

## Collaboration in research — the ALABC:Brite-EuRam lead/acid electric-vehicle battery project

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### Abstract

As part of its programme, the Advanced Lead–Acid Battery Consortium (ALABC) has a US \$4.4 million project with European Community funding (under the Brite-EuRam programme). This has been initiated by the European members of the ALABC. The background and structure of the four-year project are described, together with some of the research results that have been obtained during the first two years of the work. While many of the individual tasks contain battery test programmes to evaluate research results, the ultimate aim of the project is to bring together the various developments into prototype advanced lead/acid batteries for electric-vehicle applications. These will be bench-tested by Eucar, the joint research body of the European motor industry.

**Keywords:** ALABC; Lead/acid batteries; Electric vehicles; Conductive additives; Electro-osmotic promoters; Phosphoric acid; Separators; Lead alloys; Curing; Absorptive glass-mat separators; Formation

### 1. Background

The original research programme of the Advanced Lead–Acid Battery Consortium (ALABC) envisaged the expenditure of US \$19.3 million raised, roughly equally, from industry and from government sources. It was not surprising, therefore, that the European membership suggested applying for funding from sources amongst the various research funds sponsored by the European Commission (EC).

Initial contacts were made with the Commission through Metaleurop and, from these discussions, it appeared that the most promising option was through the Brite-EuRam (Industrial Materials and Technologies) Programme, rather than through the more energy-related initiatives such as the Joule or Thermie Programmes. From the ALABC's point of view, however, there were difficulties to be overcome. To be eligible for funding, membership of EC-sponsored research programmes was limited to organizations based within the European Community and tie industry funding had to be from European sources. Under the ALABC membership rules, subscriptions were paid to the International Lead Zinc Research Organization, Inc. (ILZRO) in the USA, who administered the overall programme. Not surprisingly, ILZRO were unwilling to remit these funds back to the European members, unless they were convinced that the rest of the ALABC members would have access to the results of any research performed under any Brite-EuRam programme —

the ALABC was set up to be run as an open programme with full dissipation of all research findings to its members.

Following further correspondence with the Commission, it was ascertained that, should a consortium granted Community funding unanimously assent to share or exchange results with other parties, they were free to do so on notifying the Commission of their intentions. On this basis, ILZRO agreed to release funds in the event of a successful application.

Work on the proposal to the EC started in Oct. 1992. Some 30 projects were solicited by the European member companies of the ALABC. These projects had to be assessed not solely on scientific merit, but also on eligibility under EC rules. In order to maximize funding, the final proposal did not include any work from organizations outside the Community. Some of these other proposals did in fact get support from the ALABC itself and, therefore, were able to start earlier. In the end, eight proposals were chosen as tasks within the final submission to the EC. In addition, during this time, contacts had been made with the Joint Research Committee of the European Motor Industry (now Eucar) and this body agreed to participate in an additional task to test battery variants developed as a result of the combined research. Finally, two other tasks were added to the Brite-EuRam programme: one to consider battery recycling (to ensure that no hindrances to the proven recyclability of the lead/acid battery

Table 1  
Members of ALABC Brite-EuRam Consortium

Company	Country	Sponsor	Research
AEA Technology	UK		✓
Bitrode Ltd.	UK	✓	
Britannia Refined Metals	UK	✓	
CMP Batteries Ltd.	UK	✓	✓
Cookson Entek Ltd.	UK	✓	✓
Digatron	Germany	✓	
ENSC de Toulouse	France		✓
Enthoven and Son	UK	✓	
FIAMM SpA	Italy	✓	✓
Hagen Batterie AG	Germany	✓	✓
Hawker Batteries Ltd.	UK	✓	✓
Metaleurop Recherche	France	✓	✓
Renault (Eucar)	France	✓	✓
Rheinische Zink	Germany	✓	
University of Kassel	Germany		✓
University of Nancy	France		✓
VARTA Batterie AG	Germany	✓	✓
ZSW	Germany		✓

were introduced as a result of the research), the other to take care of the project coordination.

The author was commissioned by the members to draft the proposal. Great care was taken to ensure that this was done in strict accordance with the EC rules on eligibility; in earlier calls for proposals, some 20% of the applications failed because they did not meet these criteria. Close contact was established with the Commission during the drafting process, and this proved to be very valuable. The Commission considered the consortium to be very strong as it consisted of battery companies, suppliers to these companies, and the end-users of the batteries. In all, the final consortium was made up of 18 organizations, of whom 13 are now contributors of funds. The members of the consortium and their respective roles are identified in Table 1.

The project proposal was submitted on 26 Feb. 1993 and news of the success of the proposal was received in July 1993. Following contract negotiations, the project commenced on 1 Jan. 1994 with funds of ECU 3.78 million (US \$ 4.4 million). Brite-EuRam contributed ECU 1.75 million (US \$ 2.02 million) of these funds. As no one member company was willing to act as Project Coordinator, a European Economic Interest Group, the EALABC (EEIG), was set up to undertake this function. In essence, this body has the same legal standing as a company, but can be established without capital. At its first meeting, the EALABC (EEIG) passed the resolution to share all information with the ALABC and informed the EC accordingly. This has enabled the flow of information to proceed as planned.

## 2. Project structure

The work schedule of the Brite-EuRam Project (No. BE 7297) envisaged the tasks to be grouped into five categories of which three would be carried out concurrently over the first three years of the programme. This is illustrated in Fig. 1. Following evaluation of the results from these tasks, battery cells and modules will be built to incorporate the improvements, either separately or in combination, for laboratory bench-testing, in conjunction with Eucar, during the fourth year. Concurrent with this testing, the implications for recycling of advanced battery designs will be evaluated. This will include recovery of any high-value materials that may be added to the battery to improve performance.

The principal research tasks were planned within five broad categories. These, together with the organizations carrying out the work (the first-named organization is the task manager), are as follows.

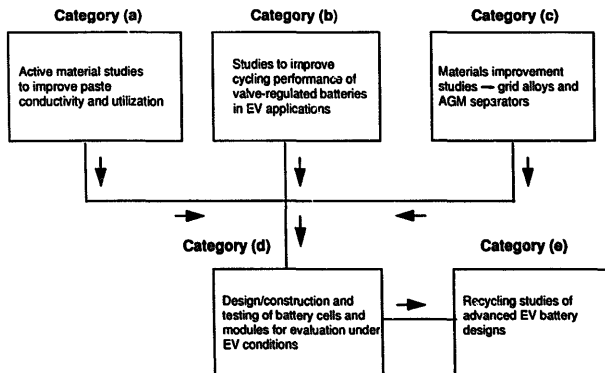


Fig. 1. Flow diagram of ALABC:Brite-EuRam lead/acid electric-vehicle project.

### 2.1. Category (a)

Task 1: The effect of electronically conducting additives to the positive active-material on the high-rate performance of lead/acid cells; Varta/ZSW.

Task 2: The electro-osmotic capacity enhancement of lead/acid electric-vehicle batteries; CMP Batteries/AEA Technology.

Task 3: The evaluation of positive active-material enhancement by the addition of conducting titanium sub-oxides in pasted-plate batteries; Hawker Batteries.

### 2.2. Category (b)

Task 4: The improvement of cycle life under electric-vehicle discharge and recharge conditions; Varta/University of Kassel.

Task 5: The influence of curing and formation parameters on cycling behaviour at high discharge rates; Hagen.

Task 7: Studies into the combined effect of the rate of discharge and the depth-of-discharge on the cycle life of lead/acid electric-vehicle batteries; CMP (Sonnenschein)/ZSW.

### 2.3. Category (c)

Task 6: Separator optimization for valve-regulated lead/acid batteries for electric-vehicle applications; Hawker Batteries/Cookson Entek.

Task 8: Examination of the effects of alloying elements on the mechanical properties, corrosion resistance and the passivation of the positive grid; Metaleurop Recherche/University of Nancy/CMP (CEAC)/ENSC de Toulouse.

### 2.4. Category (d)

Task 9: Manufacture and bench-testing of prototype maintenance-free advanced lead/acid batteries for electric-vehicle applications; FIAMM/Renault (Eucar).

### 2.5. Category (e)

Task 10: Development of recycling technology for advanced lead/acid electric-vehicle batteries; Hawker Batteries.

### 2.6. Conclusions

The main thrust of the programme of research is to improve battery performance by increasing paste utilization and conductivity. In addition, specific initiatives are aimed at improving battery life, by investigation of the phenomenon of premature capacity loss (PCL) and other detrimental factors.

### 3. Project progress

Most of the tasks started according to schedule and have progressed largely according to the work programmes agreed,

with the exception of Task 3. It was agreed that the start of this particular piece of work should await the outcome of another ALABC Project (AMC-002) in which titanium sub-oxide additions were being tried in tubular plates. In the event, it proved impossible to obtain high-quality grades of the sub-oxide, i.e. grades that consisted principally of the highest conductivity compound, and, accordingly, the test results were disappointing. Thus, it was agreed not to proceed with this work and to submit an alternative project to the EC for approval. This aims to optimize the fast-charging of electric-vehicle batteries and is based upon the use of a novel on-board charging system developed by Wavedriver in the UK. This equipment consists of a compact power-coupler that functions both as the vehicle drive-controller (converts d.c. power from the battery into a.c. for the traction motor) and as the charger (accepts a.c. line input and provides d.c. for recharging at high rates). The combined functions of the power coupler provide an economic approach to fast-charging; rates of up to 100 kW are potentially available. If successful, this would enable opportunity charging to be performed with a much reduced infrastructure cost. The Wavedriver system also incorporates power quality enhancement features that limit the impact on the electrical grid when the unit is operating in the charging mode. Permission for the change in research was granted by the EC and work started during May 1995. The new task is also under the management of Hawker Batteries.

With the Brite-EuRam Project now approaching its half-way stage, it is appropriate to review some of the progress made to date. This is done on a task-by-task basis.

#### 3.1. Task 1: Conductive additives

The concept behind this work is to try and increase the utilization of the positive active-mass in lead/acid cells, by trying to minimize the electrical isolation of portions of lead dioxide by the discharge product, lead sulfate. The strategy is to add an electronically conductive, chemically and electrochemically inert matrix to the active mass in order to assist current flow during discharge, and thus to increase the total amount of lead dioxide that participates in the discharge process.

A screening process has been carried out to identify potentially suitable additives. This has involved examination of properties such as conductivity, influence on oxygen evolution, and stability in the battery environment. Several possible dopants have been identified, i.e. four titanium compounds ( $\text{TiSi}_2$ ,  $\text{TiN}$ ,  $\text{TiC}$  and  $\text{TiB}_2$ ), tin oxide (doped with antimony oxide), and carbon fibres coated with doped tin oxide (the coating protects the carbon fibre from oxidation in the battery). Various methods of applying a stable coating to the fibres have been investigated and one capable of scale-up has been identified.

The addition of conductive materials may help to improve the positive electrode performance whenever the potential drop in the active material is appreciable, for example:

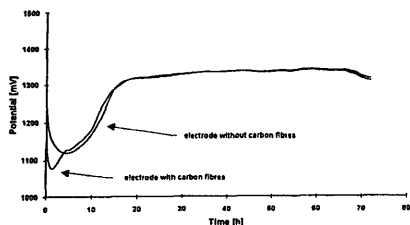


Fig. 2. Formation curves of model electrodes with and without carbon fibres.

- at high-rate discharge (high current), especially towards the end of discharge
- at high active-material utilization (high active-material resistance)
- with inhomogeneities in the material, e.g. cracks or softening that lead to high resistance

It is the goal to replace volume units of lead dioxide particles which would be present, even at the end of discharge in the absence of a conductive additive, by volume units of conductive additive. The degree of this replacement has to be chosen such that the conductivity is improved, but not at the expense of so much potentially available active material to cancel out this favourable effect. Therefore, maximum contribution to conductivity has to be obtained by a minimum volume of additive.

Some initial experimental work has been performed with the carbon fibres; the formation curves for electrodes with and without carbon fibres are shown in Fig. 2. At the beginning of formation, the potential of the electrodes is lower if carbon fibres have been added to the active mass. This correlates with results found in Task 4 (see below) which show that on formation of tribasic lead sulfate (3BS) material, it takes appreciable time for a conducting  $PbO_2$  network to become established all over the electrode pellet. By contrast, with an additive (as in these experiments) the conductive network is formed very early. Results to date have not shown any significant enhancement of capacity with carbon fibres. This could be due, however, to the grid design which had very small pellets and an already high active-material utilization, namely, 55% of theoretical. Studies are to be performed on more typical grid designs, where the limiting role of the mass conductivity should be more relevant.

### 3.2. Task 2: Electro-osmotic capacity enhancement

The discharge performance of lead/acid positive plates is limited, at high rates of discharge, by the diffusion of sulfuric acid. It is thought possible that the capacity may be improved by electro-osmotic irrigation of the (porous) plate. Previous work at AEA Harwell in the UK has shown that sulfonated polyvinylidene difluoride (SPVDF) can enhance acid availability within the positive plates of lead/acid batteries by electro-osmotic pumping. The latter is induced by the passage

of the discharge current and is driven by the high zeta potential of SPVDF. This effect was demonstrated by both dip-cell determination of the flow rates as a function of current and by measurement of the rate of electrolyte displaced from a pair of back-to-back positive plates. Initially, attempts were made to apply the SPVDF asymmetrically to the positive plate by spraying it dissolved in a solvent. This proved impractical, however, due to persistent blocking of the spray nozzle. A simple painting technique was then tried on an unformed plate, followed by air drying, but these plates returned lower capacities than untreated plates. A number of causes may be responsible for the inferior performance, e.g. local pore blockage at the surface of the plate that arises from poor penetration of the solvent and the hydrophobic nature of the air-dried coatings. Pore blockage will result in an occlusion of active material and an increase in resistance, while hydrophobic coatings will inhibit the effectiveness of wetting and, thus, the effectiveness of any electro-osmotic effect. Subsequent single-plate tests, with SPVDF applied in an improved fashion, have shown a 15% enhancement in capacity at the  $C_5/5$  rate after the first five cycles.

Earlier work at AEA Harwell had used a different solvent and Fig. 3 shows results obtained when experiments reverted to the use of this solvent. Plate number A70 was discharged at the  $C_5/5$  rate, washed in water, and then dried. It was then treated with SPVDF in the solvent prior to immersion in water to precipitate the SPVDF. The plate was initially cycled at  $C_5/5$  rate for seven cycles before the discharge current was raised to 8.9 A. A comparison between treated and untreated plates between cycles 5 and 7 showed that the former returned a capacity of 23.8 to 24.7 Ah compared with 19 to 21.3 Ah for the latter. This is a mean enhancement of 20% in capacity. At the higher discharge rate from cycle 8, the capacity dropped to 14.6 Ah for the treated plate and 14.1 Ah for the untreated. The latter fell progressively to less than 6 Ah at 15 cycles, while the treated plate sustained a capacity of 12-15 Ah between cycles 15-58. This stable, longer life was assisted by the low initial cycles because if cycling of the treated plates was initiated at 8.9 A, the capacity fell to between 7.5-10.7 Ah between cycles 15-28 (plate A71). It is interesting, and unexpected, that treatment with SPVDF seems to prolong plate life in the unsupported condition. The reasons for this

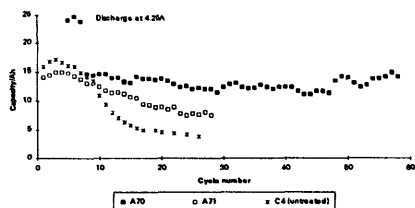


Fig. 3. Capacity of single plates, with and without SPVDF, at the  $C_5/2.4$  rate. Single-plate cycling at 8.9 A after SPVDF treatment of discharged plates.

are not yet clear but may be associated with the concentration and distribution of SPVDF in the plate.

More recently, the focus of the work has shifted from the fabrication of test plates incorporating SPVDF and their subsequent cycling, to the investigation of the effects of the preparation and impregnation methods on the wetting and electro-osmotic pumping behaviour of both SPVDF and an alternative additive. In addition, other means of incorporation of the promoter into the paste itself, or elsewhere in the battery, are being investigated.

### 3.3. Task 3: On-board fast-charging with Wavedriver power coupler

As has been indicated earlier, this is a replacement task and has only recently been initiated. Genesis G120 batteries from Hawker have been tested and delivered to Wavedriver and initial charging profiles have been circulated to consortium members for comment. The work will be carried out on a 312 V ( $26 \times 12$  V) string of batteries. Equipment for the testing is near to completion and experimental work should start in the third-quarter of 1995.

### 3.4. Task 4: Improvement of cycle life

Changes in the positive active-material structure during cycling induce changes in plate performance and may limit cycle life. The type and degree of these changes depend on the operating conditions of the battery, as well as on construction parameters such as electrode thickness, mass porosity, electrolyte concentration, grid alloy, etc. Discharge and recharge current rates, depth-of-discharge and rest times are some of the crucial operational parameters. High-rate discharge pulses and low recharge rates, which are typical for EV applications, seem to be unfavourable for cycle life.

To investigate the influence of different recharge conditions, such as different initial recharge current densities, and to compare constant-current/constant-voltage (CC-CV) with constant-current (CC) regimes, test series have been carried out with EV monobloc batteries and with single cells. The single cells are used to investigate half-cell potentials, and have strict temperature control. Two types of 6 V monobloc EV batteries have been investigated; both with pasted plates (Barton-pot oxide, 3BS curing), lead-calcium-tin positive grid alloy, and gelled electrolyte containing 5.1 M  $\text{H}_2\text{SO}_4$ . In one of the batteries, the electrolyte was doped with  $30 \text{ g l}^{-1}$  of phosphoric acid.

Results to date have indicated that cells without phosphoric acid yield lower capacity as the initial recharge current is lowered. This is true with both CC-CV and CV recharge regimes. The CC recharge is found to yield better performance than the CC-CV method. On the other hand, with cells of the same design, but with phosphoric acid additive, the influence of initial recharge current density is negligible.

It has been the belief that addition of phosphoric acid is liable to reduce discharge capacity, but data supporting this

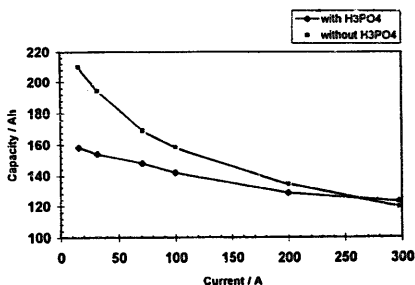


Fig. 4. Discharge capacity as a function of discharge rate for cells with and without  $\text{H}_3\text{PO}_4$ .

has been obtained at the  $C_5/5$  rate. In Task 4 work, however, it was noticed that for identical batteries (both with and without the  $\text{H}_3\text{PO}_4$  additive), a somewhat higher capacity was obtained with the variant containing the additive at the usual discharge rate employed during these studies, i.e. at  $C_{1.5}/1.5$ . These results, while contradictory at first glance, could be explained if the addition of phosphoric acid to the electrolyte influenced the rate capability, i.e. have different influences on capacity at the high and low discharge rate. To investigate this, the rate capabilities of cells which had done some 200 cycles were tested; the results are shown in Fig. 4. It is obvious that the addition of phosphoric acid reduces the discharge-rate dependency of the capacity markedly; it gives a lower capacity at low discharge rates, but higher capacity at very high rates. Therefore, the pulse discharge capacity of the battery can be improved, even if capacity at the  $C_5/5$  rate is reduced.

At the University of Kassel, work is being carried out on the in situ measurement, in a specially designed test cell, of positive active-mass conductivity and grid/mass interface conductivity. With the same equipment, forces originating from the active material are recorded. Experimental parameters are discharge and recharge conditions, as well as current-collector alloys, active-mass formulations, i.e. 3BS or tetrabasic lead sulfate (4BS) curing, and additives to the electrolyte. Results indicate that the forces arising during the course of formation and cycling of the positive active-mass induce internal pressure, or changes of pressure, of the order of 1 bar. The positive mass formed from 3BS shows less (expanding) pressure during formation than does that formed from 4BS. During cycling, however, the situation is reversed: the changes of pressure within one discharge/recharge cycle are greater with mass that originates from 3BS. The pressure is inwardly oriented during discharge (shrinkage), but outwardly oriented (expansion) during recharge for both types of material. These findings were fully reported at the Fourth European Lead Battery Conference [1]. Recent results are showing significant differences between both the thickness and the adhesion of the corrosion layers formed at the metal/active-material interface for different types of alloy.

### 3.5. Task 5: Influence of curing and formation on cycling at high rates

The objective of Task 5 is to define the influence of production process variables on battery cycling behaviour at high discharge rates. Initially, the work concentrated mainly on the preparation of unformed plates by using two paste densities ( $4.0$  and  $4.3 \text{ g cm}^{-3}$ ) and three different curing processes (high, medium and low temperature). The two different paste densities were used to obtain plates with high and low porosity. The three different curing processes produced cured plates with active masses that consisted of (other than PbO): 4BS only, 3BS only, or a mixture of 3BS and 4BS in a ratio of about 1:1. In total, this means that plates with six different combinations of porosities and crystal structures were produced.

From X-ray diffraction (XRD) phase analysis, pore-size distribution and scanning electron microscopic (SEM) measurements, the conclusion can be drawn that all plates cured at high temperature ( $80^\circ\text{C}$ ) have, besides PbO, 4BS as the main component. Virtually no 3BS is present. This finding is true for both paste densities, but, as expected, porosity and apparent density change with different paste densities.

Following this, the soaking process in sulfuric acid with three different specific gravities (1.06, 1.12 and 1.20) was investigated by XRD analysis to obtain information about the changes to the cured plates during this stage of processing. The plates were exposed to different periods of soaking, namely, 0.5, 2, 5 and 24 h. Low-temperature curing gave, even with 1.06 sp. gr. acid, a very fast formation of the lead sulfate. The latter was the main product, even after a short soaking time. Plates from high-temperature curing always had, after soaking, more monobasic lead sulfate (1BS) and markedly less lead sulfate in comparison with plates from low-temperature curing. The results from plates cured at a medium temperature were between those obtained from low- and high-temperature curing.

The six different types of cured plates, prepared during the first half of the year, were subjected to formation. As was expected, plates from high-temperature curing, i.e. high 4BS content and low surface area, were more difficult to form than those from low-temperature curing (no 4BS, high surface area). The first  $C_5/5$  capacity test, immediately after plate formation, confirmed this behaviour. The results showed that the higher the surface area, the smaller the crystals and the higher the porosity, the better was the initial capacity of the formed plates. Some of the plates were investigated after formation. The content of the lead dioxide was analysed chemically and was found to be variable. This result fits well with SEM investigations and the different initial capacities observed for the plates. The differences became much smaller after further capacity tests and this behaviour is typical of 4BS plates during discharge/charge cycling.

After formation, an accelerated cycle test was carried out with single plates, an excess of electrolyte (sp. gr. 1.30), and two negative counter plates. The results, with both paste den-

sities, showed that high-temperature curing produced the best cycle life while low-temperature curing displayed inferior performance, although the higher paste density gave slightly better endurance.

As the influence of porosity, curing and formation on cycle life at high discharge rates could be different in valve-regulated batteries, (i.e. under conditions of compression from an absorptive glass-mat separator (AGM) and a starved electrolyte), it was decided to perform, in addition to the traditional single-plate tests with an excess of electrolyte, some more tests with specially prepared cells of the AGM type. These were 2 V AGM cells, with three positive plates (enveloped by glass-mat separators) and four negative plates. For this test, all six different types of positive mass were used. In all cases, constant-current formation and a soaking time of 2 h was used. The cycle tests are continuing. From the results to date (80 cycles), it has not been possible to demonstrate any marked benefit of 4BS in AGM cells, as was found in the first experiments with flooded cells. Although only postmortem analysis can give information on the cause for any capacity loss, the results of some pre-tests have shown that, in fact, the decay of capacity during such cycling is mainly due to a softening of the positive active-mass.

Work has started on an investigation of the effect of seven different types of formation programme: (i) constant current; (ii) constant-current/constant-voltage; (iii) charging with discharge steps, and (iv) four different pulse-formation programmes. At present, only results for one paste density ( $4.0 \text{ g cm}^{-3}$ ), cured at high and low temperature, are to hand. The first  $C_5/5$  discharge after formation showed the expected differences between 4BS and 3BS, but there was also a marked influence due to the formation programme. The best results were given by a constant-current charge with a discharge step of 4 h. All pulse-formation programmes proved more effective than constant-current formation. Thus, the inclusion of a discharge step in the formation schedule, or the use of a pulse regime, overcomes the otherwise poor formation efficiency of 4BS plates.

### 3.6. Task 6: Separator optimization

The aim of the research is to optimize the fibre type and compression characteristics of AGM separators for valve-regulated lead/acid (VRLA) batteries. These features are being investigated via stratification and charge/discharge cycling tests. A  $3 \times 3$  matrix experiment has been designed, i.e. three different types of separator (50, 60 and 70% fine fibre, all-glass) and three different compression levels (20, 25 and 30% compression).

The single-test cells have been constructed by Oldham France and use this company's 2RGT 120 design (120 Ah,  $C_5/5$  rate). The cells have a special positive grid alloy, separators as specified, and a traction paste for the positive active-mass. The cell pack has 12 positive plates pasted to a nominal 2.6 mm, and 13 negative plates pasted to a nominal 2.0 mm. Plate dimensions are  $136 \text{ mm} \times 136 \text{ mm}$  with a

Table 2  
Compression levels in Task 6 cells

Fine fibre (%)	50			66			75		
Target compression (%)	20	25	30	20	25	30	20	25	30
Average compression (%)	21.6	25.2	30.5	21.8	25.6	30.2	23.1	25.2	30.1

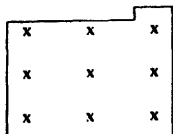


Fig. 5. Location of acid sp. gr. measurements.

separator overlap of 5 mm at the sides and the top of the plates. The case width is 90.6 mm and there are 24 layers of separator per cell.

In all, 126 cells have been assembled and formed (14 cells for each configuration). Actual compression levels achieved for the various separator types are shown in Table 2.

In the stratification test, the cells are cycled to 100% depth-of-discharge (DOD) at the  $C_5/5$  rate to a terminal voltage of 1.70 V/cell at ambient temperature. Ten cycles are performed and the capacity and overcharge factor are recorded for each cycle. After cycling, the cells are disassembled in order to measure the stratification in the separator. This is done by measuring the acid sp. gr. at nine locations (see Fig. 5) in a separator located in the centre of the cell, and also in one close to the outer plate. With these measurements, an average stratification is determined. These results are shown in Table 3. Clearly, stratification decreases with increasing fine-fibre content and increasing compression.

The cycling tests have been carried out on the basis of a discharge of 3 h at the  $C_5/4$  rate (75% DOD) and the recharge for 12 h with a voltage limit of 2.35 V and a current limit of  $C_5/5$ . Capacity checks have been carried out at 10, 50 and 100 cycles, and then every 100 cycles. This check is carried out at 25 °C with a discharge at  $C_5/5$  to 1.7 V/cell and then recharge with a voltage limit of 2.35 V and a current limit of  $C_5/5$ . Three capacity discharges are carried out in sequence for each capacity check. The end-of-life of the cell is taken as  $\leq 75\%$  of the initial  $C_3$  capacity after three capacity discharges. The capacity values (listed in Table 4) closely mirror the stratification results. The best performance is given by cells with 75% fine fibre and 30% compression.

### 3.7. Task 7: Influence of DOD as a function of discharge rate on battery life

The DOD is thought to influence the life of lead/acid batteries, i.e. increase in DOD decreases life. In practice, therefore, it is assumed to be important to avoid deep discharging in order to protect battery life. It is also known that the Ah capacity of a battery decreases with increasing dis-

Table 3  
Stratification (in points of sp. gr.) after 10 cycles at 100% DOD, Task 6

Fine fibre (%)	Compression (at 20%)	Compression (at 25%)	Compression (at 30%)
50	82.5	63.5	55.0
66	75	52.5	51.5
75	66	52.5	39.0

Table 4  
 $C_3$  Capacity (Ah) results after 200 cycles, Task 6

Fine fibre (%)	Compression (20%)	Compression (25%)	Compression (30%)
50			83
60	85	82	83
75	86	80	96

charge rate. Thus, if the damage to cycle life by deep-discharging is caused by excessive lowering of the amount of residual  $PbO_2$  in the discharged plate, the influence of DOD on cycle life would become less important at higher discharge rates. In other words, a higher DOD may be allowable with increasing discharge rate.

The objectives of Task 7 are therefore to ascertain:

- the DOD that is equivalent to 75% discharge conditions at the  $C_5/5$  rate for discharges at the  $C_5/1$  and  $C_5/1.8$  rates
- the relation between the discharge voltage and the permitted limitation of the DOD of the active mass, as a function of the discharge rate

Initially, it had been intended to test at four discharge rates but, in view of the high equipment cost, this was reduced to three rates. Necessary redesign of the test equipment resulted in a four-month delay in starting the task. The tests are being carried out on Dryfit, traction, gelled-electrolyte batteries (3TZ AX7) supplied by Sonnenschein. These are 6 V batteries with a nominal  $C_3$  capacity of 160 Ah.

The determination of the original performance of the batteries has shown that the performance is better than expected. The cutoff voltage and the Ah capacity that has to be discharged for the different DODs at the corresponding rates of discharge are given in Table 5.

Three batteries are cycled for each discharge rate and each DOD. This means: (i) three strings for the three discharge rates; (ii) each string has five modules that correspond to the five different DOD values, and (iii) each module has three batteries. Thus, 45 batteries in total are being cycled. Discharge starts 1 h after the last battery of each discharge rate has finished the charge phase. All batteries are being dis-

Table 5

Cutoff voltage and Ah capacity to be discharged for different DOD at corresponding discharge rate

Discharge rate (A)	Achieved capacity (Ah)	100% DOD	90% DOD (Ah)	75% DOD (Ah)	60% DOD (Ah)	50% DOD (Ah)
$C_5/1 = 160$	110	cutoff 1.5 V/cell	99	82.5	66	55
$C_5/1.8 = 90$	130	cutoff 1.6 V/cell	117	97.5	78	66
$C_5/5 = 32$	160	cutoff 1.7 V/cell	144	120	96	80

charged in series with different discharge rates to a different DOD. After a certain DOD is achieved for the module, it will be disconnected. Disconnection of an individual battery or module is achieved via a switching device to allow continuation of current flow through the string. Batteries are charged by using a constant-current/constant-voltage characteristic; the charging starts 0.5 h after the last battery for a given discharge rate has finished its discharge. A capacity check is carried out every 50 cycles and the test will be deemed to have finished if the capacity drops below 70% of the nominal capacity.

Testing is still in the early stages (150+ cycles). To date, there have been no marked differences between the performance of batteries discharged between 100 and 50% DOD. If anything, there seems to be a slight dependence on the discharge rate: the capacity decline at high discharge rates is higher than that at the  $C_5/5$  rate. There is also a tendency for capacity to recover after capacity checks.

### 3.8. Task 8: Effect of alloying elements on grid properties

One way to improve the energy density of the lead/acid battery is to reduce the grid weight relative to the active material. As far as the positive grid is concerned, this means the development of stronger and more corrosion-resistant alloys.

In Task 8, tin and other dopant materials (such as silver, indium and germanium) are being added to a base lead-

calcium-tin alloy and an examination is then made of any changes to the mechanical properties, corrosion performance, and corrosion-layer characteristics, i.e. chemical composition, structure and electrical properties. The base alloy is Pb-0.10wt.%Ca-0.56wt.%Sn. The effect of tin (up to 5 wt.%) on the ageing phenomenon at room temperature of cast Pb-Ca-Sn samples is shown in Fig. 6. The influence of silver additions to the alloy is given in Fig. 7. These effects are interesting but are slow; the hardening process takes up to three months.

In the second half of the research programme, it has been decided to examine a similar range of alloys cast under typical conditions and then annealed at 60 °C for a period of 72 h to simulate the curing and formation processes of battery plates. This procedure has the benefits of: (i) speeding up the hardening process; (ii) being more representative of the grid in the finished battery, and (iii) revealing any alloy sensitivity to overageing. Values of the physical properties attained for some of these alloys are listed in Table 6.

Corrosion tests have indicated that the test candidates generate corrosion layers that are similar to the actual corrosion of grids in batteries. Microprobe analyses have shown the segregation of the tin in the grain boundaries, as well as its diffusion into the corrosion layer.

Silver doping at a low level does not appear to modify the base alloy crystallization characteristics. By contrast, the cooling rate during casting has an influence on the micros-

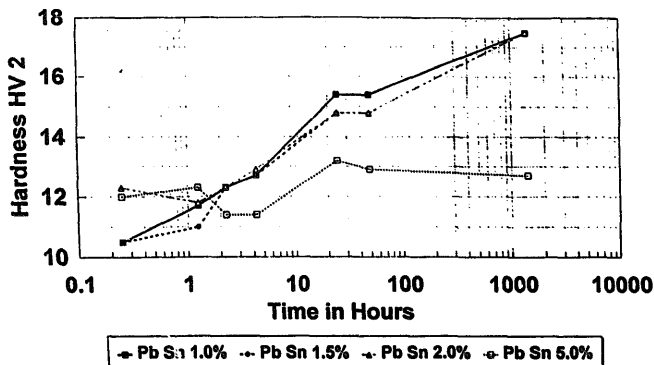


Fig. 6. Effect of tin content on alloy hardness.



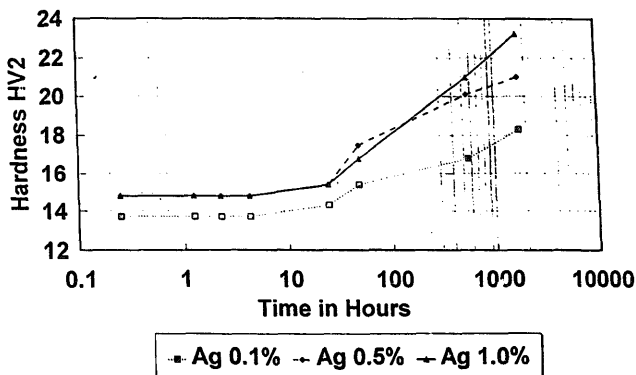


Fig. 7. Effect of silver content on alloy hardness.

Table 6  
Alloy properties

	Base alloy *	Ag-doped (0.05 wt.%)	Ag-doped (0.1 wt.%)	Sn-rich (1.5 wt.%)
Tensile strength (MPa)	36.0	50.2	58.0	60.8
% Elongation	32.1	15.4	9	8.1
Hardness (HV2)	11	15.1	17.8	19.8

\* Base alloy: Pb-0.06wt.%Ca-0.56wt.%Sn.

structure of the tin-rich alloy: at a high rate, large dendritic crystals are formed; at low rates, equiaxed structures are normal. As both mechanical properties and corrosion behaviour are linked to microstructure, work is now being concentrated on the industrial casting of selected alloys into grids to obtain information on a practical level.

Studies have been made of the passivation of the lead-calcium-tin alloys in a borate medium. These demonstrate the ability of electrochemical methods to characterize the corrosion rate and the conductive properties of the corrosion layer. Results have shown that the passive layers on the low-tin alloys (below 0.8 wt.% tin) have no electronic conductivity, but only ionic conductivity. The electronic conductivity increases sharply when the alloying tin content increases from 1.0 to 1.5 wt.% and attains a plateau between 1.5 and 2.5 wt.% Sn. There is evidence to suggest that tin decreases the thickness of the PbO layer. This work was reported at the Fourth European Lead Battery Conference [2].

In summary, the research indicates that alloys with elevated tin contents, and possibly with added silver, possess some very attractive properties for battery grids for electric-vehicle applications. The work is now moving towards testing of the alloys in batteries and will utilize thinner than normal grids (initially, by some 10-15%) to assess the benefit of the improved properties.

### 3.9. Task 9: Manufacture and testing of prototype batteries

This task is not scheduled to commence until mid-1996 but already thought is being given to the design of six battery variants for initial parameter testing. A Task Advisory Committee has been set up to help decide on the form these battery types will take. It is intended to use a standard FIAMM case to save expense and early thought is being given to grid design to allow tooling to be obtained in good time. Once the final battery designs have taken shape, Task 10 will look at any implications for recycling from the new generation of batteries.

## 4. Conclusions

The ALABC/Brite-EuRam Project is now almost half-way through its scheduled period. It has proved to be a most interesting example of how battery companies can work together on pre-competitive research, with financial and technical assistance from other partners. There have, of course, been some differences of opinion. Nevertheless, the commitment remains firm to further the advancement of the lead/acid battery and to make it the battery of choice for the first generation of electric vehicles, as is the wish of the ALABC as a whole. It is hoped that the work reported here will result

in further projects, by which the industry as a whole can benefit from the collective wisdom of its many respected experts.

#### Acknowledgements

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