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Research results from the Advanced Lead–Acid Battery Consortium point the way to longer life and higher specific energy for lead/acid electric-vehicle batteries

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Abstract

Amidst the welter of publicity devoted to the newer battery chemistries, the remarkable progress made by lead/acid battery technologists in response to the needs of the emerging electric-vehicle market has tended to be overlooked. The flooded design of battery, launched by Gaston Planté around 1860, has given way to a valve-regulated variant which has a history dating only from the 1970s. The key parameters of this 'maintenance free' battery have been improved markedly during the course of the development programme of the Advanced Lead–Acid Battery Consortium (ALABC), and it is likely that lead/acid will continue to feature strongly in motive-power applications as a result of its cost advantage and of its enhanced effectiveness. © 1998 Elsevier Science S.A. All rights reserved.

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1. Electric-vehicle battery essentials

Electric vehicles have a history which spans the whole length of the twentieth century. At the beginning of the century, electric automobiles competed successfully with vehicles powered by the immature internal combustion engine. In 1973, and again in the early 1980s, international concerns over crude-oil supplies regenerated an enthusiasm for the development of a means of transport that was no longer directly dependent upon hydrocarbon fuels. Progressively since that time, there has been an added motivation arising from widespread concern over increasing atmospheric pollution in urban communities. In 1996, domestic oil consumption in the USA was over 18 M barrels per day, of which 46.2% was imported [1] and over half was consumed in internal-combustion-engined vehicles [2]. This level of dependence on overseas oil is of concern because it is expected that a permanent decline in global oil production rate will begin within 20 yr [3]. Further, today, more than half the US population live in areas that do not comply with national ozone standards [4]. These twin motivations for developing a means of transport that does not depend upon crude oil supply have never been stronger. The key to a successful contribution being made by an electric automobile, however, is the manner in which customer expectations will be met, essentially by comparison with the equivalent internal-combustion-engined vehicle.

Customer acceptance of the electric vehicle as an alternate means of transport awaits the provision of a full charging infrastructure, but is also bound to be strongly influenced by the vehicle cost/performance ratio. Once the vehicle manufacturing cost is able to benefit from the economies of scale, it is widely felt that the electric vehicle will cost no more than the internal-combustion engined vehicle; perhaps less, since it will involve fewer moving parts. Service costs, too, may be lower for the electric vehicle, except that tyre replacement may be required more frequently. The major focus of the price/performance issue has been the vehicle's main battery—the energy-storage system that will replace the fuel tank of the internal-combustion-engined vehicle.

An acceptable battery will need to exhibit at least the following attributes:

- low purchase price
- high specific power (in order to provide the vehicle with adequate acceleration)

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Table 1
Raw materials prices, production and consumption for nickel and lead in 1997

	London metal exchange price (US¢/lb)	Western production (MMT)	Western consumption (MMT)
Nickel	340	730	915
Lead	32	4.8	5.1

- good cycle life (to provide low lifetime costs)
- good specific energy (range per charge)
- ability for rapid recharge (for maximum availability)
- low self-discharge
- high energy efficiency
- high recyclability
- safety.

There has been much discussion over the appropriate ranking of these several factors. A preoccupation with specific energy has been the major driving force for the interest in novel battery chemistries in recent years, but an appreciation of the likely costs (for example, see materials costs shown in Table 1) tends to restore interest in the lead/acid battery as a prime contender for electric vehicles particularly since, as will be shown below, this system can be rapidly recharged. The lead/acid battery also exhibits good specific power (so that the General Motors EV1 is able to offer an acceleration of zero to 60 mph in less than 9 s), energy efficiency, recyclability and safety. Much development work has been devoted to maximizing specific energy and cycle life, as well as to exploring the prospects for rapid recharge, through the function of a world-wide collaboration by the Advanced Lead–Acid Battery Consortium (ALABC).

2. The Advanced Lead–Acid Battery Consortium

The responsibility for ensuring that the best possible lead/acid batteries become available to support the growing electric-vehicle market has been accepted by the ALABC. This organization comprises 90% of the world's lead producers, 85% of the lead/acid battery manufacturers, and a variety of companies from related industrial sectors. This vertically integrated group came together in 1992 with the declared aim of making electric vehicles a reality within a decade. It is not the purpose of the ALABC itself to design the ultimate electric-vehicle battery. Rather, the aim of the ALABC is to foster a central R&D program for all its members to use as a 'research pool' to assist their own battery development activities, both for electric vehicles and for other applications. In other words, the ALABC is an open resource—the research results are disseminated freely to the members and thus benefit the industry as a whole. In this respect, European, North American and Pacific Rim members take the most promising outcomes from their respective research programmes and work together to build a new generation of lead/acid batteries.

As a starting point, it was decided that the electric-vehicle battery must be maintenance free. Thus, the flooded lead/acid battery that was introduced around 1860 was set aside in favour of the valve-regulated design that appeared during the 1970s.

Benefitting from research results of the ALABC programmes, advanced valve-regulated lead/acid batteries are already capable of meeting all but one of the mid-term criteria of the US Advanced Battery Consortium. Existing and commercially available advanced lead/acid batteries are capable of providing electric vehicles with daily commuting ranges of 90 mile or more, recharging times of a few minutes, and lifetimes of approximately 3 yr.

As indicated in Table 2, the fuel cost per mile of running a lead/acid powered electric vehicle has already dropped by an order of magnitude during the course of the

Table 2
Key parameters for lead/acid batteries for electric vehicles[a]

	Purchase price (US$/kW h)	Specific power (W kg^{-1})	Specific energy (W h kg^{-1})/ range (mile)	Recharge time	Cycle life (cycles)	Cost of ownership US$/mile
ALABC targets	150	150	50/100	50%, 5 min 80%, 15 min 100%, 4 h	500	0.07
1992	200	150	25/50	100%, 8 h	75	1.07
1995	150	150	35/75	50%, 5 min 80%, 15 min 100%, 4 h	500	0.10
1998	100	150	48/100	50%, 3 min 80%, 10 min 100%, 30 min	800	0.04

[a] Assumptions; (i) US$0.10/kW h for electricity; (ii) 16 kW h battery in vehicle; (iii) 80% efficiency; (iv) 80% depth-of-discharge.

ALABC's programme. Assuming energy costs at US$.10/kW h, fuel costs will drop further to US$0.04 per mile in 1998 and make the EV running cost competitive with the cost of fuelling a conventional internal-combustion-engined (ICE) automobile.

Towards the end of 1996, General Motors introduced the EV1 for public acquisition in California and Arizona. The vehicle was powered by a valve-regulated lead/acid battery. At about the same time, a further 3-year programme (1997–1999) was set in place by the ALABC with membership that had expanded to 58 companies and organizations world-wide.

Progress in improving the parameters shown in Table 2, that are all to be achieved with the valve-regulated lead/acid battery, is described in Section 3.

3. Advances in valve-regulated lead/acid electric-vehicle battery technology

The major advances in the development of valve-regulated lead/acid batteries for electric-vehicle applications have taken place in the areas of cycle life, specific energy, and rapid recharge.

3.1. Cycle life

When the valve-regulated lead/acid battery was first operated under deep-discharge duty, cycle life was often found to be very short. Two mechanisms for this so-called 'premature capacity loss' were proposed: the first suggested the formation of a high-resistance corrosion layer at the surface of the current-collector (grid); the second involved a degradation of the microstructure of the positive active-mass that resulted in a breakdown of inter-particle connectivity. Elegant experiments carried out by the research team at the Technical University of Brno showed that there was a strong correlation of the progressive fall in capacity as the battery was cycled with the decrease in the conductance of the active mass, but that there was no correlation with the conductance of the interphase between the grid and the active mass [5]. This observation was found to hold both for grids based on lead–antimony alloys and for grids based on lead–calcium–tin alloys. Meanwhile, Hollenkamp [6] articulated a unified theory to explain premature capacity less entirely in terms of degradation of the positive active-mass microstructure. This degradation process undoubtedly arises from the tendency of the active mass to swell at each discharge because the molar volumes of the discharge products are substantially greater than those of the charged materials. It appears that this mode of failure can be overcome by putting the active material under sufficient constraint to prevent it from swelling during deep-discharge cycling. In the plane of the battery plate it is the creep resistance of the grid alloy that is the key [7]. The replacement of lead–antimony alloys by lead–calcium alloys when valve-regulated designs were introduced reduced the creep resistance by a substantial factor and it was soon found that swelling of the active material caused the grids to grow substantially during the course of their deep-discharge cycled life. ALABC's contractors in France [8] have shown that the addition of 1 to 1.5 wt.% tin to the lead–calcium alloy and the use of a degree of work to the manufactured grid surface largely restored the creep resistance of the grid and prevented grid growth. In the direction perpendicular to the plane of the plate, the prevention of swelling of the active mass depends upon a compressive force applied to the stack as a whole [7]. In this connection, recent results (Fig. 1) illustrate the effectiveness of applying adequate compressive force to the plate stack in order to ensure a long deep-cycle life. Here, it is important to recognize that the improvement resulting from the use of the better stack compression applies equally well for lead–antimony and lead–calcium–tin grids. A crucial factor in such considerations is likely to be the physical performance of the AGM separator. Evidence is beginning to emerge from the research programme at CSIRO in Australia [9] that the application of high pressures to AGM separators that are presently in commercial use results in separator distortion so that much of the compressive force applied to the stack is dissipated by collapse of the separator rather than being applied to the active mass as intended. Development of adequate separator materials, applied in an optimum fashion is

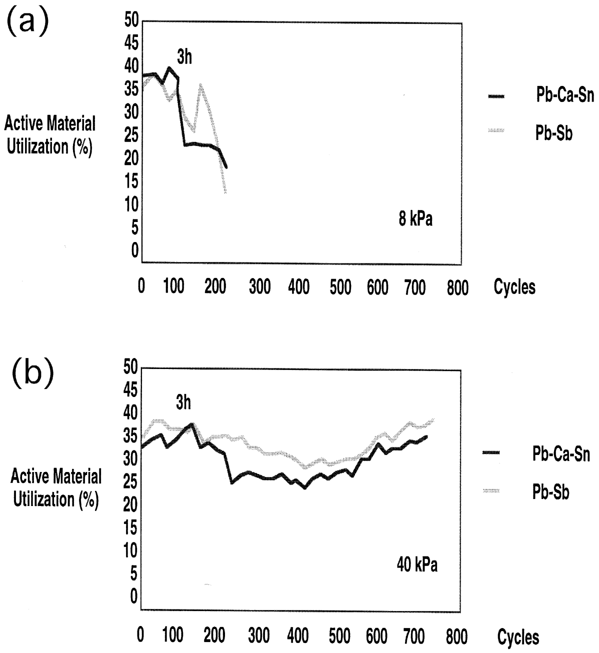

Fig. 1. Effect of compression on the 100% DoD cycle life of two types of flooded cells with Pb—0.08 wt.%, Ca—0.3 wt.%, Sn and Pb—1.6 wt.% Sb positive grids, respectively, discharged at the 3-h rate. (a) 8 kPa compression; (b) 40 kPa compression. (Data taken from ALABC (CSIRO Project No: AMC-007).

clearly a vital area requiring optimization if long cycle lives are to be maintained.

In summary, therefore, the achievement of long cycle life by overcoming premature capacity loss requires attention to at least three factors: (i) compression of the stack in a direction perpendicular to the plane of the plate; (ii) the use of alloys with sufficient creep resistance to prevent growth in the plane of the plate; (iii) accurate control of the charging process, (see below).

3.2. Specific energy

Two major approaches to improving the specific energy of the system are to reduce the weight of the structural components of the cell and to improve the utilization of the active materials. The latter depends upon choosing a design of cell with minimal diffusion lengths and possibly the deployment of additives that enhance electrolyte supply. The gravimetric issue can be addressed by utilizing lower gauge grids which combine improved corrosion resistance (so that less sacrificial material needs to be provided) with high strength. Fortunately, the alloys which have been developed with increased tin content [8] do indeed combine these two virtues. Fig. 2a shows how the corrosion weight loss during a period of 5 days exposure decreases with increasing tin content of a lead–calcium alloy, and Fig. 2b shows how the creep resistance increases with increasing tin [8].

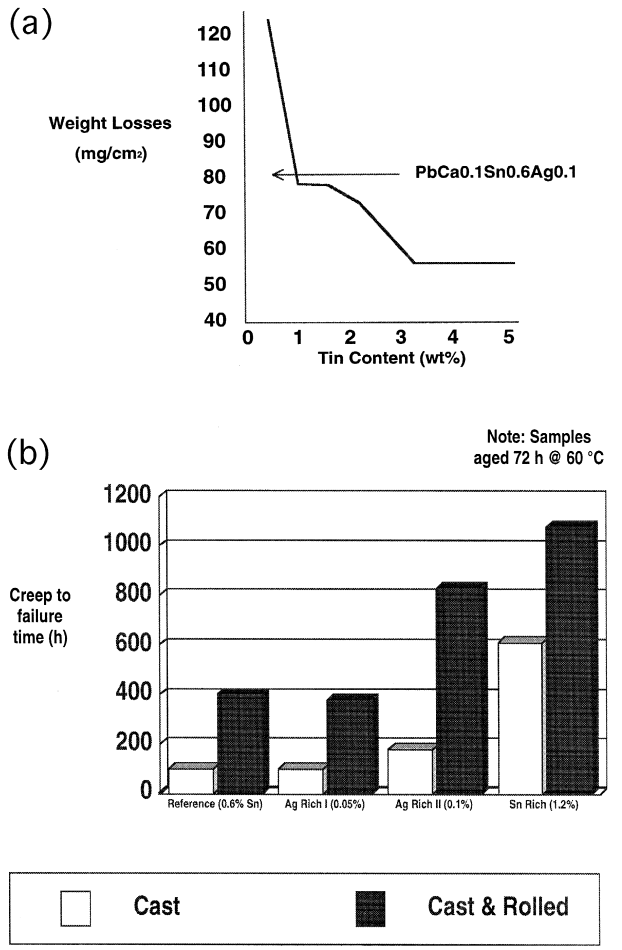

Fig. 2. Addition of tin and silver to lead–calcium alloys; (a) decrease in the weight loss during a 5-day test as tin content of Pb—0.1 wt.%, Ca—0.6 wt.%, Sn—0.01 wt.% Ag alloy is increased; (b) increase in time to creep failure (at 27 MPa) as tin and silver are added to Pb—0.08 wt.%, Ca—0.6 wt.%, Sn—0.03 wt.% Ag alloy and as the casting operation is followed by rolling [8].

Projects within the new ALABC programme are directed towards making use of these alloys in batteries with thin grids and flat plate or tubular plate design in order to achieve long life together with high specific energy.

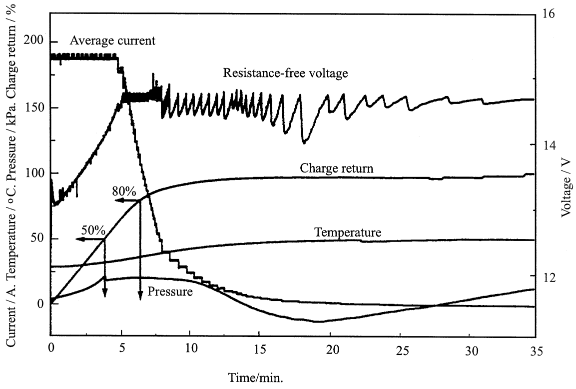

Fig. 3. Charging characteristics of a VRLA battery recharged according to an interactive pulsed-current/constant-voltage algorithm. (Data taken from ALABC/CSIRO Project No. RMC-008).

3.3. Rapid recharge

Although it flies in the face of conventional wisdom to do so [10], a significant effort in the ALABC programme has been devoted to recharging deep-discharged valve-regulated lead/acid batteries in the shortest possible time. The initial incentive for this work was as a convenient means of offsetting the somewhat limited range achievable with a battery offering a specific energy of no more than about 50 W h kg^{-1}. Despite the so-called 'Ampere-Hour Rule' [10], it was quickly found that valve-regulated batteries can be substantially charged within a few minutes (Fig. 3). In fact, repeated treatment in this way has shown [11] that it leads to a substantial increase in cycle life. The origins of this improvement are being vigorously sought in ongoing technical programmes, but the early indications are that rapid recharge produces an active material with a small particle size and much higher surface area than does regular charging (Fig. 4). This is probably the reason for the increase in line broadening which occurs in X-ray powder diffraction patterns of lead dioxide charged at

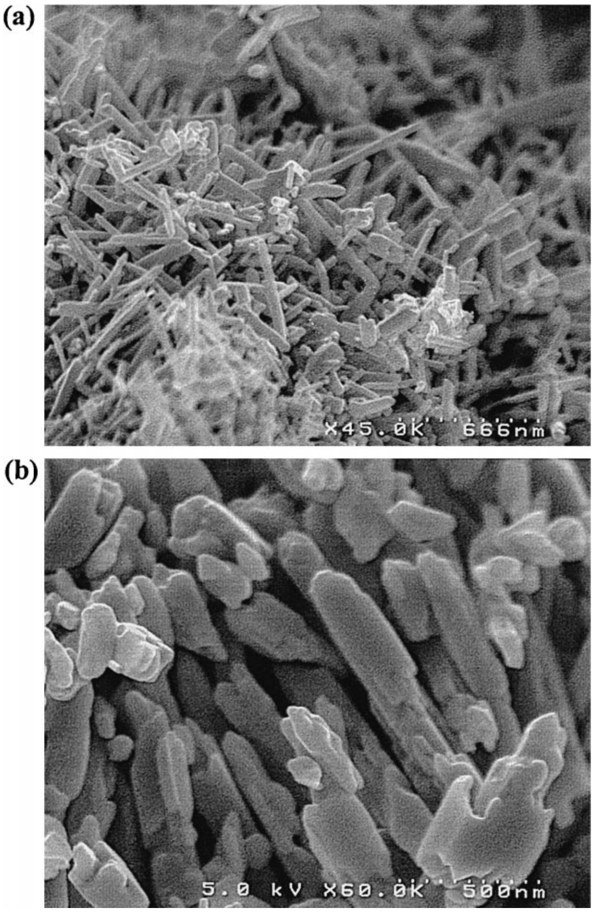

Fig. 4. (a) High-rate charging of VRLA batteries restores the positive active material in a high surface area form characterized by a needle-like habit. (b) When the battery is recharged at lower rates the positive active material forms larger particles. (Data taken from ALABC/CSIRO Project No. AMC-009).

higher rates. It is therefore possible that fast charging may produce a bonus benefit beyond its original purpose. The utility of fast charging as a means of daily range extension has been dramatically illustrated in December 1996 by a team from Delphi-E and Aero Vironment who drove an electric vehicle a distance of 1025.5 mile within 24 h on the streets and highways of Los Angeles. This demonstration illustrates that, with the convenience of fast charging, an electric vehicle equipped with lead/acid batteries suffers no significant range limitation during a day's drive.

4. Conclusions

The present state of the technology indicates that, with the projects currently in train, valve-regulated lead/acid batteries with a performance anticipated in Table 2 are on schedule for development before the end of 1998. The achievement of such a performance will represent a spectacular advance by the lead/acid battery community during the course of the 1990s and offers the prospect of an electric automobile with a range per charge of over 100 mile, repeatable several times within a day and over 500 times during the lifetime of a battery pack.

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