Improved oxides for production of lead/acid battery plates

D.P. Boden *

Hammond Group, 2308 165th Street, Hammond, IN 46320, USA

Abstract

For many years, the plates of lead/acid batteries have been produced from leady oxide, a mixture of finely divided lead ('free-lead') and lead monoxide. Although this material is generally satisfactory, it suffers from the disadvantages that it is variable in composition and requires complicated and lengthy processing after pasting to remove the residual free-lead. Plates made from leady oxide also require cycling before they achieve their full performance, and this can result in either depressed initial capacity or additional processing cost. There is a growing trend towards the use of pure lead monoxide (β-PbO) for the production of positive plates. This material is particularly valuable in valve-regulated batteries where cell-to-cell uniformity is essential for proper control of battery performance. It also reduces processing cost since it does not require time-consuming curing to remove free-lead. Red lead (Pb_3O_4) is also being more widely used in industrial batteries since it reduces formation time, and improves initial and high-rate performance. The methods of production of leady oxide, β-PbO and red lead are briefly reviewed and the characteristics of battery-grade materials are described. Particular emphasis is placed on optimum particle-size distribution, and how this can affect the battery performance. The benefits in processing and performance are described together with information on how pure litharge and red lead are used in battery plates. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Leady oxide; Lead monoxide; Lead/acid battery; Red lead; Barton pot; Ball mill

1. Introduction

A discernable trend is taking place in the type of oxide used to produce industrial batteries. Leady oxide is being replaced in some types of battery, most noticeably valve-regulated types, by pure litharge, (α-PbO). Additionally, producers of industrial batteries are using increasing quantities of red lead in their positive plates to take advantage of the performance-enhancing properties of this oxide.

In this paper, the characteristics of the various types of lead oxides used in batteries will be reviewed, their manufacturing methods described, and their advantages and disadvantages outlined.

2. Characteristics of lead oxides

The structures of the two polymorphic forms of lead monoxide are shown in Fig. 1 and the structure of red lead is shown in Fig. 2 [1]. The alpha or red form of the monoxide (the mineral litharge) is tetragonal, and the

crystals are tabular on the (001) plane. The beta or yellow form is orthorhombic (the mineral massicot) and the crystals are tabular on the (100) plane. Some physical data for α-PbO and β-PbO are shown in Table 1, and for Pb_3O_4 in Table 2 [2].

The lead monoxide manufactured by the ball-mill process is almost pure tetragonal (α-PbO) while that produced by the Barton-pot process can contain up to 10 wt.% of the orthorhombic form (β-PbO) depending on the temperature during the process.

The characteristics of leady oxide that are most important to battery manufacturers, with typical values for automotive and industrial applications are shown in Table 3. These data are for Barton-pot oxides which are the most widely used in the USA Oxide produced in a ball-mill has a higher acid absorption value (~ 240 mg g^{-1}) and a greater surface area than Barton oxide. In a survey [3] of a considerable number of Barton-pot and ball-mill oxide samples, Barton-pot material had BET surface areas ranging from 0.55 to 0.84 m^2 g^{-1} while the corresponding range for ball-mill oxide was 1.16 to 1.79 m^2 g^{-1}. Interestingly, the values for total pore volume and median pore diameter did not differ appreciably. The total pore volume
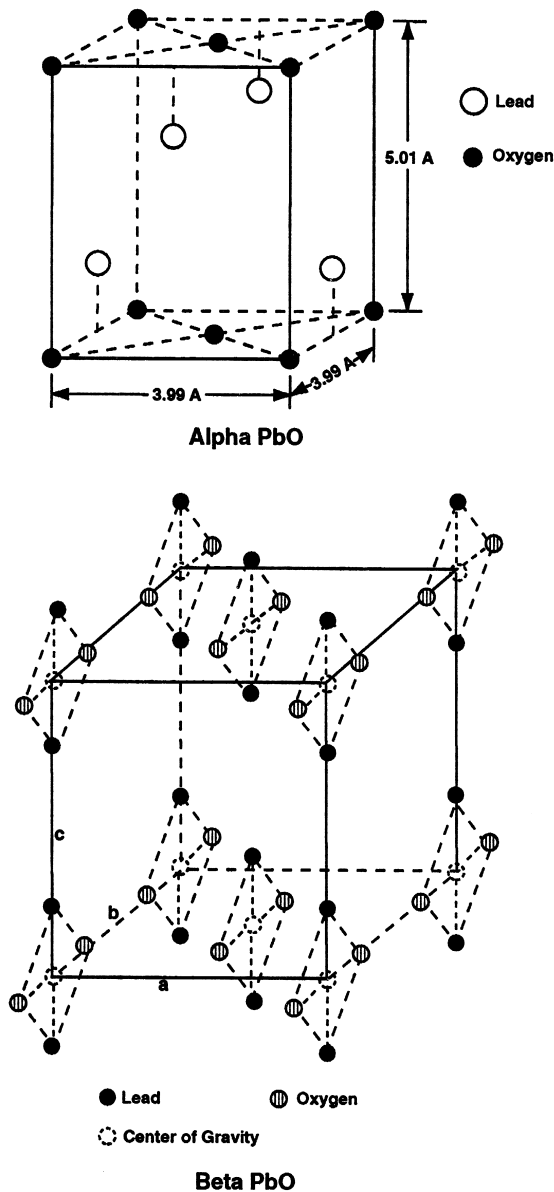
Alpha PbO

Lead

Oxygen

5.01 Å

3.99 Å 3.99 Å

Lead Oxygen

Center of Gravity

Beta PbO

Fig. 1. Crystal structures of α-PbO (Tetragonal) and β-PbO (Orthorhombic).

Table 1
Physical data of α-PbO and β-PbO

	α-PbO	β-PbO
Structure	Tetragonal	Orthorhombic
Mohs hardness	2	2
Density (g cm^{-3})	9.14	9.56
Refractive index	$w_{Li} = 2.665$	$^{n}_{Li} x = 2.51$
	$\epsilon_{Li} = 2.535$	$y = 2.61$
		$z = 2.71$
Lattice constants (Å)	$a_o = 3.96$	$a_o = 5.476$
	$c_o = 5.01$	$b_o = 5.486$
	PbO–O = 2.30	$c_o = 4.743$
		Pb–O = 2.221
Dielectric constant	32	35
Electrical conductivity (Ω cm)$^{-1}$	$\sim 10^{-14}$	$\sim 10^{-14}$

a range of 1.50 to 2.64 μm, and for the ball-mill samples, 1.67 to 2.67 μm. Since there is little perceived difference between batteries made from Barton-pot and ball-mill oxide, this may suggest that pore volume and diameter are more important characteristics than surface area and acid absorption.

2.1. Pure lead monoxide

Calcined orthorhombic β-PbO is becoming more widely used as a starting material for battery plates. Typical characteristics of battery-grade β-PbO are shown in Table 4.

This oxide differs from leady oxide in a number of important respects. Most important is the absence of free-lead. The particle size is larger and the acid absorption is lower than generally required for automotive batteries, but approximately equivalent to leady oxide used in industrial batteries. It is noteworthy that the acid absorption of pure β-PbO is higher than would be expected from its particle-size distribution. This is probably due to its greater reactivity (J.L. Nordyke, Hammond Lead Products, private communication).

The absence of free-lead significantly improves the reproducibility of the paste mixing and curing processes. With a leady oxide, some of the free-lead is oxidized during paste mixing and further oxidation takes place

for the Barton-pot samples had a range of 0.192 to 0.264 cm^3 g^{-1}, and for the ball-mill samples, 0.20 to 0.298 cm^3 g^{-1} For the median pore diameter, the Barton samples had
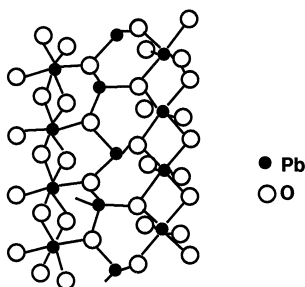

Pb
O

Fig. 2. Crystal structure of Pb$_3$O$_4$.

Table 2
Physical data for red lead (Pb$_3$O$_4$)

Property	Value
Structure	Tetragonal
Mohs hardness	2–3
Density (g cm^{-3})	4.6
Refractive index	$^{n}_{Li} = 2.42$
Lattice constants (Å)	$a_o = 8.788$
	$c_o = 6.551$
Dielectric constant	20
Electrical conductivity (Ω cm)$^{-1}$	$\sim 10^{-12}$

Table 3

Characteristics of leady oxide (Barton-pot process) for different battery applications

Characteristic	Automotive batteries	Industrial batteries
Free-Lead (wt.%)	18–24	22–28
Apparent density (g in.$^{-3}$)	18–24	23–29
Acid absorption (mg g^{-1})	170–210	130–155
Particle size:		
Median (μm)	2.2	2.8
% below 1	10–15	5–10
Alpha:beta ratio	96:4	96:4

Table 5

Typical specifications for battery-grade red lead

	25 wt.% red lead	80 wt.% red lead
wt.% Pb_3O_4	25	80
wt.% PbO	75	20
wt.% Pb	2.5 max	0.5 max
Apparent density (g in.$^{-3}$)	19–25	16–19
Acid absorption (mg g^{-1})	170–200	200–230
Median particle size (μm)	3.0	2.0

during pasting and curing. The amount of free lead oxidized at each step in the process is often variable and results in changes in the paste characteristics, and in the composition of the finished plate. This can result in variability in cells made from these plates. The latter can be a significant problem in valve-regulated batteries where cell-to-cell voltage repeatability is very important for proper long-term operation under oxygen-recombination conditions.

Another advantage of β-PbO is the elimination of the lead oxidation step in the curing process. This significantly reduces curing time and allows the process conditions to be designed to produce the optimum ratio of tribasic and tetrabasic lead sulfate in the plates.

2.2. Red lead

Red lead is beneficial in improving the electrochemical performance of cells and batteries. The lead is in a higher oxidation state than lead monoxide (ratio of Pb:O = 1.33) and its electrical conductivity is also greater. Batteries made with red lead in the positive paste can be formed quicker, and their initial capacity is higher than those made from leady oxide pastes.

The red lead is normally used in either of two ways. A high percentage red lead (> 80 wt.% Pb_3O_4) can be blended into the paste mixture to produce the desired amount in the finished plate, or the paste can be made from a lower percentage red lead (~ 25 wt.% Pb_3O_4) which is substituted for leady oxide. In either way, paste mixing and plate processing are very similar to those with

conventional leady oxide. Typical specifications for battery-grade red lead are shown in Table 5. The particle size decreases and the acid absorption increases as the percentage of Pb_3O_4 in the red lead is increased. Consequently, if a paste mix is being produced that contains 25 wt.% Pb_3O_4, a better result is generally obtained when this is added as the high percentage material because of its greater reactivity.

3. Production methods

Most of the lead oxide used by the battery industry in the USA is produced by the Barton-pot process because of its flexibility and low cost. Barton-pot oxide is also used as the raw material feedstock for the production of pure PbO and red lead. A schematic flow chart of the process used to
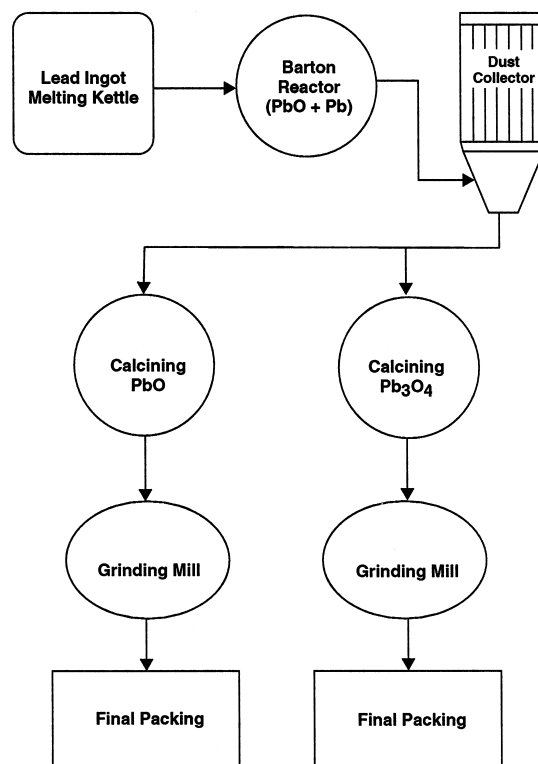
Table 4

Typical characteristics of battery-grade, orthorhombic, β-PbO

Characteristic	Value
Free-lead (wt.%)	0.1
Apparent density (g in.$^{-3}$)	26–32
Acid absorption (mg g^{-1})	125–150
Particle size:	
Median (μm)	4.5
% < 2 μm	20
% < 1 μm	5
wt.% Beta-PbO	90

Fig. 3. Schematic diagram of flow process for production of leady oxide, lead monoxide, and red lead.

produce leady oxide, pure PbO and red lead is shown in Fig. 3. Lead, of the required purity, is melted in a kettle and then fed into a reaction vessel fitted with a rotating paddle. Air is drawn through this reactor and leady oxide is drawn off by the air stream and classified by conventional methods. By careful control of temperature, air flow and paddle speed, oxide of varying characteristics can be produced. Generally, the temperature will influence the amount of free-lead in the product, and the ratio of alpha- to beta-PbO. The velocity of the air flow will influence the free lead and the particle size of the material.

Pure β-PbO and red lead are produced in calcining furnaces in which the raw material is agitated while being heated at the optimum temperature for oxidation to the required product. In the case of pure β-PbO, the temperature is held at 600°C while for the production of red lead a range of 450 to 500°C is used. In the case of red lead, the furnace is discharged when the desired amount of Pb_3O_4 has been reached. Oxide with 25 wt.% Pb_3O_4 can be made in 5–6 h, while production of an oxide with 80 wt.% Pb_3O_4 may require 16–18 h of calcining.

3.1. Particle-size control

The particle-size distribution is the most important physical property of battery oxide. It strongly influences both the performance characteristics and the life of the battery. Such measurements as apparent density and acid absorption, which are widely used by the battery industry, are reasonably good indicators of the particle-size distribution. The lower the particle size of the oxide, the higher will be the acid absorption and the lower will be the apparent density.

Although Barton-pot systems are capable of some degree of particle-size control by adjustment of process parameters, a much greater degree of control and of flexibility is achieved when the system incorporates a hammer mill. In a hammer mill, a number of hammers are fitted to a rotating shaft with a variable speed drive. A stream of air is drawn through the mill which can be adjusted by a damper setting. Consequently, the dwell time of the material in the mill can be varied. Depending on the air velocity, the number of hammers, and the speed of rotation, the material being fed into the mill can be ground to wide range of particle-size distributions. Process settings have been developed which allow a high degree of control over the median particle size and the amount of fine particles in the product.

A typical example of the particle-size distribution of leady oxide before and after milling is shown in Fig. 4. In this series of experiments, the mill was equipped with four hammers and the speed of rotation was kept constant.
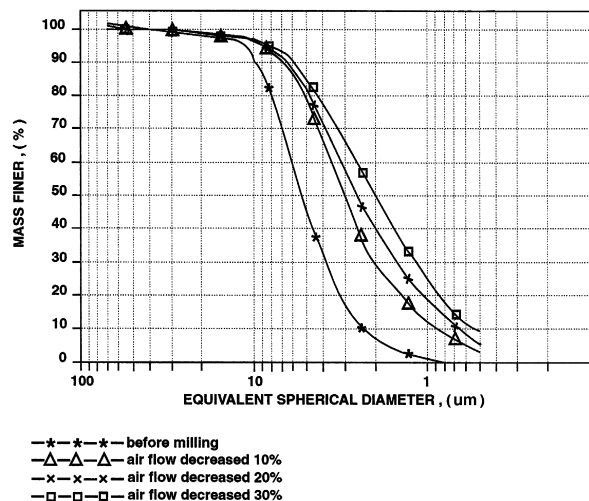

Fig. 4. Effect of mill on the particle-size distribution of leady oxide.

Changes were made to the air velocity by adjustment to the damper. By reducing the air velocity it was possible to make significant changes to the particle-size distribution. The median particle size was reduced from 5.3 to 2.1 μm and the amount below 1 μm was increased from 1 to 24%. Further comminution of the material is possible by increasing the number of hammers and/or the speed of rotation.

4. Conclusions

Pure lead monoxide (β-PbO) and red lead, as active materials in batteries, can yield a number of benefits compared to with leady oxide. Pure β-PbO gives improved reproducibility in paste mixing and simplifies the curing process. The absence of free-lead results in reduced plate-to-plate variation which, in turn, leads to more uniform float voltages in standby and valve-regulated batteries. Red lead can yield such benefits as reduced formation time, improved initial capacity, and superior high-rate performance.

Barton-pot systems coupled with a hammer mill are extremely flexible and are capable of producing oxides with a wide range of particle-size distributions suitable for automotive and industrial applications.

References

[1] H.E. Brown, Lead oxide, Properties and applications, international lead zinc research organization, 1985.
[2] M. Neuberger, Lead oxide, Air force materials laboratory, Research and technology division, Contract AF 33 (615)-2460, 1967.
[3] G.L. Corino, R.J. Hill, A.M. Jessel, D.A.J. Rand, J.A. Wurderlich, J. Power Sources 16 (1985) 141–168.