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The advanced lead–acid battery consortium—a worldwide cooperation brings rapid progress

Patrick T. Moseley *

ILZRO / ALABC, PO Box 12036, Research Triangle Park, NC 27709-2036, USA

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Abstract

The development of valve regulated lead–acid (VRLA) batteries has, in recent years, been carried forward rapidly through the collaborative efforts of a worldwide consortium of battery manufacturers and related elements of industry; the Advanced Lead–Acid Battery Consortium (ALABC). This group has set aside its competitive instincts in order to achieve acceptable goals in respect of those parameters that are key factors controlling the marketability of electric vehicles (EVs): cost, cycle life, specific energy, specific power and rate of recharge. This paper provides an overview of the principal themes of the ALABC research and development programme. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The Advanced Lead–Acid Battery Consortium (ALABC) represents a collaborative effort shared by the world's lead producers, battery manufacturers, component suppliers, and related industrial sectors pooling research and development resources to a common purpose. Formed in 1992, the consortium is carrying out a worldwide programme aimed at making electric vehicles (EVs) a viable element in the vehicular marketplace. From the outset, the membership of ALABC believed that substantial development of the lead–acid battery was possible and indeed was essential if EVs were to be launched successfully within the next few years. The introduction to the marketplace in late 1996 of General Motors' EV1, powered by lead–acid batteries, indicates that this assessment was probably correct.

Of course, the lead–acid battery has a long history dating back to the work of Gaston Planté in 1859. For the greater part of its development, the lead–acid battery has been presented with its plates immersed in a mobile electrolyte and provision has been made for gas produced during overcharge to be freely released into the external atmosphere. Flooded batteries designed for deep discharge duty are capable of delivering 35 W h kg^{-1} and cycle lives of 1000 but the gasses allowed to escape represent loss of water from the electrolyte which has to be replaced in a regular maintenance operation.

It was generally agreed at the start of the ALABC programme that for a lead–acid battery to be successful as an EV power source, it would have to be maintenance-free. It was thus necessary to develop a valve regulated form of the battery that is a significant departure from the flooded design.

The valve regulated lead–acid (VRLA) battery is a relatively new technology having been introduced in the 1970s. The VRLA battery is designed to operate an internal gas cycle in which oxygen evolved during overcharging of the positive electrode transfers through a gas space to the negative electrode where it is reduced. There are two alternative designs that provide the gas space—in one the electrolyte is held in an absorptive glass mat (AGM) separator and in the other the electrolyte is immobilised as a gel. The oxygen cycle depolarizes the negative electrode and reduces hydrogen evolution to very low levels. A pressure release valve is provided to ensure that even the residual low level of hydrogen production does not generate a high pressure.

In order to assist the reduction in gas production, lead antimony alloys were eliminated from the VRLA battery and early application of the system to deep discharge duty experienced rather short cycle life. The task for ALABC

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* Tel.: +1-919-361-4647; Fax: +1-919-361-1957

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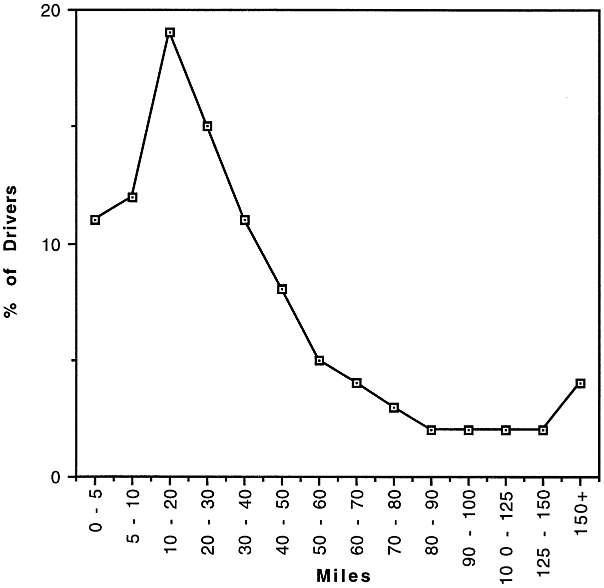

Fig. 1. Distribution of drivers by mileage in one day in 1995 [2].

therefore was initially to raise the performance of the VRLA battery to a level equivalent to that of the flooded design and then to make further improvements to meet a set of performance goals perceived to be required for EV duty.

Ever since the Air Resources Board in California proposed, at the beginning of the 1990s [1], to mandate the sale of large numbers of EVs by the major automobile manufacturers, there has been a vigorous debate over what are the essential features that an EV ought to offer in order to be acceptable to the majority of the purchasing public. Initial preoccupation with the sole issue of range-per-charge of the battery, and hence specific energy, has given way to a recognition that cost is a major issue and that range-per-charge is much less of a problem provided that it is possible to recharge the vehicle battery quickly. Indeed, it is clear that if it is not possible to recharge the vehicle battery quickly, then specific energies of even 2 or 3 times greater than that of lead–acid may not render the prospect of an EV sufficiently attractive to a potential purchaser.

A recent survey of the daily driving ranges of drivers in North America [2] (Fig. 1) shows that a range of 80 miles would satisfy the needs of 90% of drivers and that there is a residual fraction requiring a range of well over 150 miles, probably to 300 or 400. The message here is that a reasonable range-per-charge (around 100 miles), coupled with the ability to recharge quickly, will be far more useful than a range per charge of 150 miles followed by a period of hours when the vehicle is out of commission. A recent paper from the Ford Motor Company [3] proposes that: ‘‘fast charge technology can lead to increased capability while minimising cost. This synergism makes fast charge a particularly important consideration in the commercialisation of EVs.’’ Further: ‘‘although the energy stored on board the vehicle might only be sufficient for a 50 to 100 mile range, if the customer has the opportunity to quickly restore that energy supply, the number of miles per day can be significantly increased. If one or two fast charges are included in the daily operation of the EV, the range can be doubled or trebled, without the increased cost of additional batteries.’’

Goals selected for the ALABC technical programme were:

- Specific energy of 50 W h kg^{-1} to give a driving range of at least 100 miles
- Specific power of 150 W h kg^{-1}
- Cost of no more than US$150 per kW h
- Cycle life of at least 500
- Rapid recharge: 50% in 5 min and 80% in 15 min.

The rapid recharge parameter initially appeared to be a serious challenge since traditionally the lead–acid battery was believed to need a long, slow, charge [4] in order to minimise the effects of gassing and temperature rise. However, fast charging was seen as a tactical necessity for the reasons set out above.

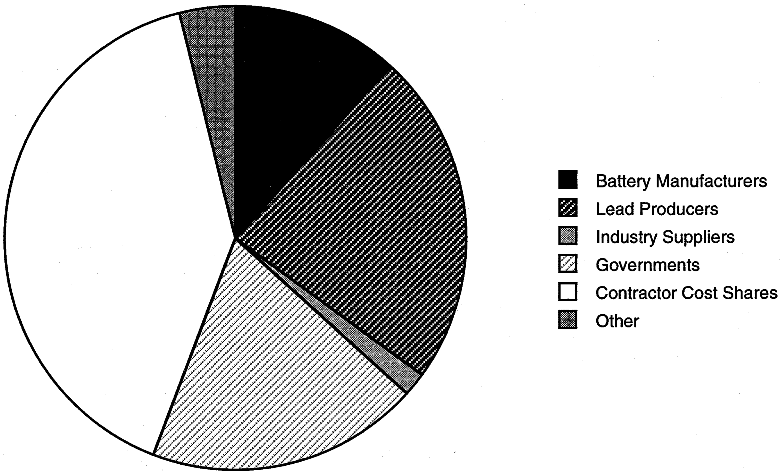

Fig. 2. Advanced Lead–Acid Battery Consortium. Sources of income for second phase (1997–199).

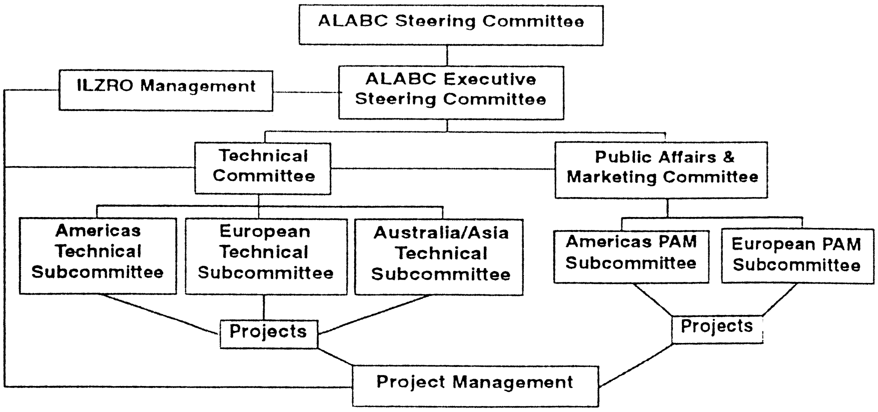

Fig. 3. Advanced Lead–Acid Battery Consortium. Committee structure.

The consortium programme dedicated to achieving the required development has addressed projects across a broad front in laboratories, factories, and research institutes around the world. Some components of the consortium's programme in the US have been supported by the U.S. Department of Transportation, Federal Transit Administration, and the programme in Europe has been co-funded by the European Commission through its Brite-Euram Programme. The present phase of the Consortium's programme is due to run from 1997 through 1999 and is funded at US$15 million deriving from the several sources shown in Fig. 2. The membership currently stands at 60, hailing from 13 separate countries, and is carrying out projects ranging from materials development in order to achieve greater active material utilisation and to identify improved alloys for current collectors, through advanced recharge algorithms, to full-scale EV demonstrations. Accountability is maintained through a system of committee approvals for all project work. The ALABC committee structure is shown in Fig. 3, where it will be seen that management of the ALABC is the responsibility of the International Lead Zinc Research Organisation. The results of the ALABC's technical programme have been a gratifying demonstration of the value of eliminating duplicated effort in order to drive technology forward at the maximum rate. During the 1990s, the performance of the valve regulated lead–acid battery developed for EVs has advanced beyond recognition.

2. Technical progress

Although five separate parameters were identified as bearing crucially upon the suitability of a battery for EV duty, both cost and the specific power performance of VRLA batteries were perceived to be within the desired range from the outset. The technical programme has therefore focused on the remaining three factors: specific energy, cycle life, and rapid recharge rate.

2.1. Specific energy

Technical programme has addressed the need to increase specific energy—without reducing life—from two directions: reduction of the mass of grid/current collector material in the battery and increase in the utilisation of the active masses.

The reduction of mass has been facilitated by the identification [5] of lead calcium alloys with high tin content (up to 1-1/2%) that exhibit improved corrosion resistance and creep strength as compared with the lead calcium alloys that had been used previously. These alloys allowed the use of thinner, lighter grids without sacrificing creep strength or life. Three ALABC programmes seek to exploit the use of the high tin alloys in the form of lightweight grids: one in a flat plate design, one in a tubular design (with finer diameter spines than usual), and one in a tubular design with strap-shaped rather than circular cross-section spines. The signs are that all three designs will result in improved specific energy. Early results from the strap-shaped tubular design being produced at Yuasa have yielded positive active material utilisation of over 50% at the 3-h rate and the projected specific energy for the system is 42 W h kg^{-1}.

The second part of the drive toward higher specific energy aims to achieve yet higher active material utilisation through the incorporation of additives, particularly in the positive plate. This development is being carried out at the Trojan Battery Company in California, where the practical programme is being supported by a modelling study at the University of Idaho, and at CSIRO in Australia. Most promising of the Trojan additives appears to be a porous polypropylene where both predictive modelling and the experimental data indicate specific energy enhanced by over 10% compared with cells containing no additives. The additives appear to be most effective at high rates, which is consistent with their function as an acid supply enhancer [6], and their effectiveness is sustained over hundreds of cycles.

When the lightweight grids and the additives are deployed in a single design, it is to be expected that the overall specific energy will approach the ALABC target figure.

2.2. Cycle life

When VRLA batteries were first adopted for deep cycle use, it was found that their capacity fell from its initial value to an unacceptable level within a few tens of cycles. This phenomenon was dubbed ‘premature capacity loss’ and overcoming this shortcoming has been a major task for the ALABC. Several factors probably contribute to the early loss of capacity. First, the elimination of antimony from the grid alloys resulted in grids with very poor creep strength. As a result, the growth of a corrosion layer on the grid with a larger molar volume than the metal from which it derived tended to force the grids to expand in the plane of the plate. This tendency was resisted well by antimony-containing alloys but not by the lead calcium alloys that replaced them in VRLA batteries. The expansion of the grids allowed loss of cohesion within the positive active mass and capacity dropped as a result. The solution to this part of the problem has been the adoption of the high tin alloys mentioned earlier since these exhibit much higher creep strength combined with lower corrosion rates, and grids of high tin alloys do not grow to any significant degree.

The second factor contributing to capacity loss operates within the active masses. It has been recognized for a long time that continuous deep cycling encourages the active material to swell in a direction perpendicular to the grid. This swelling causes progressive loss of interparticle contact and, as an increasing fraction of the active material becomes isolated from the current collector, so the capacity falls. In an elegant experimental programme at the Technical University of Brno [7], it was shown that the loss of capacity exactly follows the increase in resistance of the positive active mass. Initially it was thought that the tendency to swell was due to the large increase in molar volume that accompanies the discharge of both PbO_2 and Pb to form $PbSO_4$. However, more recently, workers at both the University of Kassel [8,9] and the Technical University of Brno [10] (Fig. 4) have shown that, at least under some sets of conditions, the tendency to swell occurs during charge rather than discharge. In any event, if capacity is to be maintained, the tendency to swell must be resisted and this is accomplished simply by constraining the stack in the direction perpendicular to the plane of the plates with an adequate force. The increase of a compressive force from 8 kPa to 40 kPa was shown [11] to be sufficient to increase cycle life from around 200 to over 700 by a team from CSIRO.

An important factor in avoiding plate swelling is the provision of adequate separators that do not collapse and release the pressure that is applied to the stacks. A variety of different separator/compression systems is currently under development to ensure that this aspect of VRLA design is adequately provided.

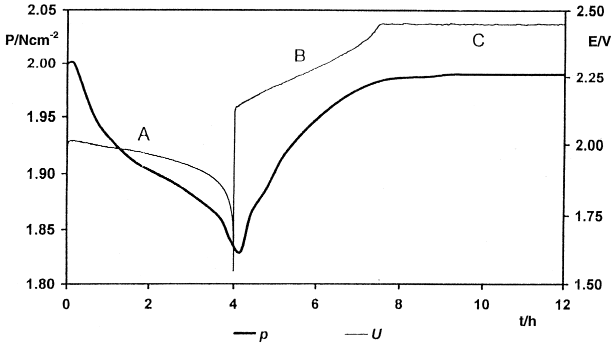

Fig. 4. Time-dependence of cell voltage (fine line) and pressure (bold line) during discharge (A) and during recharge (B + C) of cell. Pressure in the stack falls during discharge and rises during recharge [10].

A further crucial step towards the achievement of good cycle life is to ensure that a correct recharge regime is employed. It is becoming apparent that this is a more exacting demand for VRLA than for flooded lead–acid batteries. If insufficient recharge is applied, then of course, capacity walk-down is rapid. However, because the correct operation of VRLA batteries involves the optimum (but perhaps minimal) operation of the internal oxygen cycle, the accurate management of the battery around top of charge is vital both in terms of how much charge is returned and in terms of the rate at which charge is returned.

One final feature bearing on cycle life is beginning to emerge: as the problems of the positive plate are beginning to be overcome, so the negative plate is becoming the limiting factor. The problems of a negative plate relate to loss of surface area since, after a large number of cycles, the expander material becomes less effective. In order to address this issue, ALABC programmes are in progress both in the US and in Europe to identify improved sets of expander materials that should be able to endure for a greater cycle life.

2.3. Fast charging

Despite the predictions of the A h rule [4], the pursuit of fast charging of the lead–acid battery met with early success. A survey of some 30 commercially available lead–acid batteries was carried out by the Cominco research team and showed that all of them could be recharged to 50% in 5 min and 80% in 15 min [12] as required by the ALABC targets. Indeed, most of the batteries could be repeatedly recharged at these high rates and it appeared that VRLA batteries performed better in this regime than did flooded SLI batteries.

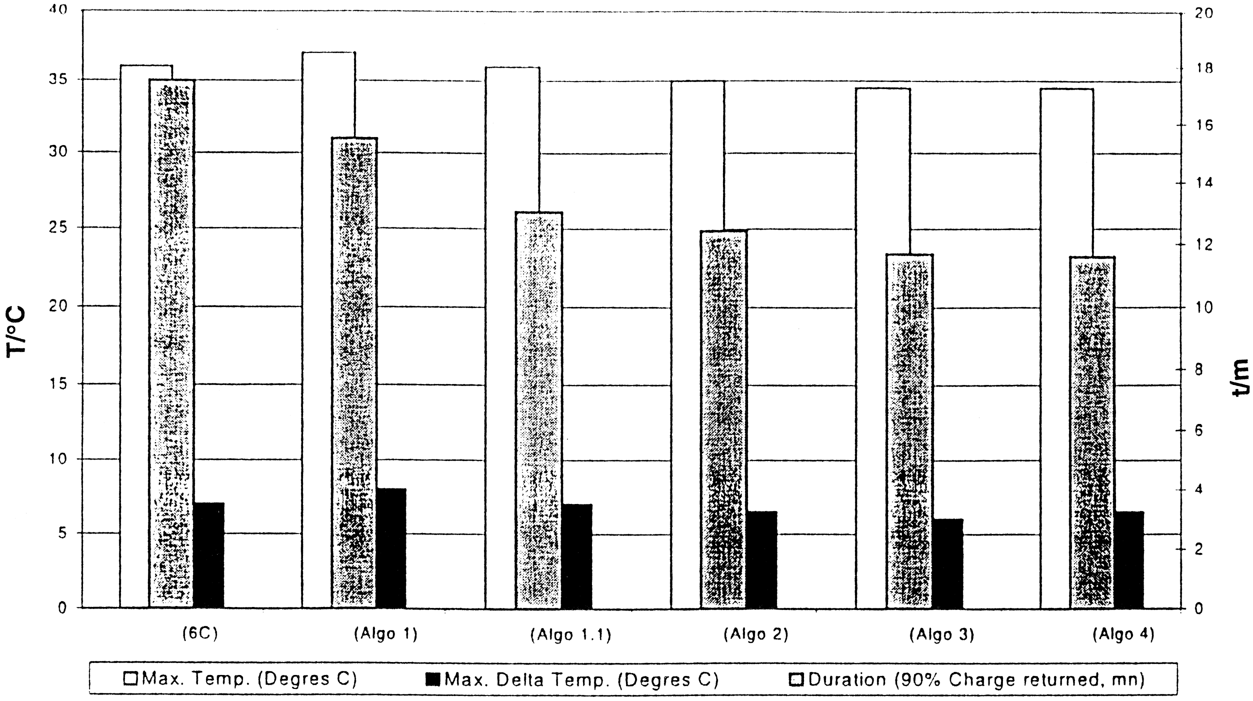

Fig. 5. Variation of maximum temperature, module temperature gradient, and time to 90% charge return for a pack of 14, 38 A h, Hawker Energy batteries charged with different charge algorithms. The left-hand bar set is a control showing the figures for a commercially available charge algorithm.

During this work, it became increasingly evident that far from being deleterious, the fast charging that these batteries were receiving actually led to an enhanced performance when compared to their duty in a normal cycling regime. This effect was most dramatically demonstrated in the test during which two samples of the spirally wound 12-V battery were cycled, one with a conventional charge regime and one with a rapid recharge [13]. In the conventional scheme, the battery was charged for 10 h with a current limit of 10 A and deep discharged at the 2 h rate to 11.6 V with a discharge to 10.5 V every 50 cycles and fully charged for 3 cycles before continuing the routine. The other battery was charged for 15 min each cycle with a maximum current level of 250 A (a 5 C rate) and then discharged at the 2-h rate to 11.6 V and again every 5 rapid charge cycles was followed by a 4-h charge with a current limit of 100 A and after every 50 cycles the battery was discharged to 10.5 V. The results of this test were, in the fast charge case, benefits to both the charge efficiency and the number of cycles achieved [13]. After 250 cycles, the conventional charging test was completed because the battery was no longer able to return 80% of its initial capacity. By contrast, the fast charged battery was still healthy after 900 cycles. Because of the difference in the cycling regime in the two cases, a direct comparison in terms of the two cycles is imperfect but there is no doubt that the number of ampere hours stored and returned during the useful life has been over three times greater in the fast charge case than in the conventional charging case [13].

Fast charging has been extended beyond monoblocks to complete battery packs, both on the bench and in on-the-road vehicles. Fig. 5 shows that, with the appropriate charge algorithm, it is possible to recharge a pack of 14, 38 A h, Hawker Energy batteries to 90% charge return in under 12 min.

It is clearly important to understand the origin of the improvement that is seen when the battery is charged quickly. It may be that the charging cycle adopted provides more protection to the active material at top of charge than does the conventional case. This possibility will undoubtedly be pursued in further research.

3. Conclusions

During the programme to date, the ALABC has identified the origins of the processes that were causing the life of VRLA batteries to be shorter than those of the flooded battery from which it was derived and has demonstrated means of correcting these. In addition, it has been shown that lead–acid batteries can be rapidly recharged so that daily ranges can be very much greater than the range-per-charge. During the course of the 1990s, the VRLA battery developed for EVs has advanced in cycle life by a factor of about 10, and in specific energy by a factor approaching two, and has reduced recharge time by an order of magnitude.

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