Most of the free lead and β -PbO in the precursor leady oxide has reacted during curing.

PEAKS[®] analyses undertaken on cured plates and pastes permit information to be obtained about:

- (i) changes in phase abundance resulting from alterations in the prevailing conditions in the curing chambers;
- (ii) the reactivity of the starting leady oxide;
- (iii) the residual lead content after curing;
- (iv) the ratio of 4BS to 3BS as a function of curing time and conditions.

For example, Fig. 4 shows the variation in phase composition for 150 plates taken from a batch of factory-cured plates [12]. The residual amount of α -PbO is shown to be relatively uniform at about 55 wt.%, but a substantial proportion of the plates has 3BS contents varying between 15 and 35 wt.%, together with 1BS and HC contents of up to 10 and 20 wt.%, respectively. Variations in phase abundance of this magnitude are likely to exert a significant influence on battery performance and this highlights the importance of controlled curing.

In another application of PEAKS[®] (Fig. 5), it has been demonstrated that the phase composition of plates cured at temperatures between 40 and

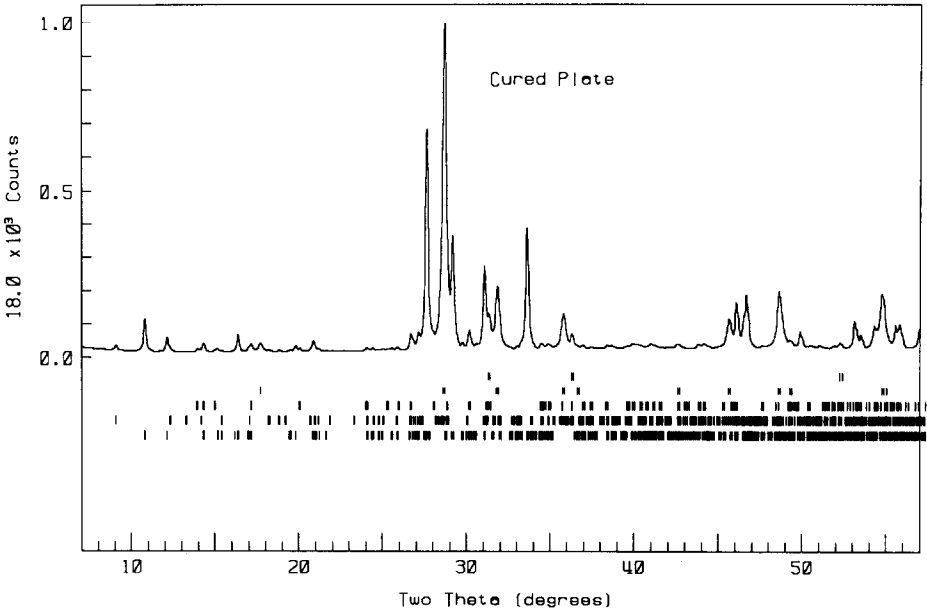


Fig. 3. Cu K α XRD pattern for cured-plate material (PEAKS[®] data given in Table 2). Rows of vertical tick marks below the pattern correspond to positions of all diffraction peaks, in descending order, arising from Pb, α -PbO, 1BS, 3BS and 4BS.

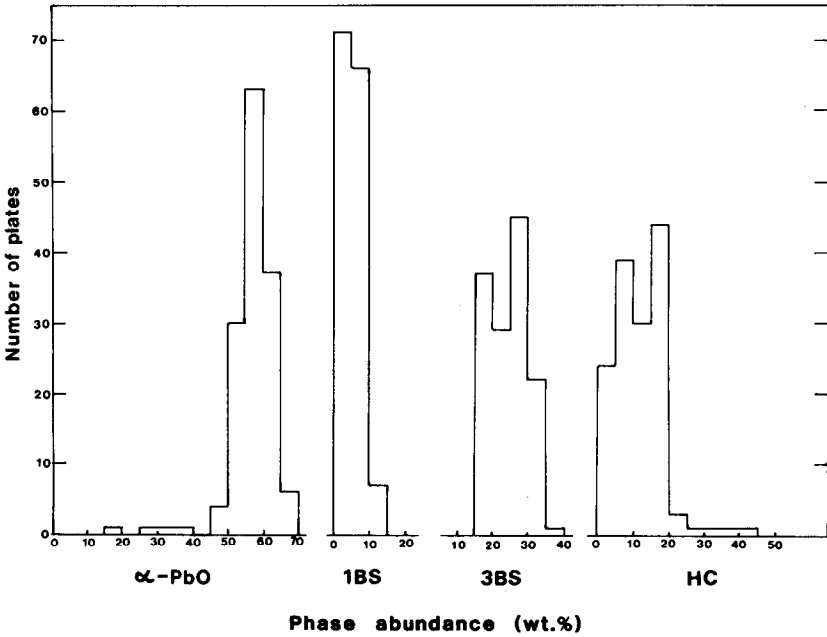


Fig. 4. Frequency of occurrence of various proportions (wt.%) of α -PbO, 1BS, 3BS and HC in 150 commercially produced cured plates, as measured by PEAKS[®].

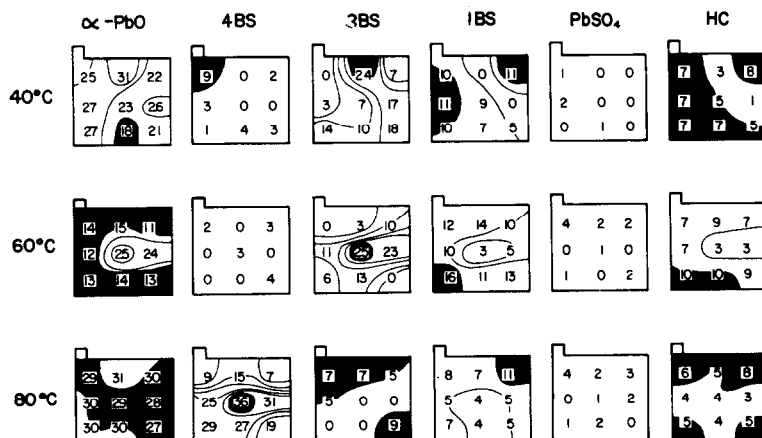


Fig. 5. Phase analyses (wt.%) at nine locations in cured plates subjected to various thermal treatments during curing. Lines are 5 wt.% contours. Areas of lowest (α -PbO) or highest (other phases) concentration have been highlighted.

80 °C can vary dramatically within a given plate. These phase “contour maps” show that “hot” spots in the centre of some plates can give rise to much larger quantities of 4BS (see the plate cured at 80 °C), while plates cured at lower temperatures (*e.g.*, 60 °C) can exhibit sharp variations in the reactivity of the leady oxide. Monitoring these phase changes provides a valuable means for controlling the quality of the final product.

Discharged positive plates

The results of a PEAKS[®] analysis undertaken on a sample taken from a charged positive plate after extensive cycling in a golf-cart battery are listed in Table 2; the corresponding diffractogram is given in Fig. 6. The plate comprises mostly β -PbO₂, with a minor amount of α -PbO₂ and a substantial quantity of PbSO₄. The presence of the sulphate indicates that the plate probably failed due to electrical isolation of the material from the grid.

PEAKS[®] analyses of this kind are useful for obtaining information about: (i) the ratio of the two polymorphs of lead dioxide, α -PbO₂ and β -PbO₂, after formation of the plate (and during subsequent battery service); (ii) the efficiency of the plate formation process; (iii) the level of sulphation of heavily cycled plates. For example, Fig. 7 shows data obtained for a series of otherwise identical positive plates that were discharged to various degrees as part of our continuing studies of the factors controlling the formation of “hard” sulphate [13]. In this work, samples were taken from the top, middle, and bottom of selected plates at each stage of discharge. As found in earlier studies [7], the rate of discharge of α -PbO₂ is much slower than that of β -PbO₂, so that most of the PbSO₄ results from the reduction of the β -PbO₂. In addition, the results also show that the bottom of each plate experiences a slightly greater depth-of-discharge than the top, due to the higher sulphate content of the electrolyte in this region of the cell.

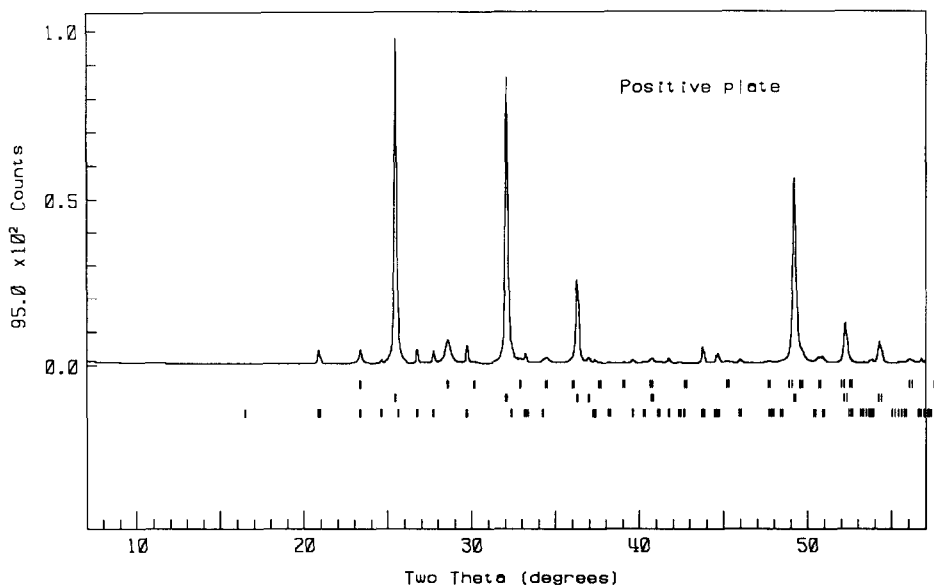


Fig. 6. Cu K α XRD pattern for charged positive-plate material from a cycled golf-cart battery (PEAKS[®] data given in Table 2). Rows of vertical tick marks below the pattern correspond to positions of all diffraction peaks, in descending order, arising from α -PbO₂, β -PbO₂, and PbSO₄.

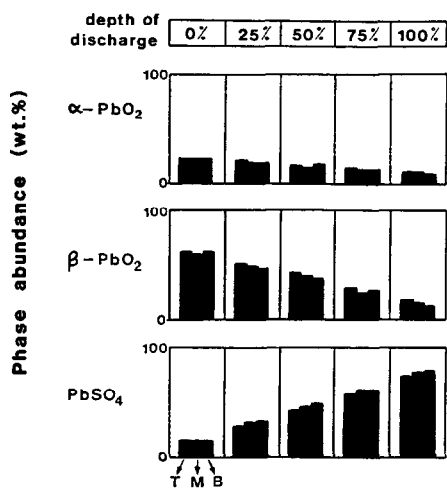


Fig. 7. Phase composition (wt.%) of freshly formed positive plates at various stages of discharge. Analyses are arranged left to right for T = top, M = middle, and B = bottom of the plate.

The importance of controlling the phase composition of formed plates (especially the PbO₂ polymorph ratio) is clearly demonstrated in Fig. 8 [7]. There, the initial post-formation ratio of α -PbO₂ to β -PbO₂ is plotted against

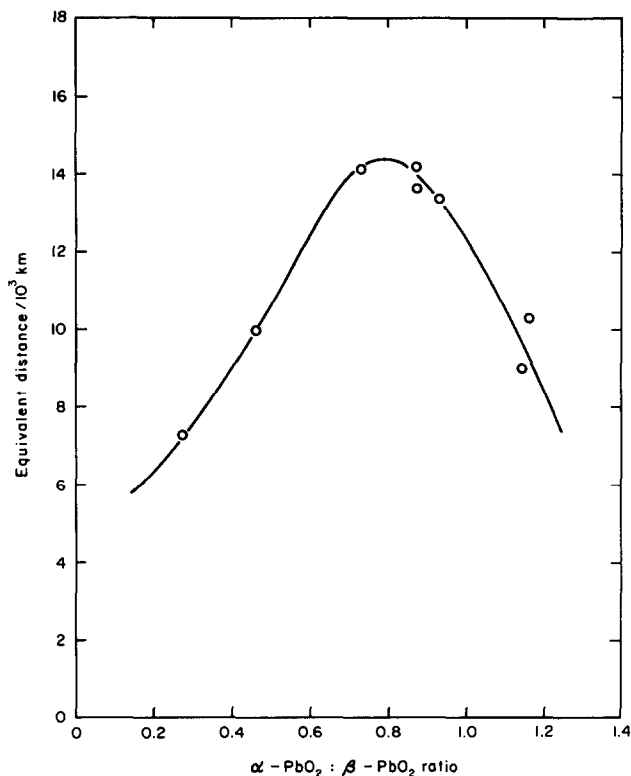


Fig. 8. Equivalent service distance (km) under simulated electric vehicle service as a function of starting ratio of α -PbO₂ to β -PbO₂ in positive plates.

the performance of the plate under deep-discharge conditions, as measured by the equivalent distance travelled under simulated electric-vehicle duty. The advantage of targeting a polymorph ratio of around 0.8 is obvious, and has now been adopted as a desirable design criterion for motive-power batteries [14].

Amorphous content

Finally, Table 2 gives the results of a PEAKS[®] analysis conducted on a synthetic mixture of 32 wt.% CeO₂ and 68 wt.% AR-grade PbSO₄. The XRD-measured CeO₂ content was 29 wt.%, close to the as-weighed value of 32 wt.% and within the error of the determination (about 10% relative, or 3 wt.% absolute). Since normalization of the CeO₂ content to 32 wt.% would produce a small *negative* value for the amorphous content of PbSO₄, the sample can be assumed to be fully crystalline. In other work with electrochemically-prepared samples of battery phases, it has been found that large amounts of amorphous material can be present, and that the presence of this poorly crystalline material may influence battery performance [4, 6, 7, 15].

Availability of PEAKS®

Copies of the PEAKS® software (on 3.5 or 5.25 in. floppy disk) and a detailed Users' Manual (at present for measurement of crystalline material only) are available from Mr W. F. Gillian, Pasmenco Metals, 114, William Street, Melbourne, Victoria 3000, Australia.

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