

Changes in the demands on automotive batteries require changes in battery design

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Abstract

The electrochemical storage of energy in automobiles faces the possibility of a major change, in that the electrical systems planned for vehicles are expected to be far more extensive than hitherto. These advanced electrical systems will require the electrical energy-storage element (one or more batteries) to operate at a partial-state-of-charge for most of its life and at unprecedented high rates (so-called ‘HRPSoC duty’). The remarkable advances achieved with valve-regulated lead-acid (VRLA) battery technology for electric vehicles (EVs) during the past 8–10 years will be of only passing value in overcoming the challenges posed by HRPSoC duty. This is because the battery failure modes seen in HRPSoC operation are quite different from those faced in EV (deep-cycle) use. The replacement of the 12 V automotive battery will not take place rapidly. If the applications that take its place are to be satisfied by a lead-acid product (probably VRLA), rather than by a battery of a different chemistry, a programme of development as successful as that mounted for deep-cycle duty will be required. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction—future automotive batteries

For most of the 20th century, batteries in road vehicles have been called upon to satisfy three functions, namely: starting the engine, supplying current for the lights when the vehicle is not running, storing electrical energy to support the ignition process. Collectively, these are referred to as ‘SLI duty’. Batteries, initially 6 V and later 12 V, have become established, low-cost, components in automobiles.

Significant changes are foreseen in automobile designs. In particular, new-generation vehicles are expected to incorporate a far greater degree of electrical functionality. A variety of justifications for such changes have been proposed. All of the designs are expected to improve fuel economy (and hence to reduce emissions) to a greater or lesser extent. Thus, ideally, customers will benefit from reduced fuel costs and, simultaneously, their vehicles will have a less harmful effect on the quality of urban air. Additionally, much has been written [1] about the benefits of replacing mechanical functions in the vehicle (steering, braking, engine accessories, air-conditioning, etc.) by electrical equivalents to provide enhanced safety, comfort and cost.

Some of the changes require systems at higher voltage, while others appear to be achievable with the system voltage pegged at 12 V, but in a dual-battery scheme. There is no clear consensus about the number of designs that could be viable. Seven variants that are under consideration are listed in Table 1 [2]. The first three configurations are intended to provide the electrical power that is necessary for an increasing range of electrical ancillaries. It should be noted that configurations 2–5 employ a 36 V battery together with a 42 V alternator, and are commonly referred to as ‘36 V/42 V systems’ or ‘42 V PowerNets’. Configurations 4 and 5, as well as 6 and 7, make use of both electric and internal-combustion engine propulsion; these vehicles are generically termed ‘hybrid electric vehicles’, or more briefly, ‘HEVs’.

Some of the variants shown in Table 1 have already been developed. Indeed, world sales of vehicles in category 6 have already passed 200 000, and many automobile manufacturers are now pursuing the development of vehicles in category 1. In the latter system, the challenge of providing high electrical energy and high electrical power on the same vehicle is met by the incorporation of two batteries, one configured for optimum energy and one configured for optimum power.

The prospect that a significant portion of the future market for automotive batteries may be aimed at vehicles in one or more of the above-mentioned configurations introduces

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Table 1
Proposed changes to electrical systems in automobiles

Design	Operating characteristics
1. 12 V dual-battery	Lowest-cost, lowest-risk approach Provides additional power for new vehicle ancillaries Improves system reliability Increases maximum power and availability Already offered in high-end (luxury) cars in Europe Can even support stop–start function (designed to shut-off ICE during stop to save fuel and reduce noise level in cabin) Can accept regenerative-braking energy
2. 42 V ‘upscale’ automotive battery ^a	Higher voltage makes it possible to power new comfort and driveability ancillaries without increasing currents In some cases, the ancillaries themselves operate more efficiently at higher voltage
3. 42 V with stop–start ^a	Combination of options 1 and 2 for vehicles with large ancillary loads (e.g., air-conditioning) during engine-off idle stand Supports increased number of engine-start events per drive Ensures higher reliability
4. 42 V ‘soft’ hybrid ^a	Adds soft electrically assisted launch from stop and recuperation of regenerative-braking to option 3
5. 42 V ‘mild’ hybrid ^a	Electrical motor used for longer periods and more frequently Stop–start and regenerative-braking requirements same as for option 4 Provides power-assist during low-speed acceleration that facilitates down-sizing of ICE and gives fuel, weight and volume savings
6. High-voltage ‘full’ hybrid	Low-end requirements overlap those of option 5 Provides longer and more frequent power assist to high-end cars, e.g., sports utility vehicles
7. ‘Plug-in’ hybrid	Vehicle can be driven in electric-only mode with full power and functionality, but for a limited range

^a System with 36 V battery and 42 V alternator.

serious consequences for the lead-acid battery community. At present, approximately 75% of the world production of lead-acid batteries is devoted to conventional automotive use. Batteries designed for this purpose are unable to provide adequate performance in any of the electrical systems under investigation. This is because, in future automobiles, the battery unit will operate at a partial-state-of-charge and will be discharged and charged at rates that can be far higher than in any previous automotive application—so-called ‘HRPSoC’ duty. A comparison of some of the key parameters for a typical automotive (SLI) battery, a deep-cycle battery and a battery undergoing HRPSoC duty is given in Table 2.

2. The challenge of high-rate partial-state-of-charge operation

When a lead-acid battery, which has not been designed for the purpose, is exposed to HRPSoC duty, it rapidly loses capacity due to an accumulation of lead sulfate on the negative plate [3]. This might be viewed as a disappointing phenomenon since the charge acceptance of the negative plates is usually (i.e., at normal rates of charge, around $1C_1$ and below) very high until the battery is almost fully charged [4]. Evidently, operation at extraordinarily high rates is sufficient to alter priorities amongst the possible reactions at the negative plate on charge.

Table 2
Typical duty and performance characteristics for VRLA batteries in different categories of present and new-generation vehicles

Parameter	Application		
	SLI, 12 V	Electric vehicle	Future automotive
Duty	High-rate start	Deep-cycle	High-rate PSoC
State-of-charge	85–90%	20–100%	42 V PowerNet: 70–90%, HEV: 60–70% ^a
Maximum normal discharge ^b	$10C_1$	$4C_1$	$15C_1$
Maximum normal charge ^b	$0.5C_1$	$0.5C_1$	$8C_1$
Failure modes	Corrosion, shedding	PCL 1, PCL 2 ^c	Under-charge and sulfation of negative plates

^a This is the normal operating range for the Honda *Insight*, but the battery-management system of this vehicle will allow a wider range of operation between 30 and 80% state-of-charge if so required by the driving pattern.

^b In multiples of 1 h rate.

^c These are two forms of premature capacity loss [10].

Table 3
Possible reactions during discharge and charge of a lead-acid cell

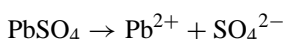
Positive electrode	
Reaction occurring on discharge	
$\text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	(1)
Reactions occurring on charge	
$\text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^-$	(2)
$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$	(3)
$\text{Pb} + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{H}^+ + 4\text{e}^-$	(4)
Negative electrode	
Reaction occurring on discharge	
$\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$	(5)
Reactions occurring on charge	
$\text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \rightarrow \text{Pb} + \text{HSO}_4^-$	(6)
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{heat}$	(7)
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	(8)

The reactions that are thermodynamically favourable in the VRLA cell during discharge and recharge are shown in Table 3. During discharge, there is only one reaction available at each of the plate polarities, i.e., reactions (1) and (5). On increasing the rate of discharge, the reaction becomes limited by the diffusion of species in solution and, accordingly, the discharge voltage of the cell decreases. During recharge, the situation is quite different. The intended reversal of the respective discharge processes are given by reactions (2) and (6). There are, however, four other processes, namely, reactions (3), (4), (7) and (8), that are allowable when the cell is on charge and these are thermodynamically preferred over the main charge reactions. Fortunately, these reactions, which have been designated ‘secondary reactions’ in the literature, proceed only slowly under normal charge regimes and, at modest rates of charge (up to around the 1 h rate, $1C_1$), it is possible to bring the charge reactions (2) and (6) to completion without much gas evolution [5].

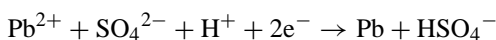
At high rates, on the other hand, a number of factors conspire to tilt the balance away from the charge reactions (2) and (6) in favour of the secondary reactions. The accumulation of sulfate on the negative plate when the VRLA cell is operated in an HRPSoC regime indicates that the recharge reactions are no longer proceeding more effectively than the secondary reactions, even at intermediate states-of-charge. Clearly, the charge reactions are more adversely affected by high rates than are the secondary reactions. The following process is implicated.

The charge reaction at the negative plate (reaction (6)) actually proceeds in two stages, namely, dissolution of lead sulfate, followed by deposition (precipitation) of metallic lead, i.e.,

- Stage 1



- Stage 2



Since the solubility of lead sulfate decreases as the concentration of acid increases, especially at elevated temperatures [6], a high rate of production of sulfuric acid, arising from high rates of recharge, can overcome the rate at which HSO_4^- ions diffuse away from the reaction sites. The result is that the rate of the recharge reaction becomes self-limiting.

Both processes involve diffusion limitations and are aggravated by the build up of sulfate that has been observed on the surfaces of negative plates [7], and that acts as a barrier to diffusion between the main body of the electrolyte and the interior of the plate. In both cases, the rate of the charge reactions becomes constrained by limited mass transfer at progressively higher rates, and an increasing proportion of the current accepted by the cell is taken up by secondary reactions.

Fortunately, several possible remedies show some promise of overcoming the problems associated with HRPSoC operation, as outlined below.

3. Approaches to extending the life of VRLA batteries in HRPSoC operation

A research and development programme of the Advanced Lead-Acid Battery Consortium has begun to shed light on those aspects of the function of a VRLA battery that presently limit its life under the expected HRPSoC duty required by future automotive batteries. The overall aim of this research is to enable battery operation at very high rates to proceed without the benefit of a regular full charge and to resist life-limiting mechanisms for an acceptable service life. The general strategy is to encourage the primary charging reaction (by minimising diffusion constraints) and simultaneously to discourage the secondary reactions (reactions (7) and (8)). Three areas of research show particular promise.

3.1. Grid design for high power

For charge and discharge at normal rates (e.g., $1C_1$ and below), the distribution of current density across a plate within a planar stack is fairly uniform. As the rates of charge and discharge are increased, however, the current becomes increasingly concentrated nearer to the current take-off (tab) at the plate corner. As indicated in Fig. 1, the consequence is that active material in the more remote parts of the plate then makes a reduced contribution to the available capacity.

One approach to alleviating the problem of non-uniform current density at high rates is to provide each plate with a second tab at a position symmetrically opposite to that of the usual tab [8]. This allows half of the current to flow out of each tab so that much material that would otherwise contribute little capacity immediately becomes accessible. Furthermore, the second tab provides an additional route for removal of the heat generated within the plate.

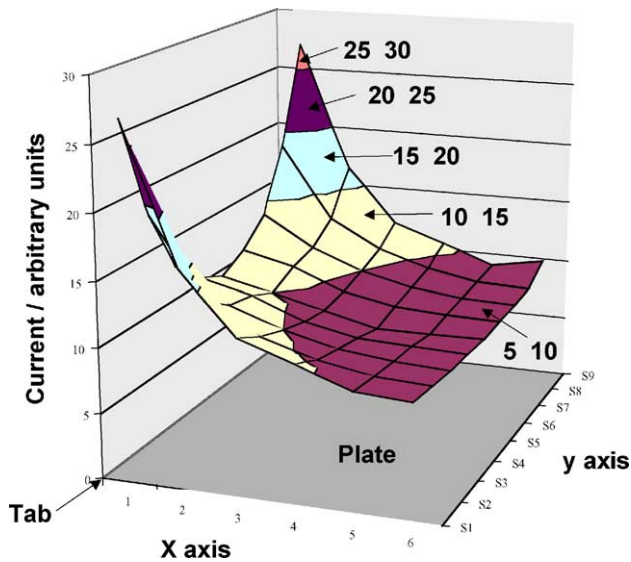


Fig. 1. Schematic of current density across a plate operated at high rates in a stack in which the current take-off tabs for plates of the two polarities are located at corners (0, S1) and (0, S9), respectively. At high rates, regions of the plates remote from the tabs contribute less capacity than regions close to the tabs.

In a demonstration of the benefits of this approach, a 36 V pack of spiral-wound, dual-tab, VRLA cells has been tested under a very demanding regime based on real-world driving of a Honda *Insight* hybrid car. The battery sustained 44 h of continuous operation without any conditioning, as shown in Fig. 2 [8]. By comparison, a single-tab pack gave only 25 min of service. This result provides a good indication that a VRLA battery must have an appropriate grid design in order to cope with the high-power requirements of an HEV defined by category 6 in Table 1. For such a battery to continue this type of operation and have an acceptable life, it is necessary to make adjustments to the active material, and particularly to that of the negative plate.

3.2. Changes to expander mix in negative active-material

It is routine for a combination of materials (collectively known as an ‘expander’) to be mixed with the active material of the negative plate in order to maintain the surface area at a high level, and to provide other beneficial effects. In the absence of an expander, the surface area decreases with cycling and the capacity of the plate declines. The expander generally comprises a mix of: organic material, which is usually a lignosulfonate; barium sulfate, which serves as a nucleating agent for lead sulfate; and carbon black, which is traditionally present at a level of 0.1–0.2 wt.%. Research at the CSIRO laboratories in Australia has shown that increasing the proportion of carbon from 0.2 to 2 wt.% in a matrix of negative active-material increases the conductivity by some five orders of magnitude [7]. Building on this result, the team at CSIRO has shown that increasing the carbon inventory above 0.2 wt.% also delays the onset of a dramatic increase in end-of-charge voltage that occurs during HRPSOC cycling and signals the onset of hydrogen gassing. The data presented in Fig. 3 show that the type of carbon, as well as the quantity, is important in providing this beneficial effect [7]. Further studies are in progress.

3.3. Trace element control

Small amounts of trace elements can cause major changes in the overpotentials at positive and negative plates, and thus can alter the rates at which the gassing reactions proceed. A thorough study undertaken by CSIRO in Australia [9] has found that elements not required by the fundamental stoichiometry of the cell reaction can influence gas evolution—either individually, or in combination when subtle synergistic effects can occur. For example, early indications show that zinc has a strong ability to suppress hydrogen gassing at the negative plate, and that a combination of antimony and iron can suppress the oxygen-gassing

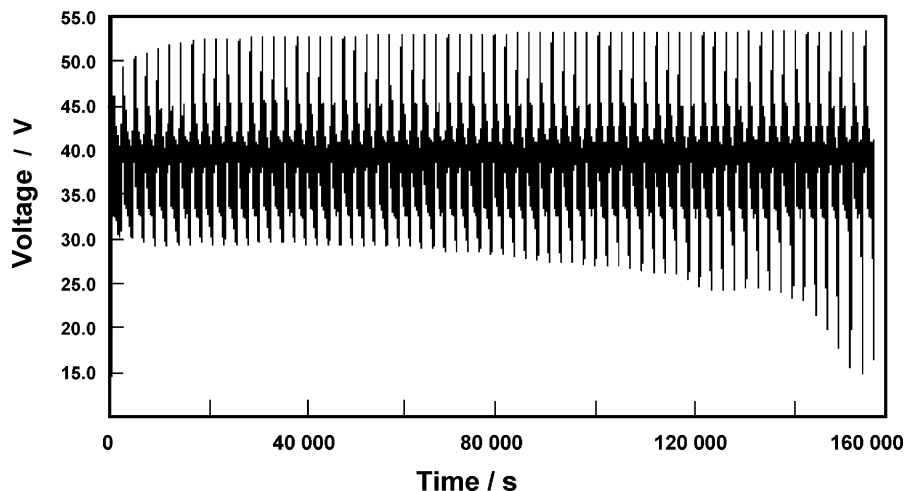


Fig. 2. Voltage versus time for dual-tab battery through 65 simulated HEV cycles—equivalent to continuous driving for 44 h without rest or conditioning [8].

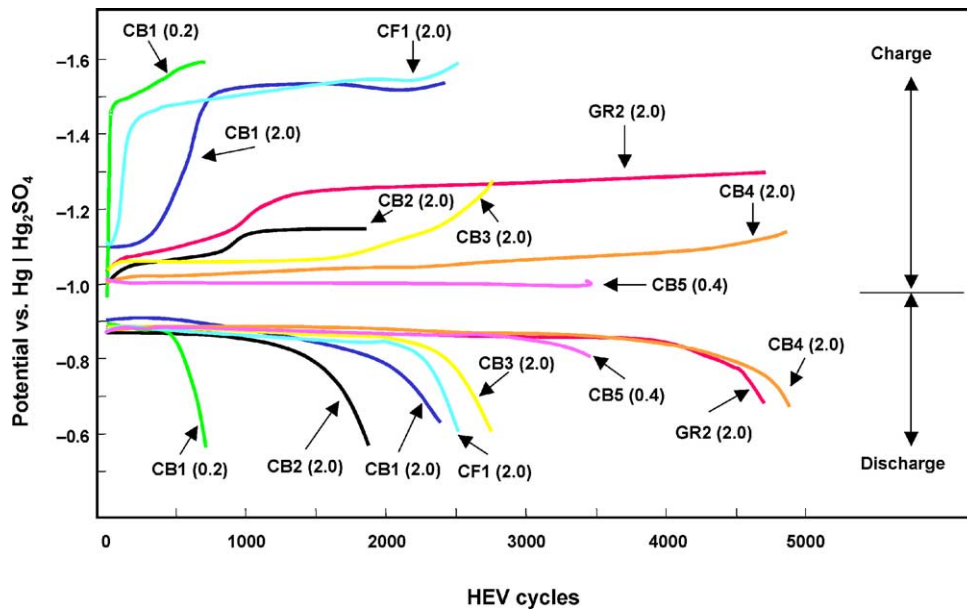


Fig. 3. End-of-charge and end-of-discharge potentials of negative plates in prototype cells during cycling under simple HEV duty. CB1–CB5: carbon black; CF1: carbon fibre; GR2: graphite. Numbers in parentheses represent wt.% of carbon species [7].

effect of some transition metals at the positive plate. The CSIRO study has determined the concentrations of each element that must not be exceeded if the float current, the hydrogen evolution current and the oxygen evolution current are to be maintained at, or below, their respective critical levels to achieve an acceptable battery life (Table 4).

3.4. Other factors

Two other lines of development may also prove fruitful in the pursuit of sustaining the life of VRLA batteries in HRP-

SoC cycling. The first is through improved engineering of the separator in order to control the flux of oxygen to the negative plate. Oxygen reduction (reaction (7)) must be limited in order to allow the negative plate to become fully charged. The second is to provide the necessary control system to allow the cells within the battery to be conditioned, even while the battery is on load. The feasibility of this approach will be tested during the later stages of an ALABC-supported project which is presently in progress [8].

4. Conclusions

In summary, it has been established that in HRPSoC service, which batteries will have to undergo in future automobile electrical systems, VRLA batteries are plagued by a tendency to accumulate sulfate on the negative plate. This phenomenon is largely the result of the peculiarly high rates of charge (and perhaps discharge) that will be required. Furthermore, since the HRPSoC duty will not require the battery to be brought to a full state-of-charge, the accumulation of sulfate is the prime failure mode. Appropriate design of the plate grid can enhance the ability of the battery to deliver and receive charge at the required rate. Furthermore, the introduction of additives to the active material can delay the onset of gassing, and hence assist recharge of the negative plate.

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Table 4

Maximum allowable levels of trace elements for maintaining float, hydrogen and oxygen currents below critical levels

Elements	Level (ppm)			Maximum allowable level (ppm)
	I_{float}	I_{hydrogen}	I_{oxygen}	
Ni	4	16	4	4
Sb	6	5	6	5
Co	4	7	4	4
Cr	7	16	7	7
Fe	–	–	–	10
Mn	5	5	5	5
Cu	33	13	34	13
Ag	76	142	66	66
Se	2	1	2	1
Te	1.5	0.5	1.4	0.3
Tl	25	25	25	25
As	5	–	5	5
Sn	41	–	40	40
Bi	543	–	522	500
Ge	673	250	658	10
Zn	915	–	905	500
Cd	756	–	722	500

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