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ALABC 2000 — the way ahead

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Abstract

Many battery energy-storage applications are currently undergoing a progressive change away from the traditional flooded lead–acid battery to a valve-regulated design which offers convenience both in operation (spill-proof, able to be rapidly recharged) and in reduced maintenance. At the same time, there are large changes in prospect in the applications themselves. In the transport sector, it appears that at least part of the largest of all present markets, the 12/14 V starting, lighting and ignition (SLI) battery, will be replaced by a 36/42 V system. Also, there may be some substitution of electric and/or hybrid electric vehicles for vehicles that employ internal combustion engines alone. There is also, currently, rapid growth in the use of valve-regulated lead–acid batteries for telecommunications and there is enormous potential for future growth in remote-area power supplies (RAPSs). The present paper reviews some of the salient aspects of the research and development programs that are being carried out in order to meet these challenges. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: ALABC; Battery; Flooded; Lead–acid; Service life; Valve-regulated

1. Introduction

Towards the end of the 20th century, the lead–acid battery underwent a significant functional revision. For most of its long history, the battery had operated with its plates immersed in a mobile electrolyte and provision had been made for oxygen and hydrogen produced during overcharge to be released freely into the atmosphere. The dissipated gases represented a loss of water from the electrolyte and therefore had to be replaced in a regular maintenance operation.

The modern, valve-regulated lead–acid (VRLA) battery operates on an ‘internal gas cycle’ in which oxygen evolved during the latter stages of charge, and during overcharge, of the positive electrode transfers through a gas space to the negative electrode where it is reduced to water. This cycle shifts the potential of the negative electrode to a less negative value and thus reduces hydrogen evolution to a very much lower level. A pressure-relief valve is provided to ensure that even the small amounts of hydrogen produced do not generate high pressure.

The changes made to the construction of the battery in the move to the valve-regulated design have brought new challenges for the materials scientist in efforts to overcome the traditional life-limiting mechanisms of the lead–acid battery: paste softening; electrolyte stratification; incomplete charging and grid corrosion [1]. The reward for a complete resolution of these issues is a battery that requires no maintenance, presents no threat of acid spill, and can be deployed with a minimal footprint.

Further, major changes are expected in the principal uses of medium and large rechargeable batteries during the next few years.

The nature of on-road transport (and much off-road too), which is currently dominated by internal combustion engine (ICE) vehicles with 12 V lead–acid starting, lighting and ignition (SLI) batteries, is likely to change in at least two ways.

1. Environmental and oil cost pressures will encourage some substitution in the sector by electric vehicles (EVs) and by hybrid electric vehicles (HEVs).
2. Demand will grow for increased electrical power in vehicles that continue to make use of the ICE as the sole means of motive power. This is expected to lead to a progressive replacement of the 12/14 V SLI system (12 V battery, 14 V alternator) by one operating at 36/42 V. Such a shift will allow the deployment of a wide range of enhanced functions, including combined starter/alternator, steer-by-wire, brake-by-wire, etc. in future vehicles.

Two other large uses for batteries command attention at this time.

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Table 1
The changing markets for large rechargeable batteries

Present market sector	World sales 1999 (US million $)	Direction of change
12 V SLI	10000	36/42 V, HEV and EV
Telecommunications	1300	Growing at ~8% but life limited in some cases
RAPS	500	Enormous potential

First, the market for uninterruptible power supplies (UPSs), and for batteries for the telecommunications sector, is growing at an enormous pace. This growth is taking place despite the fact that the adoption of the VRLA battery in this application has been hampered by a lack of appreciation of the differences between the flooded and the valve regulated designs. For example, VRLA batteries require that far more attention be paid to the management of the electrolyte inventory and to the internal oxygen cycle than is necessary for flooded batteries. Suitably designed batteries must be selected and must be used in an appropriate manner if life expectations are to be met. The operating requirements for VRLA batteries are somewhat different from those of the flooded type. For example, VRLA batteries require more attention to monitoring and control.

Second, the enormous potential of the contribution that remote-area power supplies (RAPSs) can make in bringing electric power to the one-third of the world's population which currently lack access to an electrical grid, appears to be on the brink of realization. The cost of photovoltaic (PV) units is steadily falling and the deployment of batteries, which are a sine qua non in such systems, is now being undertaken in a disciplined manner which should ensure that short life times brought about by incorrect installation and operating procedures will become a rarity.

The size of the markets involved and the incentive for change are shown in Table 1.

As a result of the changes mentioned above, there is currently a high level of research and development of the lead–acid battery, much of it carried forward through the mechanism of the advanced lead acid battery consortium (ALABC) [2]. This paper is intended to provide an overview of the principal themes that will occupy this activity during the next few years.

2. Duty cycles and failure modes

Medium and large secondary batteries are used in a variety of different tasks. Fig. 1 shows schematically three important categories of duty cycle.

The dominant failure mechanisms of VRLA batteries tend to be different in each of these limiting cases. In standby power applications (UPS telecommunications, etc.), the battery is only required to deliver current very occasionally during its working life. For the remainder of the time, the battery stands near top-of-charge and is supplied with a small charging current which is designed to maintain this state-of-charge. This mode of operation avoids the damaging effects of repeated cycling of a large fraction of the active masses through the discharge/recharge process but does require a careful balance to be maintained between the several possible reactions (oxygen evolution, oxygen reduction, positive grid corrosion, etc.) [3].

Deep discharge, as in the EV application, subjects the active masses to the maximum stress in terms of the cyclic tendency to swell and shrink (see Section 3.2) so that degradation of the positive active mass can be a serious threat.

In partial-state-of-charge (PSoC) operation, the battery cycles over a relatively small range centered on some intermediate state-of-charge. This is the mode employed in HEVs (at relatively high rates of charge and discharge) and in PV–RAPS systems (at relatively low rates). PSoC operation offers two major advantages.

1. It avoids the battery spending time near the gassing zone at top-of-charge.
2. It does not give rise to large volume change related stresses in the active masses.

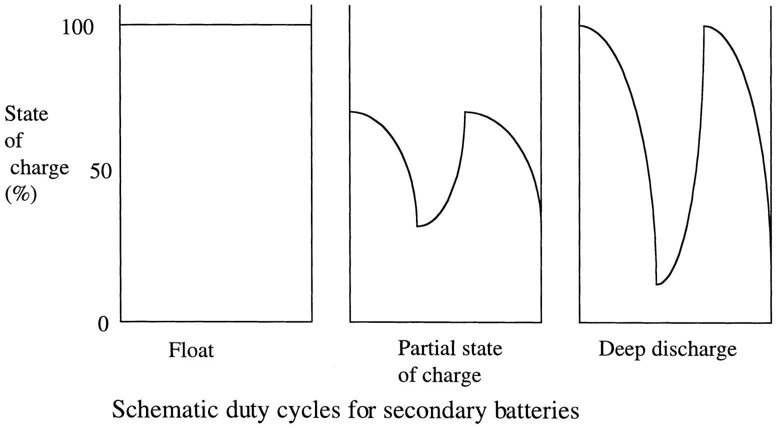

Fig. 1. Schematic of three types of duty that are experienced by secondary batteries in different tasks.

Thus, it should not be a surprise that cycling a battery in a PSoC regime has been shown to achieve an exceptionally long life in terms of total ampere-hour throughput [4].

In the PSoC duty, there is no direct requirement for the battery to be brought to a full state-of-charge. When, however, the battery comprises a series-connected string of cells, as will be the case in both HEVs and in RAPS, there will be a need to find some way of ensuring that the individual cells in the string retain a closely matched capacity. The cells in the string must also remain at a similar state-of-charge, one with another. If this is not achieved then weaker cells fall out of step, become overworked, and quickly fail. This is a failure mode which is peculiar to series-connected strings and has not been found to be a problem in the market that has so far been the largest for lead–acid, namely the 12 V SLI unit.

In order for VRLA batteries to succeed in all the applications shown in Table 1, the principal requirements are for reliability and life. The main thrusts of research are to understand and overcome the failure mechanisms in all three main types of duty (Fig. 1) so that the battery presents a viable cost-of-ownership option.

3. State of the art

When the VRLA battery was first introduced into deep-cycle duty, its cycle life was very much shorter than that of the flooded battery which it had replaced. In the telecommunications field, too, some experiences with VRLA were disappointing. It has become clear that VRLA is not quite a ‘‘drop-in replacement’’ for the flooded battery and probably ought to be treated as a different battery chemistry that happens to offer almost the same voltage characteristics. A prime target for current research and development programs, therefore, is to invest the VRLA battery with a performance which matches that of the flooded battery as closely as possible. Simultaneously, there is a need to make adjustments which will cope with the modified requirements of the batteries in the new and evolving applications. An example would be in HEV batteries where the challenges of long string operation must be met in a regime which does not need to be brought to top-of-charge other than for cell equalization.

In connection with the first objective, we take note that the change in performance that was experienced during the transformation from flooded to valve-regulated operation occurred as a consequence of specific changes to the cell design. It is logical to scrutinize these modifications first in the course of the search for improvement. The modifications in question are summarized in Fig. 2. This shows a schematic of a section through a valve-regulated lead–acid cell. The components which have been modified with respect to the flooded design are marked by asterisks. Antimony was left out of the grid alloys because, when present, this element lowers the hydrogen overpotential at the negative electrode and thus encourages the evolution of hydrogen there. Gas space, to allow the operation of the internal oxygen cycle, was created by replacing the conventional sheets of separator with either a layer of glass mat or a gel. Both materials absorbed and immobilized the sulfuric acid electrolyte. Finally, the top of the cell was closed but was provided with a valve to release excess pressure.

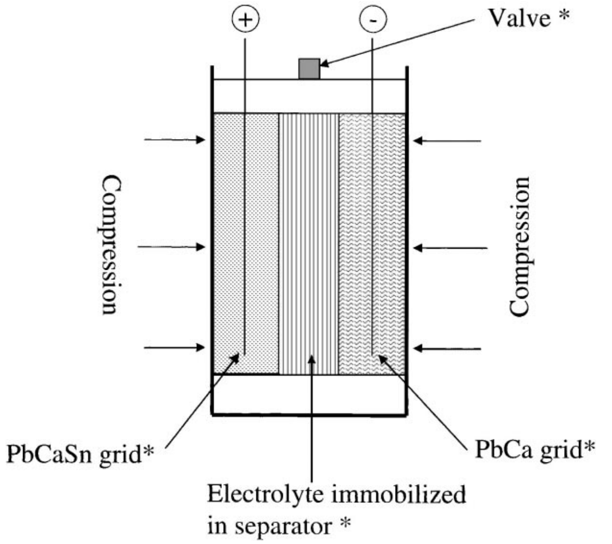

Fig. 2. Schematic of a section through a valve-regulated lead–acid cell with the components that have been modified in the course of the change from the flooded design marked by an asterisk.

The performance shortfall which was experienced during early deep cycling of VRLA cells was labeled ‘‘premature capacity loss’’, or PCL. It was soon found that more than one mechanism can contribute to PCL. As shown in Fig. 3 the several degradation mechanisms labeled PCL kick in progressively, and if they are overcome in the same order then the service life of the battery can be extended significantly.

Several failure modes that can shorten the service life of the battery, together with the status of the search for antidotes that can restore a long life, are reviewed below.

3.1. PCL 1

The first form of premature capacity loss to be identified appeared within a few tens of deep-discharge cycles. This

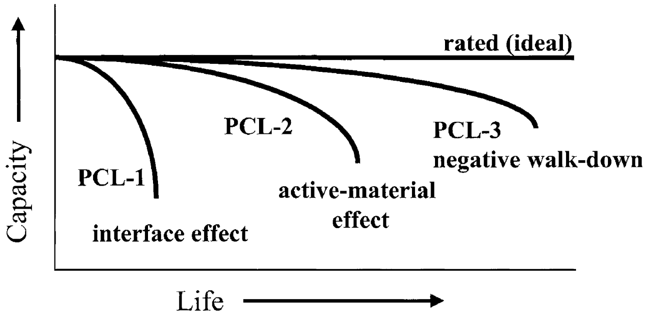

Fig. 3. Three broad categories of premature capacity loss (PCL).

occurred with cells containing antimony-free grids and involved the development of a substantial resistance in the vicinity of the interface between the positive grid and the positive active mass. PCL 1 was ameliorated by the incorporation of 1–1.5 wt.% of tin in the alloy used for the positive plate [5,6].

3.2. PCL 2

A second important degradation mechanism involved the swelling of the positive active mass which results in loss of connectivity (hence high resistance) and, ultimately, to shedding. Although this failure mode is well known for flooded batteries, it is aggravated in the case of VRLA batteries for two reasons. In the plane of the plate the removal of antimony from the positive grid alloy reduced creep strength and allowed the corrosion process to "stretch" the plate. Fortunately, the same addition of tin used to overcome PCL 1 restored the creep strength to the grid alloy.

The second potential source of PCL 2 in the VRLA design is the separator. In order to overcome swelling of the active mass in the direction normal to the plane of the plate, it is standard practice to subject the stack of plates to a compressive force maintained by the case walls, as shown schematically in Fig. 2. The success of this strategy, as a means of preventing swelling, depends on (1) the constraint being transmitted successfully right through the stack of plates; and (2) the compressive force not being dissipated by collapse of the separator material.

Of the two electrolyte immobilization systems that are prevalent in VRLA batteries, glass mat (AGM) does indeed tend to reduce in thickness when compressed, while gel does not. Gel batteries are characterized by long cycle lives, and novel incompressible separator materials also show promise in this regard (Fig. 4).

3.3. PCL 3

As progress is made towards overcoming the failure mechanisms involving the positive plate, attention turns to the negative plate. It is clear that in order to achieve a long effective life for the whole battery, both the plates must retain their full capacity. Of particular concern is the observation that in long deep-cycling tests, the negative plate takes over from the positive as the life-limiting element [8]. In particular, it has been found that premature failure in float service is often associated with selective discharge of the negative plate — the result of the combined action of a high hydrogen evolution rate and a high oxygen recombination efficiency [9]. A key challenge is the difficulty in bringing the negative plate to a full state-of-charge in the latter stages of life of a VRLA cell, when the oxygen cycle is becoming progressively more efficient.

There are a number of possible causes of the progressive capacity loss that besets the negative plate of VRLA batteries. These include

1. Reduction in surface area of the electrodes, possibly following loss of the organic expander; this might be a problem which is peculiar to the VRLA design in that oxygen reaching the negative plate is destructive to organic molecules.
2. Electrolyte stratification, which is likely to be more severe the more open is the pore structure of AGM separator materials.

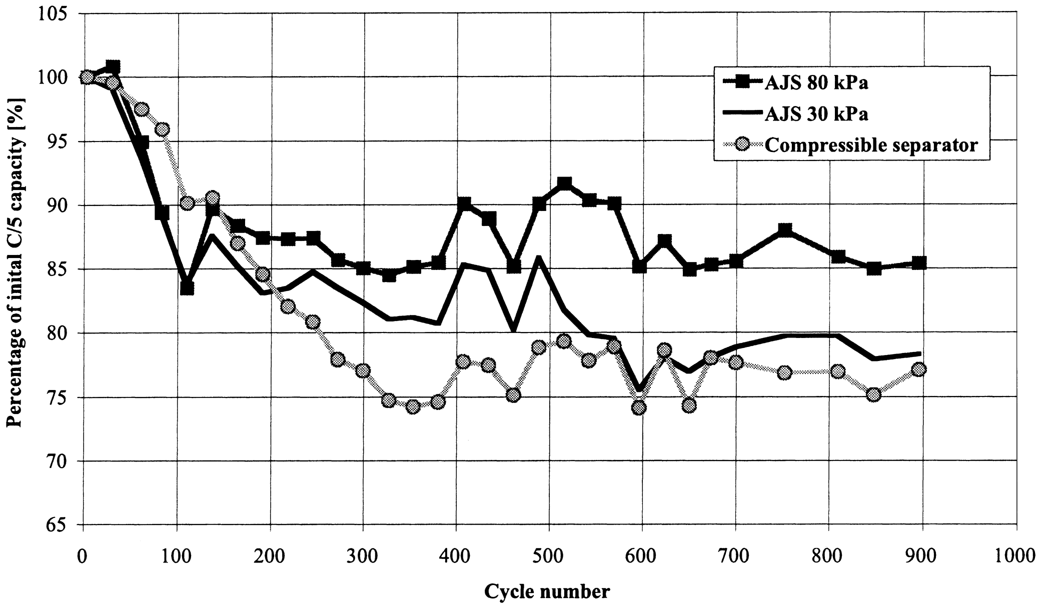

Fig. 4. Maintenance of capacity ($C_2/2$) for a lead–acid battery with an AJS (incompressible) separator under 80 kPa compression through a long cycle life (discharging to 1.6 V) [7].

3. Depression of the potential of the negative plate due to highly efficient oxygen recombination.
4. High hydrogen evolution due to impurities.
5. Recharge inefficiency due to a selective discharge of the plate.

In any event, it is encouraging to note that, whichever of these is (are) the culprit(s), the problem of the negative plate is not of universal severity. There are some cases, even in stand-by applications [10], when a long life is being achieved, and in these instances the degradation of the negative plate is evidently being held at bay.

3.4. Series-connected string issues

As mentioned earlier, individual modules within a series-connected string can vary substantially in capacity, due to manufacturing and/or temperature differences; and after a limited number of cycles, particularly at the deep discharge levels needed for EV operation, module voltages can diverge significantly. Such divergence can cause some modules to be overcharged and others to be over-discharged during the course of cycling, which gives rise to premature failure of the pack.

String imbalance can be overcome by a process of rigorous full recharging (equalization) which is practicable for deep-discharge cycling, or by the use of battery management and control systems.

In PSoC cycling, the problems of string balance are less severe but are still sufficient to limit battery life to an unacceptable extent. In applications such as HEVs and RAPS it may be inconvenient to bring the battery to a full state-of-charge at regular intervals. In such cases, a system of maintaining equalization without a full excursion to top-of-charge would be a great asset.

3.5. Active-material utilization

It has been a frustration for lead–acid battery technologists over the years that, at the discharge rates used in most applications, it is normally only possible to access around 30% of the theoretical discharge capacity. This limitation arises partly because the product of the discharge reactions is an insulator and partly as a result of diffusion limitations. Greater utilization of active mass is achieved with thin plates where diffusion distances are short.

4. ALABC 2000 R&D program

Projects within the ALABC 2000 research and development program are being designed to address the remaining problems and shortcomings of the VRLA battery, as described above. The fit between the projects and the challenges is broadly as shown in Table 2.

The need for a separator material, that is able to resist dendrites and is not susceptible to crushing, has been defined in connection with PCL 2 above. In addition, the first three of the potential problems listed under PCL 3 also may implicate the separator to some degree. A separator that would (1) prevent an excess of oxygen access from destroying the expander; (2) restrict the amount of heat generated by the recombination reaction in the negative plate; and (3) not depress the electrode potential too far, while simultaneously discouraging stratification, would make a major contribution. Thus, projects are under way to understand better the function of the separator in the valve-regulated lead–acid cell and to identify materials with optimum physical properties for the purpose.

In order to address the negative plate directly, a study will examine the mechanisms associated with the oxygen cycle in VRLA cells during overcharge. This work will provide a comprehensive picture of current distribution among the various overcharge processes and the physical states of the positive and negative plates throughout cycling. The effect of charging conditions on current densities over the plate surfaces will be measured, and this will provide information about the influence of the oxygen cycle on the mixed potential nature of the negative plate. Special attention will be paid to the first 50–150 cycles where it is common for VRLA cells to experience a drop of 10–15% in capacity. The eradication of this characteristic is given a high priority in this project. Other negative plate projects will develop strategies for maintaining the discharge capacity of the negative plate in PSoC applications, and will explore the influence of residual elements (impurities and beneficial

Table 2
Correlation of ALABC 2000 projects with outstanding VRLA technical challenges

ALABC projects	PCL 2: swelling of positive mass	PCL 3: negative walk-down	Life limitations peculiar to the PSOC regime	Improve active material utilization
Separator development	✓	✓		
Negative plate studies		✓		
Impurity studies		✓		
Twin tab studies for HEV batteries			✓	
Maintaining equalization in PsoC duty			✓	
Battery mgt. and design in RAPS			✓	
Novel grid design				✓

elements) in float duty of VRLA batteries. It is known that VRLA batteries manufactured with very pure materials can provide very long float duty (13 years) [10], but the limits of the effectiveness of "residual" elements in VRLA cells are not known as yet. Control of the balance between the reactions that decide the life-limiting function may yet be achievable through the use of catalysts [11].

Batteries used in HEVs will experience high rates of charge (as in regenerative braking) and discharge. High charge and discharge rates accentuate temperature rises and tend to aggravate the problem of pack balance. An important measure which will help alleviate temperature rise is to provide each grid with a second tab placed symmetrically opposite the first. Such a system allows half the current to pass through each tab and limits temperature rise because the heat generated also has two routes for escape. Two projects will investigate the efficacy of twin tab systems for HEV batteries. One will use flat plates and the other will use spiral wound plates. In both cases, it is expected that the presence of the second tab will help to reduce the tendency for sulfation to concentrate in certain regions of the plate. Reducing the current density in the plate should permit higher charge rates to be used without negative plate rundown and uneven material utilization.

Additionally, projects aimed at improving the prospects for HEVs will investigate the use of cell management and control systems to keep series-connected strings equalized.

Strategies for the maintenance of string balance will also be sought in the case of RAPS batteries. Here, it may be possible to perform occasional maintenance charging successively to sections of the battery by redistribution of energy amongst the cells comprising the battery.

Finally, a modest effort will be directed at a novel approach to increasing active material utilization. A novel method of preparing a lead foam has been identified. It is proposed to fill the interstices of a sheet of the foam with active material in order to prepare the novel electrodes. In this way, no particle of active material will ever be more than about 500 μm from an element of the current collector. In some conventional plates some of the active material is situated as much as 3 mm from the current collector. This is an ambitious approach, but if successful it should achieve extraordinarily high levels of active material utilization.

5. Conclusions

The present program is aimed to take the life and reliability of the VRLA battery forward by another large stride in all the major applications where this battery is a candidate. We have already seen the deep-cycle life of the battery extended by two orders of magnitude during the course of the past decade [2]. The programme of research and development that will be undertaken by the ALABC during the period 2000–2002 will seek to achieve similar progress in PSoC duties (e.g. 100,000 miles in HEVs, and 20 years in RAPS) and in float applications. By the end of the program we should have some idea of the ultimate capabilities of the battery in new and traditional tasks.

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