A high performance lead–acid battery for EV applications

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Abstract

Some recent work in the development of a high energy density lead–acid battery for electric vehicle application is described. Two separate methods are used to achieve this objective. Significant total cell weight savings can be achieved by the use of an electrolyte management system. This minimises the quantity of water used in the electrolyte. The second feature concerns the form and utilization of the lead–paste active materials. The positive and negative pastes are carried as a slurry and are agitated during the charge/discharge cycle. This maximises the utilisation of the active materials and reduces premature sulphation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In any review of power sources for future road transport vehicles, the performance of existing petrol powered motor cars is likely to be the yardstick against which all other power sources will be compared. The power sources most likely to provide a favourable comparison are those which can display comparable range and speed, exhibit a long and reliable life, and can be manufactured at a cost similar to the petrol powered competitor. Any vehicle which fails in any of these requirements is unlikely to achieve anything but a niche market share. To achieve these ends, the power source must have a high energy density and yet be economic to manufacture.

For electrically powered vehicles relying upon a secondary battery system, the lowest cost option is the lead–acid battery, with its nearest cost competitor being several times more expensive. While such a cost differential would not be so important in say a mobile phone or portable computer application, in the case of the electric vehicle where the battery may account for half the total cost, it is a major factor. Unfortunately, the lead–acid battery has a history of poor energy density. Current commercial traction batteries produce some 30 W h kg^{-1} while some more advanced research designs do well to achieve 50 W h kg^{-1}.

This paper describes an ongoing project to re-examine the lead–acid cell taking a pragmatic approach to developing options which will permit the attainment of an energy density of the order of 70–80 W h kg^{-1}. To achieve such an improvement in performance, the researcher has to examine methods of making dramatic weight reductions in addition to ensuring that all chemical conversions take place as efficiently as possible within the cell. These two approaches are described in this paper. With any battery design, which displays a doubling of battery energy density, the reader will not be surprised to observe that it bears little resemblance to current commercially available lead–acid batteries.

The final part of this paper describes a lead–acid battery desk-top design exercise which produces an energy density in excess of 80 W h kg^{-1}.

2. Reduction of lead–acid cell weight

To improve the energy density of a lead–acid battery, the designer can either reduce the total weight of the battery or increase its output (or better still, do both). In this part of the paper, the opportunities for reducing its weight will be explored.

The weight of a lead–acid cell is made up of two parts. Firstly, there are the elements which are necessary for the storage and provision of electrical energy and secondly, those items which are present to provide the necessary infrastructure. The first group, the active components, consists of the positive and negative active lead oxide/lead pastes and the sulphuric acid-based electrolyte. The quantity of these items may be accurately calculated from electrochemical equations and the required cell capacity. For a nominal 1 A h cell, 4.46 g of (+ve) lead oxide, 3.86 g of (−ve) lead and 3.64 g of concentrated sulphuric acid

are required. This gives a total weight of 11.96 g. These figures assume that the total conversion of all of the active substances (from lead and lead oxide to lead sulphate and the acid to water) occurs during the discharge cycle. In practice, the conversion is not ideal; hence, the cell's theoretical output is not realized. For reasons to be discussed later, it is also necessary to dilute the concentrated acid with water to achieve a specific gravity of approximately 1.25. This adds some 7.3 g of weight.

The second group of components consist of the hardware necessary for containing the contents of the cell and the electrical conductors needed for collecting the electrical current and connecting one cell to the next. Because of the aggressive chemical environment within the cell, all of the electrical components have to be made of lead-based metals. In a typical commercial cell, the additional weight of this second group of components is likely to be 20 g A^{-1} h^{-1}. The electrical hardware can be reduced in weight by using some form of composite construction such as a sandwich material consisting of a lead outer with a lighter metal core. More basic design changes, such as the use of bipolar construction (where this can be accommodated) can also reduce the total hardware weight.

The importance of cell weight is illustrated by Fig. 1 which shows the relationship of total cell weight to the energy density for a 1 A h cell. A cell voltage of 2 is assumed. The theoretical total weight of active material (11.96 g) is marked, which gives a corresponding energy density of 167 W h kg^{-1}. It is also of interest to note that as the total cell weight is reduced, the gain in energy density accelerates. A 10 g weight reduction from 80 to 70 g produces an increase of 3.5 W h kg^{-1} whereas saving 10 g from 40 to 30 g produces an increase of 17 W h kg^{-1}.

As was mentioned earlier, to reduce sulphation and

premature destruction of the spongy lead active material, the concentrated sulphuric acid electrolyte has to be diluted with water until its specific gravity is approximately 1.25. This means that for a 1 A h cell, the 3.64 g of acid requires a further 7.3 g of water. This increases the total weight of active components from 11.96 g to 19.26 g. Reference to Fig. 1 will show that by diluting the electrolyte in this way, the theoretical energy density has, at a stroke, fallen from 167 to 104 W h kg^{-1}—a loss of some 63 W h kg^{-1}. However, this performance loss does not have to be, since this excess weight penalty can be minimised by the use of an electrolyte management system.

The electrochemical requirement for active materials is a function of cell capacity and time. Consequently, although a 1 A h cell will require 3.64 g of acid (suitably diluted), this is not needed all at once. If discharge is evenly spread over 1 h, then a supply of acid at the rate of $3.64/60 = 0.06$ g min^{-1} would suffice. Whereas, the full weight of acid (i.e., 3.64 g A^{-1} h^{-1} capacity) would need to be available, the same is not true for the water dilutant. This is because the electrolyte specific gravity falls as the cell is discharged and further water is not needed, just a top up with acid to maintain the specific gravity at, or near, 1.25.

Fig. 2 illustrates an electrolyte management system. For reasons of clarity, only a single cell is shown and parts such as the electrolyte monitoring and control system are omitted. The system works as follows: A cell is designed to have a minimum volume of electrolyte. Facilities are provided to permit the pumping of electrolyte in and out of the cell. The cell is initially filled with acid diluted to a specific gravity of 1.25. As the cell is discharged, the electrolyte strength falls and this is monitored until it reaches a pre-determined level. At this point, the elec-
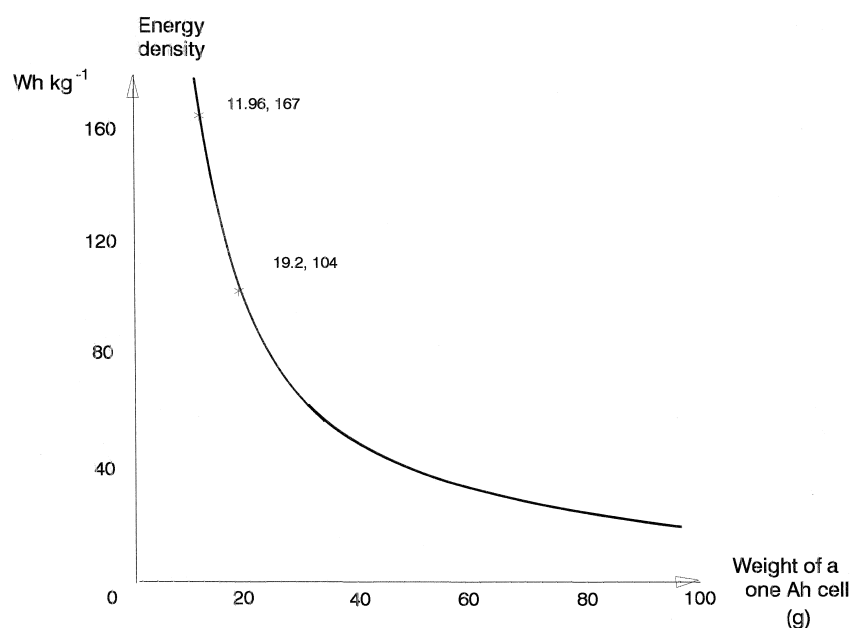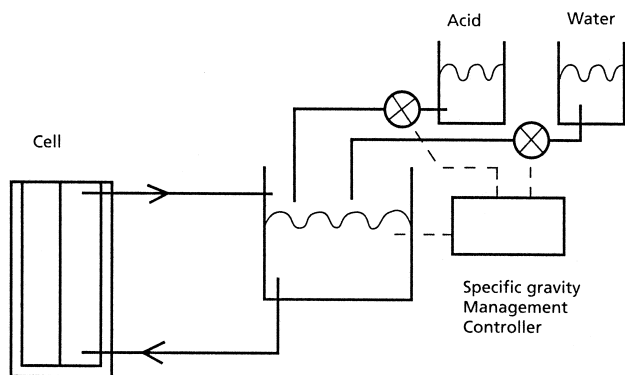

Fig. 1. Energy density against total cell weight.

Fig. 2. Electrolyte management system.

Fig. 3. Capacity against plate thickness at various discharge rates.

trolyte is dosed with concentrated acid to restore its specific gravity to the target level. This process continues cyclically around each cell until no further acid is available. This should coincide with the full conversion of the lead and lead oxide into lead sulphate.

The cell charging commences with all electrolyte at 1.10 specific gravity. This rises to 1.25 as charging continues. During this recharging cycle, additional water has to be added to the circulating electrolyte to ensure that the full conversion of the lead sulphate back into lead or lead oxide takes place. When finally the active materials are all in a recharged state, the final stage of the process is initiated. Valves adjacent to each cell are closed and the remaining electrolyte in the separate store is heated by an integral, mains-powered, heater. The resulting vapourised water is condensed and returned to the water store. The remaining concentrated sulphuric acid is returned to its on-vehicle store for use during the next discharge cycle. The cell is then ready for the next discharge cycle. The water used in the above described cycle is only required when recharging is taking place so its added weight does not need to be carried by the vehicle but stored off vehicle adjacent to the vehicle charging point.

The use of an electrolyte management system can allow a saving in weight of cell fluids amounting to some 40–60%. If such a system was applied to a conventional traction battery, suitably modified to have a reduced electrolyte volume, an energy density improvement from say 30 W h kg^{-1} to 33 W h kg^{-1} could be expected.

Such an electrolyte management system does require some extra components. These being pumps, solenoid valves and a mains-powered acid reforming unit. Software would be needed to continuously control the overall process and, in particular, monitor the specific gravity of each cell. These extra components would be shared by all cells so their weight on a per cell (or per A h) basis would be small.

3. Lead–acid cell conversion efficiency

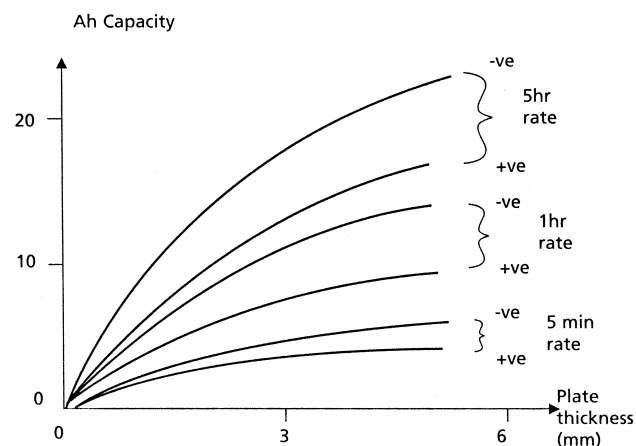In commercially available traction cells, the amount of lead/lead oxide active material, for a given ampere hour output, is often approximately twice the theoretical value. This implies that the material conversion efficiency, over the charge/discharge cycle, is often only 50%. Various researchers have documented the variation in positive and negative active material conversion efficiency for different discharge rates and material thickness. Typical results are shown in Fig. 3. [1].

The low efficiency of the cell is caused by several mechanisms. These include the sulphation of the active material leading to the inclusion of high-resistance lead sulphate. Large particles of active material only permit reaction on their outer surfaces. Problems of mass transport are caused by restricted diffusion of active materials —which in turn causes a fall in active material porosity.

To get over these problems during the deep cycling of active material and to raise the cell conversion efficiency, two alternative approaches can be considered.

The first is to use lead/lead oxide pastes milled to the finest practicable size and applied to the grid/collector plates as thinly as possible. The sizing of the cell should allow for a low rate discharge. Reference to Fig. 4 will show that if the above measures are taken, then a cycle
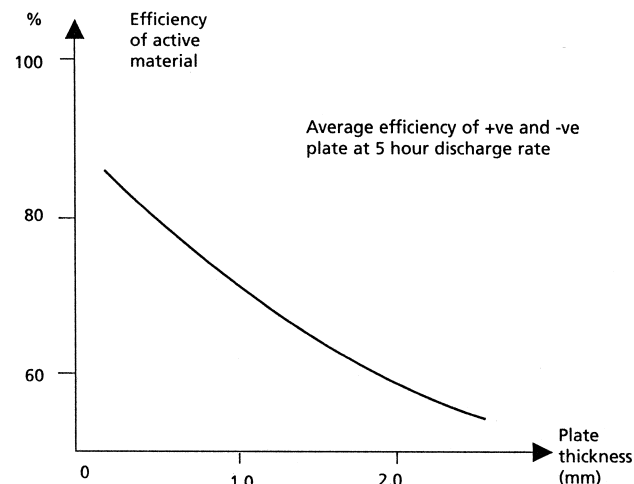

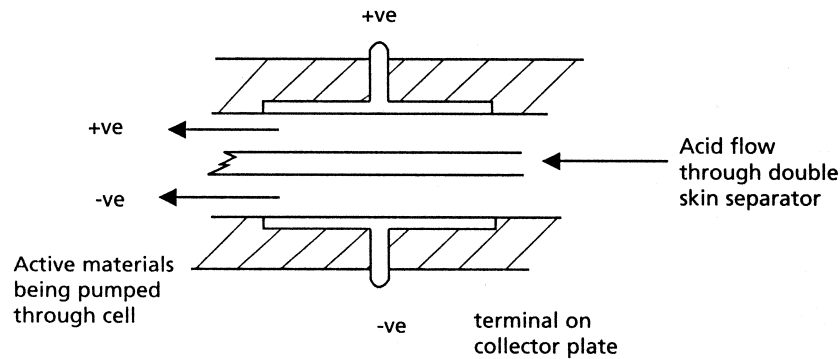Fig. 4. Conversion efficiency against plate thickness.

Fig. 5. Cell with pumped active materials.

conversion efficiency of some 70–80% may be achievable. Of course, such a strategy does create other problems, since these very thin layer of active material means that plate areas will become excessively large and need grids that are heavier than conventional ones. The use of bipolar construction is unlikely to be practical.

The second solution is to turn to a different cell construction—one based on a dynamic approach. If the positive and negative active materials are held in a slurry (rather than the normal statically 'solid' form), they then can be subjected to one of several forms of movement. This will ensure that the particles of active material are always changing their position relative to their neighbours and hence, the scope for the formation of inter-particle sulphation is greatly diminished. Because of the way that the active material is contained and used, it can be maintained in a much thicker state (than if it was coated on a plate or contained in a tubular assembly). This permits a more compact arrangement.

Various alternate configurations are possible. The active materials can be pumped from a store, through the 'cell'

which could consist of two, small area, grids with a central separator containing electrolyte (Fig. 5), or the active material could be static while the grids move relative to it.

The arrangement, which appears to hold the most promise, is shown in Fig. 6 and consists of a cell with a central separator made from a double-walled ceramic material through which the electrolyte is pumped. On each side of the separator, a slurry of active material is placed and electrical connection is via thin lead plates or grids. The slurry now has to be agitated and this can be achieved in a variety of ways. A stirrer/oscillator situated in either compartment of the cell, or a flexible floor to the two sides of the cell which rises and falls by mechanical or fluidic means, are methods which have been tried. Using a relatively thick layer of active material, these arrangements allow high grid loadings to be utilised and so the bipolar battery arrangement becomes an attractive option.

4. Design for a high performance EV battery

By applying the electrolyte management system to the agitated active material design, a very compact and efficient cell can be made. For an EV battery, many cells would be built together, using a bipolar form of intercell connection.

The following desk-top design exercise is based upon test results obtained from a small scale prototype cell—see Fig. 7. In the photograph, the pneumatic pipes to the oscillating floor and the electrolyte circulation tubes can be clearly seen.

The design is for a battery module capable of providing 10 kW of power for 3 h. It consists of 50 bipolar connected cells (100 V), each rated at 300 A h at the 3 h rate.

Each cell has a plate/separator dimension of 250×250 mm^2. The positive and negative grid plates (which also double up as intercell connectors) consist of a 2 mm thick plate of porous glass or ceramic material. The porous spaces in these plates are filled with lead, either by casting or electroplating [2]. The plates then form a chemical barrier from one cell to the next while providing an extremely low resistance for intercell connection. The need
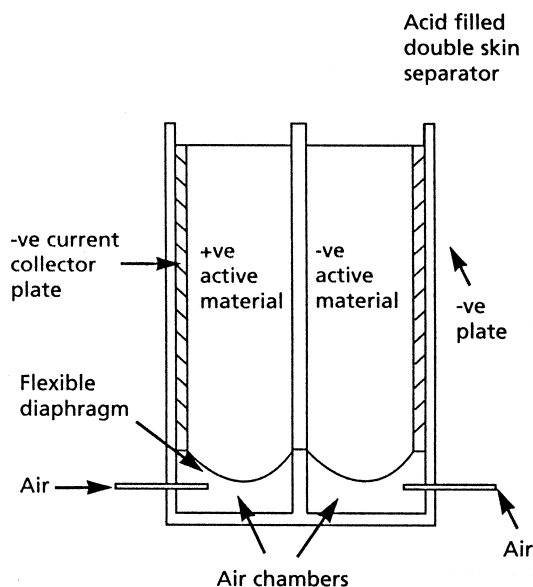

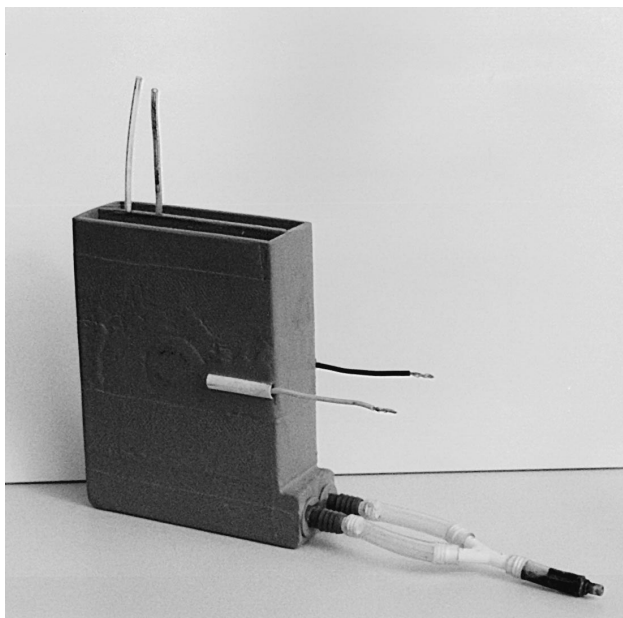Fig. 6. Cell with agitated active materials.

Fig. 7. Prototype cell with acid pumping and active material agitation.

for rigid plates rather than a thin lead foil is to provide a wear surface for the adjacent active material as it moves relative to the grid plate. Similarly, the double-walled separator is made from a ceramic material (porcelain mullite) having a maximum hole size of 1.0 μm and a porosity of approximately 50%. Electrolyte is pumped through the central space thus, providing a constant supply of replenished acid.

The slurry of active lead/lead oxide fills the space between the conducting grids and the separator. A grinding agent (i.e., sand) and emulsifier to aid movement may be added to the slurry.

In the prototype cell used to trial this design, an agitation system based on a rising and falling cell floor was used. This was achieved by introducing and then exhausting compressed air into a separate chamber at the base of each cell.

For the 30 kW h battery module described, an estimate of total weight and energy density can be made. For the active materials, three conversion efficiencies of 70%, 65%., and 60% are used. While the full amount (plus 10%) of acid is included, only 25% of the normal water content is included—the balance being stored off vehicle. From these assumptions, a total on-vehicle weight of active components can be calculated. $300 \times 50 \times$ (positive +

negative + acid + water) which gives: 253.4 kg (70%), 267.0 kg (65%), 283.0 kg (60%). The non-active components of 50 separators, 51 grid plates, the module case, agitators, pumps, valves and fluid stores have an estimated total weight of 106.6 kg.

Assuming an average cell voltage of 2.0, the above weights result in energy densities of:

83.0 W h kg^{-1} for the 70% conversion efficiency,

80.3 W h kg^{-1} for 65%,

77.0 W h kg^{-1} for 60%.

The external dimensions of the 10 kW module would be approximately $280 \times 350 \times 900$ mm^3, or 0.09 m^3.

By a process of further optimisation, especially in the areas of electrolyte volume, conversion efficiency and the weight of ancillary items, energy densities exceeding the values estimated above, should be possible.

5. Conclusion

This paper has shown how the humble, low cost, lead–acid battery can be re-engineered to provide a greatly improved energy density and become a major player in the emerging EV market. By using an electrolyte management system to reduce the total battery weight and at the same time improve the conversion efficiency of the active materials, an energy density twice that of commercially available batteries may be obtained.

A glimpse under the bonnets of a modern petrol engined car and its 100 year old ancestor will illustrate vividly just how great progress can be made when there is sufficient commercial and competitive pressure to force such progress. Perhaps the time has come for the same radical changes to be applied to the lead–acid battery. The current design of which, while the subject of a steady stream of detailed improvements, still is firmly based on the late 19th century work of Planté and Faure.

The way ahead is exciting and full of promise.

References

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