
**TECHNICAL AND RESEARCH ASPECTS OF LEAD/ACID BATTERY
PRODUCTION**

W. F. GILLIAN

Pasminco Metals, 114 William Street, Melbourne, Vic. 3000 (Australia)

A. M. HARDMAN

*Chloride Technical and Trading, Wynne Avenue, Swinton, Manchester
M27 2HB (U.K.)*

R. KIESSLING

Hagen Batterie AG, Coesterweg 45/POB 1461, D4770 Soest (F.R.G.)

D. W. H. LAMBERT

*CBS Batteries Ltd., Gillibrands Road, East Gillibrands, Skelmersdale
NN8 9TT (U.K.)*

J. E. MANDERS

Pasminco Metals, 114 William Street, Melbourne, Vic. 3000 (Australia)

D. A. J. RAND

*CSIRO Institute of Minerals, Energy and Construction, Division of Mineral
Products, P.O. Box 124, Port Melbourne, Vic. 3207 (Australia)*

Topics under discussion

| | |
|--|-----|
| ● Alloy Technology | 219 |
| Purity level | 219 |
| Effect of bismuth | 220 |
| Pressure die-cast grids | 221 |
| ● Battery Oxide | 221 |
| Level of free lead and apparent density | 221 |
| Effect of red lead | 221 |
| Granular oxide | 223 |
| Influence on paste mixing | 224 |
| ● Plate Processing | 225 |
| Influence of cured state | 225 |
| Pickling of tubular plates | 226 |
| Tackless formation | 226 |
| Plate buckling | 227 |
| ● Gas-recombination (RE) Batteries | 228 |
| Operating principles | 228 |
| Effect of impurity levels | 228 |
| Acid requirement | 228 |
| Charging conditions | 229 |
| Effect of bismuth | 229 |
| ● Positive-plate Performance | 229 |
| Effect of α -PbO ₂ : β -PbO ₂ composition | 229 |
| Effect of grid alloy composition | 233 |
| Effect of polymer binders | 234 |
| Effect of bismuth | 234 |
| ● References | 234 |

ALLOY TECHNOLOGY

Question: *What is the purity of lead required for use in valve-regulated lead/acid batteries?*

W. F. GILLIAN

With the advent of valve-regulated, or 'sealed', lead/acid batteries, concern has shifted from the traditional problem of grid corrosion effects to the more subtle area of gassing effects. The metals industry now has to face two levels of specification for lead and its alloys — one for flooded-electrolyte battery designs, the other for immobilised-electrolyte (sealed) types.

The first level of specification, applicable to conventional batteries, assumes impurity levels of <0.001 wt.%. The second level of specification, for valve-regulated batteries, focuses on purity levels in the region <0.0001 wt.% or <0.00005 wt.%. For example, Table 1 shows the limits for antimony, arsenic, nickel, selenium and tellurium [1]. These elements have been identified as the principal gas-generating impurities.

TABLE 1

Impurity limitations of pure lead for sealed batteries [1]

| Element | Maximum allowed concentration (wt.%) |
|-----------|--------------------------------------|
| Antimony | 0.0001 |
| Arsenic | 0.0001 |
| Cobalt | 0.0001 |
| Manganese | 0.00005 |
| Nickel | 0.0002 |
| Selenium | 0.00005 |
| Tellurium | 0.00003 |

Question: *Is lead of adequate purity available for valve-regulated batteries?*

W. F. GILLIAN

Most major primary smelters can meet the purity requirements for lead used in valve-regulated batteries. Unfortunately, however, the battery industry is not the only sector demanding high-purity lead. Thus, competition for this resource has placed, and will continue to place, pressure on availability and price.

There is more concern in the metals industry over the backlash against the use of *secondary* lead for the production of both grid alloy and leady oxide for valve-regulated batteries. As secondary smelting is a fast-growing industry, the implications of this new attitude among battery manufacturers are very significant. For example, the RSR Corporation in the U.S.A. recently announced that all of its metal-production facilities will be upgraded and existing pyrometallurgical processes will be replaced by electrowinning techniques. Although this change in policy was claimed to be based on environmental grounds, the move will also ensure that RSR has on-going capacity to meet the increasing demand for high-purity lead. In Europe, a major study has been initiated by a number of secondary lead producers in an attempt to identify and quantify more precisely the offending elements, or combination of elements, that have caused their lead to be excluded from valve-regulated batteries.

Finally, mention should be made of the difficulties encountered in obtaining accurate measurements of trace amounts of impurities. A recent survey conducted by Pasminco Metals on the levels of detectability of impurities achieved by a number of laboratories,

within both the smelting and battery industries, revealed a general inability to reach the low limits quoted in specifications for lead used in valve-regulated batteries. There is, therefore, an urgent need for an improvement in analytical techniques, for the standardisation of reference samples of lead, and for the certification of laboratories claiming to provide expert services.

Question: What effect does the presence of bismuth have on the corrosion behaviour of the positive grid?

W. F. GILLIAN

Although some work has been carried out in this area, a good deal more needs to be undertaken before any unequivocal conclusions can be made. Studies completed to date show that microstructural considerations come largely into play when attempting to determine the effect of bismuth on the corrosion behaviour of positive grids. For instance, Fig. 1 shows a plot of weight loss *versus* bismuth content [2]. If this were to be considered on its own, it could be concluded that there are specific windows of bismuth content at which corrosion proceeds at a slow rate. However, an examination of a plot of grains per mm² *versus* bismuth content for the same electrodes (Fig. 2) reveals that there is a striking (inverse) correlation between grain size and corrosion rate. Thus, further work must be conducted on the influence of alloy fabrication methods before the role of bismuth can be fully understood.

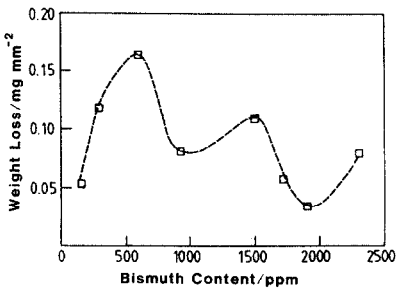


Fig. 1. Corrosion rate of Pb-Bi alloys at 1.5 V in 5 M H₂SO₄ [2].

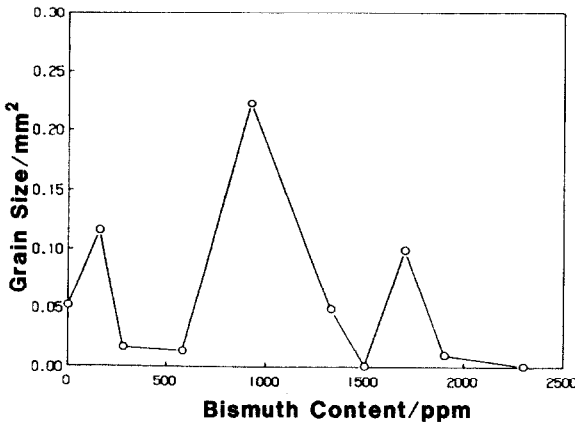


Fig. 2. Grain size of Pb-Bi alloy series [2].

Question: *Compared with gravity casting, does pressure die casting of tubular plates give rise to increased porosity and corrosion?*

R. KIESSLING

Die casting causes a markedly different grain size compared with gravity casting. This difference in grain size changes the corrosion mechanism from one of intergranular attack to one of surface attack. The latter is a much slower process and, hence, manufacturers choose the die-casting approach when designing batteries to have a long cycle life. In the die-casting process, the lead freezes from the surface towards the centre of the spine. During this freezing, the specific gravity of the lead increases, *i.e.*, the lead has a smaller volume in the solid than in the liquid state. This results in a certain degree of porosity in the centre of the spine. Other plate degradation processes occur well before this 'buried' porosity is exposed to the corrosion process. Hence, the porosity arising from die casting does not exert an influence on the service life of tubular-plate batteries.

BATTERY OXIDE

Question: *What is the preferred range of free lead in battery oxide and the preferred range for apparent density?*

A. M. HARDMAN

Battery oxides with low levels of residual lead are the preferred types, because such oxides with correct processing minimise the risk of any free lead remaining in the positive plate prior to formation. When using either ball mills or reaction pots, however, the cost of production rises as the percentage level of residual lead in the oxide decreases, thus a balance has to be reached between oxide manufacturing costs and efficient plate processing and curing in order to achieve the desired product quality. In order to limit variability during the curing and drying processes the use of controlled hydrosetting procedures will be preferred compared with natural curing and drying.

Probably the more important factor is particle size. The finer the powder the greater the apparent density and the greater the surface area per unit weight. You will note that I have not given you any hard figures, since Chloride do not normally divulge such proprietary information. However, using oxide containing 25% free lead and 99% passing a 300BS mesh would be a good starting point. The problem with oxide outside a satisfactory range is that the product does not perform very well!

Question: *Does red lead have any significance in flat-plate manufacture other than providing a means for plate identification?*

D. W. H. LAMBERT

Whilst the inclusion of red lead in the positive paste makes for easy identification of the cured plate from the negative, this is not the reason for its inclusion in the paste formulation. Red lead (Pb_3O_4) or 'minium' is added in the proportion 10 - 25 wt.% to the positive paste mix of flat-plate automotive and industrial batteries for the following reasons:

- the coulombic efficiency for the oxidation of red lead is high, as shown in Fig. 3 [3], and therefore assists in the formation of the positive active material (PbO_2) from the precursor lead oxides and basic lead sulphates of the cured plate;
- red lead has a lower heat of mixing with sulphuric acid than leady oxides and therefore the addition of red lead to the blend of leady oxides, prior to paste mixing, reduces the heat generated during mixing [4];
- red lead improves the initial plate capacity after formation by favouring the production of the β - PbO_2 polymorph, Fig. 4 [5].

Note, however, red lead is an expensive alternative to leady oxides and, therefore, the above benefits are achieved at a price.

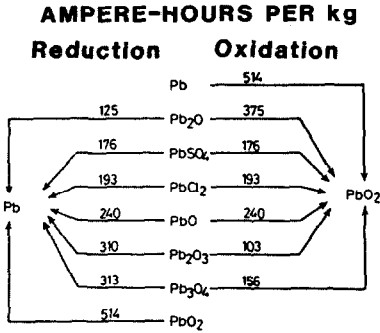


Fig. 3. Quantity of electricity required to reduce or oxidise lead compounds [3].

| Precursor or Condition | Product |
|--|--------------------------|
| Alpha PbO (Orthorhombic) $\xrightarrow{H_2SO_4}$ | PbSO ₄ · 4PbO |
| Beta PbO (Tetragonal) $\xrightarrow{\quad}$ | PbSO ₄ · 3PbO |
| PbSO ₄ · 4PbO $\xrightarrow{\text{Charge}}$ | Alpha PbO ₂ |
| PbSO ₄ · 3PbO $\xrightarrow{\quad}$ | Beta PbO ₂ |
| PbSO ₄ $\xrightarrow{\quad}$ | Beta PbO ₂ |
| Pb ₃ O ₄ $\xrightarrow{\quad}$ | Beta PbO ₂ |
| 2PbCO ₃ · Pb(OH) ₂ $\xrightarrow{\quad}$ | Beta PbO ₂ |
| PbO-M (Orthorhombic) $\xrightarrow{\quad}$ | Beta PbO ₂ |
| PbO-L (Tetragonal) $\xrightarrow{\quad}$ | PbO _{1.91} |
| Pb $\xrightarrow{\quad}$ | Alpha PbO ₂ |
| High Density Paste $\xrightarrow{\text{Favours}}$ | Alpha PbO ₂ |
| Low Density Paste $\xrightarrow{\quad}$ | Beta PbO ₂ |
| High Gravity Forming Acid $\xrightarrow{\quad}$ | Beta PbO ₂ |
| Low Gravity Forming Acid $\xrightarrow{\quad}$ | Alpha PbO ₂ |
| High Current Density $\xrightarrow{\quad}$ | Alpha PbO ₂ |
| Low Forming Temperature $\xrightarrow{\quad}$ | Alpha PbO ₂ |

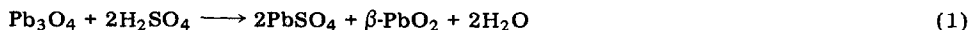
Fig. 4. Relationship of various lead compounds and plate formation conditions [5].

D. A. J. RAND

For many years, the assertion of Ritchie *et al.* [6], back in 1971, that red lead (Pb₃O₄) is inert during both the paste-mixing and the curing stages of flat-plate manufacture has remained largely unchallenged in the literature. Recent studies conducted by CSIRO [7] in a factory producing tubular plates by a wet-fill process have, however, cast doubt on this view. X-ray phase analysis measurements showed that the initial Pb₃O₄ content decreased by up to 50% during paste mixing and then decreased further, or even increased, during the subsequent curing period. The change in Pb₃O₄ content during

curing was dependent upon local temperature/humidity conditions. The unexpected occurrence of an increase in the amount of Pb_3O_4 was attributed to the breakdown of tetrabasic lead sulphate (4BS). This suggestion awaits confirmation by experiment.

Of late, Pavlov and Kapkov [8] claim that Pb_3O_4 decomposes via one, or both, of the following reactions when mixed with leady oxide and made into a paste with dilute sulphuric acid and water:



The extent to which either of these reactions takes place is dependent upon the order in which the paste ingredients are mixed together. In an important discovery, the authors have found that certain mixing procedures reduce the size of 4BS crystals that are produced during high-temperature curing. This change in morphology overcomes the low-initial-capacity problem of 4BS-based plates without impairing the superior cycle-life performance of such plates.

These recent developments suggest that there is considerable scope for optimizing the use of red lead in plate manufacture.

Question: *What is the significance of BET surface area on the performance of tubular-plate batteries and how is this altered by the use of granular oxide?*

D. W. H. LAMBERT

The Brunauer, Emmet and Teller (BET) gas adsorption method of determining internal surface area, in conjunction with XRD phase analysis (*e.g.*, PEAKS [9]), particle-size distribution and porosity/mean pore-size data, provides the battery designer with an indication of the expected electrical performance and cycle life of the tubular-positive electrode.

The particle-size distributions of granular oxide, red lead and Barton pot leady oxide are shown in Table 2 [10]. Shimadzu ball-mill oxide is even finer, typically 30% < 2 μm and 60 - 70 < 20 μm [12]. The BET surface area of granular oxide has been compared with a conventional blend of red lead and leady oxide used for tube filling [13]. The BET surface area of granular oxide at 1.7 - 1.82 $\text{m}^2 \text{g}^{-1}$ is more than twice that of blended oxide, *viz.*, 0.84 $\text{m}^2 \text{g}^{-1}$.

Motive-power tubular-plate cells containing granular oxide, when compared with tubular-plate cells containing blended oxide, have been shown to exhibit superior initial

TABLE 2

Particle-size distribution of battery oxides

| Granular oxide | | Barton-pot oxide ^a | | Red lead (Pb_3O_4) ^b | |
|----------------|------------------------------|-------------------------------|------------------------------|-------------------------------------|------------------------------|
| % | Size range (μm) | % | Size range (μm) | % | Size range (μm) |
| 100 | < 1500 | 97 | < 30 | 99 | < 20 |
| 40 | < 500 | 94 | < 20 | 7 | 10 - 15 |
| 18 | 250 - 500 | 15 | 10 - 12 | 10 | 8 - 10 |
| 13 | 125 - 250 | 50 | 8 - 10 | 18 | 6 - 8 |
| 9 | 63 - 125 | 7 | 6 - 8 | 25 | 4 - 6 |
| 12 | < 63 | 8 | < 6 | 38 | < 4 |

^aData taken from Baldsing *et al.* [11].

^bData supplied by Cookson Group Research Laboratories.

capacity and equivalent cycle-life capability [14]. Therefore, the high BET surface area, balanced particle-size range, and more porous structure of the granular oxide afford better access of the acid to the active material and contribute to its improved performance.

Question: *What is the significance of acid absorption, water absorption and BET surface-area measurements of leady oxide on the manufacture of leady oxide pastes and battery performance?*

D. W. H. LAMBERT

Acid absorption, water absorption, BET surface-area measurement and other techniques such as X-ray diffraction (XRD), neutron diffraction (ND), scanning electron microscopy (SEM), electron probe microscopy (EPM), mercury porosimetry, atomic absorption spectrophotometry (AAS) and differential scanning calorimetry (DSC) are all commonly used to characterise the physical and chemical parameters of the various leady oxides used in the manufacture of lead/acid batteries. These parameters include:

- reactivity
- surface area
- pore-size distribution and mean pore diameter
- particle-size distribution
- particle morphology
- chemical phase composition
- impurity levels

Acid- and water-absorption of leady oxides

In preparing a paste for flat plates, it is important to control the paste consistency. This is achieved by adding only sufficient 'initial water' to the leady oxide in the mixer to give a uniform and moist mass that will not stick together prior to adding the acid.

Acid absorption is not routinely used at CBS Batteries owing to the difficulty in obtaining reproducible results with the fine Sovena ball-mill oxide that is manufactured in our plant. Generally, a high acid-absorption value indicates a small particle-size, high surface-area oxide. Typical acid absorptions on CBS ball-mill oxide range from 230 - 250 ml g⁻¹. It is claimed [5] that acid absorption results are affected by light, heat, temperature, humidity, static electricity and the type of storage container.

The water absorption values (typically expressed as ml H₂O/100 g oxide) are a qualitative indication of the suitability of the leady oxide for paste mixing and can be used by the paste-mixing operator to adjust the initial quantity of water added so that a paste with optimum consistency is achieved.

BET surface area

The BET surface area of positive active material is strongly influenced by the paste density, plate formation conditions [15], and the type of precursor leady oxide used in the manufacture of the paste.

The properties of the leady oxide vary markedly with the method of manufacture. Compared to ball-mill oxides (brand names: Shimadzu, Tudor, Hardinge, Heubach, Sovena), Barton oxides (brand names: Linklater, Balox, Minimet, Hammond, Chloride) generally have larger particle-size distributions and mean particle diameters, lower acid- and water-adsorption values, higher β -PbO content, lower surface area (*i.e.*, less reactive), and longer shelf-life [16]. These differences result in corresponding differences in the processing of the two types of oxide and the resulting performance of the finished battery plate. For example, it is claimed that Barton-pot oxide is easier to handle and process, whereas the ball-mill method produces an oxide that is more reactive and that gives rise to plates with greater initial capacity and strength. The composition of leady oxides also changes during storage owing to continued oxidation of the particles of free lead to the α -PbO polymorph.

The BET value gives an indication of oxide reactivity (with H₂SO₄) and therefore assists in determining the correct paste formulation.

PLATE PROCESSING

Question: *In flat (pasted) plates, what is the relationship, if any, between the chemical phase composition of the cured material (i.e., tetrabasic/tribasic lead sulphate ratio) and that of the ensuing formed material (i.e., α -PbO₂/ β -PbO₂ ratio)?*

D. A. J. RAND

The curing process is that stage in the manufacture of flat (pasted) plates during which the paste of lead particles, lead oxides, dilute sulphuric acid and water is converted into a cohesive, porous mass that has good adherence to the supporting grid. Hardening and strengthening of the plate material is brought about by the development and growth of basic lead sulphates, principally: tetrabasic lead sulphate, 4PbO·PbSO₄ (=4BS), and tribasic lead sulphate, 3PbO·PbSO₄·H₂O (=3BS). The relative proportion of 4BS to 3BS is strongly influenced by the conditions under which the curing process is conducted. Provided the material is maintained in a moist state, temperature is the major determinant of cured-plate composition, with the formation of 4BS being favoured over that of 3BS at temperatures in excess of 70 °C [17 - 25].

Irrefutably, the performance of pasted positive plates is strongly influenced by the phase composition and morphology of the cured material. In this respect, it is now part of battery lore that 3BS-rich material gives capacity and is therefore the best route for automotive battery manufacture, whilst 4BS-rich material imparts cycling capability and should be used for industrial batteries.

There is clear evidence that the particle size of the cured material determines the capacity of the resulting formed plate. The conversion of either 3BS or 4BS to PbO₂ is metasomatic [26], that is, the PbO₂ is similar in crystal size and shape to its precursor. Since 3BS crystals are usually much smaller than their 4BS counterparts, plates formed from 3BS-rich material contain correspondingly smaller crystals of PbO₂. The latter have a high active surface area and, accordingly, the formed plate has a high initial capacity. By contrast, further studies [10] have shown that the large crystals of PbO₂ produced metasomatically from 4BS interlock to produce a reticular structure that provides greater plate strength. It was concluded (without, it should be noted, the support of direct experimental evidence) that the reticular structure in the formed plate is composed of α -PbO₂ [27 - 29]. This has given rise to the common assumption that 4BS favours the formation of this polymorph and, by analogy, 3BS converts preferentially to β -PbO₂. Thus, it has become widely believed that a direct relationship exists between the chemical phase composition of formed material (i.e., α -PbO₂/ β -PbO₂) and that of the precursor cured material (i.e., 4BS/3BS).

Whether 4BS is converted to α -PbO₂ *per se* (and likewise 3BS to β -PbO₂) has yet to be resolved. As pointed out by Culpin in a recent review [30], the situation is confounded by the fact that the production of α -PbO₂ is favoured in weakly acidic to alkaline media, and that various battery-related parameters influence the local pH conditions within the interior of the plate. Thus, physical factors such as increasing paste density (i.e., decreasing plate porosity) and increasing plate thickness will progressively hinder the penetration of sulphuric acid into the plate and cause a corresponding increase in α -PbO₂ content. The production of α -PbO₂ is also assisted by a decrease in the degree of sulphation of the paste (i.e., by an increase in the amount of unreacted PbO), and by an increase in the formation temperature. Given this complex set of parameters, it is not surprising that manufacturers find difficulty in both achieving and maintaining a specified composition for formed plates.

Question: *Can organic additives be used to inhibit the growth, and therefore the size, of crystals of tetrabasic lead sulphate during plate curing at high temperature?*

D. A. J. RAND

As discussed previously, plates produced from cured material containing a high proportion of tetrabasic lead sulphate (4BS) tend to exhibit a lower initial capacity than

plates prepared from cured material rich in tribasic lead sulphate (3BS). This is because the 4BS crystals are larger than their 3BS counterparts and, on plate formation, give rise to equally large PbO_2 crystals with concomitant lower electrochemical activity. On the credit side, however, the 4BS crystals are arranged in a network structure that increases the mechanical integrity of the plate material in both the cured and formed states.

The above situation suggests that means should be found for reducing the size of the 4BS crystals without destroying their network structure. It has been suggested [31] that manipulation of crystal size and shape could be achieved by adding suitable crystal-morphology modifiers to the paste. To date, there have been no published reports on the use of organic additives for this purpose. Attention must be drawn again, however, to the recent discovery [8] that red lead can be used to reduce the size of 4BS crystals without decreasing plate strength.

Question: Why is pickling a required step in the production of tubular plates and what important mechanisms are involved in this stage?

R. KIESSLING

During the production of tubular plates, the annular space between the spine and tube is filled with active material, either by a powder or by a wet (slurry) process. The basic material is normal leady oxide and in most cases is blended with red lead. The next stage involves soaking, or 'pickling', the tubular plates in sulphuric acid solution for several hours. The reaction between the material in the tubes and the sulphuric acid and water initiates a process somewhat akin to the curing process involved in the manufacture of flat pasted plates. This is to say, the oxidation of free-lead particles in the leady oxide is promoted by the water and both the resulting and the starting lead oxide are partially converted into basic lead sulphates. At the same time, corrosive attack takes place on the surface of the spines. These two processes serve to bond the crystals of the material into a strong structure with good contact with the spines. These features are maintained during conversion of the active material to PbO_2 in the following plate formation stage.

Question: What are the requirements for a successful 'tackless formation' process?

D. W. H. LAMBERT

There are four basic essentials for successful 'tackless formation':

- good quality plates
- a reliable formation 'circuit'
- controlled plate formation process
- trained, 'quality conscious' operators

Plate quality

Good plate quality is the first essential requirement for successful tackless formation and may be achieved by establishing well-defined working procedures at all stages of plate manufacture prior to the formation process. The relevant production processes that must be under strict quality control are:

- oxide production
- paste mixing
- pasting and 'flash' drying
- curing or 'hydro-setting'

Formation circuit equipment

The size of the installation must be decided: each 'tank' or 'box' requires a 3 V d.c. supply. The maximum d.c. voltage under which it is permitted to work in a room depends on the safety regulations of the respective country. At CBS, we operate 45 'in-series' box circuits (150 V). The rectifier output current will depend upon the maximum plate loading per box, that is, on the mass of dry, cured positive paste to be formed (typically

20 - 25 A kg⁻¹ for a 16 - 20 h formation time). The plate loading will also vary with the local climatic conditions. In temperate zones (<35 °C ambient), three 'double' plates are placed in each slot; this should be reduced to two 'doubles' for tropical regions. The rectifier must have a polarity reversal switch and, ideally, provision for programming the formation schedule.

Control of plate formation

Continuous operation of the formation circuits and careful attention to the following operating conditions will ensure maximum plant throughput, low (<2 - 5%) rework and, minimal scrap:

- working temperature controlled between 40 and 60 °C
- formation acid density controlled between 1.030 and 1.070 at 20 °C
- polarity switching of the formation circuit is carried out 30 - 60 min after commencing the charge; the plates must therefore be loaded into the boxes in reverse, *i.e.*, positive plates commence formation as 'negatives', before switching the circuit; the negative bar surface, being lead, ensures good positive plate-to-bar contact
- polarity of the box contact-bars is changed after each process by loading the positive plates onto the 'negative' bar
- contact bars of new circuits, or circuits that have stood idle for 4 - 5 days, are given a 'freshening charge'
- formation tank acid is renewed after 60 - 90 days of use; this prevents the build-up of impurities.

Question: What are the causes of, and remedies for, positive-plate buckling or distortion during formation?

D. W. H. LAMBERT

During the pasting process, particularly by machine rather than by hand-pasting, 'densification' of the paste occurs on the 'hopper side' of the plate as a result of 'working' the paste into the grid. This results in plates with a high-to-low gradient of paste density from the hopper-to-belt side. Such plates, as a result of the volume changes that occur in the cured material during electrochemical formation to PbO₂, will tend to buckle or distort: the belt side becomes 'dished' or concave. Plate buckling is also accentuated by inadequate curing of the positive plate, *i.e.*, by high (>2 - 3 wt.%) residual free lead and excessively high formation current densities (>50 - 100 A m⁻²).

The remedies are, therefore, self-evident:

- well-defined paste-mixing process, *i.e.*, sequence of water and acid additions, constituent quantities, maximum process temperature, and temperature of the finished paste-mix
- good control of paste quality, *i.e.*, consistency (neither too soft nor too stiff) and density
- efficient curing of the plates to give low residual-free-lead
- optimum plate formation current.

A. M. HARDMAN

Plate buckling is quite a common problem and, on occasion, can be the result of simple malpractice in plate manufacture. Plates are generally passed through belt-pasting machines. When the paste is squeezed into the plates, the air it replaces must be allowed to escape. This cannot happen if the belt is worn and glazed. In such circumstances, unskilled operators will tend to screw down the paste hopper and apply more pressure. Such action will cause paste densification and result in plate buckling. Therefore, in instances of plate buckling, look at the condition of the pasting belt first.

GAS-RECOMBINATION (RE) BATTERIES

Question: In relation to flooded cells and RE cells in float applications, what is the significance of the Tafel or polarisation curve? Also, what factors in battery design affect the shape of the curve and therefore cell float behaviour?

A. M. HARDMAN

In RE cells, the Tafel (or polarisation) curve explains why oxygen recombination occurs. The reason is that the oxygen recombination reaction occurs at lower, or less negative, potential than hydrogen evolution and is thus the preferred reaction. In practice, however, the charging current is split between the two reactions and a mixed potential is observed.

With RE cells, the factors that affect the shape of the negative polarisation curve are those that also affect the oxygen-recombination process. These design factors include, amongst others, separator thickness and mean pore size, degree of compression of the cell group, and both plate and separator saturation levels.

The mechanisms affecting polarisation curves for flooded products are of course well documented in literature and standard text books.

Question: What is the effect of impurity levels (in the oxide, electrolyte, etc.) on the performance of sealed lead/acid batteries? Also, are there any particular impurities that cause major problems?

A. M. HARDMAN

Any impurity, whether it be contained within the oxide, electrolyte or indeed any other component of the cell, that can depress the hydrogen overvoltage with respect to pure lead is anathema to the oxygen-recombination cell.

Probably the single most important poison is antimony. Should the lead-calcium alloy be sourced from secondary smelters, then great attention must be paid to removing all antimony (and arsenic) from recovered lead, before converting it to lead-calcium alloy. In Chloride's experience to date, only virgin pure lead can produce the appropriate quality oxide suitable for incorporation into RE-type products. Oxides produced from secondary pure lead — taken from a number of sources — have all proved to be unsatisfactory for RE products. This conclusion has been reached despite no detectable differences in impurity levels being found compared with virgin pure lead, even using the most sophisticated analytical techniques [32].

Question: What are the effects of too much or too little electrolyte in RE batteries using absorptive-mat technology? How is the required electrolyte addition determined?

A. M. HARDMAN

The effects of too little electrolyte are:

- (i) the recombination efficiency is increased;
- (ii) the cell's capacity at both low and high rates of discharge is reduced;
- (iii) the cell's internal resistance (impedance) and thus back e.m.f. is increased;
- (iv) capacity run down on open circuit will increase unless the vent design is genuinely 100% non-return;
- (v) because of uneven saturation of the separator, there will be an increased risk of leading-through and premature failure.

The effects of too much electrolyte are:

- (i) the recombination efficiency is decreased;
- (ii) electrolyte leakage via the vent could occur when the cell is on charge, especially if the cell is mounted with the vent positioned on a vertical surface;

(iii) in cases of significant excess electrolyte, separator erosion or degradation occurs, especially in duties subject to vibration: an example being a battery mounted on a common frame holding a diesel generator set.

The correct volume of acid depends on the application, and particularly the current, at which recombination is required to occur. The best way to determine the volume of acid required is empirical using trial and error methods. There is, however, a general formula that can be used as a starting point, but it is not definitive and fine tuning will be required:

volume of electrolyte $> 0.8(X + Y)$

where X is the pore volume of the dry separator and Y is the pore volume of the dry charged positive and negative active materials. Only electrical tests and laboratory trials can refine the final figure since pore volumes of both separator materials and pasted/formed plates vary from batch to batch.

Question: In RE batteries, under what conditions of temperature and charging current is there a need for temperature compensation of the charging voltage?

A. M. HARDMAN

Regardless of the application, RE batteries require temperature compensation in precisely the same way as do conventional flooded products. The need for temperature compensation with RE products is, however, more important than with conventional flooded products because of the risk of temperature variations from cell to cell within a given battery and because the recombination reaction is exothermic. It is advisable to make allowances for both these features, especially if the battery is being charged at higher than normal currents/voltages.

No RE battery system should be contemplated without its associated charger system being fully temperature-compensated. The temperature probe in an RE battery charger system *must* be placed in (or on the side of) a centrally located cell and not in the charger cabinet itself, as is usual with flooded-battery systems equipment.

The one point on the temperature axis where no voltage compensation is required is merely of academic interest.

Question: What effect does the presence of bismuth in the various components of a lead/acid cell have on gassing rates?

W. F. GILLIAN

It has been demonstrated in a number of studies that the inclusion of bismuth in the negative plate results in the suppression of the hydrogen evolution reaction on overcharge. Inclusion of bismuth in the positive plate, whether in the grid or the active material, results in a slight increase in oxygen evolution. Recent work has shown, however, that for the complete lead/acid cell, overall gassing is reduced when bismuth is present in the system. Thus, it can be concluded that the reduction in hydrogen evolution at the negative plate outweighs the slight increase in oxygen evolution at the positive plate.

POSITIVE-PLATE PERFORMANCE

Question: How does α -PbO₂ exert a lasting effect on positive-plate cycle life given that the polymorph is irreversibly converted to the β form during the discharge/charge process?

D. A. J. RAND

It is generally recognised that α -PbO₂ gives positive plates a good cycleability. This is difficult to understand in view of the fact that the initial α -PbO₂ content rapidly decreases

to a low value during the early stages of charge/discharge cycling: α - PbO_2 is irreversibly converted to β - PbO_2 via the PbSO_4 discharge product. Thus, it could be argued that a high α - PbO_2 content foreshadows, but is not directly responsible for, an improved cycle-life performance, and that other parameters, although promoting the formation of α - PbO_2 , are more important than the presence of the polymorph itself. For example, α - PbO_2 production is encouraged by increasing the paste density and/or plate thickness, but these design factors taken alone will cause an increase in cycle life. Nevertheless, the intrinsic influence of α - PbO_2 on cycleability has been demonstrated by careful studies on plates having the same physical characteristics. In particular, it is now accepted that an initial α - PbO_2 / β - PbO_2 weight ratio of ~ 0.8 results in the best deep-discharge performance [33].

How then does α - PbO_2 affect cycle life? The following studies conducted in the CSIRO laboratories offer a possible explanation. First, it has been established [34] that there is a difference in morphology between α - PbO_2 and β - PbO_2 : the α polymorph consists of compact arrays of dendritic, elongated crystals (Fig. 5(a)), whilst the β polymorph is present as loose aggregates of ill-defined (anhedral) crystals together with 'necklaces' of smaller crystals (Fig. 6(a)). These inherent features remain the same irrespective of whether the polymorph is produced from cured-plate material rich in tribasic lead sulphate (3BS) or in tetrabasic lead sulphate (4BS). There is a tendency, however, for the α - PbO_2 network derived from 4BS to be coarser grained and more massive than the corresponding structure obtained from 3BS. This network is considered to be responsible for the superior mechanical strength of 4BS-based plates under deep-discharge service.

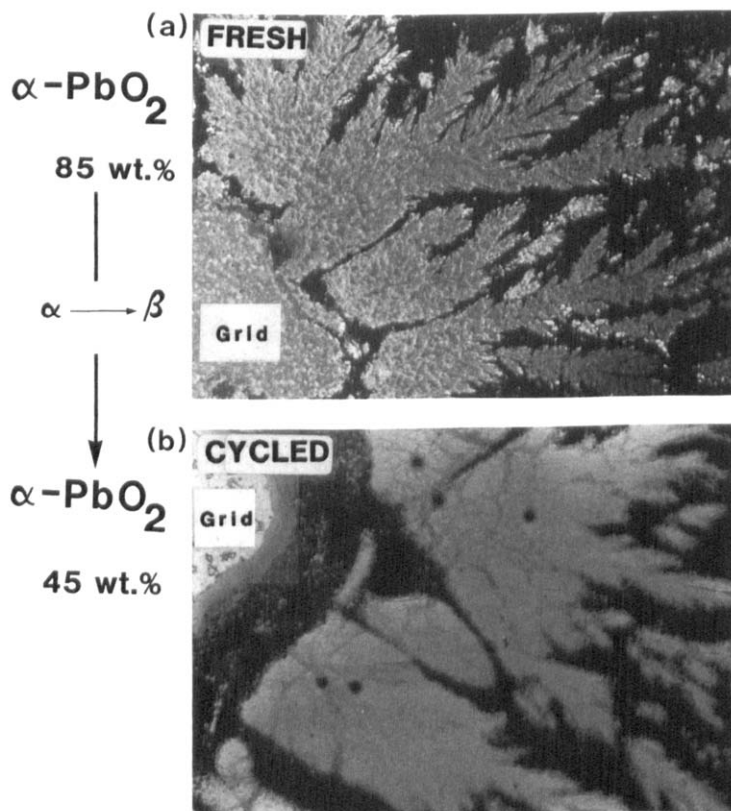


Fig. 5. Electron micrographs of α - PbO_2 in: (a) fresh and (b) cycled positive plates.

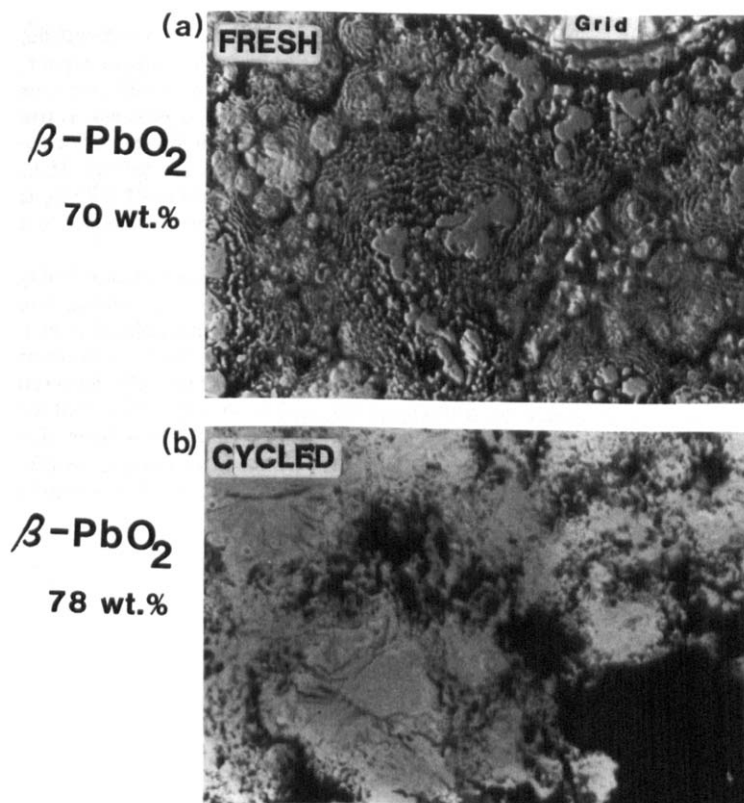


Fig. 6. Electron micrographs of β -PbO₂ in: (a) fresh and (b) cycled positive plates.

TABLE 3

Specific surface (BET) area ($\text{m}^2 \text{g}^{-1}$) of PbO₂ phases [34]

| Curing temperature (°C) | α -PbO ₂ | | β -PbO ₂ Fresh |
|-------------------------|----------------------------|--------|---------------------------------|
| | Fresh | Cycled | |
| 50 | 0.10 | 1.30 | 1.26 |
| 90 | 0.45 | 1.48 | 1.96 |

The compact nature of the α -PbO₂ does, however, result in plate material with a low specific surface area and, hence, a low capacity (Table 3). Incidentally, the aforementioned differences in morphology explain readily the existence of an optimum ratio for α -PbO₂ and β -PbO₂: the α phase provides the plate with a life-preserving 'backbone' or 'skeleton', whilst the β phase provides an avenue for facile acid diffusion and hence capacity.

After the recognition of inherent differences in the morphology of α -PbO₂ and β -PbO₂, the second important step in establishing the α -PbO₂/improved-life theory is the determination of the influence of charge/discharge cycling on this morphology. Scanning electron microscopic studies show that the initial 'strong' macrostructure of α -PbO₂ is

retained during conversion of the polymorph to the β form (Fig. 5(b)). In other words, plates rich in α - PbO_2 demonstrate a 'memory effect'. The aged structure is less compact, however, owing to the division of the bulk material into a large number of small particles separated by fine pores. This change in microstructure results in a marked increase in the specific surface area (to a value close to that for fresh β - PbO_2 , see Table 3) and a concomitant increase in plate capacity during the α - PbO_2/β - PbO_2 conversion period (*i.e.*, usually within ~ 50 charge/discharge cycles). By contrast, the macrostructure of β - PbO_2 is completely transformed by cycling service — the initial aggregates are broken down to a nondescript mass of very fine particles (Fig. 6(b)).

Finally, it is interesting to speculate on the nature of β - PbO_2 produced from α - PbO_2 via PbSO_4 , as opposed to that obtained directly from cured-plate material during the plate formation process. Recent CSIRO studies [35] using a scanning tunnelling microscope have shown that pure, electrodeposited α - PbO_2 and β - PbO_2 both display a nodular surface microstructure that is due to the emergence of crystallites of the bulk material (Fig. 7). The average crystallite diameter of α - PbO_2 (~ 35 nm) is greater than that of β - PbO_2 (~ 20 nm). It has been further discovered that α - PbO_2 is virtually free from surface pores or cracks, but β - PbO_2 exhibits large regions in which considerable microcracking is present (Fig. 8). Penetration of these cracks into the bulk of the β - PbO_2 results

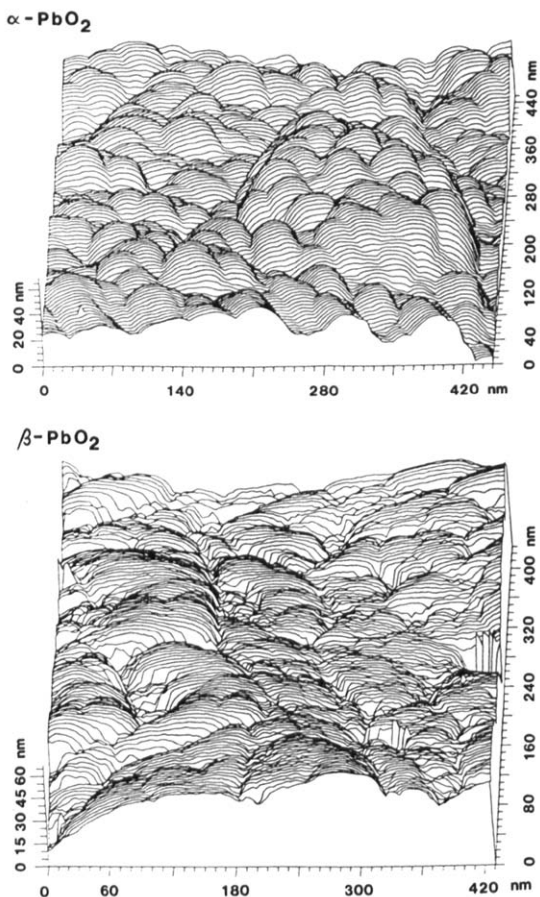


Fig. 7. STM images showing linescans of α - PbO_2 and β - PbO_2 taken over a 450×450 nm area. The surface microcrystallites are resolved [35].

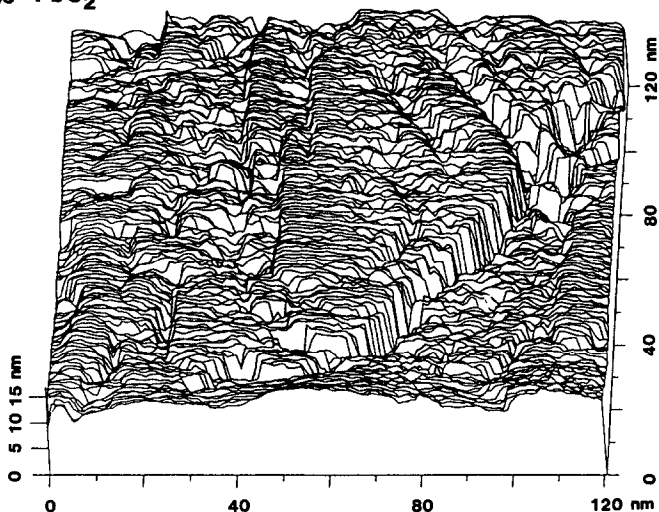
β -PbO₂

Fig. 8. STM images showing cracks on surface of β -PbO₂ (crack width <10 nm) [35].

in a large degree of internal surface area (and, hence, a high total surface area, see Table 3) but, more importantly, causes the polymorph to be mechanically weaker than its α counterpart. In the case of battery plates, an intriguing possibility is that the stronger, crack-free features of α -PbO₂ may be transmitted through to the β -PbO₂ formed on charge/discharge cycling. Therefore, despite the phase change, the plate strength is maintained and the importance of the initial α -PbO₂: β -PbO₂ weight ratio becomes self evident. This hypothesis is currently being tested in the CSIRO laboratories.

Question: The electrical resistance of antimonial-lead alloys approaches that of lead-calcium alloys at about 1 wt.% antimony. Does, therefore, a positive plate using a Pb-1 wt.% Sb alloy give similar performance to a positive plate using Pb-Ca alloy under deep-discharge cycling regimes?

R. KIESSLING

The critical limit above which antimony exerts a beneficial effect on positive-plate performance appears to be around 1 wt.% of the metal in the grid alloy. Antimony is leached from the grid during the corrosion process — part of this antimony remains in the corrosion layer, a smaller amount goes into the active material. The antimony influences the changes in morphology that take place in the plate material during charge/discharge cycling. It seems that antimony acts as a form of 'glue' for the PbO₂ of the active mass and thus prevents early shedding of plate material. This gluing action comes into full effect at a grid antimony concentration of 1 wt.%. For this reason, modern maintenance-free automotive batteries use low-antimony alloy in the positive plates and lead-calcium alloy in the negatives.

Question: Does a decrease in the antimony content of the positive grid result in a corresponding decrease in the specific capacity (A h kg⁻¹)?

R. KIESSLING

The antimony content of the grid alloy does not influence the initial capacity but does have a strong effect on the development of capacity during service life. Antimony provides plates with good cycleability. By contrast, when making antimony-free batteries

manufacturers have to obey strict production methods and controls in order to avoid premature failures.

Question: *What is the effect of polymer binder on the performance of positive and negative plates?*

R. KIESSLING

If the manufacturing process for lead/acid batteries is controlled carefully, then polymer binders are not necessary. The use of polymeric binders is popular in some exotic batteries and possibly this may encourage their application in lead/acid batteries. There is little recorded evidence, however, that significant benefits can be achieved through the incorporation of binders in the plate material. Indeed, PTFE binders are quite expensive and this factor alone argues against their use.

Question: *What is the effect of the presence of bismuth on the positive active material?*

W. F. GILLIAN

There are strong indications that bismuth contents $>0.1\%$ give rise to shedding of the positive active material. It has also been determined that bismuth will leach from the positive plate and be deposited on the negative electrode. It has been claimed by some that this leaching effect will result in an improvement in the porosity, thereby allowing greater utilization of the plate material. On the other hand, tests have also shown bismuth enhances the nucleation of lead sulphate which, despite giving rise to a higher initial discharge current, will ultimately enhance the isolation of active material and reduce plate capacity. Just which of these two effects will be dominant has not yet been determined. The question is largely academic, however, since at levels below 0.05% the bismuth will be removed by the leaching action of the electrolyte.

REFERENCES

- 1 D. Prengaman, New alloys for advanced batteries, *Proc. Symp. Lead Power for the 90s, Paris, France, April 28 - 29, 1988*, Lead Development Association, London, U.K.
- 2 N. Papageorgiou, M. Skyllas-Kazacos and D. A. J. Rand, in T. Tran and M. Skyllas-Kazacos (ed.), *Proc. Seventh Australian Electrochemistry Conf., The University of New South Wales, Kensington, N.S.W., Australia, February 15 - 19, 1988*, pp. 32 - 35.
- 3 D. H. Collins (ed.), *J. Power Sources*, 2 (1977/78) 73.
- 4 D. H. Collins (ed.), *J. Power Sources*, 2 (1977/78) 68.
- 5 T. Blair, in *Improvements in Alloys, Oxides and Expanders for Lead Batteries*, Lead Development Association, London, 1984, pp. 8 - 14.
- 6 H. B. Stephenson, C. L. Hixson, H. S. Long, J. S. Bryson, J. D. Purdum and E. J. Richie, Pastes and grids for the lead-acid battery, *ILZRO Project LE-82/LE-84*, Final Report, Dec. 31, 1971, Int. Lead Zinc Res. Org. Inc.
- 7 D. A. J. Rand, R. J. Hill and M. McDonagh, Improving the curing of positive plates for lead/acid batteries, *Proc. LABAT-89, Int. Conf. Lead/Acid Batteries, Drujba, Varna, Bulgaria, May 29 - June 2, 1989*, Paper No. 65; *J. Power Sources*, to be published.
- 8 D. Pavlov and N. Kapkov, Lead/acid battery positive plates manufactured from $4\text{PbO}\cdot\text{PbSO}_4$ pastes prepared from leady oxide and red lead, *Proc. LABAT-89, Int. Conf. Lead/Acid Batteries, Drujba, Varna, Bulgaria, May 29 - June 2, 1989*, Paper No. 63; *J. Power Sources*, to be published.
- 9 A. M. Foxworthy and R. J. Hill, PEAKS, a program for quantitative X-ray diffraction phase analysis of lead-acid battery materials, CSIRO/Pasminco Metals, Melbourne, 1989, V3.5.
- 10 M. J. Weighall, D. W. H. Lambert, D. A. J. Rand and W. G. A. Baldsing, in T. Keily and B. W. Baxter (eds.), *Power Sources 12*, Int. Power Sources Symposium Committee, Leatherhead, 1989, pp. 77 - 92.

- 11 W. G. A. Baldsing, K. K. Constanti, J. A. Hamilton, P. B. Harmer, R. J. Hill, D. A. J. Rand and R. B. Zmood, *Lead/Acid Batteries for Remote-Area Energy Storage, Commun. MCC 745*, CSIRO Div. Mineral Chem., Port Melbourne, Dec. 1986, 59 pp.
- 12 N. E. Hehner, in E. J. Ritchie (ed.), *Lead Oxides*, Independent Battery Manufacturers Association Inc., Largo, 1974, p. 12.
- 13 M. J. Weighall, A new granular lead oxide for improved lead/acid batteries, ILZRO Battery Seminar, Florida, U.S.A.
- 14 D. W. H. Lambert, *J. Power Sources*, 28 (1989) 187 - 199.
- 15 J. M. Stevenson and A. T. Kuhn, in L. J. Pearce (ed.), *Power Sources 10*, Int. Power Sources Symposium Committee, Leatherhead, 1984, pp. 555 - 567.
- 16 G. L. Corino, R. J. Hill, A. M. Jessel, D. A. J. Rand and J. A. Wunderlich, *J. Power Sources*, 16 (1985) 141 - 168.
- 17 J. N. Mrgudich, *Trans. Electrochem. Soc.*, 81 (1942) 165 - 173.
- 18 S. Ikari, S. Yoshizawa and S. Okada, *J. Electrochem. Soc. Jpn.*, (overseas edn.), 27 (1959) E167 - 169.
- 19 H. Bode and E. Voss, *Electrochim. Acta*, 1 (1959) 318 - 325.
- 20 S. C. Barnes and R. T. Mathieson, in D. H. Collins (ed.), *Batteries 2*, Pergamon, Oxford, 1965, pp. 41 - 52.
- 21 J. Armstrong, I. Dugdale and W. J. McCusker, in D. H. Collins (ed.), *Power Sources*, 1966, Pergamon, Oxford, 1967, pp. 163 - 176.
- 22 D. Pavlov and V. Iliev, *Elektrokhimia*, 11 (1975) 1735 - 1737.
- 23 D. Pavlov and G. Papazov, *J. Appl. Electrochem.*, 6 (1976) 339 - 345.
- 24 V. Iliev and D. Pavlov, *J. Appl. Electrochem.*, 9 (1979) 555 - 562.
- 25 T. G. Chang and M. M. Wright, *J. Electrochem. Soc.*, 128 (1981) 719 - 725.
- 26 J. Burbank, *J. Electrochem. Soc.*, 113 (1966) 10 - 14.
- 27 A. C. Simon and E. L. Jones, *J. Electrochem. Soc.*, 109 (1962) 760 - 770.
- 28 A. C. Simon, in D. H. Collins (ed.), *Batteries 2*, Pergamon, Oxford, 1965, pp. 63 - 78.
- 29 J. R. Pierson, *Electrochem. Technol.*, 5 (1967) 323 - 327.
- 30 B. Culpin, *J. Power Sources*, 25 (1989) 305 - 311.
- 31 D. A. J. Rand, *J. Power Sources*, 23 (1988) 267.
- 32 B. Culpin, M. W. Pilling and F. A. Fleming, *J. Power Sources*, 24 (1988) 127 - 136.
- 33 *Battery Reference Book*, Bitrode Corporation, Fenton, MO, U.S.A. and TBS Engineering, Cheltenham, U.K., 1989, p. 167.
- 34 D. A. J. Rand, P. B. Harmer, R. J. Hill and J. A. Wunderlich, in T. Tran and M. Skyllas-Kazacos (eds.), *Electrochemistry: Current and Potential Applications, Proc. Seventh Australian Electrochemistry Conf., The University of New South Wales, Kensington, N.S.W., Australia, February 15 - 19, 1988*, pp. 20 - 23.
- 35 B. A. Sexton, G. F. Cotterill, S. Fletcher and M. D. Horne, A scanning tunnelling microscopy study of the surface microstructure of alpha- and beta-lead dioxide, *Proc. STM '89, 4th Int. Conf. Scanning Tunnelling Microscopy/Spectroscopy, Oaraki, Ibaraki, Japan, July 9 - 14, 1989*.