

RESEARCH HIGHLIGHTS IN LEAD/ACID BATTERIES

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Market trends

World lead sales depend heavily upon the use of the metal in the manufacture of lead/acid batteries. These batteries are widely employed to start internal-combustion-engined vehicles, to provide standby power, to propel specialist vehicles, and to operate portable appliances. Potentially enormous new markets lie in electric road vehicles, mains-electricity load-leveling facilities, and remote-area power-supply systems. The increasing demand for better electrical output and longer service life, together with trends towards reduced weight and lower maintenance, requires the deep-discharge performance of all types of lead/acid batteries to be lifted.

In pursuit of better electrical performance

The basic parameters to consider here are energy density (*i.e.*, Wh kg^{-1} or Wh l^{-1}) and power density (*i.e.*, W kg^{-1} or W l^{-1}). The energy density is the amount of electricity that can be generated per unit mass (or volume) of the battery, the power density is the rate at which this energy can be supplied per unit mass (or volume).

Practical energy and power densities are less than their theoretical (*i.e.*, maximum) values on account of: (i) electrode-kinetics and reactant-supply restrictions (*i.e.*, overpotential factors) that reduce the battery voltage on load, (ii) the internal resistance of various cell components that also act to decrease the battery voltage, (iii) the need for inactive construction/operation materials (*e.g.*, grid current-collectors, inter-cell connectors, terminals, cover and container, separators, water in the electrolyte, etc.) that contribute to the battery's weight (and volume) but are not involved in the electricity-producing reaction, (iv) the influence of various morphological, geometrical, distribution, and chemical (*i.e.*, isolation and passivation) effects that prevent the full utilization of the electrode materials during the cell reaction. Factors (ii) - (iv) are the most important in limiting the performance of lead/acid batteries.

Reducing internal resistance

The internal resistance of cells and batteries can be reduced by (i) developing thinner, lower resistance, separator materials, (ii) decreasing plate thickness, (iii) improving current-collection through the development of new grid designs, (iv) increasing grid conductivity through using lead composites, *e.g.*, copper-stretch-metal [1], (v) minimizing current pathways through introducing innovative cell designs, (vi) ensuring good inter-particle contact within the plate materials through optimizing phase chemistry and architecture, adding binders, dopants, etc

Conventional lead/acid batteries employ a monopolar plate arrangement in which a number of negative plates are parallel-connected and then joined in series to a similar (interleaved) group of positives (Fig 1) In the alternative bipolar arrangement, each interior plate serves as the negative of a cell on one side and as the positive of the adjacent cell on the other (Fig 1) The bipolar plates are stacked parallel to each other so that cell-to-cell current flow is through the whole area of the electrode, and is transmitted only through its thickness The current pathway is considerably shorter than that of the monopolar type and, hence, resistance losses are reduced appreciably The practical realization of the bipolar battery has been delayed, however, by difficulties in maintaining the integrity of both the electrodes themselves and the seals they must make with the container

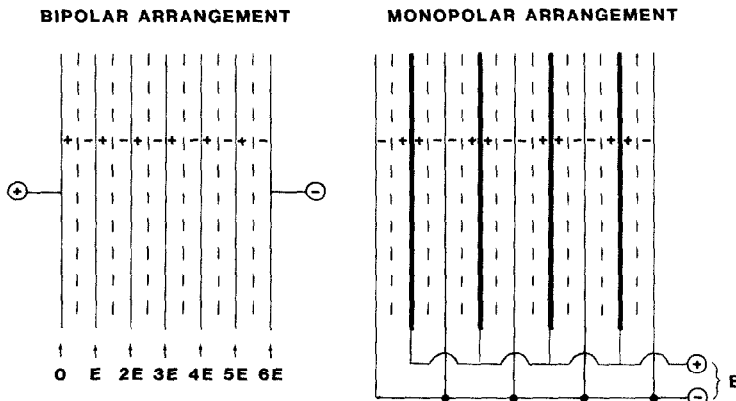


Fig 1 Plate arrangement in monopolar and bipolar cell designs

The recently introduced Dunlop "Pulsar" automotive battery has a unique construction [2] The battery consists of alternate, side-by-side, positive and negative plates mounted on injection-moulded plastic frames To produce a 12 V battery, a frame containing three positive and three negative plates is placed opposite a similar frame (with a separator frame in between) in such a manner that each plate in one frame faces another of opposite polarity in the adjacent frame The desired capacity is achieved by stacking a number of these frame pairs in series This arrangement eliminates

the need for "top lead" in inter-plate and inter-cell connections. Current collection is taken along the whole length of the vertical side of each plate, so that resistance losses are significantly decreased and, subsequently, the power output is greatly increased

Reducing the weight of inert materials

Clearly, the need to lessen the weight contribution of inert materials is strongest in mobile and portable applications of batteries. Engineering approaches are usually adopted to minimize battery hardware, although some research opportunities present themselves, *e.g.*, in the development of corrosion-resistant, low-density, lead-coated grid materials such as aluminium, copper, glass, titanium, etc. The greatest weight savings are likely to be achieved through innovative cell designs. For example, Dunlop claim that the novel plate arrangement of the Pulsar automotive battery results in up to 50% reduction in weight over conventional systems

Increasing the utilization of plate materials

Plate materials are not fully discharged during the cell reaction. Utilization at the beginning of service is a function of the delivered current density, the rate of electrolyte diffusion into the plates, the total surface area of the plate materials, the degree of electrical contact both between the particles of material and the current collector (grid) and between the particles themselves, and the intrinsic electrochemical activity of the particles. These factors are found to change both during a given discharge cycle and between subsequent cycles, so that the battery is eventually unable to supply useful energy and/or power.

Attempts to increase the utilization of plate materials have involved. (i) reduction in plate thickness, (ii) changes in cell design, (iii) forced circulation of electrolyte, (iv) increase in porosity and total surface area of the materials, (v) changes in plate preparation procedures, and/or the addition of dopants. By the latter, it is hoped to modify both the chemical composition and the size/shape/distribution of the positive-plate material particles to yield a reproducible system with optimum electrochemical activity. Although the engineering approaches of (i) - (iv) have led to improvements in both energy and power densities, they have also often resulted in premature battery failure. For example, reducing the thickness or increasing the porosity of plates has generally resulted in shorter cycle life through accelerated grid corrosion or material shedding, respectively. The flow-through cell developed by Johnson Controls, Inc in the U S A (Fig 2), whilst being capable of very high levels of material utilization (51% improvement), must use plates that contain no cracks or pinholes (both initially and throughout operation) and that also exhibit good mechanical integrity under pumping pressures, both criteria present difficult technological challenges. These problems serve to illustrate the age-old rule of battery development, namely, a basic compromise has to be made between electrical performance and service life

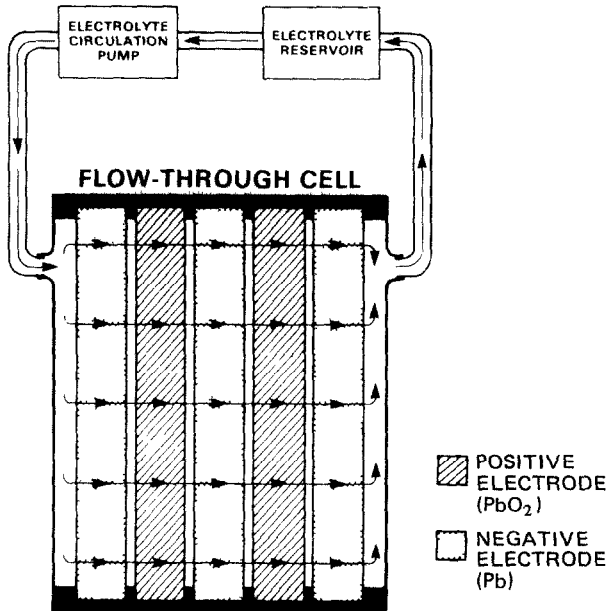


Fig 2 Electrolyte flow-through concept for lead/acid batteries [3]

The crystal-chemical approach

In research circles, increasing support is being given to the view that the best approach to enhancing lead/acid battery performance is to shift the emphasis from engineering aspects towards efforts aimed at achieving a deeper understanding of the subtle changes in both the phase chemistry and the individual crystal (*i e.*, solid-state) and total architectural properties of plate materials that occur during battery manufacture and operation. Such knowledge is considered essential for industry to obtain, first, tighter control, and second, optimization of the various plate-making stages, so that battery performance becomes both uniform and maximum. It is considered that research campaigns will benefit greatly from encouraging the involvement of both the investigative techniques and the skills of solid-state scientists in conjunction with those of electrochemists.

In pursuit of better manufacturing control

To obtain the goal of better manufacturing control, a universal physico-chemical technique is required to relate quantitatively the effect of changes in the multitudinous process parameters on the chemistry and structure of the plate materials during their successive preparation and utilization stages (those encountered with flat positives are shown in Fig. 3). Recent research in the CSIRO laboratories has shown that the technique of X-ray diffraction (XRD) phase analysis can make a valuable contribution.

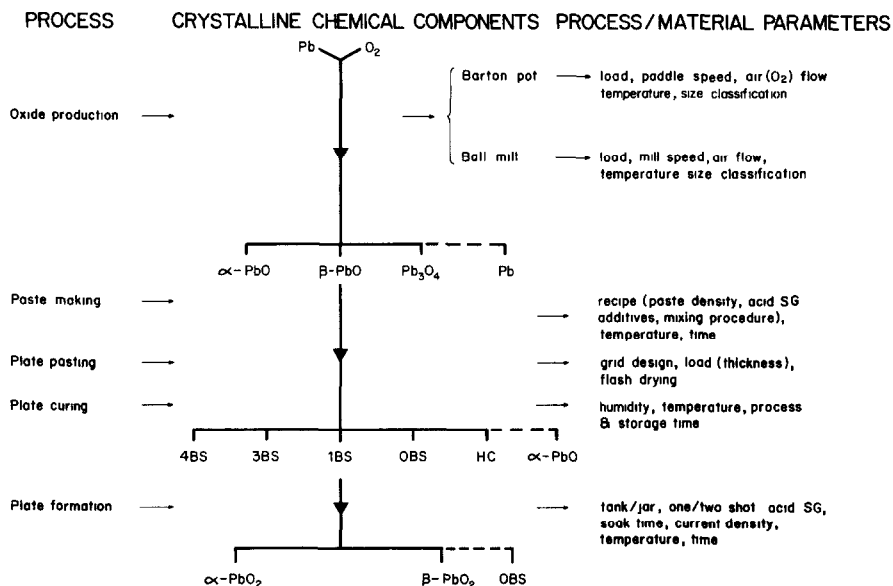


Fig 3 Crystalline chemical compounds and process parameters involved in the production of flat positive plates for lead/acid batteries 4BS = $4\text{PbO}\cdot\text{PbSO}_4$, 3BS = $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$, 1BS = $\text{PbO}\cdot\text{PbSO}_4$, OBS = PbSO_4 , HC = $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$

To date, XRD phase analysis has been applied to: (i) leady-oxide production, to achieve better quality and process control [4], (ii) plate curing, to remove variations in the subsequent service lives of cells [5]; (iii) plate formation, to provide an optimum chemistry conducive to good cell performance [6], (iv) plate service, to elucidate battery degradation processes [7]. In these studies, the phase-analysis technique has been used not only to determine the relative abundances of the various crystalline phases present in plate material, but also to distinguish between crystalline and "amorphous" material [6]. Since it is recognized that, in addition to the composition of the plates, battery service parameters also depend upon the effective surface area of the material particles and their size, shape, and spacial relationships with each other, XRD phase analyses have been supplemented by independent measurements of total plate surface-area and pore-size distributions, and by electron and optical microscopic studies. Attention has been focused initially on flat plates, but is currently being extended to cover tubular types.

In pursuit of better service life

Parameters that are considered important in determining the service life of lead/acid batteries include:

- (1) the chemical composition and physical properties of leady oxide,

(ii) the composition (including additives), density and method of application of the paste;

(iii) chemical composition and structure of cured plates (flat type) or pickled plates (tubular type),

(iv) chemical composition and structure of formed plates,

(v) composition and casting conditions of grids,

(vi) composition (including additives) of electrolyte,

(vii) choice of separator,

(viii) cell design,

(ix) storage time before use,

(x) discharging and charging mode,

(xi) temperature of operation,

(xii) uniformity of concentration and maintenance of electrolyte

Parameters (i) - (vii) depend upon the method of battery production and, hence, are known as “inner parameters” On the other hand, parameters (viii) - (xii) are determined by the conditions of battery use, and are accordingly referred to as “outer parameters” Any deleterious effect of the inner parameters on service life can be minimized through control and optimization of the materials’ processing stages, whilst any problems emanating from the outer parameters can be reduced by selecting the battery design and system features to match the operating requirements of the application Nevertheless, both types of parameters will act (to varying degrees) to bring about the eventual demise of the battery via failure of either the positive plate, the negative plate, or the separator (e g , Fig 4)

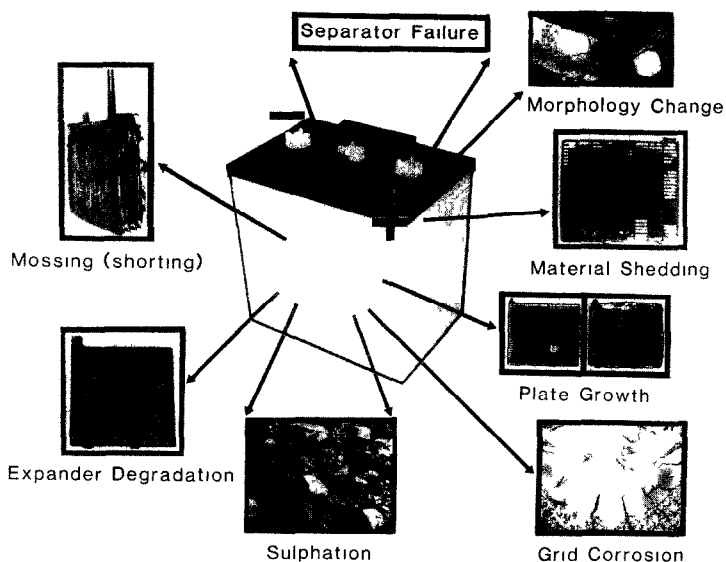


Fig 4 Examples of failure modes commonly exhibited by flat-plate lead/acid batteries

The service life of a lead/acid battery is generally limited by the performance of the positive plate, the capacity of which gradually declines on charge/discharge cycling. This loss of capacity has been attributed to a combination of the following failure mechanisms (refer Fig. 4):

- (i) loss of inter-particle contact and decrease in the total surface area of the material due to morphological changes,
 - (ii) shedding of material from the plate due to grid corrosion and morphological changes,
 - (iii) electrical isolation of parts of the material due to grid deterioration and growth, encapsulation by non-conductive lead sulphate, and formation of a barrier grid-corrosion film at the interface with the plate material;
 - (iv) plate sulphation due to acid stratification effects,
 - (v) gradual conversion of material to an electrochemically inactive form.
- These phenomena decrease the discharge capability by reducing the amount of material available for reaction and by introducing large resistance losses.

Improving material stability

The physical retention of positive material can be improved by enclosing flat plates in plastic or glass-fibre envelopes, or by using tubular electrodes clad with fabric gauntlets. The former is purely a band-aid approach, the latter introduces higher manufacturing costs. It is therefore important to understand more fully the changes in particle morphology that occur during the preparation and utilization stages of the positive material, with a view to obtaining more rigid structures that allow maximum reaction with the electrolyte, but at the same time withstand stresses caused by volume changes that accompany the chemical reactions during charging and discharging of the battery.

Research has demonstrated the importance of getting the right mix of chemistry at the plate-formation stage. Formed plates consist of α -PbO₂ and β -PbO₂, and the initial value of the α/β weight ratio has been found [7] to exert a marked effect on battery service life under deep-discharge conditions. A non-linear increase in service life occurs with increase in the initial α -PbO₂ content until an eventual maximum in performance is reached (at $\alpha/\beta \approx 0.8$ for positive-limited traction cells). The α -PbO₂ consists of prismatic crystals which, it is argued, interlock to form a rigid structure and thereby impart great mechanical strength to the plate material. Further research should be directed towards investigating how manipulation of the chemistry of each individual stage of plate-making (by adjusting process conditions) can establish a particle structure conducive to good performance in each succeeding stage.

Reducing grid corrosion

Methods to combat grid corrosion have included: (i) careful selection of grid and plate designs, (ii) use of alloying additives in the grid metal; (iii) adding dopants to the electrolyte; (iv) better control of charging conditions. Very recently, Tracor, Inc. in the U.S.A. have announced [8] the development of an extrusion process for coating small diameter glass fibres

with lead. The extruded pure lead surface is claimed to be dense and amorphous in appearance, and to have high resistance to cycling corrosion. Grids made from lead/glass composite wires have been used in a limited number of 6 V and 12 V batteries. The energy and power densities of these batteries are claimed to exceed those obtained from conventional types.

The corrosion of lead-antimonial grids, apart from resulting in eventual mechanical failure, also contributes to the self-discharge of the negative plate. During battery charge, antimony dissolves from the positive plate, diffuses through the electrolyte, and deposits on the negative plate. This results in a reduction of the hydrogen overpotential at the negative plate, and leads to hydrogen evolution during battery charge and open-circuit stand. Such behaviour increases water losses and, hence, maintenance requirements. On the other hand, the presence of antimony in the positive plate does enhance the deep-discharge performance of batteries. The detrimental gassing effect of antimony can be reduced by using grids of lower antimony content or by employing pure lead or lead-calcium substitutes. Batteries with lead grids, however, are not able to withstand the vibration and mechanical shocks experienced in some applications (*e.g.*, traction and portable power). Batteries using lead-calcium grids are more robust, but they do not exhibit satisfactory deep-discharge service lives. Thus, considerable research activity has been directed towards finding an alternative for antimony that provides its cycling benefits but avoids its electrolyte maintenance problems. Success here may come from adopting a crystal-chemical approach to study elements that form closely related crystal structures in common with antimony when combined with oxygen and/or sulphate.

Reducing acid stratification

During cycling of lead/acid batteries, acid is either consumed (*i.e.*, during discharging) or produced (*i.e.*, during charging). This results in high-density acid settling near the bottom of the plates and low-density acid near the top of the plates. The development of a resulting vertical concentration gradient of acid leads to non-uniform material utilization and current distribution. factors that shorten service life through the irreversible formation of lead sulphate, particularly on the negative plates. Acid stratification can be removed through agitating the electrolyte either by gassing on overcharge or by circulation with pumps (usually the air-lift type). The University of Alabama at Huntsville (U S A) claims [9] to have obtained a 100% increase in the cycle life of golf-cart batteries when using a pulsed, electrolyte-destratification system. In general, the degree of success in eliminating stratification is a function of the cell geometry, the design of the pump accessory system, and the cell operating procedure.

Hunting hydrogen

In addition to the above positive-plate failure modes, it has been suggested [10] that the decline in plate capacity on charge/discharge cycling

is due to the progressive loss of hydrogen species from the crystal structure of PbO_2 , together with a corresponding increase in the degree of structural order. This hydrogen-loss concept has stimulated a great deal of recent research activity. Studies in the CSIRO laboratories have shown that the electrochemical activity of crystalline PbO_2 does not change with battery service [11]. On the other hand, positive plates have been found to contain significant amounts of poorly crystalline (*i.e.*, "amorphous") material [6]. It has yet to be determined whether this material (together with any hydrogen it may contain) plays an important role in determining the electrochemical activity of positive-plate material.

Summing up

The lead/acid battery continues to satisfy an immense, worldwide demand for inexpensive and reliable electrical-energy storage. Given the huge resources invested in its production, the vital dependence of lead markets on its welfare, and the ever-present threat of one of the alternative battery systems reaching commercialization, manufacturers and material suppliers will not allow lead/acid to rest on its laurels.

Paradoxically, although lead/acid has a long and established record of commercial performance, the physicochemical characteristics of its preparation and operation continue to mystify and fascinate the enquiring research scientist and technologist alike. The driving force for research is the great scope for improvement offered by the battery, at present, the energy-storage capability is only a minor percentage of the theoretical value.

The lead/acid battery is a mature product and therefore break-throughs are likely to be few and far between. The most recent, the Dunlop Pulsar battery, has been the result of lateral engineering thought. The time is ripe for now exercising lateral research thought. The first steps in this direction are being taken by those research groups who are drawing upon the skills and ideas of colleagues in scientific disciplines that, traditionally, have not been closely associated with the lead/acid system.

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