

LEAD-ACID TRACTION BATTERIES FOR ELECTRIC ROAD VEHICLE PROPULSION -- DIRECTIONS FOR RESEARCH AND DEVELOPMENT

D. A. J. RAND

CSIRO, Institute of Earth Resources, Division of Mineral Chemistry, P. O. Box 124, Port Melbourne, Victoria 3207 (Australia)

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Summary

Little information exists on the behaviour of lead-acid batteries operating under the duty cycles normal to electric road vehicle service. Important battery requirements for the propulsion of traffic-compatible electric vehicles include a deep-discharge capability at high efficiencies of active material utilization, and a long cycle life. In order to optimize power-source characteristics to meet these criteria, especially for passenger cars, it is necessary to gain full knowledge of the influence of actual vehicle service on the performance of traction batteries. This article defines areas in which both fundamental and applied work are required to achieve this aim based on the current performance of the lead-acid system.

1. Introduction

Lead-acid batteries have a wide range of applications for which manufacturers have developed different battery designs. Of the various systems produced, traction types for the propulsion of traffic-compatible electric road vehicles are the least advanced. Batteries are required with higher energy densities than the conventional types now used in both the low-speed milk float and the in-plant fork-lift truck. Improvement here is of prime importance, since the lead-acid battery is the only one commercially available for electric vehicles. Further, a recent survey [1] of alternative battery systems has shown that the strongest competitors to the lead-acid battery still suffer from serious operational problems.

Improvements to the lead-acid battery are being sought in energy density, service life, rechargeability, and manufacturing processes and costs.

2. Achievements and ideas

2.1. Energy density

The theoretical energy density of the lead–acid battery, 171 W h/kg, is considerably greater than that available from current prototype and commercial systems, *i.e.*, around 22, 29 and 34 W h/kg at the 1-, 2- and 5-hour rates, respectively. Attempts to improve overall performance involve reducing battery weight and increasing the utilization of active materials.

2.1.1. Battery weight

About half the weight of a lead–acid battery consists of inert materials [2], *e.g.*, supports (grid metal), separators, connectors, terminals and cell containers; water in the electrolyte might also be considered in this category. Attempts to reduce the weight of support materials have involved the use of alternative cell configurations and new, low-density grid materials such as lead-coated aluminium [3, 4], copper [4], steel [5], nickel [6] and titanium [7, 8] (expanded, rolled or punched), and metal-coated plastics [9]. The introduction of carbon fibres into positive electrode grids has resulted [10] not only in a reduction in weight, but also in prolonged cycle life and increased power capability of lead–acid cells. The main factors affecting the choice of alternative grid materials are (1) good adherence of the active material to the grid, (2) good corrosion resistance, (3) good electrical conductivity, (4) good mechanical properties (*e.g.*, tensile strength, creep strength, etc.), and (5) low cost. Recently, several innovative grid designs have been developed [11] which involve less weight of grid metal but ensure good utilization and retention of active materials as well as efficient current collection. The recent introduction and development of moulding techniques has allowed the manufacture of thin-walled, high strength, heat-sealed polypropylene containers of reduced weight. Further weight savings may come from the use of aluminium for terminals and intercell connectors.

2.1.2. Active material utilization

The remainder of the battery weight (about half) consists of active materials, *i.e.*, PbO_2 , Pb, H_2SO_4 . However, the active materials are inefficiently used and less than half their amount actually takes part in the cell reaction during discharge at the high rates required in electric vehicle applications [12]. Attempts to increase the utilization of the positive active material have been discussed in a previous communication [1]. Research in this area has largely centred on studies of the morphology of the active material [*e.g.*, refs. 13 - 24] and how problems such as growth and distribution of crystals result in material unavailability. Although such investigations have, in many cases, provided theories to account for the low utilization of active material in the positive plates (and their ultimate failure — see below), no clear picture has emerged for the role of particle morphology.

In order to improve the discharge rates of negative plates, particularly at low temperatures, small amounts (~ 3 wt.%) of certain materials are added

during the paste-mixing process. These additives are called “expanders”, and among the most commonly used are barium sulphate, carbon black, lignin, and various lignin derivatives (*e.g.*, lignosulphonates). Barium sulphate in combination with an organic expander material such as lignin appears to provide the most effective expander action [25], but even under these conditions utilization of negative active material is little better than that of the positive. It is generally held that the function of expanders is to modify crystal growth during charge/discharge cycling so as to maintain a fine, porous, crystalline plate structure; in the absence of these additives the initial sponge-like active material of the lead electrode tends to coalesce and densify. This recrystallization results in a structure that is less accessible to electrolyte and therefore more difficult to discharge. However, despite the numerous detailed investigations on the mode of action of expander materials [*e.g.*, refs. 13, 15, 25 - 44], there is still little agreement on the exact mechanism by which they improve the capacity and cycle life of lead electrodes.

2.2. Battery cycle life

The cycle life of a lead-acid battery is generally limited by the behaviour of the positive plate, the capacity of which gradually falls on charge/discharge cycling*. The loss of capacity has been attributed to a combination of the following failure mechanisms: (1) “shedding” of active material (PbO_2) due to grid corrosion and other factors; (2) decrease in the total surface area due to morphological changes; (3) loss of contact between individual particles of the active material due to “paste softening”; (4) gradual conversion of active material to an electrochemically inactive form; (5) electrical isolation of parts of the active material due to grid deterioration, encapsulation by non-conductive PbSO_4 , and formation of a barrier grid corrosion film at the active material/grid interface.

2.2.1. Structure and stability of active material

Research into shedding, surface area changes and paste softening (failure mechanisms (1) - (3), Section 2.2 above) has centred largely upon optical and electron microscopic examination of the changes in morphology of the particles that occur during preparation, formation, and utilization of the positive active material. Many attempts [13 - 24, 45 - 67] have been made to relate the microstructures formed during the successive stages and to determine their respective effects on the mechanical strength and service life of the active material, but still no clear explanation is available for the decrease with cycling in the capacity of positive plates. Two polymorphic forms of PbO_2 have been found in anodic corrosion products on lead and in the initial active material of positive plates, namely $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ [45, 46, 60, 68 - 71]. The presence of $\alpha\text{-PbO}_2$ in pastes depends on plate con-

*During the initial few cycles, the capacities of batteries using antimonial lead grids pass through a maximum.

struction and method of formation [72]. In particular, the ratio of α - to β - PbO_2 is influenced by local pH changes brought about by diffusion processes within the plate. Investigations have shown [73, 74] that α - PbO_2 formation is promoted by a high pH, and electron microscopic studies have revealed [65] that this polymorph will form preferentially at the active material/grid interface. It has been reported that battery performance depends on the relative amounts of the two dioxide species in the positive active material. The α - PbO_2 polymorph is believed [13, 45 - 47, 59, 63] to extend the cycle life of positive plates by imparting greater mechanical strength to the active material structure, whereas the β - PbO_2 form has been found [47, 52, 75, 76] to provide more capacity on discharge. Further studies on commercial electrodes have subsequently indicated [77] the presence of an additional, amorphous form of PbO_2 .

Plate history determines not only the identity but also the morphology of the active material. Plates with tri-basic lead sulphate ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$) as the major cured component produce dipyrarnidal crystals of β - PbO_2 on formation [65], whereas plates formed mainly from the tetra-basic sulphate ($4\text{PbO}\cdot\text{PbSO}_4$) consist of interlocking prismatic needles of β - PbO_2 [23, 57, 59, 62]. Crystals with the latter morphology are preferred since they form a more rigid mass than dipyrarnidal crystals. Studies by Simon *et al.* have shown [17, 19] that after formation, PbO_2 has a uniform, closely-packed structure which is transformed during cycling into a "coralloid structure" characterized by large voids and a dense network of PbO_2^* . The development of the coralloid structure was found to be independent of the methods used for curing and forming the plates, but the number of cycles required for its appearance depended on the rate and depth of discharge. The structure was found to consist of columns of PbO_2 with dense interiors and extremely rough and porous surfaces. The coralloid structure was observed to break up towards the end of cycle life leaving a nondescript mass of loosely connected particles. At the end of discharge of plates with the coralloid structure, particles of unreacted PbO_2 were found to be embedded in the lead sulphate crystals. These were considered to be an inactive form of PbO_2 (evidence of inactive and active forms of PbO_2 had been obtained previously from n.m.r. [78] and d.t.a. [77] investigations) and to be responsible for the emergence of the well-defined PbO_2 coralloid structure on repetitive charge/discharge cycling.

2.2.2. Electrochemically inactive material

A decline in plate capacity is observed as the coralloid structure develops, but it is not yet clear exactly what role the structure plays relative to battery

*This is considered to be different from the "reticulate structure" reported earlier [46]. A reticulate structure is thought to evolve during plate formation when large amounts of tetra-basic lead sulphate crystals are present, and to consist of a network of inactive PbO_2 .

performance. It has been argued that whereas the structure offers a large active surface area favourable to electrode performance, the dense interior renders most of the PbO_2 inaccessible to reaction. Loss of plate capacity has also been explained [17] by an increase in the amount of inactive material during cycling (failure mechanism (4), Section 2.2. above) — an effect attributed to a change in microstructure [72] and also to the amount of hydrogen, or hydroxyl, species in the lead dioxide lattice [77]. The identity of inactive PbO_2 has yet to be established.

2.2.3. Grid corrosion

Corrosion of the grid structure supporting the active material is the other main cause of positive plate failure in cycled lead-acid batteries (failure mechanism (5), Section 2.2. above). Deterioration of the grid can lead to electrical isolation, and eventual disintegration of the plate. Generally, lead-antimony alloys (> 4 wt.% Sb) have been used for grids owing to their good mechanical properties and good castability (*i.e.*, ease of fabrication); also, they improve paste adherence [46, 58, 63, 64, 67, 79 - 81]. Further, there is evidence that the presence of antimony retards positive grid growth and corrosion [69]. Recent attempts to improve corrosion resistance have included adding cobalt and silver inhibitors to either the active material or the electrolyte [82].

Apart from leading to eventual mechanical failure, anodic corrosion of the grid also contributes to self-discharge of the negative electrode [69, 83 - 86]. 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 of the negative plate, and leads to hydrogen evolution during battery charge and on open-circuit stand. This detrimental side-effect is reduced with grids of lower antimony content. With recent improvements in plate casting, handling, and pasting equipment, the strength required for adequate grid stability has decreased considerably, and low-antimony alloys (~ 3 wt.% Sb) are now part of commercial design throughout the world.

3. Directions for research

3.1. Energy density and cycle life

Current research into active material utilization should be directed towards the development of new forms of active material with improved electrochemical activity. Furthermore, since there is always a compromise between capacity and cycle life, the morphology of the active material has to be such as to allow maximum reaction with electrolyte without any accompanying loss in mechanical strength of the battery plate. A current ILZRO research programme is aimed along these lines and is attempting to produce oxides that have uniform, consistently reproducible physical characteristics combined with high charge acceptance, high energy density, and

extended cycle life. This research project includes a detailed examination of selected dopant materials which, it is hoped, will change both the chemical composition and the size, distribution, and shape of the positive active material particles to produce an optimum crystal system.

3.2. *Effect of low-antimony alloy grids*

The performance of cells with low-antimony alloy positive grids under the deep-discharge conditions of electric road vehicle use has not been studied in close detail. Previous studies [87] have only involved examination of electrode behaviour under low-rate, continuous-current discharge, and plate failure under these conditions is possibly different from that experienced during variable-load, high-rate discharge in traction applications.

The influence of dissolved grid antimony on physical features of the positive plate such as mechanical stability of the active material mass, particle morphology, and adherence of active material to the grid is still not fully understood. For example, there is no clear consensus of opinion on the major effect of antimony on the crystallization processes occurring during the formation and charge/discharge cycling of positive plates. Antimony is thought to increase the α - PbO_2 content in the formed active material [58, 75] and to improve the adhesion of PbO_2 to the grid [63]; both these factors will lead to improved cycle life. It has also been suggested [64, 75, 80, 81, 88] that the presence of antimony preserves small particle size, large specific area, and prismatic morphology of the lead dioxide particles during cell operation. Other work has shown [67] that antimony acts as a nucleation catalyst for β - PbO_2 in the corrosion product formed on the positive grid surface. Finally, recent research has indicated [89] that the development of the so-called coralloid structure in cycled positive plates [Section 2.2.1.] is connected with antimony species entering and leaving the active material structure. From this wide range of information, it is clear that further work is required to determine the exact nature of the process, or processes, by which antimony modifies the crystal growth of lead dioxide in positive plates.

The electrochemical effects of adding minor amounts of alloying elements (*e.g.*, Ag, As, Ba, Bi, Cd, Ce, Cu, Hg, Li, Mg, Mn, Na, S, Se, Sn, Sr, Te, Ti, or Tl) to improve the mechanical strength of low-antimony grids, are also not well characterized. In particular, more information is required on the relationship between deep-cycle life and the characteristics of corrosion films formed between grids and the adjacent positive active material. Further, since previous work has shown that the charge acceptance of both positive and negative electrodes depends to some extent on the composition of the grid alloy, other research is needed to determine the extent to which the presence of minor component grid metals influences charge acceptance at the charging rates and cell temperatures encountered in electric vehicle applications.

Thus, the effect of reduced antimony content on the physical and electrochemical properties of battery plates operating under traction duty

cycles requires detailed investigation. In such studies, electrochemical, optical and electron microscopic, and crystallographic techniques will provide valuable information on the processes taking place during charge/discharge cycling.

3.3. *Effect of lead-calcium grids*

The major maintenance operation of a lead-acid cell is the addition of water to make up that lost by electrolysis and self-discharge reactions. A major trend in the recent development of lead-acid systems has been the use of grids cast from lead-calcium alloys with some tin added to improve castability. The hydrogen overvoltage of lead-calcium alloys is about 0.2 V higher than that of lead-antimony alloys. This results in significant reductions in gassing rates at normal charging voltages. Furthermore, calcium does not migrate to the negative plate to cause self-discharge of the battery — a problem encountered with conventional systems using lead-antimony grids where antimony transport processes lead to a lowering of the hydrogen overpotential at the negative electrodes and an induced higher rate of self-discharge [see Section 2.2.3. above]. Lead-calcium grids also have better electrical conductivity than those made from lead-antimony alloys [67].

Although Pb-Ca “maintenance-free” batteries have been used for many years in standby and load-levelling applications (*e.g.*, for auxiliary power in submarines, telephone exchanges, etc.), and are now even marketed as automotive starter batteries (particularly in the U.S.A., *e.g.*, the Delco Remy Freedom Battery [90]), they have not yet been proven to be satisfactory for electric road vehicle propulsion. Apart from drossing problems in producing grids of the composition (0.03 - 0.09 wt.% Ca) required for good mechanical and electrochemical performance, the main drawback in the use of Pb-Ca grids lies in the reduced stability of the positive plate under the deep discharge conditions of electric vehicle service — there are only minor problems with Pb-Ca negative grids. The shorter cycle life of these positive plates is due to the poor adherence of the active material to the grid. This has been attributed to changes in the morphology of the PbO₂-active material [43], and to the build-up of a lead sulphate “barrier layer” at the grid/active material interface [88, 91, 92]. Further research on the metallurgy and electrochemical behaviour of the Pb-Ca system is urgently required before a maintenance-free lead-acid system will become economically viable for motive power applications.

3.4. *Effect of temperature*

Electric vehicle batteries are usually composed of modular cells tightly packed within a confined space in the lower part of the vehicle chassis. Under these conditions, the temperature in the battery can rise markedly during normal vehicle operation. Three possible sources of heat during charge are (1) electrochemical polarization (a function of electrode area, ageing effects and temperature); (2) ohmic resistance (a function of battery design — particularly resistance of grid and inter-cell connectors); and (3) entropy-

related thermodynamic thermal effects (*i.e.*, the cell reaction has a substantial entropy change that causes exothermic heating during charge). Increase of cell temperature may affect the physical and chemical properties of the electrodes, electrolyte, and other cell components. The charge and discharge characteristics, cell performance, and cell cycle life may also be affected by the variation of temperature. For example, the service life of lead-acid batteries has been found [93] to be greatly reduced by operation at a temperature higher than 45 °C, and above 55 °C a battery can fail in a few tens of cycles. Attempts have been made to avoid adverse temperature rise by fitting batteries with cooling systems (*e.g.*, heat exchangers) or by circulating the electrolyte of individual cells. However, equipment such as this reduces the specific energy of the system and introduces engineering problems.

Although the kinetics of the electrochemical reactions taking place in a lead-acid system have been studied in some detail for low temperature operation [94 - 97], relatively little attention has been paid to the effect on battery performance of working temperatures above 25 °C. Information on the high temperature performance of lead traction batteries is of vital importance to countries such as Australia, where temperatures may rise to 40 °C during summer months.

3.5. Effect of variable load in traction service

Although considerable effort has been directed towards improving the energy density and cycle life of the lead-acid battery, very little published information exists on the behaviour of lead-acid batteries operating under the duty cycles normal to electric vehicle service. In particular, detailed information is lacking on the relationship between battery capacity and rate of discharge with varying load, *i.e.*, continuous or pulsed high-rate discharge interrupted by (a) regenerative charging pulses during deceleration, (b) intervals at open circuit corresponding to temporary halts of the vehicle at traffic signals, and in road congestion, etc., and (c) boost charging during parking.

3.5.1. Pulsed discharge

Many on-the-road electric vehicles are fitted with solid-state switches (transistor or SCR) for stepless speed control. These electronic devices are turned on and off at a fairly high frequency (~ 300 Hz) and have the effect of chopping the constant voltage of the battery into a series of rectangular voltage pulses at the armature terminals of the motor. The average armature voltage is varied by changing the mark/space ratio of these pulses, *i.e.*, by either maintaining constant pulse repetition frequency and allowing the pulsewidth to vary, or by maintaining a constant pulse-width and varying the frequency, or by some combination of these two techniques. This method of regulating the energy delivered to the motor is known as "chopper control".

There is some controversy [98] over the behaviour of lead-acid batteries operated under intermittent, as opposed to continuous, constant-current discharge conditions. For example, Jayne obtained [99] a marked im-

provement in capacity from batteries subjected to high-speed pulse discharge, but Cataldo observed [100] no discernible increase in battery capacity at pulse discharge rates equivalent to those encountered in electric vehicle use. Furthermore, whereas Jayne found the capacity to be unaffected by interruptions to the discharge, Taylor and Siwek observed [101] an actual reduction in capacity when discharge was regularly broken by short periods at open circuit. The latter authors found increases in capacity only from batteries which were rested for long periods (minutes) between successive discharge pulses (*vide infra*). The increase in capacity of lead-acid batteries under such intermittent discharge conditions has been attributed [24, 99, 101, 102] to a capacity recuperation, or "recovery", phenomenon which occurs either during the pulse discharge itself [99] or during the rest periods between high-rate discharge pulses [101, 102]. This phenomenon is associated with better utilization of the active material by increased penetration of acid into the pores of the electrodes during the period at which the battery is at rest.

Studies of physicochemical phenomena such as crystal morphology, diffusion rates, reaction kinetics, conductivity, grid corrosion, temperature fluctuations, etc., are required to determine the effect of high-speed, high-current, pulsed discharge on battery capacity and life.

3.5.2. Regenerative braking

With regenerative braking, the kinetic energy of an electric vehicle can be used during deceleration, or when it is running down hill, to drive energy back into the battery from the traction motor, now acting as a generator. The consequent load on the motor exerts a useful braking force. However, the true benefits of this type of braking are still being debated. It has been suggested that the main advantage of regenerative braking is a gain in the range of a vehicle, *e.g.*, Kasama *et al.* have reported [103] that automatic field control of regenerative braking can improve the urban driving range of electric vehicles by 16%. A 6.6% range improvement was obtained [104] with the Copper Electric Town Car. On the other hand, it has been argued [105] that the real advantage of recovering kinetic energy is not to extend the vehicle range but to decrease maintenance costs by reducing wear on the conventional braking system, and by extending battery life through the use of shallower discharge cycles. Although it is generally held that regenerative braking is beneficial to battery life, detailed studies of its effect on the physical and electrochemical processes occurring within the battery are lacking and further research is needed to support this claim.

3.5.3. Rest periods

The batteries in an electric vehicle experience steady and continuous discharge conditions only if the vehicle is run without stops at a constant speed until all the available energy has been consumed. In practice, the batteries in a vehicle are subjected to intermittent discharge under the normal stop/start conditions of urban and, to a lesser extent, rural driving.

TABLE 1

Directions for research and development of lead-acid traction batteries

Aim	Development areas	Research areas
Improved energy density	1. Reduced battery weight and volume - lower weight container - low density grids - minimum battery hardware	1. Increased utilization of active materials - structural aspects, <i>e.g.</i> , particle morphology, porosity, surface area, electrical isolation - morphological changes on cycling - phase transformations, <i>e.g.</i> , α/β -PbO ₂ ratio - electrochemical inactivity
	2. Alternative cell configurations - improved grid design - more efficient plate geometry and arrangement - decreased internal resistance	2. Effect of dopants - plate additives, <i>e.g.</i> , expanders: BaSO ₄ , lignin - electrolyte additives, <i>e.g.</i> , H ₃ PO ₄ , Co ²⁺
Increased cycle life	3. Improved separator materials - reduced attack by active materials, metal dendrites, temperature	3. Stability of active material - cohesion and adhesion and particle morphology - electrolyte action, <i>e.g.</i> , erosion, dissolution - with new grid alloys
	4. Control of temperature - heat exchangers - circulating electrolyte	4. Effect of contaminants - dissolved grid metals, especially Sb - trace impurities in materials
	5. Control of electrolyte concentration - circulating electrolyte	5. Reduced grid corrosion - new grid alloys - effect of additives - control of self discharge
Reduced maintenance	6. Control of gas evolution	8. Decreased gassing
	7. Control of self-discharge	- new grid materials, <i>e.g.</i> , Pb-Ca-Sn alloys
	8. Charger optimization	9. Improved charge acceptance

Nevertheless, little is known concerning the effect on battery performance of rest periods comparable with those experienced under practical driving conditions, *e.g.*, temporary halts of the vehicle at traffic signals, and in road congestion, etc. Discharge-rest trials carried out in CSIRO Laboratories showed [24] that noticeable increases in lead-acid battery capacity (8 - 14%) occurred when the length of the rest period was greater than the discharge period.

4. Conclusion

In view of the current interest in electric vehicles as a means of conserving oil reserves and the fact that the lead-acid battery is the only system available for motive power, a high level of support for lead-acid battery research and development can be expected in the next few years. The directions to be taken are for increased energy density, greater cell lifetime (especially under deep cycling with variable load profile), and reduced maintenance requirements. To achieve this, continued effort is needed in those areas currently under investigation together with the initiation of new lines of research aimed at developing the capabilities of the lead-acid battery to meet the needs of electric road vehicles. The major research and development areas demanding attention are listed in Table 1. Such investigations should relate closely to the performance of batteries operating under actual service conditions in electric vehicles.

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