

## APPLICATION OF DIFFRACTION TECHNIQUES IN STUDIES OF LEAD/ACID BATTERY PERFORMANCE

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### Introduction

During its 120 year existence, most of the major improvements in the performance and reliability of the lead/acid battery have resulted from changes in system design and engineering. These have been achieved largely through trial-and-error methods with little commitment of extensive fundamental research effort. Until the recent past, this essentially empirical approach has produced a continuously improving product which has been adequate for most applications. However, the increasing utilization of the lead/acid battery in areas such as large-scale energy storage and limited-mission electric vehicle service has placed more stringent demands on its performance that engineering changes alone cannot satisfy.

Despite improvements in battery design, it should be remembered that, ultimately, it is the "active" materials on the positive and negative plates that store/supply the energy, and that optimization of their physico-chemical properties is essential for satisfactory performance. The significant limitations on the performance of the lead/acid battery are the initial electrochemical activity of the material in the positive plate and the rate at which this activity declines during charge/discharge cycling. Utilization of the active mass at the beginning of service is a function of the discharge current density, the rate of electrolyte diffusion into the plates, the total surface area of the active material, the degree of electrical contact between the particles in the plate and between the particles and the current collector (grid), and the intrinsic electrochemical activity of the particles themselves. These factors change both during a given discharge and between successive charge/discharge cycles such that the battery is eventually unable to supply sufficient energy at a useful rate.

In spite of extensive study using a wide variety of physical, chemical, and electrochemical techniques, no *clearly defined* explanation of the decline in battery capacity with cycling has yet emerged [1 - 3]. However, the application of each technique has resulted in an increase in the understanding of the very complex array of solid, liquid, and interfacial processes upon which successful operation of the lead/acid battery is dependent. This is certainly no less true in the case of X-ray diffraction than for any of the other physicochemical techniques applied to date in battery studies.

Indeed, as research turns to the more fundamental aspects of the solid-state chemistry of the active mass, diffraction techniques of one sort or another can be expected to play an increasingly important investigative role.

This article presents a resumé of the most significant contributions to lead/acid battery research made by X-ray, neutron, and electron diffraction techniques. In addition, those areas of research are defined which show the most promise in achieving improvements in the performance of the lead/acid battery.

## X-ray diffraction studies

### *Phase identification and abundance*

The traditional application of X-ray diffraction (XRD) to the study of the lead/acid battery has been for the identification of constituent phases and/or for the estimation of changes in the abundance of these phases as a function of battery charge/discharge cycling. However, in practice, the lead oxide/lead sulphate system does not lend itself easily to XRD methods of analysis because of problems arising from severe diffraction peak overlap, from high X-ray scattering and absorption coefficients, and from uncertainty in the degree of crystallinity, variability of particle size, and extent of structural distortion [4 - 6].

Phase identification by XRD techniques is often a difficult task since many of the phases have similar diffraction patterns and the samples are often poorly crystalline. Accurate determination of phase abundance is also difficult since peak intensities are not, in the general case, a simple linear function of phase concentration in multiphase systems [7].

For quantitative analytical studies calibration curves of phase abundance vs. diffraction peak intensity must be obtained prior to the analysis -- either experimentally using standard mixtures of the materials with or without the addition of an internal standard [6, 8 - 14], or theoretically using powder diffraction data calculated directly from the crystal structures of the individual phases [15 - 21].

Since battery performance is usually limited by the failure of the positive plates, most XRD studies have concentrated on examination of formed positives [4 - 6, 8 - 13, 15, 16, 22 - 30]. By contrast, the negatives have received considerably less attention [28, 31, 32], although some of the XRD investigations of the anodic corrosion products of lead and its alloys [33 - 35] are also relevant to these plates.

Early XRD analyses of the positive-plate active material [22 - 24] revealed the presence of  $\beta$ -PbO<sub>2</sub> and its discharge product PbSO<sub>4</sub>, but the first record of  $\alpha$ -PbO<sub>2</sub> in charged plates did not occur until 30 years later [25]. Since then, the relative proportions of the two forms of PbO<sub>2</sub>, their distribution throughout cross-sections of plates, and the changes in their abundance as a function of cycling history have been carefully examined. The relative proportions of the two forms of PbO<sub>2</sub> have been found to

influence the discharge capacity [8, 9, 26, 36, 37], mechanical strength [9, 38], oxygen overvoltage characteristics [37], particle- and pore-size distribution [6, 36, 37], and surface area [6, 36] of the active material. In addition, XRD measurements of the amount of  $\text{PbSO}_4$  produced on discharge and/or left unconverted at the end of charge, have provided information about the efficiency of the charge/ discharge process and the nature and whereabouts of any material which is not participating in the cell reaction.

Dodson [8] was the first to demonstrate the significance and beneficial effect of  $\alpha\text{-PbO}_2$  in positive plates. He observed that plates containing high initial amounts of  $\alpha\text{-PbO}_2$  had a low initial capacity, but that this capacity increased with cycling and the plates slightly outlasted those containing no  $\alpha\text{-PbO}_2$ . Recent work [15, 16] has confirmed these observations and has indicated that the optimum ratio of  $\alpha\text{-PbO}_2$ : $\beta\text{-PbO}_2$  for batteries operated under simulated electric vehicle service at 25 °C may be in the vicinity of 0.75.

Studies of the distribution of  $\alpha$ - and  $\beta\text{-PbO}_2$  in positive plates [26, 27, 36, 39 - 42] have shown that whereas  $\beta\text{-PbO}_2$  predominates in the outer layers of plates, the inner zones may contain appreciable amounts of the  $\alpha$  form. This distribution of the polymorphs arises because the  $\alpha\text{-PbO}_2$  which is converted to  $\text{PbSO}_4$  during battery discharge is converted back to  $\beta\text{-PbO}_2$  during recharging [8, 11, 25, 26, 33, 43]. The amount of  $\alpha\text{-PbO}_2$  in a positive plate therefore declines during cycling of the battery and the amount that remains tends to be concentrated in the central portions of the plate and next to the grid, where electrolyte access is restricted.

In recent studies of batteries operated at temperatures up to 60 °C [16, 44], it has been shown that with increasing temperature the amount of  $\alpha\text{-PbO}_2$  declines more rapidly with cycling, yet a correlation still pertains between battery cycle life and the initial  $\alpha\text{-PbO}_2$ : $\beta\text{-PbO}_2$  ratio. This suggests that the amount of  $\alpha\text{-PbO}_2$  itself may not be the important factor but rather the conditions of the plate curing and formation which ultimately give rise to the high initial  $\alpha\text{-PbO}_2$  content.

Quantitative XRD measurements of the relative utilization of  $\alpha\text{-PbO}_2$  and  $\beta\text{-PbO}_2$  in battery plates [16, 44] have shown that although the conversion efficiency of  $\beta\text{-PbO}_2$  is higher than that of  $\alpha\text{-PbO}_2$ , the  $\beta\text{-PbO}_2$  utilization declines more rapidly than  $\alpha\text{-PbO}_2$  utilization during cycling. Furthermore, since the  $\text{PbSO}_4$  content of the charged positive plate remains low throughout battery life, the decline in battery capacity is due to a failure of the  $\beta\text{-PbO}_2$  to be reduced to  $\text{PbSO}_4$  on discharge rather than to a failure of the  $\text{PbSO}_4$  to be converted back to  $\text{PbO}_2$  on charge. This suggests that electrical isolation of the  $\beta\text{-PbO}_2$  particles between themselves is the cause of battery failure rather than the development of extensive insulating  $\text{PbSO}_4$  corrosion films on the grid. However, at low temperatures of battery operation (< 40 °C), variability of phase composition between individual positive plates can be quite large and the occasional development of a few, heavily sulphated, charged plates can lead to failure of the entire battery even though the majority of the plates are not sulphated.

XRD methods have also been extensively used [14, 31, 32, 45 - 54] to study the complex array of phase transformations that take place during plate curing and formation, especially since it has been suggested [31] that plates retain a memory of their formation procedure and that the history of this treatment determines subsequent plate capacity and cycle life.

The specific conditions chosen for the curing and formation processes not only determine the identity and abundance of the phases produced in the plate, but also control the detailed microstructure of the plate particles, and the ultimate mechanical strength and durability of the bonds between the particles themselves and between the active mass and its supportive grid structure [1 - 3]. It has been claimed that tetrabasic lead sulphate is the preferred compound for the creation of a rigid mass of  $\text{PbO}_2$  in the formed plate [45, 55, 56]. On the other hand, a high initial content of  $\text{PbO}$  in the paste promotes the formation of  $\alpha\text{-PbO}_2$  in the formed plate [9, 26], thereby lending higher mechanical stability to the active material during cycling. XRD phase analysis studies are, therefore, of considerable importance in attempts to understand and assess the optimum paste composition and formation conditions for maximum battery capacity and cycle life.

#### *Poorly crystalline and/or amorphous material*

In addition to the crystalline phases in battery plates, numerous XRD studies have documented the presence of poorly crystalline or amorphous\* material, and have reported changes in its abundance according to the method of plate preparation and cycling history [5, 6, 11 - 13, 30, 57 - 60].

The presence of non-trivial amounts of non-diffracting, amorphous material in the positive plates severely hampers attempts at quantitative XRD phase analysis since the "standard" materials used for the determination of calibration constants are also likely to contain amorphous components. One approach to the solution of this problem is to examine samples of the phase from a variety of sources and to use the material with highest crystallinity for the analytical standard [5, 13, 17]. A second, and perhaps more desirable, method is to derive the calibration curves from calculated XRD patterns as described above [15, 16, 21].

Kordes [6] observed that the amorphous content of  $\alpha\text{-PbO}_2$  samples was in the range 40 - 70 wt.% and that of  $\beta\text{-PbO}_2$  samples in the range 18 - 50 wt.%, depending upon the method of preparation. The positive active material from plates with an  $\alpha\text{-PbO}_2\text{:}\beta\text{-PbO}_2$  ratio of 0.5 contained about 34 wt.% of amorphous material, with the outer portions of the plates being more poorly crystalline than the interiors. In addition, the size and shape of particles, as well as the total surface area of the samples, were determined by X-ray scattering measurements at very small angles for comparison with gas absorption estimates.

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\*The term "amorphous", as used in this paper, refers to material which does not give rise to normal X-ray diffraction peaks, either because it is truly structureless, or because the particle size is very small (i.e., less than  $\approx 100 \text{ \AA}$  in mean dimension).

In recent XRD studies [16, 44] of positive plates operated under simulated electric-vehicle service, the amorphous content has been found to lie in the 10 - 29 wt.% range, and to increase slightly as cycling proceeds. Comparison of these results with wet chemical analysis data showed that the amorphous  $\text{PbO}_2$  component discharges at a rate similar to that of the crystalline component, but that the amorphous material utilization declines somewhat more rapidly with cycling.

The  $\alpha\text{-PbO}_2$  component was confirmed to have a lower crystallinity than  $\beta\text{-PbO}_2$  when prepared electrolytically, especially as a corrosion product of the grid metal. The lower than expected X-ray diffraction intensity obtained from the  $\alpha\text{-PbO}_2$  component in known mixtures of the two polymorphs of  $\text{PbO}_2$  [4] may, therefore, be explained by the relatively higher proportion of amorphous material in the  $\alpha\text{-PbO}_2$  which contributes to the mass of this component but not to the intensity of its diffraction peaks.

### *Crystallite size*

There have been many determinations of the particle size, porosity, and surface area of the active masses in lead/acid batteries using optical and electron microscopy, and gas absorption techniques [1 - 3 and references therein]. However, unless these particles are single crystals, the sizes so determined will not correspond to the true size of the crystalline material under examination. In fact, relatively few studies have been devoted to the determination of crystallite dimensions in lead/acid batteries [6, 12, 26, 61 - 63]; all of these have utilized XRD methods.

The determination of crystallite size using XRD rests on the fact that the breadth of a diffraction line from a particular material increases as the size of the crystals decrease [7]. Many methods of estimating size from peak width exist, each with its own degree of accuracy and experimental difficulty. The most commonly employed method relates the crystallite size to the peak broadening using a combination of the Scherrer [64] and Warren [65] equations, but the results obtained with this technique are of uncertain quality in anything but a relative sense, and only apply to crystallites with sizes less than about 2000 Å. Of course, for crystals with dimensions less than 100 Å or so, the diffraction peaks become so broad that they eventually disappear into the general background and their contribution to the sample is then incorporated as an "amorphous" fraction in a quantitative phase analysis.

In spite of these difficulties, there is general agreement that the crystallite size of fresh battery  $\text{PbO}_2$  material formed at 25 °C is around 180 - 500 Å, and that this value rapidly increases (for  $\beta\text{-PbO}_2$  at least) to several thousands of angstroms after only a few charge/discharge cycles [6, 12, 26, 61 - 63]. Ikari *et al.* [26] observed that the crystallite size of  $\beta\text{-PbO}_2$  was larger than that of  $\alpha\text{-PbO}_2$  at a given temperature, that the size of both polymorphs increased with the temperature of formation, and that the maximum size of crystallites was achieved with formation acid densities of  $\approx 1.07 \text{ g cm}^{-3}$ .

Broadening of diffraction peaks can also result from non-uniform lattice strain brought about by the presence of non-stoichiometry and/or defects in the crystal structure of the material under examination, rather than by a real decrease in crystallite size [62]. Therefore, it has been suggested [57, 61, 66 - 68] that the observed decrease in peak width as  $\beta$ -PbO<sub>2</sub> is cycled in a battery actually represents a change in the  $\beta$ -PbO<sub>2</sub> crystal structure towards a more stoichiometric, defect-free variety that is less electrochemically reactive. However, comparisons of battery capacity with changes in crystallite size have indicated that the increase in size occurs well before the capacity decline begins to take place [63].

### *Corrosion films*

Corrosion of the positive-plate grid is a fundamental problem in lead/acid batteries that produces many undesirable effects. One of the most serious of these effects is the formation of loosely adherent layers of various oxides and sulphates of lead. These can act as electrical barriers and produce disruptive internal stresses between the grid metal and the surrounding active material [1, 69 - 71]. Lead corrosion in batteries is complex because of (i) the large variations in electrolyte concentration and voltage which occur during operation, (ii) the creation of potential and concentration gradients across the corrosion film, and (iii) the fact that the film consists of a series of ill-defined "intermediate" lead oxides [62, 72] and basic sulphates [47, 73].

In studies of the corrosion of lead and its alloys it is important to establish the nature and rate of the processes taking place, the morphology and structure of the reaction products, and the effect of deliberately and accidentally introduced impurities and imperfections in the grid metal. XRD techniques have played a significant role in the elucidation of these processes, not only in the identification of the corrosion products [32, 33, 73 - 80], but also in the determination of their spatial relationships [33, 74, 76 - 79], lattice orientation [75], and crystallite size [80].

Unfortunately, conventional XRD measurements are not always able to resolve the patterns from the many compounds which form in the corrosion film, cannot separately analyze the distinct layers in very thin films, and are not easily undertaken *in situ* for the study of the sequential formation of corrosion products [73]. One recent solution to this problem has been to use micro-XRD procedures [81] on 10  $\mu$ m samples picked from corrosion films [82]. When used in conjunction with microprobe laser Raman spectroscopy and standard electron optical techniques, this application of the XRD method should prove to be particularly fruitful, not only in corrosion studies, but also in detailed analysis of the bulk active material.

### *Crystal structure*

Until the detailed crystal structure of a compound has been determined, there remains a degree of doubt about the *exact* chemical formula of the material and, as a result, an uncertainty about its true physicochemical

and thermodynamic properties. Unfortunately, this is particularly true in the case of the phases in the Pb-S-O-H system because of the common occurrence of non-stoichiometry, variable valence state, very small particle sizes, structural defects and poor crystallinity. In fact, a recent survey of the 20 or so phases relevant to the lead/acid battery [21] has shown that almost half of these phases have unknown crystal structures. Moreover, many of these poorly characterized phases are basic lead sulphates [83 - 86], basic lead carbonates [87, 88], and intermediate lead oxides [72, 89 - 92], all of which are proving to be important in relation to the curing, formation, and corrosion processes which take place in batteries.

XRD is of limited use in the determination of the crystal structures of these phases because of the large difference in X-ray scattering abilities of Pb, O, and especially C and H: the XRD patterns from most of the phases are almost completely dominated by the presence of Pb, and little information can, in general, be obtained about the locations of the "lighter" atoms in the structures. With only a few exceptions [60, 63, 93 - 95], therefore, most of the crystal structure determinations have been the preserve of neutron diffraction (see below).

Nevertheless, XRD methods are capable of providing *indirect* evidence of phase non-stoichiometry, structural disorder, and crystallinity by accurate measurements of diffraction peak width (described above) and unit cell dimensions. Chiku [28] related the observed changes in the unit cell dimension of Pb in negative plates to the decline in discharge capacity of these electrodes. Since then, there have been similar attempts to relate changes in positive-plate capacity to changes in the degree of structural order and hydrogen content of  $\beta$ -PbO<sub>2</sub> [57, 61, 66 - 68]. However, recent accurate XRD determinations [63] of the unit cell dimensions of  $\beta$ -PbO<sub>2</sub> samples taken from the positive plates of batteries cycled under a simulated electric vehicle service have failed to demonstrate a correlation with battery capacity and, furthermore, have set an upper limit of 0.5 mole% for the hydrogen content when coupled with Pb<sup>2+</sup>/Pb<sup>4+</sup> substitution in this phase.

### Neutron diffraction studies

High-flux monochromatic neutron sources are far less accessible than their X-ray counterparts and, for this reason, the direct application of neutron diffraction to the study of the lead/acid battery system has, until recently, been relatively rare [6, 59, 96 - 98]\*. However, neutrons offer several advantages over X-rays when used as the probing radiation in diffraction studies, the most important of which are (i) the smaller, and random, variation in scattering power for elements with dramatically different atomic

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\*Since the major emphasis of this paper is devoted to diffraction (elastic scattering) processes, only passing reference will be made to the application of recent inelastic/incoherent neutron scattering experiments to battery systems.

number, enabling the accurate location of C, O, and H atoms as well as Pb, (ii) the invariance of neutron scattering power with diffraction angle, resulting in higher diffraction intensities at high scattering angles, and (iii) the generally very low neutron absorption coefficients of most materials, enabling the experiment to "see" further into the sample. The major disadvantage of neutron diffraction is that relatively large samples (*i.e.*, more than about 10 g) are required in order to obtain statistically meaningful data.

Kordes [6] was among the first to apply neutron diffraction techniques to the positive plate material in the lead/acid battery. He examined the distribution, size, and crystallinity of both  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> within the plates, and used small-angle scattering to obtain estimates of changes in the particle shape factors of the PbO<sub>2</sub> grains during the course of charge/discharge cycling. Utilizing the greater penetration of neutrons relative to X-rays, Kordes showed that the interior of the plates was less crystalline (30%) than the outer surfaces (40 - 60%). Furthermore, the amorphous material participated more readily in the discharge reaction. Failure of the plates was attributed to a gradual anhedralization of the PbO<sub>2</sub> particles leading to a "softening" of the paste.

Prior to the work of Kordes, and until recently, the use of neutron diffraction was mainly restricted to the determination of the crystal structures of individual phases occurring in the lead/acid battery, with little or no accompanying discussion of the relevance to battery performance [99 - 104]. However, the renaissance in powder diffraction which has occurred with the advent of the full-profile Rietveld method of crystal structure refinement [105 - 108] has led to an increased interest in the neutron diffraction analysis of battery materials.

One recent suggestion for the failure mechanism of positive plates in lead/acid batteries is that the decline in the electrochemical activity of the positive plate is related to the progressive loss of a hydrogen species from the crystal structure of  $\beta$ -PbO<sub>2</sub> as the battery is cycled, ultimately leading to the formation of a phase which resembles the chemically prepared (apparently inactive) product. Much of the new wave of neutron studies has, therefore, concentrated on the determination of the detailed stoichiometry of the  $\beta$ -PbO<sub>2</sub> material and on the location of any H atoms which may be present in its crystal structure [59, 97, 98].

As a result of these studies it is now clear that the traditional view of  $\beta$ -PbO<sub>2</sub> as a substantially oxygen-deficient structure is incorrect. If anything, the neutron diffraction data indicate that there is a slight deficiency of lead atoms relative to oxygen. Any hydrogen that is present in the crystal structure of  $\beta$ -PbO<sub>2</sub> may, therefore, be incorporated in one of at least two different ways: the hydrogen atoms may merely compensate for the lead atom vacancies, or they may be involved in a coupled substitution of Pb<sup>2+</sup> for Pb<sup>4+</sup> [59, 97, 98]. However, not only have ordered structural sites for this hydrogen not been found, but there is very little, if any, difference between the crystal structure of  $\beta$ -PbO<sub>2</sub> from a fresh battery plate,  $\beta$ -PbO<sub>2</sub> taken from failed batteries, or samples prepared chemically [59, 63, 96 - 98]. The

proposal that battery capacity declines as a result of the loss of a hydrogen species from the  $\beta$ - $\text{PbO}_2$  structure, therefore, seems unlikely.

While the crystal structure of  $\beta$ - $\text{PbO}_2$  samples from a wide variety of sources has been refined quite successfully [59, 96 - 98] using neutron diffraction data, the refinement of the  $\alpha$ - $\text{PbO}_2$  structure has only been achieved in the case of chemically prepared material [59]. Electrolytic samples of  $\alpha$ - $\text{PbO}_2$  contain significant quantities of poorly-crystalline material, have severe cation disordering over the octahedral sites, display evidence of lattice strain and unit cell incoherency, and contain up to 15% vacancies on the lead atom site [59]. However, these properties of  $\alpha$ - $\text{PbO}_2$  have not received much attention because  $\alpha$ - $\text{PbO}_2$  is usually not the major phase present in lead/acid battery positive plates and, in any event, the amount present declines rapidly during the early stages of battery operation [8, 11, 25, 26, 33, 43].

Significant quantities of hydrogen (up to 0.26 atoms per  $\text{PbO}_2$  formula unit) have been measured in bulk samples of electrochemically prepared  $\alpha$ - $\text{PbO}_2$  and  $\beta$ - $\text{PbO}_2$  using chemical analysis [1, 5, 109], nuclear magnetic resonance [66], thermogravimetric analysis [57], X-ray photoelectron spectroscopy [110], and inelastic neutron scattering [97, 111]. However, since neutron diffraction studies have been unable to locate these hydrogen atoms within the  $\text{PbO}_2$  structure itself, it seems likely that the chemically-determined hydrogen contents originate from surface adsorbed water species and/or water or hydroxyl species occupying lattice vacancies near the crystal surface. These disordered, proton-rich, surface layers may indeed play a significant role in the electrochemical activity of the  $\text{PbO}_2$  particles in lead/acid batteries, but since the layers do not have long-range ordered structures their detailed properties cannot be studied by X-ray or neutron diffraction. Similarly, the presence of disordered hydrogen atoms and/or vacancies in the dioxide structure, but at levels insufficient to be detected by X-ray or neutron diffraction, may also be important in determining the electrolytic activity of the crystals. Investigations of these structural features require the use of electron diffraction techniques before a full understanding of the effect of hydrogen and other defects in the  $\text{PbO}_2$  structure can be reached.

### Electron diffraction studies

As indicated previously, the size, morphology, and spatial relationships of the particles in the electrodes can have a significant effect on the performance of the lead/acid battery. For this reason, the literature abounds with optical and, more recently, electron microscopic examinations of the surface of the active material [1, 2, and references therein]. Both of these techniques permit the observation of features in the active material to dimensions of only a few micrometers, much smaller than the sample sizes analyzed by neutron diffraction, and even below the limit of micro X-ray diffraction. However, unless polished cross-sections are prepared, only the

surface features of the particles can be observed in microscopic examinations and, further, no information can be obtained about crystal structure.

On the other hand, when an electron beam is passed *through* a very thin specimen of material, rather than merely being backscattered by the surface of the sample, images of the real space crystal structure (*via* its diffraction pattern) can be obtained with a spatial resolution of only a few angstroms. This technique — transmission electron microscopy — provides information about crystal structure and order/disorder effects on the unit cell scale, rather than information about features of the spatially-averaged, long-range ordered structure, which are obtained by X-ray and neutron diffraction.

Transmission electron microscopy has recently been applied [60, 111] to various samples of both  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> and has revealed a number of structural features of the dioxides which had previously passed undetected by conventional diffraction techniques. In particular,  $\alpha$ -PbO<sub>2</sub> has been shown to be composed largely of crystals with extensive structural faulting perpendicular to the [001] direction in the unit cell. The presence of this faulting is, no doubt, the reason why attempts to refine the crystal structure of  $\alpha$ -PbO<sub>2</sub> have met with only limited success [59, 60, 98]. Furthermore, the structural defects themselves may be related to the higher level of cation disorder and non-stoichiometry observed in electrolytically prepared samples of  $\alpha$ -PbO<sub>2</sub> [59].

By contrast, the level of structural faulting in  $\beta$ -PbO<sub>2</sub> crystals is observed to be much lower than in  $\alpha$ -PbO<sub>2</sub>, consistent with its near-stoichiometric Pb:O ratio and with the ability to achieve satisfactory structure refinements for all samples [59, 60, 96 - 98]. However, the fact that both  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> contain structural defects, to one degree or another, allows the possibility that the presence of these defects, and/or any hydrogen atom incorporation associated with their presence, could have an influence on their electrochemical activity in a battery.

### Directions for research

From the above discussion, it is clear that diffraction techniques have already made many significant contributions to our understanding of the processes that take place during the manufacture and operation of lead/acid batteries. Furthermore, as research and development efforts shift from battery engineering towards the investigation of more subtle solid state properties of the active material, it is to be expected that the application of diffraction methods will prove to be even more valuable. Areas of research that are amenable to study with diffraction experiments and that are in need of further attention include the following:

- (i) Crystal structure determinations on the remaining poorly characterized basic sulphates, basic carbonates, and intermediate oxides of lead.
- (ii) An extension of the quantitative XRD positive plate phase analysis methods to the compositions of cured plates, including the determination

of the effect of different phase compositions on the electrochemical activity of the formed plates.

(iii) Studies of the influence of the conditions of leady oxide manufacture on the size and shape of the crystallites formed and of their ultimate effect on plate performance.

(iv) A more detailed characterization of the nature and chemical composition of the amorphous phases in the active material, including examination of the role of any hydrogen species present in these phases.

(v) A clear definition of the role of  $\alpha$ -PbO<sub>2</sub> in maintaining the mechanical stability and electrochemical performance of positive plates, and its relationship to the  $\beta$ -PbO<sub>2</sub> content.

(vi) Micro-diffraction studies of the corrosion films on positive plate grids, including detailed analyses of the spatial relationships between component phases and their influence on the nature of the bond between the paste and the grid.

(vii) Further transmission electron microscope studies of the nature of the defects in the PbO<sub>2</sub> crystal structures and of their possible influence on the electrochemical activity of the plate material in batteries.

(viii) Further determinations of crystallite size and shape variations in positive plates as a function of cycling history, current density, depth of discharge, and temperature of operation.

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