ELSEVIER

Journal of Power Sources 59 (1996) 81–86

JOURNAL OF POWER SOURCES

Lead/acid battery myths

P.T. Moseley

The Advanced Lead–Acid Battery Consortium, A Program of the International Lead Zinc Research Organization, Inc., 2525 Meridian Parkway, Suite 100, Durham NC 27723, PO Box 12036, Research Triangle Park, NC 27709-2036, USA

Received 28 October 1995; accepted 13 November 1995

Abstract

The lead/acid battery deserves a more positive image than has been traditional heretofore — particularly with respect to a number of aspects that relate to its utility as a power source for electric vehicles. Recent results from a large internationally coordinated research programme indicate that: (i) with proper attention to construction, valve-regulated lead/acid batteries can be deep-discharged many times without capacity loss; (ii) lead/acid batteries can be recharged extremely rapidly so that long journeys of electric vehicles become a realistic possibility; (iii) ranges of over 150 km between charges are achievable, and (iv) the introduction of significant numbers of lead/acid-powered electric vehicles does offer a beneficial environmental impact.

Keywords: Lead/acid batteries; Deep-cycle performances; Capacity; Recharging facilities; Environmental impact

1. Introduction

As a consequence of its long history of development, lead/acid battery technology is set about with a variety of folklore, and some of its reputed disadvantageous characteristics are erroneously attributed. Once erroneous attributions have appeared, it can be very difficult to dislodge them from the 'conventional wisdom', despite the tendency of the research community to revisit each aspect of the system on a regular basis. It is the purpose of the present paper to take a sideways look at a number of myths that have been harboured within the lead/acid battery community over a number of years, particularly those which would appear to bear on the prospects for success in the most demanding of applications, namely, the deep-discharge cycling required for electric-vehicle use.

2. Discharge capacity

Specific energy is seen to be the principal factor that limits the suitability of lead/acid batteries for electric-vehicle duty. This is the quantity of energy that can be delivered during each discharge cycle per unit weight of battery. Specific energy is obviously influenced unfavourably by the weight of the components (lead and lead compounds) employed in the system. There is little that can be done to ameliorate this problem in conventional battery designs, beyond paring down the physical dimensions of the grid members to the minimum level compatible with resisting corrosion through a full operational life. On the other hand, attempts to increase the amount of energy that is withdrawn from the active materials deployed within the grids have been an active preoccupation for lead/acid battery technologists since the earliest stages of development of the system. In most conventional batteries discharged at $C_1/1$ to $C_3/3$ rates, it is found that only 25 to 30% of the active mass in the positive plates is actually able to be discharged. This fractional 'utilization' of the active material represents a substantial limitation on the ultimate specific energy of the system. It is also the focus of the limitations on cycle life of deep-discharge batteries. The life of the batteries is normally gauged by the number of deep-discharge/recharge cycles accomplished before the measurable discharge capacity falls below a certain percentage (normally, 80%) of the initial value. The factors that limit the utilization, and hence the specific energy, are also the factors that ultimately determine the end of cycle life by the progressive reduction of discharge capacity.

It has been found that, in some circumstances, the deep-discharge capacity required for electric-vehicle applications of lead/acid batteries falls quite rapidly with cycling and, thereby, results in a very short life. The process by which this decay occurs has been termed 'premature capacity loss' (PCL) [1].

In theory, a wide range of factors could influence the discharge capacity and the development of capacity loss that can

0378-7753-95-$15.00 © 1996 Elsevier Science S.A. All rights reserved
SSDI 0378-7753(95)02305-4

occur in lead/acid batteries. Early explanations of these phenomena had to do with the possible existence of a form of PbO_2 that was electrochemically inactive, or with the possibility that a hydrogen species was playing an important role in the availability of discharge capacity. Extensive research programmes into these possibilities indicated that such notions were ill-founded [2]. It now appears likely that the most severe limitation on discharge capacity [3] and a prime source of PCL loss both lie within the positive active-mass. The limitation is imposed simply by the microstructural requirements of the electrode which must accommodate large volume changes during the discharge/recharge reaction, allow acid ingress at all stages, and maintain electrical content with all of the dischargeable material.

An extensive study of the origins of PCL loss and of ways in which it can be overcome has been undertaken by the Advanced Lead–Acid Battery Consortium (ALABC) [4] through a working group of international battery experts and extensive experimental programmes. At the CSIRO laboratories in Melbourne, Australia, a microstructural study has been undertaken [5] with a purpose-designed cell to control active-material constraint. The findings indicate that the progressive expansion of the positive active-material results ultimately in a breakdown of conductivity throughout the porous structure. As this breakdown intensifies, less and less of the material is accessible to discharge and, therefore, capacity falls. A research programme at the University of Brno in the Czech Republic has shown [6] that the progressive decline in positive-plate performance is matched by an increase in resistance of the active mass — as the particles move apart.

The importance of the influence of microstructure on the maintenance of capacity through the discharge/charge reaction sequence is well illustrated by the scanning electron micrographs shown in Fig. 1 [1]. Here, a tubular positive plate is packed with lead dioxide and a minor weight fraction of graphite. When freshly prepared (Fig. 1 (a)), the active material appears to be tightly packed, but after an initial discharge (Fig. 1(b)), there is a considerable restructuring that leads to compaction in some areas and voidage elsewhere.

The evolution of the capacity of the above plates with discharge/charge cycling is markedly dependent on the weight fraction of graphite that is incorporated (Table 1). In the absence of graphite, no capacity is recovered because the active mass does not wet on the introduction of the electrolyte. The highest capacity is recovered with 1 wt.% of graphite and this is sustained through a number of cycles without major decrease. Electrodes with 5 or 10 wt.% of graphite show substantial initial discharge capacity, but this falls to a low level in early cycles and then progressively recovers. At 12 wt.% graphite, the discharge capacity remains low, presumably because the volume fraction of PbO_2 is below a critical value [7].

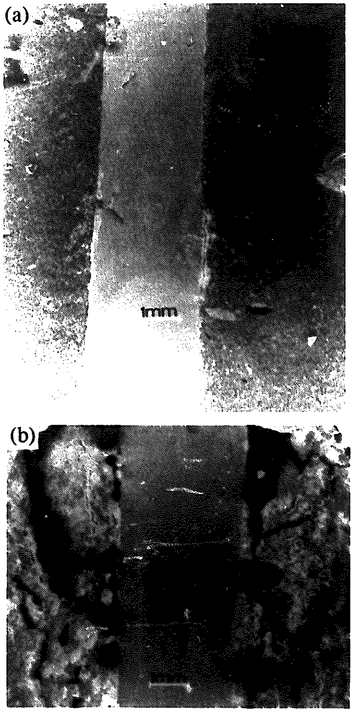

Fig. 1. Scanning electron micrographs of cross sections through tubular positive plates containing 10 wt.% graphite [1]. Central region of each image shows the grid spines with the active material on either side: (a) as prepared, and (b) after initial discharge.

Table 1
Effect of graphite addition on the evolution of discharge capacity from tubular positive plates

Graphite (wt.%)	Discharge capacity (as % of theoretical) obtained at cycle					
	1	2	3	4	5	6
0	1					
1	33	32	38	29	25	25
5	22	4	3	15	17	20
10	29	0	6	13	19	24
12	5	0	0.5	1	1	1.5

This is an extravagant demonstration of PCL that arises because insufficient material was provided in the initial packing of the tubular sleeves to keep the whole active mass under compression. Dramatic changes in microstructure and recoverable discharge capacity take place rapidly.

The CSIRO programme [5] has shown that the application of compression to the active mass, so that it is constrained from expansion, is largely effective in preventing the progressive loss of capacity.

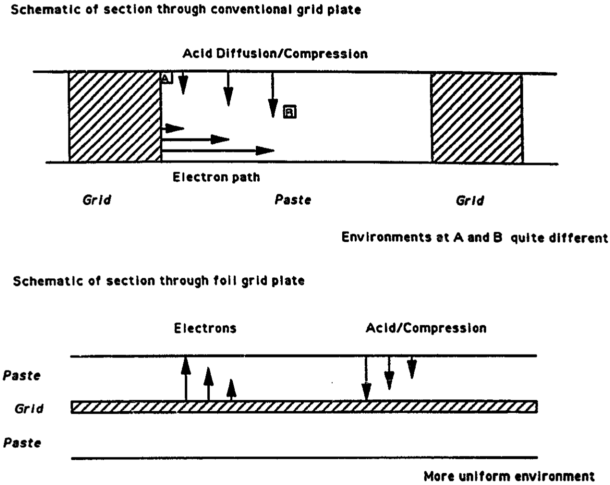

Fig. 2. Schematics of sections through positive plates with conventional or foil grids. With conventional grids, the electrochemical and compression environment of any point in the active mass is characterized by two positional parameters: one defining the distance from the grid and the other defining the distance from the plate surface. With foil grids, a reference point is simply defined by its position within the thickness of the layer.

The first point raised in this paper, therefore, is that some of the more exotic theories to account for materials' utilization/capacity loss can be set aside in favour of a straightforward consideration of whether or not the active mass remains optimally deployed. When this is achieved and when the charge regime avoids gassing (see below), it is possible to achieve large numbers of cycles with valve-regulated lead/acid (VRLA) batteries without loss of capacity.

Before leaving this topic, it is pertinent to consider the prospects for keeping the active material adequately constrained. It is possible to impose macro-constraint by packing flat plates tightly into a case, by the use of tubular gauntlets (also packed tightly), and by the use of spiral-wound designs. In addition to the overall compression that is applied to the electrode assembly, it is necessary, however, to consider the circumstances of the active material at a local level. In this connection, there may be some advantage in the use of continuous foil current-collectors, rather than conventional rectilinear grids. Fig. 2 shows schematics of the section through a conventional positive plate without over-pasting, and through a plate formed by pasting both sides of a thin foil. It is clear that the environment of the active material in the first case, in respect of current collection, acid access and compression, is more heterogeneous than in the second case. Battery design with continuous sheet current-collection could well achieve more uniform local compression and would be less prone to corrosion than designs with rectilinear grids.

3. Rate of recharge of lead/acid batteries

A second factor formerly thought to limit the potential utility of lead/acid batteries for electric-vehicle applications was the rate at which it is possible to restore charge. If the rate of charge of a cell is not controlled properly, the temperature of the cell can rise sharply and, perhaps more seriously, the electrodes can commence the formation of gas bubbles so that the active material is 'blown apart'. The well-known texts by Vinal [8] and Bode [9] quote an 'ampere-hour rule' for describing the limitations on rate of charge, as follows: 'If the charging rate, in Ah, is kept below a value equal to the number of Ah remaining to be charged, then the conditions as to gassing and temperature will be met'. This implies that it is not possible to exceed the $C_1/1$ rate in charging lead/acid batteries and indeed, in the past, charging periods of up to 8 h have been normal. This is clearly a serious impediment to the development of a market for lead/acid-powered automobiles in competition with combustion-engined vehicles. With the latter, owners are used to recharging (with liquid fuel) in a matter of a few minutes.

To lessen the recharging problem, the ALABC set out to explore the realistic limitations on fast charging. The subsequent results have been a dramatic demonstration that the technology has been labouring under yet another myth. A team of workers at COMINCO have demonstrated [10] that a variety of currently available lead/acid batteries are

Table 2
Fast charging a variety of types of lead/acid battery

Battery type	5-min return (%)	15-min return (%)	Temperature rise (°C)	Cycle no.	Capacity (% of initial)
Flooded SLI	54.3	82.7	22.2	55	<80
AGM flat plate	56.4	81.1	20.6	209	106
AGM spiral	51.0	84.9	24.2	273	120
Tubular, gel	41.4	82.8	23.3	156	104

rechargeable at very high rates over many cycles without capacity loss. Some examples of the charge returned in 5 and 15 min for three of the deep-cycling batteries are shown in Table 2; the performances are compared with those of an automotive (SLI) battery. In these tests, rapid recharges were provided by a 15 kW, 300 A, Minit Charger™ (Model MC 36) produced by Norvik Technologies. During charging, this equipment maintains a constant resistance-free voltage set by the operator. Many times per second, the charger interrupts the current, measures the resistance-free battery voltage, and adjusts the current to maintain the set resistance-free voltage. Also presented in Table 2 are the temperature rises for the batteries exposed to the fast-charging regime. These are probably confined to an acceptable level. The capacity delivered by each battery as a percentage of its initial capacity, after a given number of cycles, is also shown. It is clear that whereas the battery designed for SLI duties does not perform well under the fast-charge conditions, the three deep-discharging batteries are capable of at least 100 cycles. It is worth pointing out that these three batteries displayed no sign of PCL. On the contrary, their capacity at the end of the tests was, in each case, greater than at the start.

During the course of this ALABC project at COMINCO, some 30 different batteries have been evaluated using a rapid-recharging regime. All showed the capability of accepting 50% of charge within 5 min, except for a small number where the charger capacity was inadequate to cope with the size of the battery (as in the case of the last entry in Table 2). The importance of these fast-charging results cannot be overstressed since they indicate that, effectively, the range issue for electric vehicles is very much less of a problem than had been previously thought.

Moreover, the results are very encouraging in terms of demonstrating that lead/acid batteries can be recharged very rapidly without accelerating battery degradation. This appears to be true also when the batteries are subjected to very fast partial charging and discharging. Recognizing the importance of fast charging in the overall move towards electric-vehicle acceptability, the ALABC has devoted considerable effort towards the production of suitable fast-charging equipment and systems for monitoring the fast-charging process. A further demonstration of the effectiveness of fast charging in a realistic duty cycle is provided in the next section.

4. Range of lead/acid-powered electric vehicles

Another prevalent, but false, belief is that electric vehicles powered by lead/acid batteries are essentially confined to very small ranges, typically 50 to 70 km per charge. Nevertheless, experience shows that, provided precautions are taken with battery design to restrict capacity loss (by compression) and to charge the battery properly, a fully acceptable range is achievable.

The latter factor, i.e. proper charging, is particularly important; the process is not completely efficient. A small amount of energy is lost to parasitic reactions (heat generation, gassing, etc.) and it is always necessary to return more charge (Ah) than is withdrawn during discharge. The extent of this requirement for excess charge ranges from around 2% (in the most efficient systems) to around 20%. To return just 100% of the charge withdrawn is tantamount to undercharging the battery and guarantees capacity walk-down. For example, the capacity at the nth discharge, C_n, can be represented as [3]:

$$C_n = C_0(1-\alpha D)^n \qquad (1)$$

where C_0 is the original discharge capacity, α the fraction of recharge, D the depth-of-discharge, and n the cycle number. If a battery is cycled to an 80% depth-of-discharge with 100% of return of the number of Ah discharged, that represents, say, only a 98% return of accessible capacity (i.e., an overcharge of 2%), then αD will take the value 0.016 and the number of cycles achievable before capacity falls to 80%, C_0 will be only 14.

The ALABC study carried out by COMINCO [10] highlighted the conditions necessary for avoiding cycle-life degradation through inappropriate charging, i.e.:

- a sufficient degree of overcharge (often 10 to 20%) must be provided in order to make good the losses due to parasitic reactions; but note, a large amount of overcharge is liable to be deleterious
- a high initial charging current is beneficial; this is consistent with the fast-charging regime described above
- a sufficiently high voltage must be used; the precise threshold value depends on the type of battery to be charged

The following gives two examples of satisfactory operating experience with lead/acid-powered electric vehicles.

In January 1991, the Santa Barbara Metropolitan Transit District (MTD) introduced lead/acid-powered electric shuttles into regular transit service [11]. Each shuttle in a fleet of eight has been fulfilling a daily range of 80 miles during 8 h each day on a single charge. The public has responded very favourably to this imaginative programme and ridership has increased tenfold during the first year of all electric bus operation, i.e. from 0.1 to 1 million passengers per year. During the past four years, MTD has logged more than 0.48 million km and 60 000 h of service with the fleet of shuttles during the course of some 8000 driving cycles. Emissions of air pollutants have been prevented as a result of diesel bus replacement with the electrics. This programme is a clear demonstration that present state-of-the-art battery electric propulsion technology can be successfully applied to transit applications.

A second example, and one which illustrates the vital importance of correct battery charging, is provided by the operating experience of the Arizona Public Service (APS) Company's fleet of lead/acid-powered cars and pick-ups. These vehicles are being used in real road-driving duty, and make full use of all the electric accessories such as air-conditioning, lights, etc. Every few weeks, the vehicles are subjected to a range test on a measured track. In April 1995, the ranges of the vehicles were falling precipitously from one measurement to the next, and were well below those expected on the basis of literature produced by the manufacturers. Following consultation with the ALABC, the battery manufacturers, the vehicle manufacturers and the charger manufacturer, the APS Program Manager introduced revised charging algorithms [12]. Subsequently, the vehicles' performance has improved in a dramatic fashion to the point where ranges of over 160 km per charge are being measured on each assessment on the track. Some of these vehicles are being charged at conventional rates, while others are making almost exclusive use of very fast-charging methods with state-of-charge return from 30 to 100% in just 13 min. The improved performance following adjustments to the charge algorithms has been experienced by both the vehicles being charged conventionally and those being fast-charged.

The significance of these latter results should not be underestimated since it demonstrates not only the vital importance of correct charging in order to achieve a full range with a lead/acid-powered electric vehicle, but also shows that extremely fast-charging is a valid procedure to the point where 'range is no longer an issue'.

5. Environmental impact

Not all lead/acid myths have long histories and the final topic addressed here was raised earlier this year by a report issued by Lave et al. [13] at the Carnegie Mellon University. It was proposed, on the basis of a theoretical study, that since a growing electric-vehicle market will require the production of appreciably more lead/acid batteries, lead emissions will increase and will pose a threat to public health. This, demonstrably, is not true.

The Carnegie Mellon report (see Ref. [13]), which is based on a hypothetical electric vehicle using 'available' and 'goal' technologies, makes a number of significant errors in projecting the amount of lead emissions associated with the use of lead/acid batteries in electric vehicles. First, the stated battery mass of an 'available technology' electric vehicle, cited as 1378 kg — upon which all other calculations are based — is greater than the entire mass of, for example, the GM Impact electric vehicle, which has a curb weight of 1350 kg. Second, the authors base their projections on industry air-emission factors that date back to the mid-1970s, and on lead materials flow balances that were decades older still. By doing so, the study ignores all the benefits accrued from the very rigid standards that have been established since that time to limit the release of lead from battery plants, mines and smelters.

Further, the authors of the Carnegie Mellon study erroneously combine lead emissions from all sources and pathways regardless of form, and then equate these emissions to dispersive, airborne, tail-pipe emissions. The problem with such methodology is that it fails to consider the relative bio-availability (and subsequent risks) of the different waste streams, and also ignores the presence of modern control and management techniques employed at these stationary lead-processing facilities.

It might be added that no theoretical approach to a problem of this sort can be regarded as entirely satisfactory unless hard figures are available to substantiate the conclusions. In the present case, the figures are in dramatic conflict with the Carnegie Mellon premise. As shown in Fig. 3, during the years between 1970 and 1993 the volume of lead consumed by the US battery manufacturing industry increased from 538 000 t by a factor of about 2. During the same period, industry modernization and regulatory compliance measures resulted in tremendous reduction in both the amount of lead released to the environment and exposures to lead. As a result, the levels of lead in air around point industrial sources witnessed a dramatic decline (i.e., by a factor of approximately 2) from 1970 to 1993 [14].

Facilities in the USA that fail to comply with the National Ambient Air Quality Standard (NAAQS) for lead are required to work with local and state officials to develop implementation plans to bring their facilities into compliance with the ambient standard. Therefore, all facilities will be required to comply with the NAAQS, regardless of whether or not they experience an increase in their lead/acid battery production. Similarly, stringent regulations govern lead discharges to land and water.

The majority of emissions reported in the Carnegie Mellon study involved lead releases to land from mines and smelters. Attempts to correlate mine tailings and smelter slags with dispersive emissions resulting from the combustion of leaded gasoline are highly inappropriate. The large volume wastes generated at stationary sources are typified by low bio-availability and local management and control.

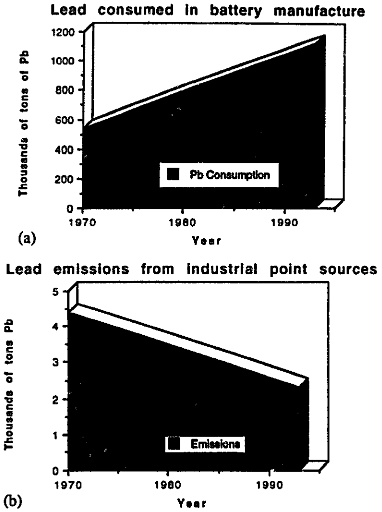

Fig. 3. Volume of lead consumed in battery manufacture between 1970 and 1993 compared with lead emissions from industrial point sources during the same period.

In summary, the adoption of large numbers of lead/acid-powered electric vehicles still offers the prospect of a dramatic improvement of the environment on the streets of major cities. Even in the manufacturing facilities where the batteries are produced, there are no prospects of environmental degradation due to the increased throughput that might be necessary — another myth.

6. Conclusions

There is an important need for a concise and reliable assessment of the status of lead/acid battery technology. Moreover, a view of this status is obscured by the existence of a number of myths that have arisen, for a variety of reasons, over the relatively long development time of the technology. It is important to set such myths aside and to recognize that:

- Discharge capacity of the lead/acid battery is limited by well-understood physical parameters that can be controlled to allow an adequate specific energy over a cycle life which, in turn, will be satisfactory for electric-vehicle applications
- Lead/acid batteries can be recharged very much more quickly than had been previously thought
- Provided the recharge is carried out according to a properly designed algorithm, an adequate range can be achieved by an electric vehicle powered with a lead/acid battery; this range can be supplemented with 'opportunity' fast charging to the point that range becomes no longer a problem
- An increase in the number of lead/acid batteries manufactured to supply a growing electric-vehicle industry does not pose an environmental threat and, indeed, the introduction of a substantial fraction of battery-powered vehicles still offers the prospect of dramatically enhancing the transport infrastructure environment

References

[1] A.F. Hollenkamp, *J. Power Sources*, *36* (1991) 567–585.
[2] S.V. Baker, P.T. Moseley and A.D. Turner, *J. Power Sources*, *27* (1989) 127–143.
[3] A.D. Turner, P.T. Moseley and J.L. Hutchison, Proc. Vol. 84–14, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 267–276.
[4] J.F. Cole, *J. Power Sources*, *40* (1992) 1–15.
[5] A.F. Hollenkamp, K.K. Constanti, M.J. Koop and K. McGregor, *ALABC Project No. AMC-003*; A.F. Hollenkamp, *J. Power Sources*, *59* (1996) 87–98.
[6] M. Calabek, P. Baca, V. Smarda and K. Micka, *ALABC Project No. AMC-003A*.
[7] D. Pavlov, *J. Power Sources*, *33* (1991) 221–229.
[8] G.W. Vinal, *Storage Batteries*, Wiley, New York, 4th edn., 1955.
[9] H. Bode, *Lead-Acid Batteries*, translated by R.J. Brodd and K.V. Kordesch, Wiley, New York, 1977.
[10] E.M.L. Valeriote, K. Tomantschger, T.G. Chang, J. Sklarchuk, D.M. Jochim and M.J. Dewar, *ALABC Project No. RMC-002*; T.G. Chang, E.M.L. Valeriote and D.M. Jochim, *J. Power Sources*, *48* (1994) 163–175.
[11] P. Griffith, *FTA Rep. No. FTA-CA-26-0019-95-1*, 1995.
[12] R. Hobbs, *Electric Vehicle Charger Test Project at Arizona Public Service*, Interim Rep. for US Department of Energy, 1995.
[13] L.B. Lave, C.T. Hendrickson and F.C. McMichael, *Science*, *268* (1995) 993.
[14] *National Ambient Air Quality Standard Trends Report*, 1993.