In pursuit of high specific energy, high specific power valve-regulated lead-acid batteries

P.T. Moseley[a,*], R.D. Prengaman[b]

[a]ILZRO/ALABC, P.O. Box 12036, Research Triangle Park, NC 27709-2036, USA
[b]R.S.R. Corporation, 2777 Stemmons Freeway, Suite 1800, Dallas, TX 75207, USA

Abstract

This paper seeks to consolidate the experiences gained from a group of projects carried out by the Advanced Lead-Acid Battery Consortium (ALABC) and aimed at achieving increases in the specific energy and the specific power of lead-acid batteries by developing grid designs of low weight. The use of corrosion-resistant alloys allows significant reductions in weight, but if this approach is taken too far problems arise with obtaining good adhesion of the active material to the grid. Some success has been achieved in the production of cells with improved specific energy and long life. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The design of valve-regulated lead-acid (VRLA) batteries often involves a compromise between specific energy and specific power. Batteries are generally designed to emphasize one of these parameters at the expense of the other. For mobile applications, however, the ideal battery would exhibit both high specific power and high specific energy. The most straightforward way to achieve good performance in both of these parameters is to remove surplus inactive lead from the design, for example by reducing the thickness of the grid, i.e. the current-collector. An additional motivation for the use of thin-plate designs of cell stems from the move to high-rate partial-state-of-charge (PSoC) operation in new automotive applications (36-/42-V powernet automobiles and hybrid electric vehicles). In this type of duty, the battery is required to accept high rates of recharge from the regenerative-braking process and the balance between the charge-consuming reactions (Eqs. (1)–(4)) may be disturbed.

Positive plate charging

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + HSO_4^- + 3H^+ + 2e^- \qquad (1)$$

Negative plate charging

$$PbSO_4 + H^+ + 2e^- \rightarrow Pb + HSO_4^- \qquad (2)$$

Oxygen evolution

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (3)$$

Hydrogen evolution

$$2H^+ + 2e^- \rightarrow H_2 \qquad (4)$$

In low-rate operations (i.e. up to $C_5/5$), both electrodes can be charged efficiently while they are in a PSoC condition, and reactions (1) and (2) proceed very much faster than reactions (3) and (4) until the cell approaches a full state-of-charge. At higher rates of charge, however, reactions (1) and (2) may become hindered by the limited rate of diffusion of HSO_4^- ions away from the reaction site (the diffusion coefficients of H^+ and HSO_4^- are 9.3×10^{-5} and 1.3×10^{-5} cm^2 s^{-1}, respectively). The applied potential can then rise, with the result that reactions (3) and (4) begin to proceed at a significant rate. Such inefficiency at higher rates of charge would not cause any problems in cycling regimes which involve a full recharge, but in PSoC duty the effects of the inefficiency are likely to be cumulative. Failure to recharge effectively results in the accumulation of lead sulfate on the plates.

Cell designs with thin layers of active material allow shorter mean diffusion distances, with the result that the failure mechanism outlined above for high-rate PSoC cycling should be less severe. It is logical that designs incorporating thin layers of active material should also employ thin grids.

* Corresponding author. Tel.: +1-919-361-4647; fax: +1-919-361-1957.
E-mail address: pmoseley@ilzro.org (P.T. Moseley).

The strategy of using grids of reduced thickness can be pursued to the point where corrosion just fails to compromise structural integrity or current-collection ability before an acceptable life is achieved. Since the rate of grid corrosion is the controlling factor, it is clear that the reduction of the mass of inactive material in the plate can be achieved by selection of a corrosion-resistant alloy with which to fabricate the grid. Several projects carried out by the Advanced Lead-Acid Battery Consortium (ALABC) have sought to build cells and batteries that employ grids of minimal thickness fabricated from alloys with high corrosion-resistance. Employment of this strategy for removing weight from the batteries, while leaving other aspects of design unchanged, is intended to result in simultaneous improvement in specific energy (Wh/kg) and specific power (W/kg), and to assist high-rate PSoC performance.

This paper sets out to describe how far this design approach has succeeded and to outline the factors that are presently limiting further progress.

2. Selection of grid alloy composition

The development of lead-acid batteries for future applications is focused on valve-regulated designs in which the grid alloys are antimony-free. Satisfactory mechanical properties are achieved by alloying the lead used in grid manufacture with small amounts of calcium and tin.

At low tin contents, the calcium precipitates rapidly behind moving grain boundaries as Pb_3Ca. At higher tin contents and below a calcium content of 0.08 wt.%, the metallurgy changes to give a continuous $(PbSn)_3Ca$ precipitate with a limiting composition of Sn_3Ca. This stoichiometry corresponds to a Sn:Ca weight percent ratio ('r' value) of 9:1. The value of this ratio has a profound influence on the evolution of the microstructure and the mechanical properties of the alloy [1].

The concentrations of calcium and tin also exercise a dramatic influence on the corrosion properties of the alloy. Within the range of calcium content normally considered for use in VRLA batteries (0.02–0.10 wt.%) an increase in the concentration of calcium results in an increase in the corrosion rate. Tin has the opposite effect, i.e. an increase in the tin content of the alloy within the range 0.5–1.5 wt.% brings about a decrease in the corrosion rate, see Fig. 1 [2]. Thus, it was found that the rate of corrosion of cast lead–calcium–tin alloys is a function of both the calcium and the tin contents [3].

The method used for grid manufacture also has a major influence on the manner in which a Pb–Ca–Sn alloy behaves in service. Rolled Pb–Ca–Sn alloys exhibit a very much finer grain structure which leads to enhanced mechanical properties in comparison with cast Pb–Ca–Sn alloys [4]. Alloys prepared in these two different fashions are also expected to display different corrosion characteristics. There is a more regular distribution of the active element in the rolled
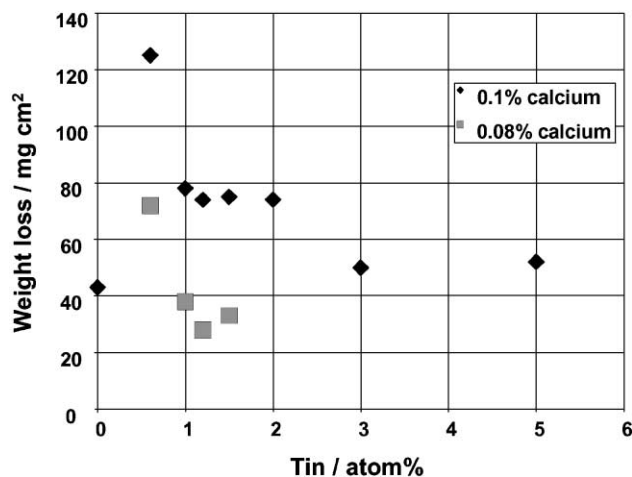

Fig. 1. Corrosion of Pb–Ca–Sn alloys after 5 days at 1500 mV in 5 M H_2SO_4 at 50 °C.

structure than in the cast one, while cast alloys show a tendency for tin enrichment at the grain boundaries [1].

Four separate projects within the ALABC technical programme examined different approaches to the use of corrosion-resistant alloys in lightweight grid designs. A range of alloy compositions with different Sn:Ca ratios, but all expected to offer low corrosion rates, was employed. In three cases, the grid alloy materials were rolled and in the fourth the alloy was pressure die-cast. Two of the cell designs used flat-plate positives, while the other two were variants of the tubular-plate design. Details of the cell designs and of their performance are given in the following sections.

3. Cell design and performance

3.1. Con-rolled grids I (AMC-008)

In an ambitious project [5] intended to miss no opportunity for exploiting low-corrosion alloys, a wide variety of cell designs was planned, including both AGM and gel types, and both con-rolled and expanded-metal grids. In order to facilitate comparisons with the other three projects, only the con-rolled AGM variant is described here. Particulars of the flat-plate design which was used are given in Table 1.

The specific energy achieved was less than expected assuming an active-material utilization similar to that in the control. Therefore, no cycling data were collected. Tear-down analysis appeared to show incipient separation of the positive active-material from the grid surface.

3.2. Con-rolled grids II (A-004.2)

This project [6] represented an attempt to overcome the factors that limited the performance of batteries in AMC-008.

Table 1
Grid parameters for project AMC-008 [5]

Parameter	Positive plate	Negative plate
Alloy (wt.%)	0.07 Ca, 1.6 Sn, 0.008 Al	0.07 Ca, 1.5 Sn, 0.008 Al
Grid thickness (mm)	0.51	0.43
Plate thickness (mm)	1.88	1.83
Weight reduction wrt control (%)	47	58
Constant-current discharge testing		
Specific energy (Wh kg^{-1}) 33.82 (14.8% increase wrt control)	–	–
Energy density (Wh l^{-1}) 73.43 (7.5% decrease wrt control)	–	–

Table 2
Grid parameters for project A-004.2 [6]

Parameters	Positive plate	Negative plate
Alloy (wt.%)	0.057 Ca, 1.287 Sn	0.057 Ca, 1.287 Sn
Grid thickness (mm)	0.7	0.7
Plate thickness (mm)	1.2	1.1
Constant-current discharge (C_5) cycling		
Cycle number	Capacity (Ah)	
1	99.3	
9	94.48	
15	84.4	

Fig. 2. Cycling performance of thin tubular plate cells.

The details of the flat-plate battery design which was employed are given in Table 2.

From the outset, the capacity was less than expected (100 Ah) and fell steadily with cycling. Cycling was discontinued at an early stage as the fundamental problems that limited capacity appeared not to have been overcome.

3.3. Fine spine tubular design (BE97-4085)

This project [7] sought to build on the robust characteristics of the tubular-plate positive design, and saved weight by reducing the diameter of the central spine. In fact, a spine with an elliptical section was used giving a maximum dimension of 2.24 mm and a minimum dimension of 1.20 mm. The spines were pressure die-cast. Design features are given in Table 3.

Thirteen-plate cells yielded specific energies of 33 Wh kg^{-1} in constant-current cycling at the 5-h rate and 29 Wh kg^{-1} in ECE 15L cycling. This represents a 60% improvement over the specific energy of standard technology.

Table 3
Design parameters for project BE97-4085 [7]

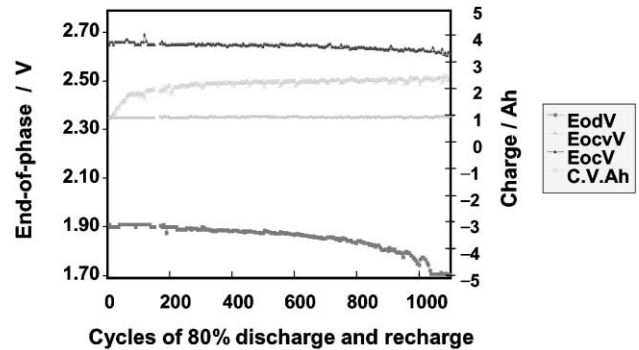| Parameter	Positive plate
Alloy (wt.%)	0.0.8−0.09 Ca, 1.2 Sn, 0.01−0.02 Al
Spine section; maximum, minimum (mm)	2.4, 1.20
Inside tube diameter; maximum, minimum (mm)	4.89, 2.70

The prototype cells achieved 1000 cycles (to 80% DoD) with a stable charge factor, see Fig. 2.

3.4. Stamped spine design (A-005.3)

This project [8] also utilized the tubular positive plate, but in this case the section of the spine was altered still further from circular. The plate was prepared by stamping from a rolled sheet of alloy to produce spines in the form of strips with cross-sectional dimensions of 0.75 mm × 10 mm. The spines are thus strips of metal rather than wires. The finished plate is shown as Fig. 5 in ref. [9]. Design features are given in Table 4.

The stamped, flat, tubular plate performed well in the initial three-plate tests. The utilization of positive active material was at a normal level initially, but increased through the first 100 (100% DoD) cycles to reach the outstanding value of 55%, Fig. 3. If this performance were to be translated into a full size battery it would provide a specific energy of 44–45 Wh kg^{-1}. Attempts to build full-size cells based on this design resulted in a far lower initial capacity

Table 4
Design parameters for project A-005.3 [8]

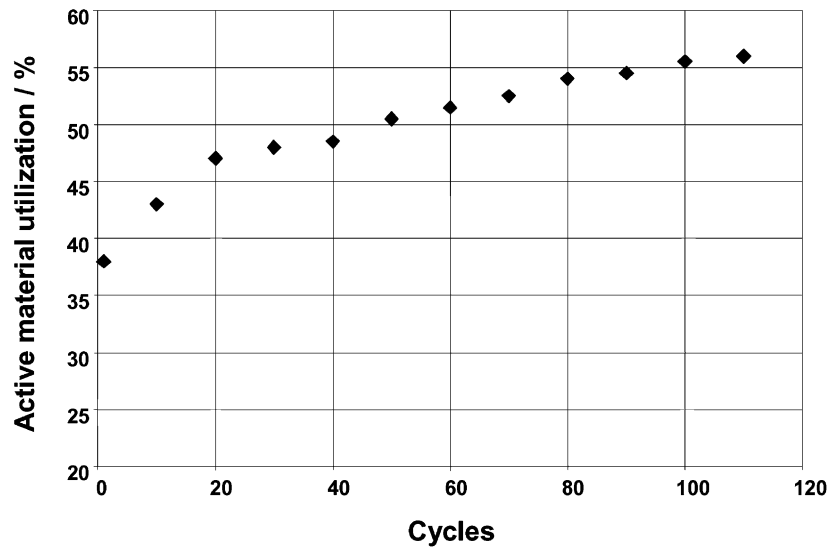| Parameter	Positive plate
Alloy (wt.%)	0.08−0.09 Ca, 1.4−1.5 Sn
Spine dimension 1 (mm)	0.7
Spine dimension 2 (mm)	10

Fig. 3. Cycling performance of stamped grid, tubular-plate cells.

and, upon tear-down analysis, evidence was found (see Fig. 4) of separation between the grid and the positive active material, and of localized corrosion on the flat faces of the spines. Failure to achieve a strong bond at this interface and the unexpected corrosion may have been due to a delay in the fabrication process; after the plates were pickled, they were stored for six months before use.

3.5. Comparison of performances

The four attempts to exploit alloys with corrosion-resistant compositions have met with varying success. Not surprisingly, none of the grid alloys used in the positive plates employed have shown any significant level of corrosion in service. Rather the problems that have arisen are characterized by early failure that appears to be attributable

Fig. 4. Cross-section through positive plate of stamped grid, tubular-plate cell that shows partial de-lamination of active material near grid. Current-collector section dimensions are approximately 0.7 mm × 10 mm.

to an incomplete adhesion between the positive active material and the positive grid surface. In other words, the grid alloy is too corrosion resistant.

It is interesting to note that Pavlov [9] reported the formation of lamellar $PbSO_4$ crystals at the active-mass-collecting-layer surface of a rolled Pb–Ca–Sn, die-cut, strap-grid tubular plate that indicated an incomplete bond between the grid and the active material. This work also showed that good cycle-life could be achieved with batteries containing this type of grid with a somewhat corrosion-resistant alloy, if high densities of positive active material were used [9].

If the corrosion-resistance of the alloy governs the four types of cell described here, then we might hope to find a correlation between the degree of success and the detailed stoichiometry of the alloy. Table 5 summarizes the behaviour of the four sets of cells and the 'r' factor (Sn:Ca ratio). The higher is the 'r' factor, the more difficult is it for the material to corrode and form a strong bond.

All the alloys used have 'r' factors greater than the value [10] that corresponds to the formation of intergranular precipitates of Sn_3Ca, but the two projects that showed low capacity from the outset employed con-rolled alloys with the highest two 'r' values. The two sets of cells with the lower 'r' ratios fared much better. That with a value of 14 and an alloy produced by pressure die-casting did not appear, in cell tests, to suffer from the loss of adhesion seen in some of the other cases. The intermediate case with an 'r' ratio of 17 and a grid stamped from a rolled sheet is interesting. The cell tests gave moderate capacity at the outset but improved progressively to yield high values after considerable cycling. One explanation of this behaviour might be that the cells initially suffer from poor adhesion, but that this defect is repairable by the action of cycling if adequate compression is maintained so that the high utilizations which the project was seeking are eventually achieved.

Table 5
Summary of projects which employ thin, corrosion-resistant grids, Sn:Ca ratios, and performance

Project	Sn:Ca ratio ('r' factor)	Manufacturing method	Performance of cells
AMC-008	20	Con-roll	Low initial capacity
A-004.2	23	Con-roll	Low initial capacity
BE97-4085	14	Die-cast	High capacity, good life
A-005.3	17	Stamped	High capacity only after considerable cycling

In the case of the battery testing with this design, it seems that the delay in the middle of the manufacturing process was sufficient to render the adhesion defect irretrievable.

There may be two lessons to be learned from the collection of results that have arisen from this set of four projects. The first would be that the alloy must be somewhat corrosion resistant in order not to be consumed in too short a life, but it must not be so corrosion resistant that it cannot form a strong adhesion between the positive active material and the grid. The Sn:Ca weight percent ratio maybe a useful guide to achieve the right balance, since it is the presence of too much surface tin beyond that necessary to form Sn_3Ca precipitates that invests the alloy with excessive corrosion resistance. Such a condition must be overcome by chemical methods that create oxide or corrosion layers on the grid surface to permit attachment of the active material.

In the presence of a high tin content, the PbO content of the corrosion layer is decreased, while the SnO_2 content is increased. Tin inhibits the oxidation of Pb [11] and may prevent adequate attachment of the active material during conventional curing.

The second lesson shows the importance of carrying the manufacturing process through to completion without interruption. The need to achieve adequate paste adhesion with a somewhat corrosion-resistant alloy probably causes the system to be less tolerant of departures from optimum manufacturing procedure.

4. Conclusions

It is feasible to achieve weight reductions in VRLA cells by means of corrosion-resistant alloys, but close attention must be paid to the ratio of the minor constituents so as not to encounter problems with adhesion of the active materials. Great care needs to be taken to optimize the manufacturing protocol in order to produce a robust structure which will allow access to all of the active material throughout life.

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