

Lead oxide for lead/acid battery positive plates: scope for improvement?

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Abstract

Among the many factors that determine and influence the performance of lead/acid batteries, one of the most important, and as yet not fully developed, is how to make the positive active mass more electrochemically reactive. The inherent characteristics of this active mass are the cumulative result of the four precursor stages of its production, namely, the leady oxide, paste mixing, curing and formation procedures. There is evidence to suggest that the method of pasting itself is also influential. Many recent studies have reported progress on techniques to increase active-material utilization, to improve plate conditioning, and to solve the vexatious problem of premature capacity loss. The purpose of this discussion is to focus attention on the role and the importance of leady oxide on battery design and performance. At present, the battery industry makes leady oxide by either the ball-mill or the Barton-pot process. It is difficult to conclude which of the two methods gives the best leady oxide. Each type of leady oxide has its champions but, in general, ball-mill and Barton-pot product both make effective automotive batteries. For deep-cycle batteries, however, many battery companies (especially in Europe and Japan) prefer ball-mill oxide; in North America, the Barton-pot variety is favoured. This investigation examines the present procedures for making leady oxide, the desirable properties of leady oxide, and the influence of the oxide on battery performance. Analysis shows that there is scope for the production of improved leady oxide — by using existing production techniques and/or by the development of new processing technology.

Keywords: Lead/acid battery; Positive plate; Leady oxide; Barton pot; Ball mill

1. Lead and its oxides

The atomic structure of lead has four valency electrons, two of which are in the 6p and two in the 6s orbitals. Because the orbitals are only partially filled, lead can form a wide variety of oxides. This has given rise to many scientific studies on the identification, usefulness and general performance of each identifiable lead oxide that is involved in the production and operation of lead/acid battery positive plates. In practical terms, however, only three lead oxides currently find use in such application.

1.1. Lead monoxide, PbO

In its simplest state, lead forms a monoxide, PbO, in which the lead: oxygen ratio is 1:1. There are two polymorphic forms of the monoxide. This ability to exist in different, but similar, crystal structures adds complexity to the preparation of a given battery 'oxide'.

The red polymorph of PbO, commonly called litharge or α -PbO, has a tetragonal crystal structure and is stable at low

temperatures. The yellow polymorph (massicot or β -PbO) has an orthorhombic structure and is stable at high temperatures. The transition temperature of α -PbO to β -PbO is around 480 °C (the actual temperature depends markedly on the oxide preparation history). Although the colours of the oxide are very different, conclusive evidence of the presence of the two polymorphs in battery oxide can be obtained only by X-ray diffraction (XRD) phase-analysis.

The 'leady oxide' currently employed in battery making is typically a mixture of 70 to 80 wt.% lead monoxide and 20 to 30 wt.% lead particles (so-called 'free-lead'). The method used to manufacture the leady oxide determines the relative proportions of the two lead monoxide polymorphs in the final product (*vi.*).

1.2. Lead tetroxide, Pb₃O₄

This oxide, known as minium or red lead, is formed when lead monoxide is heated in a stream of air at around 540 °C. Red lead has a unique tetragonal crystal structure. Sometimes, it is used in battery making (especially for tubular plates)

Table 1
Physical properties of lead oxides [11]

| Property | PbO | Pb ₂ O ₄ | PbO ₂ |
|-------------------------------|--|---|--|
| Molecular weight | 223.21 | 685.57 | 239.19 |
| Colour | α : red β : yellow | orange to brick red | dark brown or black |
| Structure | α : tetragonal β : orthorhombic | spinel | α : orthorhombic β : tetragonal |
| Density (g cm ⁻³) | α : 9.2–9.5 β : 9.5–9.9 fumed litharge: 0.7 (max) black (grey): 1.4–1.8 ground calcined oxide: 1.6–2.0 | 9.1 | reported 9.165, 9.375 and 9.40 for PbO _{1.919} |
| Transition temperature | 488.5 °C | 830 °C (in oxygen pressure) | decomposes at 290 °C |
| Melting point | 897 °C, sublimates before melting | decomposes in atmosphere at 500 °C non-conductor | |
| Electrical properties | p- or n-type semiconductor | | semiconductor (resistivity at 20 °C, 91 M Ω cm) |
| Solubility | α : 0.05 g l ⁻¹ in H ₂ O at 25 °C β : 0.107 g l ⁻¹ in H ₂ O at 25 °C | insoluble in cold or hot water soluble in HCl and HNO ₃ and warm concentrated H ₂ SO ₄ | insoluble in cold or hot water soluble in HCl; slightly soluble in HNO ₃ and H ₂ SO ₄ |
| Thermal stability | stable up to 250 °C; oxidized to PbO ₁₋₂ at 300–350 °C and to Pb ₂ O ₄ at higher temperatures | stable up to 500 °C; decomposes to PbO at higher temperatures | decomposes to lower oxides above 290 °C |

due to its ability to assist in plate formation (about one-third of the oxide is converted directly into PbO₂ before the formation charge is started). In recent times, however, the application of red lead has slowly declined because of its extra cost and handling (safety) problems.

1.3. Lead dioxide, PbO_n ($n \approx 2$)

This oxide, which in a lead/acid battery is the product of positive-plate formation, constitutes the 'active mass'. It exists in two forms, termed α -PbO₂ and β -PbO₂, in which the lead:oxygen ratio is a nominal 1:2. Due to a number of complex factors, however, the lead:oxygen ratio varies and this helps to add to the 'black magic' of battery making [1,2]. It should be noted that although α and β are the well-accepted polymorphs of PbO₂, Kirkinskii [3] has suggested that there may be a third polymorph of PbO₂ that is stable at higher than normal atmospheric pressure.

One of the major achievements of recent times has been the quantitative determination of the α and β forms of PbO₂ in positive plates by XRD phase-analysis [4], together with definition of their optimum weight ratio for various types of battery application [5].

Inasmuch as oxides of lead occur with many lead:oxygen ratios, it is tempting to 'ask' which ratio has the best electrochemical performance. Early researchers considered this matter in depth but, to some extent, their work was less than conclusive. This was due in large measure to the limitations of the analytical techniques that were then available. The publication on lead oxides issued by the Independent Battery Manufacturers Association (IBMA) [6] contains a most useful review and bibliography of this pioneering work.

The properties of the PbO₂ electrode are, of course, fundamental to battery design. In particular, the morphology of the positive active mass has a vital impact on battery performance. Further, the strength and elasticity of porous solids, such as PbO₂, is a function of their microstructure. This aspect is compounded by the fact that the shape and volume of PbO₂ and PbSO₄ (the battery discharge product) change during each charge/discharge cycle. In a mixture of the two polymorphs, it is generally accepted that β -PbO₂ contributes by far the greater share of electrochemical capacity [7–9]. On the other hand, there is much evidence to suggest that α -PbO₂ imparts structural durability to the positive active mass [10]. During cycling, α -PbO₂ is converted irreversibly to β -PbO₂ via PbSO₄. It is difficult to perceive, therefore, how any effects of α -PbO₂ can be long-lasting.

Some research has been carried out with respect to the possible use of chemically prepared PbO₂ for direct application to battery grids. So far, tests have not yielded satisfactory results.

The physical and chemical properties of PbO, Pb₂O₄ and PbO₂ are summarized in Tables 1 and 2 [11], respectively.

2. Desirable leady oxide properties

The main properties that exert significant effects on the performance of leady oxide in the active material are described below. Although the concept and rationality of each property is readily understood, it is often difficult to measure and quantify the property itself. Moreover, in some cases, standard techniques have yet to be specified and accepted by the battery industry.

Table 2
Chemical properties of lead oxides [11]

| Reagent | PbO | Pb ₃ O ₄ | PbO ₂ |
|-------------------------------|-------------------------------------|--------------------------------|--|
| Hydrogen | reduction is slow | reduced above 200 °C | reduced at 150 °C to lower oxides and water |
| Carbon | | reduced above 300 °C | reduced at 260 °C |
| Chlorine or bromine vapour | dihalide is formed | dihalide is formed | dihalide or oxyhalide is formed |
| Aqueous solutions of halogens | oxidized to dioxide | | diiodide and iodic acid are formed in presence of moisture |
| Hydrogen halides | | | oxidized to halogens |
| Sulfuric and nitric acids | | divalent salts are formed | tetravalent salts are formed |
| Hydrochloric acid | | dichloride is formed | tetrachloride is formed |
| Sulfur | sulfide is formed | | oxidized to sulfur dioxide |
| Hydrogen sulfide | | | sulfide is formed |
| Sulfur dioxide | | sulfide is formed | reacts violently to form PbSO ₄ |
| Ammonia | | | nitrogen is formed |
| Nitrous oxide | | | decomposes to PbO and oxygen |
| PbO ^o -horus | | | reacts explosively |
| Metallc oxides | fuses readily to form double oxides | | plumbates are formed |

2.1. Purity

There are established standards of lead purity for making leady oxide for use in flooded-electrolyte batteries. Not surprisingly, however, there are differences of opinion between suppliers of lead derived from ores mined in different parts of the world, especially with respect to the permissible amount of bismuth in the lead. Also, there is continuing debate on the relative merits of using primary and/or secondary lead for leady-oxide production.

A particular difficulty relates to the purity of lead required to make leady oxide for use in valve-regulated lead/acid designs, where it is vital to restrict gas generation to a low level. Experience shows that certain trace elements, either alone or in combination with other trace elements, can seriously increase gas evolution. This has given rise to a marked shift by many battery companies towards tighter purity controls for the lead that is used in oxide manufacture. Two typical specifications for lead purity are given in Table 3 [12].

2.2. Free-lead content

With present production processes, most leady oxide contains around 20 to 30 wt.% free lead. Above 30 wt.%, the material becomes so reactive in air that instantaneous combustion can occur with unpleasant consequences to production equipment and facilities.

2.3. Polymorphism

The relative proportions of the two polymorphs of PbO are important in the production of battery plates. This is because reports claim that the ratio moderates the yields of the different basic lead sulfate phases that can be formed during the subsequent curing process. In particular, α -PbO favours tribasic lead sulfate (3PbO·PbSO₄·H₂O), while β -PbO promotes tetrabasic lead sulfate (4PbO·PbSO₄) [13]. In turn,

Table 3
Typical purity specifications for lead in oxide making [12]

| Material | Flooded battery (max. wt.%) | Valve-regulated battery (max. wt.%) |
|----------------|-----------------------------|-------------------------------------|
| Lead | 99.97–99.99 | 99.99 |
| Trace elements | 0.03–0.01 | 0.01 |
| Antimony | 0.001 | 0.0005 |
| Arsenic | 0.001 | 0.0005 |
| Bismuth | 0.03 | 0.025 |
| Cadmium | 0.001 | 0.001 |
| Copper | 0.0015 | 0.001 |
| Iron | 0.001 | 0.001 |
| Manganese | 0.0005 | 0.0001 |
| Nickel | 0.0005 | 0.0002* |
| Selenium | 0.0005 | 0.001 |
| Silver | 0.005 | 0.0025 |
| Tellurium | 0.0005 | 0.0001* |
| Tin | 0.001 | 0.001 |
| Thallium | 0.01 | 0.01 |
| Zinc | 0.001 | 0.001 |

* Quantity can be crucial in some designs.

the basic lead sulfate phases produce different plate performance characteristics during charge/discharge cycling. Thus, control of the α -PbO: β -PbO ratio is fundamental to the production of leady oxide [14].

2.4. Reactivity (acid absorption)

This is a somewhat subjective characteristic, but is often determined as it gives a useful practical indicator of the paste-mixing attributes of the oxide. The parameter provides an approximate measure of the wettable surface area of the oxide. This latter property essentially depends on the number of particles and their individual surface area. Reactivity is expressed as the weight (mg) of sulfuric acid absorbed per gram of oxide [15].

The lead monoxide particles produced by a ball mill are much smaller than those resulting from a Barton pot. Thus,

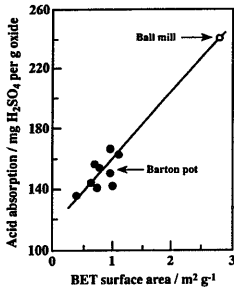


Fig. 1. Reactivity of ball-mill and Barton-pot lead oxides [16].

ball-mill oxide has a higher reactivity, i.e., a higher 'acid absorption value' (Fig. 1).

2.5. Surface area

The surface area of leady oxide is dependent upon the PbO content; a maximum area (and, hence, reactivity) is displayed at ~15 wt.% β-PbO [16], see Fig. 2. Therefore, in

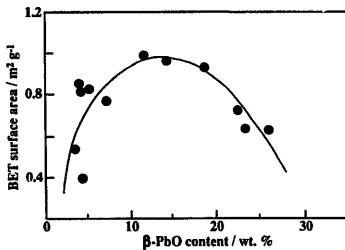


Fig. 2. Influence of β-PbO content on surface area of leady oxide.

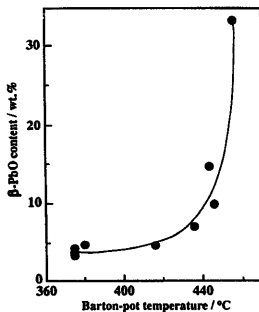


Fig. 3. Influence of temperature on β-PbO content in Barton-pot leady oxide. (Note, the absolute value of the temperature depends on the location of the sensor.)

order to obtain optimum results, it is imperative to control the level of β-PbO in the starting battery oxide, either through regulation of the oxide-making process itself (principally, the temperature of operation, see Fig. 3) or through blending with synthetically prepared β-PbO.

There is a general belief that 'flat' particles are preferable to those with a 'spherical' shape. This is one of the reasons why some manufacturers pass leady oxide through a hammer mill before paste mixing. As a further benefit, the hammer mill increases the amount of β-PbO in the leady oxide.

2.6. Apparent density

The Scott volumeter [1,15] is used to obtain the apparent density. The latter is defined as the mass of oxide divided by the total occupied volume (including pores/voids). This test gives a measurement of the combination of particle size and shape and is complementary to the reactivity test. Together, the two tests give a good description of the oxide and provide a check on consistency between different production batches.

In the Scott apparatus, oxide powder is allowed to fall gently down a vertical tube of rectangular cross section. This tube is fitted with baffles that are arranged obliquely at intervals on either side. The oxide passes into a cubed-shaped box of known volume. The surface of the powder is levelled off flush with the rim of the box and the 'cube weight' is determined.

2.7. Occupational health/handleability

Leady oxide is normally produced as a dry powder that requires special handling so as to prevent any health risk to workers in the oxide and/or battery making operations. Also, a free-flowing powder is essential for some types of battery design, especially those with positive tubular plates. In Europe, it is possible to purchase a granular type of lead oxide that has low dust properties and good flowability when filling tubular positives [17].

2.8. Stability

It is best to use leady oxide relatively soon after manufacture as some of its properties, especially free-lead level, flowability and reactivity, can deteriorate if the material is kept in storage for too long [14]. Examples of such degradation for ball-mill and Barton-pot oxides are given in Fig. 4 [18].

2.9. Active material/grid interface

An important aspect of battery design is the degree of bonding between the positive active mass and the current-collector portion of the grid. Generally, the integrity of the bond is a function of the corrosion layer that is formed between the grid alloy and the active mass. Nowadays, grid alloys are highly corrosion resistant and advanced curing and formation techniques are often needed to produce a suitable

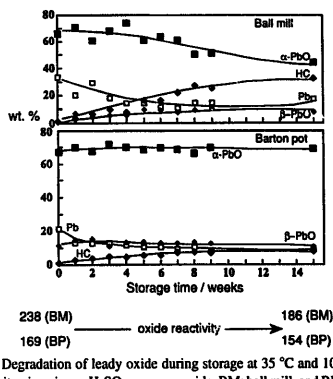


Fig. 4. Degradation of lead oxide during storage at 35 °C and 100% RH. Reactivity given in mg H₂SO₄/per gram oxide. BM: ball mill, and BP: Barton pot [18].

bond. In former times, when grids were not so corrosion resistant, it was easier to form this bond. The International Lead Zinc Research Organization, ILZRO, and others have investigated ways and means to pre-condition the grid prior to, or during, pasting so as to encourage improved bonding. The result of this work may yet prove invaluable as the industry continues to develop and use highly corrosion-resistant alloys, such as those with high levels of tin and/or additions of silver.

2.10. Cost

With approximately 50% of the lead content of batteries being in the form of oxide, the cost of this component has an important effect on manufacturing costs. Nonetheless, it is possible that the industry might accept a 'reasonable premium' over the existing cost of oxide in return for a better material.

2.11. Quantitative values of oxide characteristics

A search of the published literature [2,15,16,19,20] has yielded the summary information given in Table 4 on the desirable values for the key properties of battery oxide.

Each battery manufacturer tends to hold proprietary information on the quantitative definition of the key oxide properties for different battery designs. Obviously, it is not possible to obtain access to such data. Nevertheless, it is hoped that further numerate information will become available for evaluation and discussion, perhaps through the results of the research programme that is being conducted by the Advanced Lead-Acid Battery Consortium [21]. The objective must be to establish realistic industry target values for each essential oxide property so that progress towards the next milestone in lead-oxide performance can be charted and achieved.

Table 4
Values of key properties of leady oxide

| Property | State-of-the-art value |
|-----------------------|---|
| Purity | see Table 3 |
| Polymorphism | 60–70 + wt.% α -PbO 15–20 wt.% β -PbO |
| Particle size | 2–10 μ m |
| Specific surface area | 0.4–1.8 m ² g ⁻¹ (Barton pot) 2.4–2.8 m ² g ⁻¹ (ball mill) |
| Pore volume | 0.2 cm ³ g ⁻¹ |
| Shape | flat, ragged preferred to spherical |
| Bulk density | 3 g cm ⁻³ |
| Apparent density | 0.92 (ball mill) 1.53 (Barton pot) |
| Acid absorption | 240 mg H ₂ SO ₄ /g oxide (ball mill) 140–160 mg H ₂ SO ₄ /g oxide (Barton pot) |
| Free-lead content | 20–30 wt.%, 50 wt.% in special cases |
| Occupational health | depends on local regulations |

3. Leady oxide production: current practice

In general, leady oxide is used to make battery plates in three different ways: (i) as a paste applied to flat cast or expanded grids; (ii) as a powder or slurry to tubular grids within a ganuntlet, or (iii) as a proprietary slurry to rolled lead sheet and/or co-extruded wire grids [22].

For pasted plates, the leady oxide is mixed with water, sulfuric acid and selected additives. The resulting mixture is applied to the plates, and then cured and formed. In the case of tubular plates, the leady oxide can be applied as a dry powder or as a slurry under pressure or a vacuum; as mentioned above, red lead (Pb₂O₃) is sometimes added to the leady oxide. Dry filling of tubular plates can be a dusty process with associated health risks within the work place. Such risks can be reduced by the use of specialized filling equipment, low-dust granular leady oxide, or wet-fill techniques [17]. After filling, the plates are pickled (or, in some cases, cured) and then formed. In some new battery designs, a mixture of chemically produced PbO and water (i.e., a low sulfate, no free-lead mixture) is applied to rolled lead sheet or co-extruded lead wires. Such technology allows the curing process to be by-passed.

Nearly 50 different oxide-manufacturing procedures have been evaluated during the last 95 years. Over the past two decades or so, three basic ways of making battery lead oxide have established a proven commercial success [1,23–25]; (i) the Shimadzu ball mill (patented in the USA in 1926) with in-built screens through which the oxide passes; later variations were developed by Heubach and Tudor; (ii) the Hardinge cone ball mill, as developed by Chloride and GOX; (iii) the Barton pot, invented and developed between 1898 and 1908 by George Barton; this technique has been further modified by Balox, Chloride, Hammond, Heubach, Linklater, Minimet, Pennaroya, and others.

Today, nearly all battery leady oxide is made in either a ball mill or a Barton pot. In each case, the input material is high-purity lead produced either from mined lead ore (pri-

mary lead) or from recycled lead/acid batteries and other lead-bearing scrap (secondary lead). In both the ball-mill and Barton-pot technologies, humidified air is input to the process (note, water assists the oxidation process and, thereby, improves productivity). This often requires careful control otherwise the air-borne oxide product can contain sufficient moisture to clog the filters in the baghouse.

3.1. Ball-mill leady oxide

Two main designs of ball mill are in use. In the original mill, developed by Shimadzu in Japan and Tudor in Europe, the leady oxide produced within the mill falls continuously through small holes in the periphery of the drum on to a concentrically located, cylindrical, outer casing. A forced stream of humidified air carries the leady oxide through a series of cyclone separators where the coarse particles are collected and returned to the mill. The finer particles are fed to a hopper for temporary storage before making into paste.

Depending on the design, lead is fed into the mill either as a whole ingot, or part of an ingot. In other designs, the lead is first cast into small pieces (balls or cylinders) before introduction to the mill. Within the rotating mill (typically, 25 to 35 rpm), the lead pieces grind against each other to form smaller pieces that oxidize exothermically to produce a mixture of lead monoxide and unreacted lead particles (free lead). Due to the heat of reaction, the ball mill is water cooled. The average temperature in the mill is around 90 °C. The key elements of process control are: lead input rate, mill rotation speed, speed and humidity of air flow, feed rate of over-sized particles from the cyclone separator, degree of water cooling.

An alternative design of mill, the Hardinge mill, employs a cone-shaped chamber with a casing that does not contain holes, Fig. 5(a). Lead ingots/pieces are input to the mill. A forced stream of humidified air carries the leady oxide to cyclones for size separation, together with that part of the fraction which spills out of the cone as it is produced. This type of mill operates at around 175 °C.

3.2. Barton-pot leady oxide

Molten lead is poured into a crucible and agitated by a large rotating paddle, Fig. 5(b). Humidified air is blown through the crucible above the surface of the molten lead. The resulting oxide is passed through a series of cyclone classifiers. Over-size particles are returned to the crucible for further processing. Often, prior to being stored or used to make paste, the leady oxide is passed through a hammer mill both to flatten the typically spherically-shaped oxide particles and to increase the amount of β -PbO. This treatment increases the reactivity by about 12% over that of standard Barton-pot oxide (nominally, 140 to 160 mg H_2SO_4 per gram oxide). It has been reported [25] that additions of antimony at the 25 to 30 ppm level can result in an energy reduction of up to 5%.

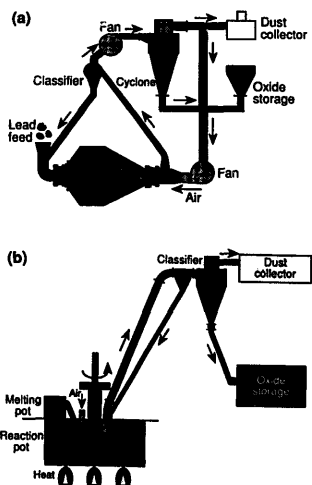


Fig. 5. Schematic of leady oxide production by (a) Hardinge ball mill, and (b) Barton pot.

The output and the quality control of the Barton-pot process is a function of: lead-feed rate, paddle design and rotation speed, air-flow speed and humidity, temperature of the crucible and its contents [26].

4. Comparison of ball-mill and Barton-pot leady oxides

Both processes make acceptable leady oxide. Despite much investigation, it is not possible to conclude with confidence which process gives the best leady oxide [14,27]. Historically, battery manufacturers have selected a process based on a number of important factors, such as those set out in Table 5 [14,15,28–30].

When selecting an oxide-making process, it is useful to consider the duty cycle of the batteries that are being made, e.g., automotive or traction service. Experience indicates that it can be helpful to evaluate factors such as:

1. coarse oxide is less reactive than fine oxide;
2. temperatures of paste mixing will be lower when using coarse oxide;
3. paste made from coarse oxide is unlikely to set rapidly;
4. coarse oxides do not result in the high plate surface-area that is desirable for cold-cranking battery performance;
5. fine oxides produce hotter pastes and, therefore, the paste-mixing process requires good temperature control to help prevent the production of 'gritty' paste that can be difficult both to apply to grids and to cure;
6. the speed of curing is related to the content of lead oxide in the paste; low-oxidation oxides tend to cure more vigorously than high-oxidation counterparts;

Table 5

Comparison of ball-mill and Barton-pot oxides

| | Ball mill | Barton pot |
|--|--|--|
| Particle size | small particles | larger particles |
| Reactivity in air | generally high; can cause storage and long-distance transport problems | generally more stable |
| Polymorphism | 60–70 wt.% α -PbO 1–4 wt.% β -PbO | 15 wt.% β -PbO |
| Acid absorption (mg H ₂ SO ₄ /g oxide) | 240 | 140–160 |
| Surface area (m ² g ⁻¹) | 2.4–2.8 | 0.4–1.8 |
| Free-lead content (wt.%) | ~30 | ~25 |
| Ease of making battery paste | makes a stiff paste which can require careful control | makes a softer paste which can result in easier pasting |
| Paste curing | capable of fast curing | average curing rate |
| Battery performance | batteries have good initial capacity, but possibly shorter life | enhances battery life, but can result in lower initial capacity |
| Deep-cycleability | usually good | sometimes good |
| Process control | easier, more consistent oxide | can be more difficult, but recent computer controls are helping |
| Typical production rate (kg h ⁻¹) | up to 1000 | 300–800 |
| Investment considerations | costs more; requires more space; noisy; costlier to maintain | lower initial cost; compact in size; relatively quiet; costs less to maintain; uses less energy to run |
| Energy use (kWh t ⁻¹) | 100–300+ | up to 100 |
| Environmental aspects | with well-engineered environmental systems (including baghouse and storage), existing emission standards can normally be met; typically, in the range of less than 0.1 mg oxide per N m ³ | |

- the tendency is to use coarse oxides for traction and stand-by batteries, but fine oxide for automotive batteries; this does not mean that fine oxides should not be used for industrial batteries, but rather, they may not be as essential as they are for automotive batteries; and
- oxide particle properties that encourage acid concentration near to the grid/active-material interface should be beneficial, especially in the acid-starved conditions prevalent in valve-regulated designs of battery.

No doubt progress and advancement will be achieved, probably through better control techniques, in the manufacture of lead oxide. Given that it is possible to quantify the characteristics needed for the optimum lead oxide, it appears difficult (and perhaps not possible) to control the Barton pot and/or ball mill to produce oxide within desired levels of tolerance and reproducibility. It may be that the combination of mechanical action, exothermic reaction and oxygen/air flow is not the best way forward.

5. Other techniques for lead oxide production

Over the years, many ingenious ways to make lead oxide have been explored, especially with respect to lead oxide for battery manufacture. Probably the most useful reviews of production techniques are contained in the publications on lead oxide by ILZRO [31] and the IBMA [6]. In 1969, for example, VARTA AG was granted a patent to make PbO by spraying molten lead on to an oscillating, high speed rotating disc [32]. Later, in 1976, the company Zakłady Bieli Cynkowej in Poland [33] reported results from a technique for oxidizing molten lead with air containing water to produce 66 wt.% PbO and 34 wt.% free lead; 68% of the PbO was of

the tetragonal form (α -PbO) and 32% was orthorhombic (β -PbO).

Looking through the many examples quoted in the ILZRO publication [31], it appears that limited research has been carried out on how to oxidize lead in a closely-controlled atmosphere of air/oxygen/other gas. As the battery industry moves towards tighter control of the production of components, it is interesting to conjecture what results will be obtained if more stringent conditions are introduced into the lead-oxide production process.

The possible enhancing effect on lead-oxide performance of various dopants has also been investigated [34]. Alas, the results to date have been largely less than conclusive as positive plates are quite sensitive to non-PbO₂ precursor substances. In general, any material not readily electrolytically oxidized to PbO₂ can be considered to be an impurity. Each 'impurity' has its own level of tolerance, above which loss of active-material performance or other problems can occur.

Fume oxide particles, essentially finely-divided orthorhombic lead monoxide (β -PbO), are much smaller than those produced by either a ball mill or a Barton pot. In the process used to make fume oxide, molten lead flows out of a small nozzle and is atomized by a blast of air blown at right angles to the direction of lead flow. ILZRO [31] and Comnico [35] have experimented with fume oxide, with and without dopants. Batteries made from such oxide had exceptional capacity, essentially due to the fineness and, therefore, high surface area of the oxide. On the other hand, the process costs were unacceptable and some reports suggested that battery capacity declined fairly quickly under deep-cycle duty. Barak [1] also reported that maintaining a desirable free-lead content in the fume oxide is difficult. This prompts the question: is it preferable to make fume (or, for that matter,

ball-mill or Barton-pot) oxide and free lead in one operation, or is it better to prepare lead monoxide by a preferred route, make the free lead separately, and then mix them together to a prescribed formulation?

Some 15 years ago, tests showed [34,36] that positive plates could be made from lead dioxide produced by chemical means. More recently, some batteries have been made with a form of electrolytically produced lead dioxide. Results have yet to be published.

6. Towards better leady oxide

The critical properties of the ideal leady oxide need to be determined more precisely, and a way to produce it commercially has to be engineered. The question to be addressed is: will the next generation of leady oxide be made by the ball mill, the Barton pot, or some other new process? Or, is this question irrelevant if the ideal active-material chemistry, morphology, bonding, etc., is established during subsequent curing and/or formation without any major influence of the precursor leady oxide?

Clearly, the battery industry would welcome any new type of leady oxide that enhances active-material performance. Commercial prudence suggests that every effort should be made to develop such material through improvements to the ball-mill or the Barton-pot process. It may be, however, that resources should be allocated to engineer a new method of making the next generation of leady oxides — oxides that are more reactive, more stable, and less expensive to manufacture.

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