

Technical Note

Aspects of lead/acid battery technology 3. Plate curing

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Abstract

Curing is the process by which strength and adhesion of paste to grid is established prior to formation. The conditions for effective curing are set out and the two basic methods, fast and slow curing, described together with problems associated with curing. The introduction of a curing stage may be necessary with tubular positives where some filling powder blends are used. Unless the free lead in the filled plate is reduced there can be a significant self-discharge in charged, fresh cells awaiting delivery.

Background

Curing is the process by which strength and adhesion is given to the active material of the plate prior to formation and is retained by the material after formation.

The composition of the unformed material is complex, but in a strongly adherent cured material the following compounds are present: lead sulfate (PbSO_4), monobasic lead sulfate ($\text{PbSO}_4 \cdot \text{PbO}$), tribasic lead sulfate ($\text{PbSO}_4 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$), and tetrabasic lead sulfate ($\text{PbSO}_4 \cdot 4\text{PbO}$). The latter two compounds form needle-shaped crystals that interlock to impart strength to the active material. In positive plates, the basic lead sulfates after formation are hard and relatively dense $\alpha\text{-PbO}_2$. The actual size of the PbO_2 crystals and the proportion in the formed positive is very much dependent on the conditions of current density and electrolyte concentration and temperature during the formation process, but the two forms of basic lead sulfate mentioned must be present initially for good material strength. The crystals of $\alpha\text{-PbO}_2$ can vary in length from 10 to 150 μm , the size depends on the formation conditions. Thereafter, this network of interlacing needle-shaped crystals is barely affected by service conditions and provides the main strength of the positive active material and its particle-to-particle cementation.

The lead sulfate and the monobasic lead sulfate react differently during formation to form very small regular polyhedra with a very uniform size between 2 and 3 μm . The crystals are very small in comparison with those derived from the other components of the unformed material and remain virtually unchanged in size, or shape, during and after the formation process.

In the negative active material, the needle-shaped crystal structure of the cured material is retained during the formation and is assisted by the presence of barium sulfate crystals with a similar crystal structure to lead sulfate.

The importance of curing cannot be overstressed. The final formed active materials can lack the essential particle-to-particle cementation that is required to provide a resilience to the regular expansion and contraction forces occurring naturally in the materials during the course of discharge and charge, unless curing is performed in a highly disciplined manner.

The purpose in curing is to produce an effective crystal structure that confers adequate strength to the material, whilst preserving a highly developed surface area presented to the electrolyte, to retain the material sufficiently intact to satisfy the life and performance requirements dictated by the market. In the case of positives, this means the retention of sufficient α -PbO₂ for life and β -PbO₂ for the maintenance of capacity output.

In the uncured plate, as dispensed from the pasting machine, there is a relatively high free-lead content since the original lead oxide from which the paste is made also contained a high proportion of free lead. Unless this free lead can be oxidized, it will remain as dense metallic lead in negative plates with a very limited surface area. It remains relatively inactive and contributes very little to the cell performance. Since restricted surfaces polarize rapidly on discharge the continued presence of unconverted lead increases the voltage loss on discharge, particularly at high discharge rates. This is important in automotive batteries, where the maintenance of a high terminal voltage at engine starting loads is a prime requirement. For positive plates, the oxidation of metallic lead to lead dioxide requires appreciably more in ampere-hour input than when converting lead oxide or lead sulfate. This sometimes results in less than full formation and, consequently, a reduction in the initial capacity. With cycling, the free lead in a positive active material will be converted, but this cannot always be tolerated, particularly in the case of traction cells required to operate in onerous working conditions where the rated capacity is required very early in life.

The effectiveness of the curing process can be assessed simply on the degree of free-lead conversion and the amount of moisture left in the material after the process has complied to the specified time, temperature, etc. The conditions for a satisfactory cure are closely tied to the amount of moisture in the uncured plate and the retention of that moisture for sufficient time for the free-lead conversion to continue to near completion. Thereafter, the material can be dried and stored.

The pattern of the crystal structure is set initially in the paste mixing by the control of the maximum temperatures in the mix to below 60 to 62 °C, and the thorough distribution of the dilute sulfuric acid throughout the mix. During the curing process, there is an interaction between the free lead, atmospheric oxygen and the moisture.

Conditions for effective curing

Free metallic lead cannot be oxidized unless there is both oxygen and moisture present. There is a ready supply of oxygen from the surrounding air but the moisture has either to be supplied from within the plate materials or from an external source to supplement that which is within the plate.

Figure 1 shows the effect of the initial moisture content of active material on the reduction in the free-lead content of plates curing in their own moisture in a

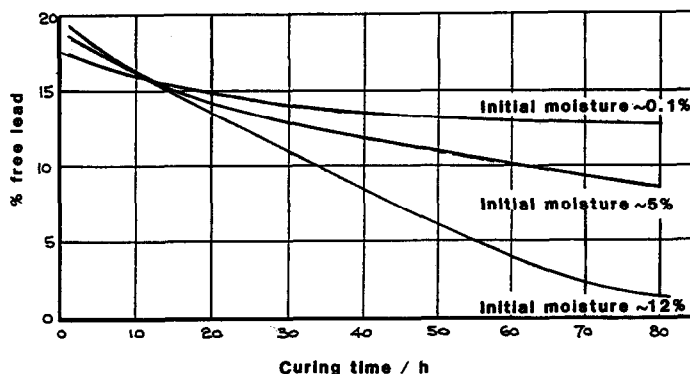


Fig. 1. Effect of initial moisture level on the reduction in free-lead level of plates curing in a static atmosphere without external moisture supply.

static atmosphere. Whilst these curves do not quantitatively represent every type of plate, they are qualitatively representative of plate curing.

The moisture level in most plates where the flash-drying oven temperature has been effectively controlled will be at least 10 to 12 wt.% at the start of the cure. With this moisture level, the reaction produces a relatively slow reduction in the free-lead content, unless the plate temperature has attained at least 30 °C. The setting of the flash-drying oven temperature has a major bearing on the speed of cure since, if the temperature can be maintained to deliver plates from the oven with no more than 10 wt.% moisture, then the rate of cure can be greatly increased and the incidence of poor curing virtually eliminated. If, however, the oven temperature has been allowed to rise and plates are delivered with 7 wt.% or less moisture, the effect of the exothermic curing reaction will be to reduce the moisture level still further and the rate of cure approaches zero. Generally, a satisfactory cure reaction occurs when the flash-drying oven temperature is just sufficient to evaporate all the surface moisture and no more.

Several laboratories have examined the effect of absorbed moisture on the rate of reduction of the free-lead content, and there is reasonable agreement that the lead oxidation reaction proceeds at its maximum rate over a relatively narrow range of moisture levels in the material. Outside this band of moisture levels, the rate at which the oxidation reaction proceeds falls dramatically. Whilst it may not be possible to ensure that all plates passing through the flash-drying oven will be dispensed with the optimum moisture contents, it is preferable to err on the high side of the optimum range. This is because the exothermic reaction, which proceeds slowly at first, will reduce the level of the moisture and the oxidation process will speed up.

The maximum rate of free-level conversion occurs when the moisture content of the active material lies between 7.0 and 8.5 wt.%. The object in starting the cure with a higher value than this is to ensure that the maximum advantage is taken of the full band-width of moisture change where only the self moisture of the plates is used. Figure 2 gives data derived from information given by Humphreys *et al.* [1]. The value of these data lies in the identification of the conditions of humidity and temperature conducive to a rapid reduction in the free-lead content without the loss of paste cohesion and adhesion to the carrier grid. Most workers also generally agree that the rate of free-lead reduction reaches a maximum at ~30 °C and falls progressively as the temperature is raised above this values.

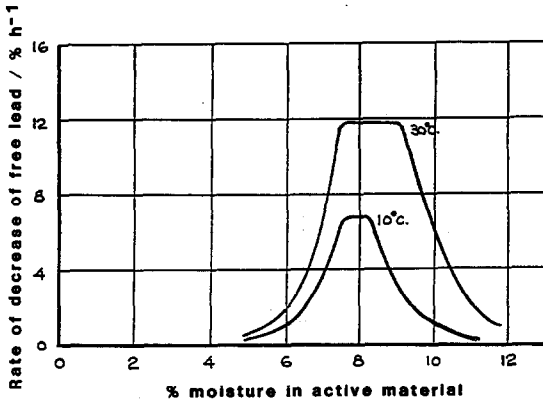


Fig. 2. Effect of moisture level and temperature on the rate of decrease of free-lead content.

Two methods of curing active materials are practical:

(i) Fast curing where the plates leaving the flash-drying oven are packed, spaced apart a distance of about a single-plate thickness, and transferred to a heated humid chamber where the humidity is maintained at saturation level and the temperature is thermostatically held at 30 °C;

(ii) Slow curing where the plates are held in close contact with each other and the heat of the curing reaction is used to maintain the temperature of the active material, whilst the self-moisture in the material is retained by the contact of one plate to the next.

Fast curing

This method is favoured by manufacturers who wish to minimize the time taken to cure and reduce the amount of 'work in progress' at the curing stage. The ideal conditions would be for the plates to be dispensed from the flash-drying oven with a moisture content close to the level of 9.5 wt.% where the reduction of the free lead is at its maximum. The passage of the plates through the oven would have ensured the temperature of the material was above 30 °C.

Even with the most careful settings of the oven control, it is difficult to achieve consistently these optimum conditions for curing, and the plate material needs to be exposed to a relatively large volume of moist, warm air immediately after leaving the oven to bring the material to the optimum cure conditions. The spacing of plates apart from each other as they emerge from the flash-drying oven is essential both to expose each material surface to the chosen ambient conditions and to bring about an equalization of moisture and temperature throughout the full rack of plates. When building up racks of plates prior to transfer to the curing atmosphere, care has to be exercised that the plates are not temporarily in a draught where the chilling air can cause a rapid reduction in the moisture and temperature just below the surface of the material. This can inhibit and, in severe cases, stop the curing process. The racks need to be assembled under extract to reduce the level of atmospheric pollution, or all operators within that area must be provided with effective respirators. The former is always the better.

There is always the risk that the extraction of air from the area surrounding the racks will produce some chilling. Therefore, as soon as a rack has been filled, it should

be covered to conserve the heat. Preferably, these covers should be impervious to air and water vapour, so that heat and moisture are retained in the temporary atmosphere surrounding the plates.

Whilst the humid ovens provided for curing can be free standing, it is often more practicable to use a low-height room in which the walls and ceiling have been treated with a waterproofing medium and into which steam is bled to provide the warm, humid, stagnant atmosphere that is ideal for fast curing. Wherever possible, the curing ovens or rooms should have inlet and outlet doors at opposite sides so that racks of curing plates can be kept in strict date sequence and the possibility of racks not receiving their full cure is eliminated.

The value of low rooms lies in the ease with which they can be controlled both for temperature and moisture content, as well as in the economy of heat usage. An alternative is the setting apart of a small section of the factory that is thoroughly screened off from the rest of the plant and is equipped with sufficient fine water sprays near the roof to create a permanent moist atmosphere. The racks of plates are then mounted in date order into permanent openings on robust shelving.

Not all manufacturers are prepared to set aside humid curing rooms and drying ovens. Rather, they are content with a somewhat slower turn-around of cured plates. In these circumstances, as plates emerge from the flash-drying oven, each level in the rack is quickly covered with wet sacking or closely woven canvas so that the lower edges of the wet covering extend at least 20 cm below the bottom edges of the plates. As the next level in the rack is filled, this is also covered so that the lower and the higher coverings overlap and enclose the upper level of plates, and so on. In this way, the plates are all enclosed in tunnels with walls that are impregnated with moisture. When the rack of several levels of plates is completely filled, it is moved into an area generally free of traffic and doors that are frequently opened and closed. The objective in selecting an area with a relatively static atmosphere is to minimize the uncontrollable cooling that could otherwise occur and that would slow down the curing reaction. The small volume of air enclosed within the wet tunnels is rapidly heated by the exothermic curing reaction and is retained within the tunnel.

In hot climates, the covers enclosing the plates need to be wetted frequently to offset the rapid loss of moisture through evaporation. An alternative method that is effective under such conditions is to build shallow brick tunnels and line them with plastic sheeting. Single racks are inserted into these tunnels with the plates evenly spaced in each rack. The racks are then covered with a plastic sheet over which is placed relatively thick covers of poor heat-conducting material. The dimensions of the tunnels are such that there is very little free space around the plates. The loss of heat to the outside is low and slow and the tunnels remain filled with water vapour that is produced by the heat of the curing reaction.

Both of the methods will produce plates with <5 wt.% free lead within 24 h, provided the plates as they emerge from the flash-drying oven are promptly covered. The danger lies in allowing operators to completely fill all levels of a rack before applying a covering of wet sacks or canvas.

After the allotted cure time, the covers are removed and the plates dried separately. In the case of the brick tunnels, the plates are removed and dried, usually in the open air.

Slow curing

This is often referred to as stack or rack curing; the objective is to eliminate special curing rooms and rely on plates in contact with each other creating acceptable

curing conditions. With automotive plates destined for container formation, it is usual for the double plates, as pasted, to be broken into single plates and these stacked one on top of another to form a pile about 30 to 40 cm high. These stacks of plates, set to one side of the pasting shop in a relatively draught-free location, are then left for ~ 72 h to self-cure. It is convenient with plates 2 mm in thickness or less to take a small pile of plates and break them at the foot-to-foot junction over a fixed metal strip.

Some firms use an open-sided wooden box into which the plates are piled. The box sides provide protection from draughts and, thereby, reduce the rate of heat loss. Other manufacturers pile the plates on a pallet and space the piles apart between 2 and 3 cm. When the pallet is filled, all the piles are covered with an impervious sheeting, such as polyethylene, and left for ~ 48 h, after which the sheeting is removed and the plates allowed to dry in the local atmosphere.

In the case of plates destined for dry charging, it is not necessary to part the double plates since they are more conveniently formed as doubles. They are stacked as doubles and subjected to the same time-curing regime.

Thicker traction plates tend to take a longer time to cure and the optimum curing time should be determined by experiment. This can most readily be done by extracting sample plates at intervals after, say, 36 h and determining the level of free lead. It is expedient to add a small safety margin to the optimum time in order to accommodate variations in processing. Most makers accept a free-lead level of not more than 4 wt.% for bulk production since the attainment of better values can often extend the curing time appreciably and upset the total production planning.

Although a satisfactory reduction in the level of the free lead can be obtained merely by putting the stacks of plates in a relatively draught-free location, the reproducibility of the cure is improved by shielding the stacks of plates with impervious sheeting that extends to below the bottom of the stacks. There is a small risk that after the cure reaction has finished, the sheeting will hinder the drying of the plates. This can be avoided by removing the sheeting when the cure reaction is complete and leaving the plates to dry naturally for a period of 24 h. This calls for a good shop-floor discipline that some firms find is best maintained by the roving quality inspector.

An alternative to stacking the plates is to rack them on horizontal runners with the adjacent plates in contact with each other and under slight pressure. There is the risk that the temperature rise, where the length of the horizontal rack exceeds 50 cm, may become too high for the retention of the necessary humidity for good curing. It is helpful to break the total length of racked plates into a number of 30 cm lengths (or thereabouts) and insert a poorly conducting spacer between each length. This effectively prevents the centre plates from becoming too hot for effective curing.

When using the racking system, it is necessary to hold the rack of plates under compression. This can be done with a simple wedge arrangement. Care must be taken not to jam the plates together too tightly. This produces hot spots that dry out too rapidly and give rise to a variable cure. Again, it is preferable to cover the racks of plates with impervious sheeting until the cure reaction has completed. The sheeting should then be removed to allow the plates to air-dry.

In between the fast and slow curing methods are hybrid methods. These include racking the plates and passing them into humid setting rooms where the humidity is created by passing hot water through mist spraying nozzles above the racks and air-drying afterwards, or slow curing followed by drying in heated ovens, etc.

Excellent cured plates can be produced by either fast or slow curing methods. The system chosen is an individual choice based on the ease or economy with which it fits the remainder of the plate processing. It is, however, generally agreed that in the case of traction plates that are thicker than 3.5 mm, a better cure can be achieved using the slower method.

Problems in curing

Although the curing process is essentially a simple one, it is subject to errors that subsequently affect adversely the final product. These are almost entirely due to undercuring that can develop for the following reasons:

(i) Poor shop-floor process discipline allows plates to be released from curing before the specified time. This usually occurs because a proper identification system (i.e., detailing plate type, data and time of commencement of curing, the earliest data for release to the next process, etc.) is not in being, or there happens to be a shortage of plates for the next process and supervision takes a chance and removes plates from the curing stack.

(ii) The temperature of the flash-drying oven is too high and removes too much moisture from the plates. In these circumstances, the rate of curing is appreciably reduced (see Fig. 1). Routine monitoring of the free-lead levels in alleged cured plates is necessary to maintain good production standards. If the tests indicate that the curing reaction has been too slow or has been inhibited by premature loss of moisture, the plates should be damped and moved to a low-heat chamber held around 35 to 40 °C to restart the reaction. The curing process is then repeated. This does not usually present a difficulty with fast-curing systems since the plates are spaced apart and can be readily wetted without sticking together. In the case of stacked plates, it is difficult to rewet and restart the cure and, therefore, it is more realistic to prevent the situation by concentrating on proper settings for the flash-drying oven.

(iii) There is no readily available free-lead analysis service. A reasonable indication of the state-of-cure of positives can be obtained by scraping away the top layers of material and comparing this with the underlying material. If the colour is substantially the same then the cure is probably complete and satisfactory. If the underlying material is of a greenish colour whilst the top material is yellow/orange, then the cure has almost certainly been arrested. In the case of negatives, the carbon and expanders colour the active material and it is difficult to determine visually whether or not the cure has been taken to a satisfactory completion. In this case, the only reliable data are those given by chemical analysis.

(iv) Plates have been allowed to cool before they have been covered with sheeting and removed to the curing location. This results in a high free-lead level. This tends to be more troublesome with fast-cure systems since the plates are spaced apart and can cool more readily. The plates should be wetted and taken into a warm area to restart the curing reaction.

Spalling

Spalling is the direct result of undercuring. It is the name given to a condition that is experienced particularly in tank formation where the positive material flakes

off (or is shed) and leaves a 'pock-marked' or grossly damaged and uneven material surface.

Whichever symptom shows up, the occurrence should be treated with concern. The completeness of the cure should be examined thoroughly and remedial action taken immediately. The real danger lies with container-formed cells and batteries since spalling, though present, can be hidden and the problems are passed to the customer. This is particularly true in the case of automotive batteries when there is slack in the element build-up and, with traction cells using flat plates, spalling usually results in short service lives.

Curing of tubular positive plates

Although it is uncommon to talk of curing tubular positive plates, it can be as important for the free-lead content to be reduced as for normal flat plates. The filling powders varies from maker to maker and this influences the extent to which there is a free-lead problem. The variation in filling powder is large — from wholly red lead to wholly lead oxide, with all the combinations in between plus additions of litharge together with none, part or all of the components being sulfated prior to use as the filling powder. These are referred to as simple or presulfated filling powders. For a presulfated powder, the simple mix or blend is made into a wet mix (i.e., similar to a paste) with dilute sulfuric acid. This mix has a texture and sulfate content that, when dried, can be readily pulverized into a free-flowing powder.

Where red lead or sulfated and pulverized red lead is used for filling, there is virtually no free lead present and no separate curing operation is needed. It is normal practice after filling, to close the bottoms of the tubes with a preformed closure and to immerse the filled plates in a weak solution of sulfuric acid. This increases the amount of lead sulfate throughout the mass of the material. Such procedure assists the subsequent formation and minimizes powder density variations over the length and width of the plates.

When using a filling powder comprising mill oxide alone or in a blend with red lead or litharge, the free-lead content will decrease as the red-lead component is increased. Even if the filling material is subsequently sulfated, some free lead will usually remain. In container-formed batteries, this promotes self-discharge either during rest periods in the formation schedule or after the formation has been completed if no rest periods are included. This self-discharge reaction is more pronounced with increase in the free-lead content; there is also an accompanying rise in temperature. If the filling comprises mainly mill oxide and little or no cell external cooling is provided, the temperature rise can be sufficient to melt the bituminous sealing compound and, thereby, cause it to run down between the edges of the cell lids and the surrounding cell container walls. The walls also bulge due to the softening of the container material. Although the temperature rise can be suppressed to some extent during rest periods with external cell cooling, it often reappears after the completion of formation with similar compound and cell container problems. Once the self-discharge has occurred, the free lead will have been reduced sufficiently for further troubles to be virtually nonexistent.

The conditions for the reduction of the free lead in tubular positive plates are the same as for flat plates, i.e., ~12 wt.% moisture and a temperature of 35 to 40 °C. The process generally requires the plates to be dipped, after dry filling, to wet the powder thoroughly. The disparity between the densities of the filling powder and

the dip (irrespective of whether plain water or slightly acidulated water is used) prevents the moisture content of the wetted plate from greatly exceeding the optimum for effective curing. There is a tendency, when the wetted plates are placed in the curing oven, for the moisture content to fall below the optimum and, consequently, for the rate of curing to slow down appreciably. It may be necessary for plates to be wetted at predetermined intervals throughout the curing period to compensate for this initial loss of moisture. The frequency and the amount of rewetting is greatest when only mill oxide is used with free-lead contents within the range 25 to 35 wt. %.

It is generally found that curing results are more favourable if the plates are not sulfated before curing. This probably is due to the increased volume of the sulfated powder reducing the volume porosity and the amount of moisture that the powder can absorb.

A reasonable objective is to reduce the free lead in the plate to below 4 wt. %. At this level, little trouble is experienced with container formation and self-discharge.

It is the practice with some manufacturers of traction cells to adopt container formation and to subject the cells to a limited discharge (called a 'protective discharge') before storing cells prior to assembly into finished batteries. This is unnecessary when the plates have been cured.

Reference

- 1 M. E. D. Humphreys, R. Taylor and S. C. Barnes, Research and development in nonmechanical electrical power sources, in D. H. Collins (ed.), *Power Sources 2*, Pergamon, Oxford, 1968, pp. 55-65.