



## Short communication

## Consequences of including carbon in the negative plates of Valve-regulated Lead–Acid batteries exposed to high-rate partial-state-of-charge operation

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## ABSTRACT

In power-assist hybrid electric vehicles (HEVs) batteries are required to operate from a partial-state-of-charge baseline and to provide, and to accept, charge, for short periods, at very high rates. Under this regime conventional lead–acid batteries accumulate lead sulfate on the negative plate and fail quickly. This failure mode can be effectively countered by the inclusion of certain forms of carbon at greater concentrations than have been used in lead–acid batteries in the past. So effective is this preventive measure that VRLA batteries benefiting from the inclusion of such carbon have been able to substitute for nickel metal hydride batteries in power-assist HEVs with no significant loss of performance. There has been much speculation about the function of the carbon that is providing this remarkable improvement. This paper aims to review the several mechanisms that have been proposed as possibly playing some contributory role.

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## 1. Introduction

Approaching legislation to control carbon dioxide emissions, combined with the continuing rise in oil-based fuel prices, has encouraged the introduction of various types of hybrid electric vehicles (HEVs) to the automotive market place. A range of vehicle types is now on offer. Microhybrids still operate with a 12-V battery, provide a stop/start function and, usually, recover energy through regenerative braking. Medium hybrids add to this basic scheme the ability to make a contribution to the vehicle motive power from an electric motor – the ‘power-assist’ system – and, in order to achieve this capability, they incorporate a battery with a higher voltage (typically around 144 V). At the top end of the HEV range ‘full hybrids’ are able to contribute a small all-electric range which can save the vehicle heat engine from the task of pulling away from a stationary position, during which operation fuel economy is notoriously poor. Full hybrids use a battery at a higher voltage still (generally above 200 V).

The task for the battery becomes more demanding through the series micro-, medium- to full-hybrid, but in all cases the requirement is to operate from a partial-state-of-charge so that regenerative braking energy can be accepted efficiently. From this baseline, the battery is called upon far more frequently than its SLI (starting, lighting and ignition) predecessor. Discharges and charge

events typically involve only a small fraction of the battery’s capacity but they occur continuously and do take place at very high rates.

Conventional lead–acid batteries, such as those designed for SLI or deep-cycle use, quickly accumulate lead sulfate on the negative plate under such a regime and the first HEVs to appear have made use of nickel–metal hydride batteries. Although these are somewhat more costly than lead–acid they are able to perform the duty without early failure.

Quite recently it has emerged that the incorporation of elevated levels of certain types of carbon into the negative plates of lead–acid batteries can overcome the mechanism that is responsible for the accumulation of lead sulfate and this discovery has allowed the production of prototype lead–acid batteries that are capable of operating successfully in the HEV mode. It is the purpose of this paper to consider the several possible mechanisms through which the presence of the carbon is able to provide this benefit in an attempt to identify which types of carbon are most effective.

## 2. The mechanism of sulfate accumulation

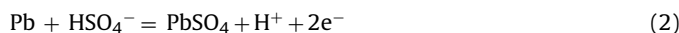
The fully charged positive plate of a lead–acid cell consists of a porous mass of PbO<sub>2</sub> surrounding a lead alloy grid, and the discharge reaction is



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The fully charged negative plate is a porous mass of lead particles surrounding a lead alloy grid and the discharge reaction is



The sulfuric acid electrolyte occupies pores within each plate and the volume between the plate, which also contains the separator. Ions from the electrolyte participate in the discharge process.  $\text{HSO}_4^-$  ions for the discharge reactions at each plate can be drawn from the region close to that plate. Also during the discharge process protons are produced at the negative plate and consumed at the positive plate. It is thus necessary for there to be a net flux of protons from the negative to the positive plate during discharge. Electrons travel round the external circuit.

The battery in a HEV is required to operate from an incompletely charged condition (partial-state-of-charge) to permit charge to be accepted during regenerative braking. From this baseline it is exposed to many short charge and discharge events at very high rates.

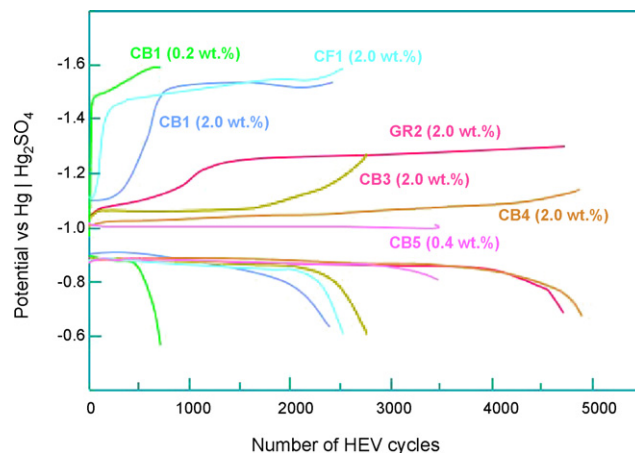
With a conventional lead–acid battery the very high rates cause the discharge reaction to take place preferentially at the plate surface, due to diffusion limitations, and near the top, because of a non-uniform potential distribution across the grid.

Since the battery must always operate at an intermediate state-of-charge there is always some discharge product ( $\text{PbSO}_4$ ) present on the plates. On the negative plate only about 25% of the lead metal is utilized in the electrochemical reactions so that, at 50% state of charge in a new battery, about 12.5% of the active material is present as  $\text{PbSO}_4$  and 87.5% of the active material is still lead metal. However, the non-uniform distribution of the discharge product impedes the subsequent recharge process and, after only a few (about 1000) short high-rate cycles, we see charge current going into the production of hydrogen instead of converting  $\text{PbSO}_4$  back to lead [1–3]. As a result, the amount of lead sulphate on the negative plate increases rapidly and the cell fails. In some cases it is possible to reduce the amount of sulphate by taking the battery up to 100% state-of-charge (conditioning) but this can be inconvenient in a vehicle.

The surface area of the active material on the positive plate is far greater than that on the negative and no accumulation of lead sulphate occurs on the positive.

### 3. The effect of adding extra carbon

Some time ago [4] it was reported that the phenomenon of sulfation of the negative plate exposed to an HEV duty cycle could be somewhat alleviated by increasing the amount of carbon in the plate. Increasing the amount of carbon by a factor of 3 gave some improvement and increasing by a factor of 10 gave even more. The failure mode was delayed rather than eliminated and the type of carbon used was not disclosed. The improvement provided by the extra carbon was attributed to an enhancement of the conductivity of the partially discharged negative active material thanks to a conductive network of carbon particles distributed between the crystals of lead sulfate. More recently [3] it has been shown that different types of carbon give rise to vastly different results when added incrementally to the negative active mass. Some types of carbon gave excellent protection against negative plate sulfation, while others appeared to provide virtually none (see Fig. 1). This variety of behaviour is, perhaps, not surprising in view of the very wide range of types of carbon that are available [5]. It has been suggested [3] that other processes might be playing a role, apart from the conductivity contribution: It was noted that carbon with high surface area was particularly beneficial and it was proposed that the carbon might impede the growth of lead sulfate crystals and/or the carbon



**Fig. 1.** Plots of the end of charge potentials and end of discharge potentials for seven different lead–acid cells each with a different form of carbon in the negative plate, at the concentration indicated, as the cells were exposed to simulated HEV cycling. CB1 is a carbon black with a surface area of  $47 \text{ m}^2 \text{ g}^{-1}$ . CB3 is a carbon black with a surface area of  $20 \text{ m}^2 \text{ g}^{-1}$ . CB4 is a carbon black with a surface area of  $80 \text{ m}^2 \text{ g}^{-1}$ . CB5 is a carbon black with a surface area of  $1400 \text{ m}^2 \text{ g}^{-1}$ . GR2 is a graphite with a surface area of  $20 \text{ m}^2 \text{ g}^{-1}$ . CF1 is a carbon fibre with a surface area of  $0.4 \text{ m}^2 \text{ g}^{-1}$ .

particles might act as nucleation centres for crystallization of lead sulfate. The observation of very poor performance in some cases prompted the reminder that, in all attempts to reduce parasitic reactions such as hydrogen production, great care must be exercised to keep trace metallic impurities below critical concentration levels.

The inclusion of 1.5 wt% of high surface area expanded graphite in the negative active material of a spiral wound cell of 24 Ah capacity allowed it to complete 220,000 EUCAR power-assist cycles, which corresponds to 5500 capacity turnovers [6].

In general the inclusion of an appropriate form of carbon has the result of preventing the concentration of lead sulfate discharge product in local regions of the negative plate. Uniform distribution of the discharge product allows complete charge acceptance, and the accumulation of sulfate is effectively avoided.

### 4. Possible functions of carbon added to the negative plate

There have been at least eight distinct functions proposed for the additional carbon that can influence the way the negative plate performs in high-rate, partial-state-of-charge (HRPSoc) cycling. Some of the suggestions are somewhat tentative but all are mentioned here in the interests of completeness. Active research is currently devoted towards discovering which of these functions is (are) responsible for the enormous improvement that carbon can bring to the negative plates of lead–acid batteries operating at HRP-SoC. This work is of great significance as it should point out which form (or forms) of carbon is (are) the ideal additive(s) for the negative plate and may even provide an indication of the optimum volume fraction(s) to be used.

#### 4.1. Electronic conductivity

The earliest suggested mechanism for the additional carbon was that it improved the conductivity of the negative active material and that this facilitated recharge. The electronic conductivity of carbon is less than that of the principal active material of the negative plate (metallic lead) but when the cell is in a partial-state-of-charge there are regions that are occupied by lead sulfate, which is an insulator. Thus, it is conceivable that carbon particles might provide an electronically conducting pathway through such regions. In a side

experiment [3] it has been shown that, as the amount of carbon added to a mixture with an insulator ( $\alpha$  PbO) is increased, a point is reached where the conductivity of the mass increases dramatically with a small increment in carbon content. This threshold occurs at a composition (wt%) close to that where the addition of carbon is shown to cause beneficial effects for HRPSoC cycling and probably corresponds to the permeation limit for conductivity through the second phase material. It should be noted that the conductivity of carbon depends strongly on the degree of graphitization of the carbon material. Graphites typically have very good conductivity, whereas activated carbon or carbons with high-surface area are typically less graphitized and can range in conductivity values from close to that of graphite to being good insulators.

#### 4.2. Restriction of crystal growth

If carbon is distributed between lead sulfate crystals it is also possible that its presence may impede the progressive growth of such crystals. Constraining the size of the lead sulfate crystals (keeping a large surface area) would then assist the subsequent charge process. Support for this possible mechanism has been provided by the demonstration [7] that the addition of titanium dioxide particles instead of carbon also provides some improvement in partial-state-of-charge cycling. It is assumed that the titanium dioxide particles are equally effective because they impede the growth of lead sulfate crystals in the same way.

#### 4.3. Hydrogen over-potential-impurities

The degradation mechanism that must be avoided in order for a lead–acid battery to continue to provide unimpaired performance in HRPSoC is the deflection of current that is intended for the cell charge reaction (lead sulfate into sponge lead) into secondary reactions—principally hydrogen evolution. Earlier work at CSIRO [8] has established the concentration levels of impurities that must not be exceeded if gassing problems are to be avoided in float charge applications. Many transition metals, for example, reduce the hydrogen over-potential and thus facilitate hydrogen emission. On the credit side, however, indications were obtained that the presence of certain elements (zinc, bismuth) is beneficial in suppressing the evolution of hydrogen at the negative plate.

Activated carbons tend to come from natural precursors (coconut, sawdust, peat, coal, etc.) and can contain large amounts of impurities such as sodium, potassium and calcium (from lignocellulosic precursors) and also iron, nickel and chromium (from the equipment used to activate them). Carbon blacks tend to be more pure because of the nature of their origins and manufacture. Natural graphites can contain many impurities as well depending on the location of the mine that produced them. Close attention must be paid to the purity of carbons that are to be included in the negative plate.

#### 4.4. Capacitive contribution

Supercapacitors are electrochemical energy storage devices that store energy based in non-Faradaic processes that involve the accumulation of charges at an interface. The structure formed in this process is called the electric double layer. The stored energy in the electric double layer is complementary to the function in a secondary battery. Capacitors can operate at extremely high rates (i.e. they offer very high power) but the amount of energy stored is very limited. Batteries store far more energy but are limited when it comes to power density. It has been shown [9] that the high-rate partial-state-of-charge duty required in an HEV can be well served by connecting a supercapacitor in parallel with a lead–acid cell.

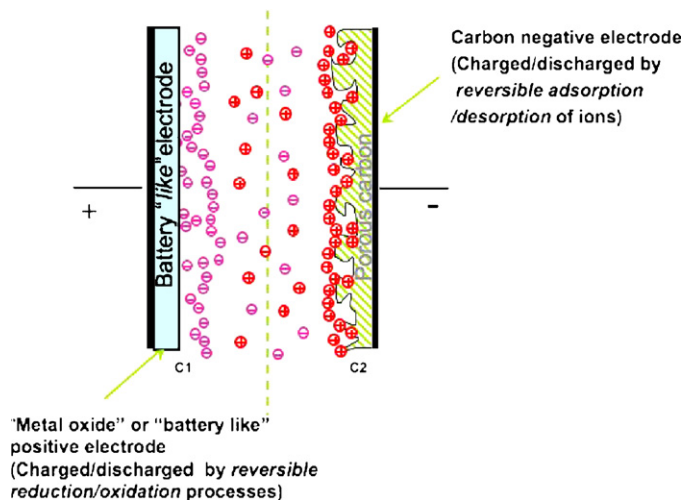


Fig. 2. Asymmetric supercapacitor.

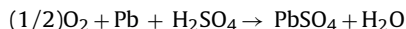
The supercapacitor acts as an effective peak power buffer accepting and providing much of the transient current, especially that at very high rates. The lead–acid cell is a bulk energy store covering for the relatively low energy storage of the supercapacitor.

This result brings to mind the function of the asymmetric supercapacitor which has one plate operating as a battery electrode and the other behaving purely as a capacitor electrode. One example (Fig. 2) has a regular lead–acid positive plate composed of lead dioxide, a sulfuric acid electrolyte, and a high-surface-area carbon negative plate. The resultant configuration offers higher energy storage than does a symmetric supercapacitor and higher power than a battery. Is it then possible that an asymmetric supercapacitor could still function if there were some lead particles mixed with the carbon on the negative plate and, in the limit, could a conventional sponge lead battery plate with a sufficiently high-carbon content behave in the same way?

During high-rate charge conditions, the highly capacitive component is able to store protons or solvated protons in an electric double layer very rapidly. Such a process could absorb charge current which would otherwise lead to hydrogen evolution in those cases where the cell charge reaction (the reverse of equation 2) is unable to cope. Non-Faradaic charging will occur at an intermediate potential between the steady-state potential of the negative plate and the potential required to produce hydrogen. The negative electrode can spontaneously, but at a lower rate, discharge the electric double layer, converting lead sulfate back to lead. Thus, the capacitive element can support charge and discharge events that occur at the highest rates, and the Faradaic part of the cell can cope with events that take place over a longer timescale. While both processes are in operation a mixed potential will exist across the electrode surface.

#### 4.5. Reactions involving the oxidation of carbon

The accumulation of lead sulfate on the negative plate is aggravated by the arrival of oxygen generated at the positive plate as part of the oxygen cycle.



Any mechanisms allowing the oxidation of carbon within the cell would deny oxygen the opportunity to assist the formation of lead sulfate in this way but such reactions would involve the transfer of carbon to the positive plate as a first step. Carbon is stable at the open circuit potential of the negative plate. Further, this

potential contribution of carbon could only operate until the supply of carbon was exhausted and it is doubtful if this mechanism can explain how the beneficial effect can be sustained for the long times that have been observed (see Section 5, below).

#### 4.6. Intercalation of hydrogen into the graphite structure

If the carbon added to the negative active material is in the form of graphite, then the possibility arises that intercalation reactions can take place. A wide variety of species can be inserted between the graphene sheets of the graphite structure [5]. When graphite is held at a positive potential in contact with sulphuric acid, for example, both ions ( $\text{HSO}_4^-$ ) and molecules ( $\text{H}_2\text{SO}_4$ ) can be intercalated, with the charge on the ions balanced by a positive charge on the oxidized graphite network. In lithium ion cells graphite constitutes the negative plate and is able to intercalate lithium ions to form products such as  $\text{LiC}_6$ . In both cases the intercalation is accompanied by an increase in electronic conductivity [5]. There are reports of electrochemical storage of hydrogen in graphite (see references in [10]) but there is little information about the form in which the hydrogen is accommodated. If there is a species analogous to  $\text{LiC}_6$  then it could contribute local storage of the protons and provide a boost to the conductivity of the material. The ionic radius of the proton is considerably less than that of the lithium ion and there is, as yet, no information on such a compound.

#### 4.7. Electro-osmotic pumping

The application of an electric field across a liquid in contact with a material bearing a suitable zeta potential can cause movement in the liquid by a process of electro-osmotic flow (EOF). EOF is fluid motion induced by the interaction between a fluid at the wall of the channel and the external applied electric field. The rate of flow is proportional to the applied voltage, the pH and conductivity of the solution, and the material of the channel wall. A process of electro-osmotic pumping has been proposed to assist the irrigation by fresh electrolyte of the positive plate of a lead–acid cell in the presence of graphite [11] but, to date, there are no reports of electro-osmotic pumping in the negative plate.

#### 4.8. Additional nucleation sites

It is standard practice in lead–acid battery manufacture to add a small amount (typically 0.2–0.4 wt%) of barium sulfate to the negative active material. This material provides a large number of nuclei on which lead sulfate crystals are able to grow. Increasing the number of crystals formed serves to increase the surface area of the discharge product and thus to assist charge acceptance. Barium sulfate is believed to be effective in this function because it is isomorphous with lead sulfate. The notion that carbon particles could function in a similar manner is less easy to accept because none of the structures that can be adopted by carbon bear any resemblance to the structure of lead sulfate and an epitaxial growth process is therefore unlikely.

### 5. The Ultra battery

Of all the energy storage systems that employ lead–acid chemistry for HRPSoc operation, that which has been most successful to date has been the Ultra battery [12,13]. This has a conventional  $\text{PbO}_2$  positive plate and a negative comprising two parts: one part has the usual sponge lead active material and the other part is a capacitor electrode containing a mixture of carbon black and activated carbon [14]. The two parts of the negative share a common contact to the external circuit and they share the same positive plate. With



Fig. 3. Honda Insight with an 'Ultra' VRLA battery in place of the original nickel metal hydride battery completed over 100,000 miles with no conditioning or equalization and without failing.

this design, the total discharge or charge current of the combined negative plate is composed of two components: the capacitor current and the regular lead–acid negative plate current. Accordingly, the capacitor electrode can act as a buffer to share the discharge and charge currents with the lead–acid negative plate and protect it from being discharged and charged at high rates.

The success of this system is not limited to laboratory tests, where the Ultra has completed over 370,000 EUCAR cycles without failure. A Honda Insight fitted with a 144-V Ultra battery, has run for over 100,000 miles with no conditioning and the battery remained in an excellent state throughout (Fig. 3).

### 6. Process of elimination

An important question now is whether or not the carbon mixed into the active mass of the negative plate is able to perform the same function as the carbon that is used in the negative system of the Ultra battery where it is in electrical contact but not in physical contact with the negative active mass.

If this is the case, then the task of discovering the key mechanism is simplified. Only those mechanisms that could still operate when the carbon is isolated from the lead active mass could remain as candidates for providing the major benefit. Conductivity effects, lead sulfate crystal growth inhibition, electro-osmotic pumping and the provision of extra nucleation sites for lead sulfate should probably all be set aside. Reaction of oxygen from the positive plate would provide an effect with only a finite life and, since the Ultra battery uses non-graphitic forms of carbon, the intercalation contribution can be eliminated. Care must be taken over the effects of impu-

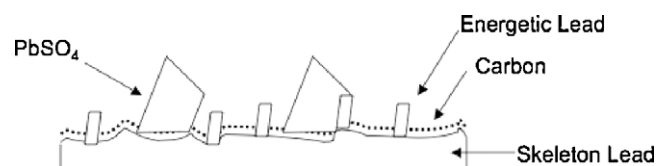


Fig. 4. Schematic of the surface of a negative active material containing an intimate mixture of high-surface-area carbon and lead at a partial-state-of-charge. The lead has a surface area of less than  $1 \text{ m}^2 \text{ g}^{-1}$  and the carbon has a surface area of  $1000\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ . The Faradaic process of charge and discharge involves the interconversion of lead and lead sulfate. The charge and discharge of the carbon involves the adsorption and de-sorption of protons at the solid surface and occurs far more rapidly.

rities whatever beneficial mechanism is in play. The only process remaining is the contribution of a capacitive effect.

Thus, it can be said that, if the carbon in a negative active material mix is operating in the same manner as is the carbon in the separated negative plates of the Ultra battery, then its most important function is to provide capacitive energy storage alongside the electrochemical storage contributed by the conventional components of the plate. The observation that high surface area carbons work well in the negative mix exposed to HRPSoC (Fig. 1) is consistent with this notion. The possibility that some of the other mechanisms could be operating simultaneously, but in a less visible manner, cannot be excluded of course and, in this connection, it can be mentioned that carbon dioxide has been found in the gas space of cells exposed to  $I$ - $U$  charging [15].

## 7. Conclusions

With the proviso mentioned above, that the carbon in a negative mix acts primarily as a capacitance, albeit diluted from the quantities in the Ultra battery and the hybrid supercapacitor, then it can be concluded that the optimum form of carbon to be used will have a high surface area and will be free from deleterious metallic impurities. Forms of carbon used in supercapacitors may be strong candidates. Additional, but less important, contributions from the carbon in the mix would then still be: to impede lead sulfate crystal growth, and to assist conductivity in any areas that become rich in sulfate. Also, high surface area forms of graphitic carbon are not eliminated and when they are used the intercalation mechanism could also play a role.

In order to achieve maximum benefit of the carbon added to the negative active material it may be desirable to increase the amount of carbon used beyond the levels explored so far.

A typical high voltage (144 V and above) lead-acid battery developed for HEV purposes will have a capacity in the region of 6 Ah (at the 1-h rate). Since the capacity is contributed equally by the positive and negative plates around 12 g of active lead would be required. Since the utilization of lead will not exceed 25% at the high rates involved it would be reasonable to provide 48 g of lead in the negative active material of each cell. This lead will be distributed partly as low-surface-area material (skeleton-structure lead [16]) contributing conductivity, but not capacity, and partly as high-surface-area material ( $\sim 1 \text{ m}^2 \text{ g}^{-1}$ )—energetic-structure lead [16], providing capacity.

In the case of a cell designed according to the concept outlined above, we can envisage the use of a form of carbon with a very high surface area ( $1000\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ ) also distributed on the skeleton-structure lead (Fig. 4). Most of the high-rate charge and discharge events called up during HEV operation make use of no more than about 3% of the cell capacity. In order for this to come from the

capacitive element the carbon will need to contribute 3% of 6 Ah (i.e. 180 mAh) or 180 mWh at 1 V. The best supercapacitors offer some  $10 \text{ Wh kg}^{-1}$  and this implies a carbon loading of 18 g. Thus, for optimum HRPSoC function, the negative plate should contain of the order of 25 wt% high surface area carbon.

This initially poses a challenge for conventional paste mixing as the presence of the carbon modifies the thixotropic properties of the paste so that processing considerations may set practical limits to the amount of carbon that could be used. Novel paste mixing technologies currently emerging, however, may go a long way to overcoming this problem.

It may also be pointed out that even the addition of 2–4 wt% of a suitable form of carbon can result in a dramatic improvement in HRPSoC performance in comparison with batteries of a conventional formulation so that a composition well short of 25 wt% carbon may well prove to be entirely satisfactory in providing a long life in a hybrid automobile.

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