

Improving active-material utilization

N.E. Bagshaw

59 Clement Road, Marple Bridge, Stockport, SK6 5AG, UK

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Abstract

A major factor controlling the specific energy of a lead/acid battery is the utilization of active material. If this could be increased, the specific energy would be increased, with a corresponding increase in range of electric vehicles using the lead/acid battery. The main parameters that affect active-material utilization are examined, namely, current density, plate thickness, active-material structure, conductivity of active material and grid, and electrolyte volume and density. Increases in utilization can be achieved by changing all these parameters and examples are given. © 1997 Published by Elsevier Science S.A.

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1. Introduction

Although the research on newer types of battery with high specific energy has intensified in recent years, these systems are not yet ready for exploitation on a large commercial scale in electric vehicles. Lead/acid and nickel/cadmium batteries remain the only products that are presently commercially viable for this application. The main technical drawback of these mature batteries is their low specific energy (Wh kg^{-1}).

The energy density (Wh l^{-1}) of lead/acid batteries is relatively high and 100 Wh l^{-1} is achieved at the 5 h rate in some submarine batteries. In this particular type of electric-vehicle application, the weight of the battery is less critical whilst space is at a premium and lead/acid batteries perform efficiently and reliably. In road electric vehicles, although volume is important, weight becomes critical and the specific energy of traction batteries at $35\text{--}40 \text{ Wh kg}^{-1}$ only allows a vehicle range of 100–150 km.

One of the major factors that controls the specific energy is the utilization of the active materials. For example, the positive active-material in a traction lead/acid battery has a utilization of about 35% at the 3–5 h rate and there appears to be scope for improvement that could translate directly into increases in specific energy and vehicle range. This paper examines the factors that control the utilization of the active materials and ways of effecting an improvement in this utilization.

2. Current density

One of the accepted properties of a lead/acid battery is the effect of discharge rate (in terms of current or time) on the utilization of the active materials. ‘High rates’ and ‘low rates’ have different meanings in different applications. In automotive and aircraft batteries, a 1 min discharge is considered as a high discharge rate and a 1 h rate as a medium rate. In traction batteries, discharges of 10–30 min are high rates and a medium discharge rate is the normal rated capacity of 5 h. Finally, in submarine batteries, a high rate is defined as 1 h, a medium rate as 5–10 h and a low rate as 60–100 h. The only way of comparing such diverse batteries, with capacities that vary from about 25 Ah (aircraft) to over 10 000 Ah (submarine), is by considering the current density on the plates [1].

The utilization of positive active-material in relation to current density is shown in Fig. 1, where typical cells for aircraft, submarine, traction and standby applications are shown. All the cells are of the flat-plate type, except the traction cell which is of tubular construction. The actual area on the surface of the tubes has been used to calculate the current density in this case. All the cells are of the conventional free-electrolyte type, except the standby cell which uses VRLA technology. All the curves illustrate the increase in utilization with decrease in current density. Obviously, for a particular type and construction, the utilization can be increased if the design can be modified to give a larger plate surface area for a given amount of active material.

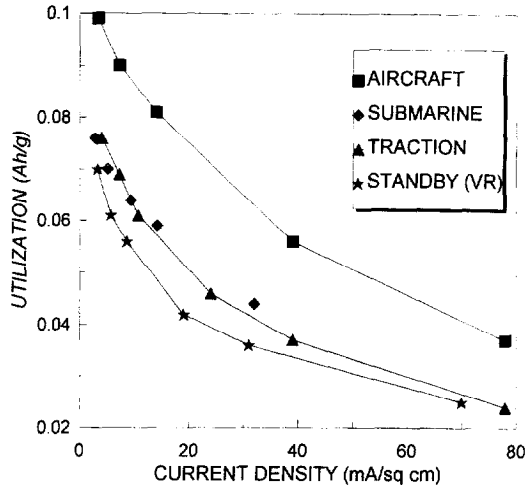


Fig. 1. Utilization of positive active-material in commercial cells.

The curves in Fig. 1 also illustrate that different constructions and designs give different utilizations at the same current density. For example, interpolation of the data shows that the positive active-material utilization at 10 mA cm^{-2} is some 33–39% higher in the aircraft type than in traction or submarine cells, and as much as 40–50% higher at 30 mA cm^{-2} . One of the major differences in design that accounts for this is the difference in thickness of the plates. This was 1.07 mm for the aircraft type and 3.9 mm for the submarine type (both flat plates). The traction plates were 8 mm thick, but these were of the tubular type and the real ‘thickness’ of a tubular plate in terms of utilization is the distance between the outside of the active-material surface and the surface of the spine, which was 2.4 mm. The standby plate thickness was 3.3 mm and the main reason for the somewhat lower utilization in terms of plate thickness is that the curves are based on rated performance and the actual average performance is somewhat greater.

3. Plate thickness

The effect of plate thickness alone can be demonstrated by single plate tests using plates of different thickness but the same paste technology. One example of such a test for negative active-material utilization in flat plates showed increases of 10% at 5 mA cm^{-2} , 35% at 10 mA cm^{-2} and 50% at 40 mA cm^{-2} , when comparing a 1.9 mm plate with a 5.7 mm plate. As would be expected, the gain in utilization for the thinner plate is greater as the current density increases. Similar results were obtained for positive plates.

A practical example of putting this into effect is the redesign of a large flat-plate cell (capacity approximately 10000 Ah at the 5 h rate) by redistributing the active material in plates of lower thickness. The positive-plate thickness was reduced from 4 to 3.3 mm (with a corre-

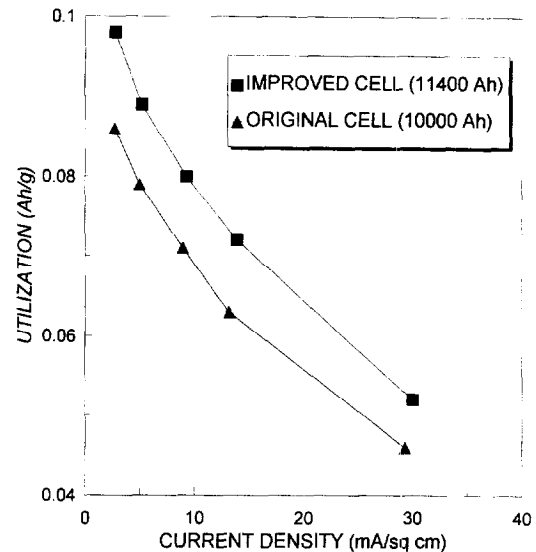


Fig. 2. Utilization of positive active-material in large flat-plate cells. Positive plate thickness: original 4 mm, and improved 3.3 mm.

sponding decrease in negative-plate thickness) such that the number of plates in the cell could be increased. The total amount of active material was approximately the same in the standard and the modified cell and only minor changes in other aspects of design were made. The effect of the change in thickness is shown in Fig. 2 where the positive active-material utilization is plotted against current density for the two cells.

At the relatively low current densities of 3 to 5 mA cm^{-2} (corresponding to discharge rates in the 10 h to 20 h range) the increase in utilization as a result of the change in thickness was 10–14%; this increased at higher current densities to 18%. For a given discharge rate (in h), however, the actual current density on the plates was lower for the modified cell because of the high total plate surface

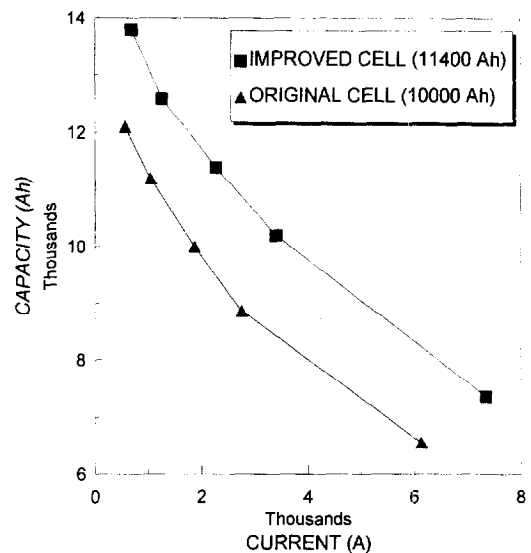


Fig. 3. Effect of improved utilization on capacity of large flat-plate cells.

area. The combined effects of lower current density and thickness are illustrated in Fig. 3 where the actual capacity is plotted against discharge current for the two cells. The combined effects resulted in an increase in capacity of 19 and 22% at 2000 and 6000 A, respectively.

It should be pointed out that the positive-plate thickness cannot be reduced without considering the effect on life. If major reductions in thickness were contemplated, the problem of grid corrosion would have to be addressed and grid alloys with higher corrosion resistance would have to be used.

4. Active-material structure

Obviously, the physical structure of the active material can have a critical effect on its utilization during discharge. Whilst processing parameters such as paste mixing and plate curing can have an influence, the original raw material — leady oxide — has a fundamental effect.

Table 1 shows the influence of the particle size of leady oxide on the utilization of positive-active material in single automotive-type plates discharged in excess electrolyte at 20 °C.

The utilization tends to increase with decrease in particle size. The effect becomes more pronounced at higher discharge rates. For example, the increase obtained by using oxide of 2.5 μm size instead of 70 μm is 35% at a current density of 250 mA cm^{-2} (10 min rate), but only 14% at 25 mA cm^{-2} (3 h rate).

Measurements of the physical properties of the pasted electrodes after curing and drying show that the essential difference is in internal surface area. The latter varies from 0.8 to 2.0 $\text{m}^2 \text{g}^{-1}$ (BET) with decreasing particle size of the original leady oxide. Pore-size distribution measurements show that the percentage of pores below 0.8 μm increases in electrodes made from finer oxides. Perhaps surprisingly, there is no clear relationship between the internal surface area of formed electrodes and the particle size of the original oxide. Semi-quantitative analysis (by X-ray) shows, however, a higher proportion of $\alpha\text{-PbO}_2$ in electrodes made from coarser oxides, no doubt because of the tendency for coarse leady oxide to contain higher amounts of free lead.

Table 1
Effect of particle size of leady oxide on positive active-material utilization

Mean particle size (μm)	Utilization (Ah g^{-1})	
	25 mA cm^{-2}	250 mA cm^{-2}
2.5	0.103	0.065
5	0.102	0.063
8	0.098	0.057
14	0.097	0.060
53	0.093	0.053
70	0.090	0.048

Active-material structures can also be modified by additives to the paste. An interesting effect on positive active-material structure has been shown by Tokunaga et al. [2,3] who added anisotropic graphite to the positive paste. This resulted in an increased porosity (mainly in the volume of pores with sizes above 2 μm) and, in turn, increased positive-material utilization. One of the reasons for this was the extra acid available in the pores of the plate.

Further attempts to modify the structure of the active material have been made [4–7]. For example, Edwards [4] examined the effects of an addition of lightweight, hollow, glass microspheres as a filler in the positive and negative paste. The performance of plates of similar porosity was evaluated in terms of the utilization of the lead dioxide and lead actually present in the plates. The effect of the glass microspheres was to reduce the utilization of the negative active material at low rates with no effect at higher rates. On the other hand, the lead dioxide utilization was increased, particularly at high rates, with a maximum effect at an addition of 4.4 wt.% of the glass microspheres. The increase in utilization was again explained by the increase in the acid/active-material ratio in the plate.

Whilst modifications in active-material structure can obviously have a significant effect on utilization, it has to be remembered that an increase in performance of the plate itself is the important criterion. If the additives to the paste displace active material, although there is an increase in utilization of the remaining dioxide, there is not necessarily an increase in capacity of the plate.

5. Conductivity of active material

Both the active materials in lead/acid batteries (lead and lead dioxide) are conductors and act as current carriers to the nearest grid member during discharge. As discharge proceeds and lead sulfate is formed, the conductivity decreases and causes an increase in plate resistance. This is one of the major reasons for limiting the discharge time and, therefore, the utilization of active material (to 35–40%). The position can be contrasted with that in silver peroxide plates (in silver/zinc cells) or silver chloride plates (in magnesium/silver chloride sea-water batteries) where the discharge product (silver) has a higher conductivity than the original active materials and, thus, results in a much higher utilization as well as a flatter discharge curve.

A utilization of about 80% for both silver peroxide and silver chloride can be achieved (with the appropriate designs) even at very high discharge rates (current densities of 0.125 and 0.375 A cm^{-2} , respectively).

The effect of the relatively poor conductivity of active material in lead/acid batteries as discharge proceeds can be shown by tests on single plates with varying pellet size. The utilization of positive active-material in automotive-size plates with pellet areas between 0.3 and 3.42 cm^2 is

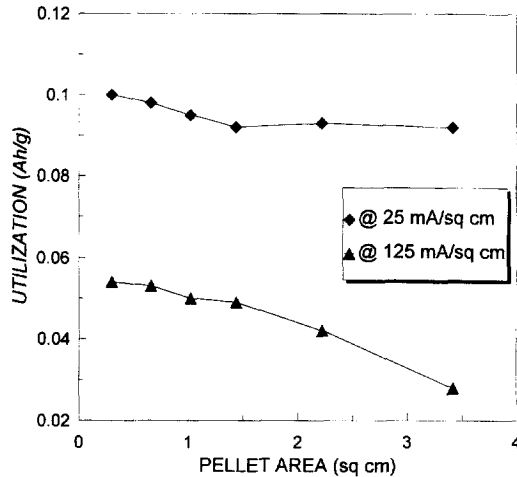


Fig. 4. Utilization of positive active-material in single plates with varying pellet size.

shown in Fig. 4. With increase in pellet size, the average distance from active material to conducting grid member increases. This results in a decrease in utilization, especially at higher current densities, and illustrates the importance if grid design in optimizing utilization.

Various attempts have been made to improve the utilization of lead/acid active materials in the original paste formulation. These include graphite [2,3] and tin dioxide coated glass flakes [5]. From a conductivity point of view, one of the potentially most useful additions is Ebonex, the trade name for the Magneli phase oxides of titanium. These oxides have the general formula Ti_nO_{2n-1} and their conductivity values were given by Hayfield in the original patent [8]. The potential uses of the Magneli phase oxides in various types of battery and fuel cells were outlined in 1990 [9]. Early work with the additive [10] showed that the formation process for battery plates could be accelerated. By contrast, experiments with tubular cells containing Ebonex powder in the active material gave disappointing results [11]. More recently, the effect of Ebonex in fibre form as an additive to flat positive plates in automotive-type batteries gave more encouraging results [12]. An addition of 2 wt.% to the positive mix resulted in increases in utilization of 15% at the 3 h and 5 h rates, but only 2% at the 20 h rate, compared with standard material.

6. Conductivity of grid

The active-material utilization is controlled both by the conductivity of the active material itself (as shown by Fig. 4) and by that of the grid. The capacity available in the plates has to be delivered at a useable voltage, and any high IR drops in the plates (from whatever source) will limit the capacity and, therefore, the utilization of the active materials. These effects are most evident in large plates and at high discharge rates.

The combined effects from the grid and active material can best be illustrated by considering the use of a high conductivity (copper) negative grid. Tests on large flat-plate cells [13] showed that the use of copper in the negative grid had no effect when the cells were discharged at a current density of 46 mA cm^{-2} on the positive plate. When copper was incorporated in both the negative and positive plates, however, increases in utilization of 18–19% were obtained. It is evident that the cell is positive limited and the resistive effect in the positive active-material prevents any increase in performance of the cell, even when a high conductivity negative plate is used.

The position is quite different in large cells using tubular positive plates. The average distance from the positive active-material to the grid is much smaller in a tubular than in a flat plate, and the resistive effect caused by the active material is therefore much smaller. In this case, the performance at high rates is limited by the negative plate and the use of a copper negative grid enables an increase in active-material utilization and, consequently, in cell performance. Lead-coated, expanded copper grids [14] have been used in tall cells since the 1970s and can result in an increase in active-material utilization and cell performance of 25% or more at high rates [15].

Obviously, the use of high-conductivity grids is less effective in smaller cells but, at high discharge rates, a significant increase in utilization can be obtained. Copper negative grids have been used in some traction cells.

The most efficient overall conductivity in a battery is obtained from a bipolar construction and a significant increase in active-material utilization (and a simultaneous decrease in weight) would be achieved by such a construction. One of the major problems in using bipolar plates in lead/acid batteries is the corrosion of the conducting barrier at the positive side. The use of a conducting oxide (such as Ebonex), as a coating on the barrier material or as a filler in a plastic barrier, or even in bulk form, is one possible approach to solving this difficulty.

7. Electrolyte

Unlike other types of battery, the electrolyte in a lead/acid cell is also an active material and is consumed

Table 2
Effect of acid volume on positive active-material utilization

Discharge duration (h)	Positive active-material utilization (Ah g^{-1})	
	Standard	High acid
1	0.050	0.050
3	0.066	0.067
5	0.072	0.074
10	0.079	0.082

during discharge. At very low rates (100 h), all lead/acid cells are limited by the electrolyte. Even at much faster rates, an increase in acid volume can have an effect. Table 2 shows the increase in positive active-material utilization caused by an increase of 10% in acid volume in a 9000 Ah cell. Increases of 3–4% can be achieved at 5 h to 10 h rates. At faster rates there is little advantage.

The alternative way of increasing the acid content is to increase the density of the electrolyte. Some industrial cells now contain acid of 1.30 sp. gr. instead of the traditional 1.27 sp. gr. The theoretical increase in capacity for each litre of 1.3 sp. gr. acid, compared with the lower density, is 16 Ah and gives a corresponding increase in utilization of active material. In actual practice, an increase in density of acid from 1.275 to 1.30 can result in an increase in active-material utilization of about 6 to 9%.

One of the problems in using extra electrolyte is that it may not be available for use if it is remote from the actual plates and cannot be transported sufficiently quickly to the plates. The problem can be exacerbated by acid stratification. It was shown by Sunu et al. [16] that agitation of the electrolyte in motive power cells could overcome such problems and could increase the capacity (and, therefore, utilization) by about 4% during discharge at rates from 1 to 5 h, simply by making the electrolyte available at the active material.

The principle of electrolyte agitation can be taken further by using forced flow of acid through the plates. Between 1978 and 1982, interesting laboratory experiments were carried out by VARTA in an ILZRO project [17]. A special arrangement, known as the 'eloflux' cell was used. This comprised a test electrode and two counter electrodes with a system for forcing excess electrolyte through the pore system in the plates. Such an arrangement enabled the utilization of active materials using acid of constant density to be determined. Utilizations of positive and negative electrodes were 250% and 165%, respectively, of those obtained with no forced flow. Although these improvements were achieved under special, idealized, laboratory conditions, it is tempting to consider the

design of a practical lead/acid system using excess acid flowing across (and through) the plates. Although this would complicate the design of the traditional lead/acid battery system, its advantages may be worth examining.

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