

Review

# The role of carbon in valve-regulated lead–acid battery technology<sup>☆</sup>

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## Abstract

The properties of different forms of carbon and their potential, as active mass additives, for influencing the performance of valve-regulated lead–acid batteries are reviewed. Carbon additives to the positive active-mass appear to benefit capacity, but are progressively lost due to oxidation. Some forms of carbon in the negative active-material are able to resist the tendency to sulfation during high-rate partial-state-of-charge operation to some considerable extent, but the mechanism of this benefit is not yet fully understood.

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## 1. Introduction

For many years, carbon has been favoured as an additive to the negative active-material in lead–acid batteries, despite the fact that there has never been universal agreement on the reasons for its use [1]. Now that the valve-regulated version of the battery (VRLA) is being exposed to high-rate partial-state-of-charge (HRPSoC) operation in various applications [2], evidence is

emerging that demonstrates clearly the beneficial effects of carbon. In particular, increased levels of certain forms of carbon act to restrict the progress of plate sulfation, the process which ultimately terminates the useful life of the battery in HRPSoC duty. There has also been a report [3] that the addition of certain types of carbon to the positive active-material can improve battery capacity and life. In view of these developments, and the diverse range of chemical and physical properties that are observed in different forms of carbon, it is timely to review the mechanisms by which carbon additions could benefit VRLA batteries in various duty cycles, and to assess the forms of carbon that are likely to provide the greatest benefit.

## 2. Allotropes of carbon and their properties

Elemental carbon participates in two distinct types of covalent bonding. In the diamond structure, each atom is joined to

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four neighbours, at a distance of 1.54 Å, by tetrahedrally oriented bonds that are formed by  $sp^3$  hybrid orbitals. There is an energy gap of 5.3 eV between the  $\sigma$  and  $\sigma^*$  bands so that the material is an insulator [4]. In the graphite structure, the atoms are arranged in planar hexagonal networks (so-called ‘graphene’ layers) that are held together by strong  $sp^2$  bonds, 1.42 Å in length. The bonding between these planar layers (van der Waals type) is relatively weak (bond length 3.35 Å). In graphite, which is the equilibrium phase under ambient conditions,  $\pi$  and  $\pi^*$  bands around the Fermi level fill the  $\sigma$ – $\sigma^*$  gap, which renders the material semi-metallic. The structure leaves the conductivity highly anisotropic, however, with the in-plane conductivity two-to-three orders of magnitude greater than that in the direction perpendicular to the plane [5]. More recently discovered forms of carbon (fullerenes, nanotubes, etc.) consist of structures in which hexagonal networks of carbon atoms are curved into spherical or cylindrical shapes.

The diamond structure tends to exhibit a high degree of crystalline perfection, although isolated point defects can occur. The layered structure in graphite, however, allows a range of defect opportunities, that give rise to considerable variability in physical properties. The normal –AB– layer stacking sequence, in which the atoms of alternate layers in the crystallographic  $c$ -axis sequence are situated identically in the  $x$ – $y$  plane, results in a hexagonal structure. The structure can, however, be re-ordered to construct a rhombohedral sequence –ABC– in which the atoms of every third layer in the  $c$  axis sequence are situated identically in the  $x$ – $y$  plane. Such re-ordering can be partial or complete. Further, a fraction of the carbon atoms can be  $sp^3$  rather than  $sp^2$  hybridized, with the result that the graphene layers become buckled. Indeed, the concentration of  $sp^3$  carbons can be quite high [4]. Disordered carbon systems with the same  $sp^2/sp^3$  ratio show a variety of different electronic structures owing to the degree of clustering of  $sp^2$  carbons into ‘graphitic domains’ [6]. A disordered distribution of  $sp^2$  sites in an  $sp^2/sp^3$  mixed system disrupts the conjugated  $\pi$  electron system even when the concentration of  $sp^3$  carbons is rather low. This ‘non-graphitic’ disorder serves to reduce conductivity, but this can be restored by thermally induced migration of  $sp^3$  defects at temperatures from 200 to 400 °C [4]. The degree of crystalline perfection is reduced to a minimum in the production of amorphous or glassy forms

of carbon. The ultimate crystallite size for carbon materials can vary over a large range, from 0.001 to 100  $\mu\text{m}$  [7]. Evidently, the specific surface area of such material can also vary widely.

Departures from the perfect structure of graphite, which can arise from the occurrence of stacking faults and/or the accommodation of  $sp^3$  carbon atoms, cause the conductance of the material to be variable over a wide range [4]. The chemical reactivity of a given carbon material is influenced by the specific area and the composition of the surface. Each  $sp^3$  carbon atom has one free bond that is not involved in holding the graphene layer together. Such bonds can accommodate a variety of chemical entities, e.g., carbonyl, carboxyl, lactone, quinone, phenol, and various sulfur and nitrogen species [7].

Two important factors affect the electrochemical behaviour of graphite, namely, the layered structure and an amphoteric disposition [8]. The layered structure of graphite, which involves strong bonds within the sheets of atoms lying perpendicular to the  $c$  axis and weak bonds between the sheets, allows a rich intercalation chemistry. A wide variety of species can be inserted between the graphene sheets and this increases the spacing between the sheets (Fig. 1) without disturbing the bonds that hold the sheets together. The earliest graphite intercalation compounds, which involved the incorporation of potassium, were reported over 160 years ago [9]. Intercalation into graphite host materials is classified in terms of ‘ $n$ ’ stages. Stage- $n$  is defined as the structure in which intercalates are accommodated regularly in every  $n$ th graphitic gallery. The structure in which intercalates occupy every graphite gallery is termed a stage-1 structure (as in Fig. 1). The process of intercalation can give rise to a large expansion in the  $c$  axis direction of the crystal structure as quite large ions and/or groups can be accommodated.

The amphoteric characteristic arises because graphite is a semi-metal (the valence and conduction bands overlap slightly [10]) in which both electrons and holes are always available to carry current. As a result, graphite can act as an oxidant towards an electron donor intercalate and as a reductant towards electron acceptor species such as acids. Pure graphite intercalation compounds can be synthesized with stages between 1 and, at least 12, depending on the nature of the intercalate and the synthesis route. Graphite intercalation compounds can exhibit remarkable properties. For example, the stage-1 lithium graphite intercala-

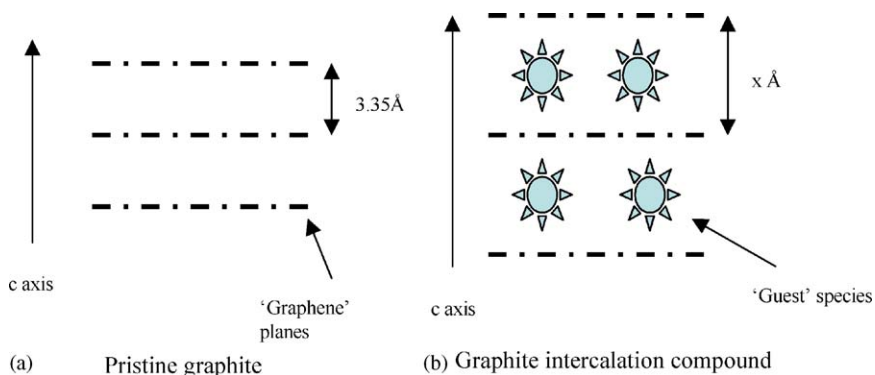


Fig. 1. Schematic of graphite intercalation. (a) An ‘edge-on’ view of the graphene planes in un-reacted graphite; (b) an edge-on view of a stage-1 graphite intercalation compound showing expansion of the interplanar spacing to accommodate the guest species. The dimension,  $x$ , can take values up to 9 Å or more without disrupting the long-range order of the crystal structure.

Table 1  
Conductivity in *a* and *c* axial directions of graphite and some graphite intercalation compounds (GICs)

Material	Formal charge on carbon	Conductivity, <i>a</i> -axis (S cm <sup>-1</sup> )	Conductivity, <i>c</i> -axis (S cm <sup>-1</sup> )	Reference
Graphite	0	1 × 10 <sup>4</sup> to 2.5 × 10 <sup>4</sup>	10 <sup>2</sup>	[15,16]
Bisulfate GIC	+	~1.6 × 10 <sup>5</sup>	~2 × 10 <sup>2</sup>	[17]
Lithium GIC	–	2.4 × 10 <sup>5</sup>	1.8 × 10 <sup>4</sup>	[11]

tion compound has a conductivity of 2.4 × 10<sup>5</sup> S cm<sup>-1</sup> within the graphene planes and 1.8 × 10<sup>4</sup> S cm<sup>-1</sup> in the direction perpendicular to the planes [11].

Graphite forms a number of intercalation compounds with sulfuric acid [12–14]. These develop when the intercalation process is assisted either by the presence of an oxidizing agent (such as PbO<sub>2</sub>) or electrochemically when the material is held at a positive potential. In general, the process involves the insertion of both HSO<sub>4</sub><sup>-</sup> ions and neutral H<sub>2</sub>SO<sub>4</sub> molecules, with the charge on the former balanced by a positive charge on the oxidized graphite network (e.g. C<sub>24</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·2.5H<sub>2</sub>SO<sub>4</sub>). The stage-1 sulfuric acid graphite intercalation compound can be prepared in 96% acid at a cell voltage just below the decomposition potential of the electrolyte [8]. At any particular oxidation level, the graphite bisulfate compound can be decomposed by a cathodic current.

The conductivities of graphite and of some graphite intercalation compounds, in the *a* and *c* axial directions, are shown in Table 1. The data show that formation of the intercalation compounds generally results in an increase in electronic conductivity.

It has recently been reported [18,19] that hydrogen can be stored in carbon single-wall nanotubes by an electrochemical process. Carbon samples subjected to a negative potential in a cell with potassium hydroxide electrolyte and a nickel counter electrode were found to take up 1–2 wt.% of hydrogen that could be released when the potential was reversed. Further, the maximum stored concentration could be increased by incorporating Group I metals (especially, lithium) into the carbon structure [19]. It is not yet clear whether this result signals the feasibility of protonic intercalation into the graphite structure, but it has been suggested [20] that there is nothing special about carbon nanomaterials (as opposed to other forms of carbon) as far as hydrogen uptake is concerned. Indeed, Frackowiak and Béguin [21] have shown that electrodes constructed from high surface-area carbon fabrics (woven bundles of activated carbon fibre) are able to store reversibly between 1.5 and 2.0 wt.% hydrogen. These authors suggested that the mechanism of storage was intercalation (of nascent hydrogen) into graphitic domains, rather than trapping of hydrogen by carbon-surface functional groups. It would clearly be valuable to establish whether or not hydrogen intercalation into graphite does occur and, if so, whether the process might enhance the electronic conductivity of the graphite in the same way as does the intercalation of lithium.

### 3. Conventional use of carbon in lead–acid batteries

Three materials are usually added, as minor components, to the negative paste mix of lead–acid batteries, namely, carbon

black (an amorphous form with a particle size in the range 0.01–0.4 μm, usually present at 0.15–0.25 wt.%), an organic material (usually a lignosulfonate, at 0.2–0.4 wt.%), and barium sulfate (0.3–0.5 wt.%). This mixture is often referred to as an ‘expander’ since its purpose is, at least partly, to maintain the active material on the plate in a high-surface-area form. The amounts of each of the three additives have, to date, been kept to a minimum, in order to displace the smallest amount of active material possible. The understanding of the function of each component of the expander is incomplete, however. It is generally agreed that the barium sulfate serves as a nucleating agent for lead sulfate (with which it is isomorphous) during discharge. The organic component is the actual expander as it acts as a dispersing agent, discouraging the increase of particle size and the concomitant decrease in surface area. It was originally felt that the primary function of the carbon black portion was to ‘clear the negative plates during formation’ and improve low-temperature performance [22]. This implies that even such a small amount of carbon may have a positive, but small, impact on negative-plate conductivity. More recent work (see Section 5) has established that larger amounts of specific types of carbon powders, flakes and fibres can have a significant effect on plate conductivity, particularly in the HRPSoc operation of hybrid electric vehicles.

### 4. Effects of carbon on the behaviour of the positive plate

Despite concern that carbon in the positive plate of the lead–acid battery would be prone to oxidation, there have been a number of investigations of the behaviour of carbon materials as additives to the positive active material (PAM). In view of the wide diversity of properties exhibited by the different forms of carbon (Section 2, above), it is to be expected that some forms are more stable in hostile environments than are others.

In 1987, it was reported [23] that the incorporation of 0.1–2.0 wt.% of graphite (99.6% purity) into the positive active-material (PAM) of a lead–acid cell improved both the discharge capacity and the cycle-life. The study provided X-ray diffraction evidence of the generation of the bisulfate graphite intercalation compound during cell formation and it was suggested that the intercalation process (which may be reversible during discharge) might enhance the porosity and, hence, the access of acid to the PAM. The presence of the graphite certainly appeared to render the distribution of PbSO<sub>4</sub> discharge product more uniform throughout the plate thickness. Interestingly, however, the beneficial effect on discharge capacity was reported to increase with graphite particle size, which appears to be the reverse of the effect of carbon size in the negative plate (see below).

An alternative (or perhaps additional) explanation of the source of the benefit provided by the addition of graphite to the PAM is that the irrigation of the plate by acid electrolyte is assisted by electro-osmotic pumping [24]. Electro-osmosis is the movement of liquid relative to a stationary charged surface (e.g., a capillary or a porous plug) by an electric field. Graphite present within the PAM is assumed to intercalate  $\text{HSO}_4^-$  ions and has been found [24] to exhibit a significant zeta potential. Zeta potential is the electric potential that exists across the interface between a solid and a liquid. Since the material in the cell is situated within an electric field (between plates of different polarity), the conditions for liquid movement due to electro-osmotic pumping may be satisfied [24]. Electro-osmotic flow-rate is directly proportional to zeta potential. Further work on the system would be necessary before this possibility could be separated from the other possible processes by which the presence of graphite might modify the performance of the electrode.

Other work [25–27] investigated the addition of 0.2–1 wt.% of carbon black to positive plates. It was found that at a level of 0.2 wt.% carbon black improved the formation process, but had little effect on cycle-life [27]. Roughly 60% of the carbon black was consumed during formation and the remainder disappeared early in cycling. Interestingly, this carbon black significantly increased the  $\alpha/\beta\text{-PbO}_2$  ratio and the total  $\text{PbO}_2$  created during formation compared with an equivalent paste without carbon black. This unusual effect was attributed to a combination of increased conductivity early in formation and a resultant increase in  $\text{PbO}/\alpha\text{-PbO}_2$  contact area, which resulted in an enhanced level of direct conversion of  $\text{PbO}$  to  $\alpha\text{-PbO}_2$ . Thus, the initial low-voltage stage of formation where  $\alpha\text{-PbO}_2$  is formed was extended [28]. Moreover, the morphology of the PAM was uniform and largely composed of spherical agglomerates, which suggests that formation occurred with moderate, uniform levels of supersaturation and at relatively low current densities.

The addition of carbon fibres to the PAM has also been reported [29] to increase both the capacity and cycle-life of test batteries. This effect may also be due to an influence of the additive expanding porosity or it may be due to the fibres providing mechanical support to the active mass [29].

Thus the evidence reported in the literature indicates that the effect of adding carbon to the PAM on the capacity and life of a lead–acid cell depends on the form of the carbon used. Carbon black has little effect [27], but graphite [23] and carbon fibres [29] are both beneficial.

## 5. Increased levels of carbon in the negative plate

The build-up of lead sulfate in the negative plate of a VRLA cell operated under HRPSoC conditions represents a unique type of behaviour not found when the cell is exposed to duty cycles such as deep cycling from top-of-charge or float (standby) duty. The phenomenon was first studied by scientists at Japan Storage Battery Company (JSB) in their development of VRLA batteries for HEV applications [30,31]. Their work focused mainly on the benefits of employing higher concentrations of carbon black

to ameliorate the effect, a theme that is discussed later in this section. Considerable detail on the characteristics of cell failure under HRPSoC operation has been demonstrated in an extended study by CSIRO, on 12-V 10-Ah VRLA batteries [32]. The batteries were exposed to a simulated HEV duty that involved cycling between 50% and 53% state-of-charge (SoC) at the 2C rate. Cycling continued until the battery voltage reached pre-set upper and lower limits at which point one ‘cycle-set’ had been completed. Prior to commencing the next cycle-set, each battery underwent a capacity-recovery process that involved repetitive full discharge–charge cycles with substantial overcharge. Even though the 2C rate is rather low compared with normal HEV operation, the characteristic mode of degradation of the negative plate was rapidly demonstrated. Overall, as summarized in Fig. 2, there was a progressive accumulation of lead sulfate. This occurred throughout the course of the simulated HRPSoC cycling, during which the nominal plate SoC was 50%. Importantly, the high levels of accumulated lead sulfate persisted into the nominally fully charged state (recorded after the battery had completed a recovery-charging sequence).

At the outset, the concentration of lead sulfate for the nominally 100% charged plates is low ( $\sim 5\%$ ), as expected (Fig. 2). Discharging to 53% SoC (the starting point for the first set of HEV cycles), sees the concentration rise by just over 15 wt.%, in line with the expected utilization level. With the completion of each successive cycle-set, however, the abundance of lead sulfate increases markedly. By the end of the third cycle-set, approximately half of the active material has been discharged to lead sulfate, and the recharge process to a nominal 100% SoC is clearly failing to reduce the sulfate level to any significant degree. This accumulation of lead sulfate correlates well with a progressive fall in both the time for which useful power is available from the battery and the total capacity (at 2C) that is available. By comparison, there is no equivalent increase in lead sulfate content in the positive plates. In fact, the average concentrations, under both the 50% and 100% nominal SoC conditions,

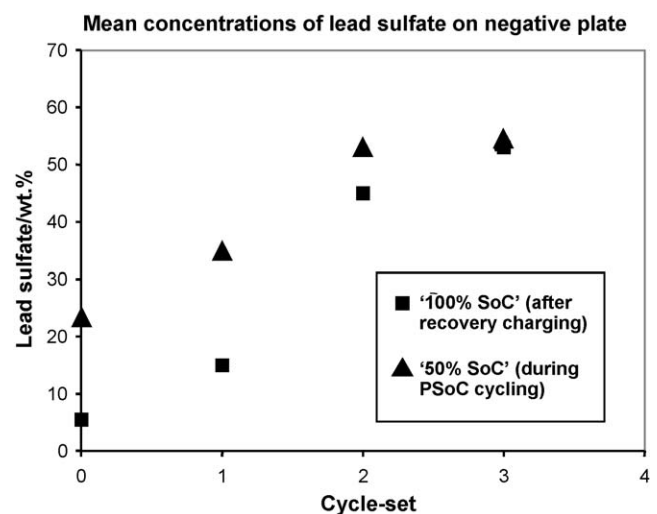


Fig. 2. Abundance of lead sulfate on negative plate, as determined by chemical analysis of total sulfur, plotted against length of simulated HEV service (see text for details).

decrease slightly from the initial values during the course of the three cycle-sets [32]. This difference in behaviour between the positive and negative plates, together with clear evidence that appreciable hydrogen evolution develops during HEV cycling, has led to the conclusion that failure of the negative plates under HRPSoC duty is fundamentally due to poor charge-acceptance. This process sets up conditions that ultimately accelerate the further accumulation of lead sulfate and hasten the demise of the cell.

As noted earlier, the first hint of a solution to the problem was reported by the JSB group [30]. They showed that an increase in the concentration of carbon black that is added to the negative active-mass helps to resist the accumulation of lead sulfate on the plate. Increases of three-times ( $3\times$ ) and ten-times ( $10\times$ ) the base concentration (not reported) retarded the build-up of lead sulfate in the negative plate and extended cycle-life. Specifically, the increase in lead sulfate concentration per cycle fell from 0.1% to 0.05% to 0.03% for the base,  $3\times$  and  $10\times$  carbon levels, respectively [30].

A subsequent study [31] focused on the influence of carbon in negative plates at the same carbon levels adopted earlier [30]. A most important observation was that at the  $10\times$  carbon level, the cycle-life was the best of the three and the lead sulfate accumulation in the negative plates was lowest, compared with the plates with lower carbon levels. Moreover, it was found that while the  $10\times$  lead sulfate amount was lowest at the end of cycling, the  $\text{PbSO}_4$  crystal sizes were the largest. Nevertheless, due to the relatively large amount of carbon present, these large crystals were recharged easily. This suggests that perhaps all lead–acid products, particularly those with long shelf life or high deep-discharge cycle-life, might benefit greatly from using increased levels of carbon in their negative paste formulations.

The CSIRO team confirmed [32] that raising the concentration of a standard carbon black from 0.2% to 2.0 wt.% produces an immediate gain in HEV cycle-life, although the negative plates, in the case studied, still evolved hydrogen from quite early in service. From conclusions reached in the earlier work [30,31], it was thought that the beneficial effect of increased concentrations of carbon was due to a concomitant increase in the conductivity of the negative active-mass. As shown by CSIRO, conductivity does increase dramatically once the carbon content is raised above a certain minimum threshold (Fig. 3). Conductivity alone was not responsible for the effect, however, because different types of carbon, which gave similar improvements in conductivity, conferred quite varied benefits on negative-plate performance. Indeed, a series of tests with different types of carbon indicated [33] that the specific surface area (SSA) may be more important, especially in the early stages of HEV service (Fig. 4). In general, the best performance came from carbons with the highest SSA which, because of this property, kept the negative plate potential well out of the range in which hydrogen evolution would occur. Importantly, though, not all types of carbon that suppressed negative plate potential conferred significantly better HRPSoC cycle-life performance [33].

During the early stages of HEV service the additive may function simply as a second phase to keep the growing crystal-

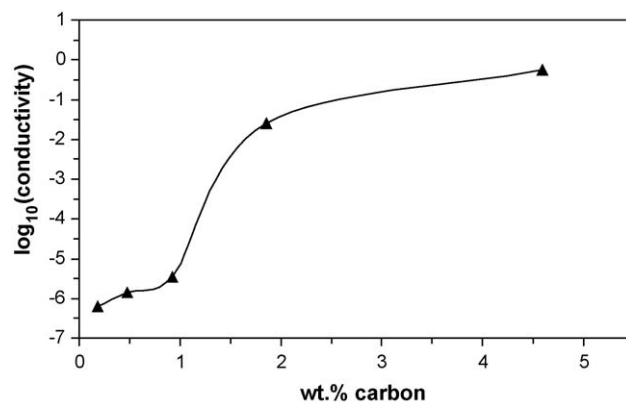


Fig. 3. Relationship between conductivity and concentration of carbon black in a specimen of a cured paste prepared from a mixture of carbon black (Raven H<sub>2</sub>O Columbia Chemical Co., Marietta, GA, USA) and  $\alpha$ -PbO. Increasing the carbon black content from 0.2 to 2.0 wt.% results in an increase in conductivity of about four orders of magnitude [32].

lites of  $\text{PbSO}_4$  apart. The results summarized in Fig. 4 show a high surface-area carbon material to be more effective than one with low surface area. Indeed, it is possible that the second-phase material does not have to be carbon in order to benefit the performance of the negative plate. The incorporation of silica fibres has been found [34] to improve charge-acceptance of the negative plate. Such fibres are also reported to have a beneficial effect on pasting, and this characteristic may be important since very high-surface-area carbon is thought to have an opposite effect in that it renders pasting more difficult. Much remains to be done in this area, particularly if a composite additive might bring optimum benefit, with one component providing the second phase func-

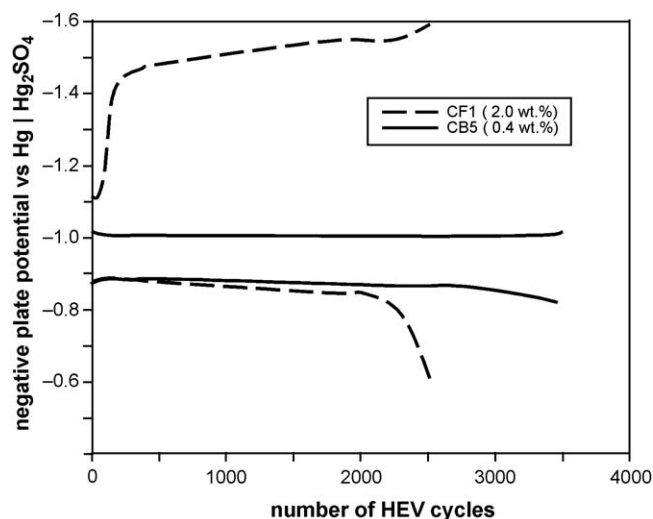


Fig. 4. Changes in negative-plate potential during simulated HEV service for prototype cells containing different types and amounts of carbon materials in their negative plates. Upper curves are for potentials measured at end of each charging step; lower curves are for potentials measured at end of each discharging step. Two sets of curves for cells containing 0.4 wt.% carbon black with a very high surface area (CB5,  $1400\text{ m}^2\text{ g}^{-1}$ ) sustain their potentials far better than curves for a cell containing 2 wt.% of carbon fibres with a low surface area (CF1,  $0.4\text{ m}^2\text{ g}^{-1}$ ) [33].

tion to maintain electrolyte access between  $\text{PbSO}_4$  crystallites and another facilitating electronic access. In this connection, we note that the dissolution–precipitation mechanism for recharge of the active material requires a high-surface-area sulfate to assist the dissolution step and good electronic access to assist the precipitation step ( $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$ ).

Since carbon materials are known to exhibit a wide range of structural disorder, to accommodate a variety of surface functional groups and to have a rich intercalation chemistry, the observation of a range of behaviour from different carbon additives in the negative plate is perhaps not surprising.

More recent work by Yuasa [35,36] has proposed the use of conductive graphite fibres in the negative paste of batteries intended for HRPSoC use in hybrid buses. With this and other materials improvements, commercially available batteries achieved HRPSoC lifetimes in excess of 300,000 cycles in the laboratory which translates into a service life of some 4 years in a hybrid electric bus.

In summary, there may be at least two ways in which carbon particles help to resist the accumulation of sulfate in the negative plate during HRPSoC duty [32]: the first as a stable second phase material separating individual crystallites of  $\text{PbSO}_4$  and thus facilitating access of the electrolyte for the dissolution stage of the recharge reaction, and the second as a facilitator for extension of the electronically conducting surface available for the precipitation of lead. These two functions might, in principle, be performed by two different materials, for example a high-surface-area silica for the first (some optimization may be needed here since too fine a material may be ineffective, or may degrade pasting properties, while too coarse a material may require too great a material loading in order to achieve the desired effect), and a highly conductive form of carbon for the second.

## 6. Asymmetric electrochemical capacitors

Ultracapacitors based on non-Faradaic (double-layer charging) energy storage and delivery have severe drawbacks with regard to high cost, low specific energy, and wide voltage swings. Nevertheless, their high-power performance on both charge and discharge makes them attractive for HRPSoC operation in HEVs.

A variant of the traditional carbon–carbon ultracapacitor is the so-called ‘asymmetric electrochemical capacitor’, or hybrid energy storage (HES) device, examples of which have recently been critically reviewed [37]. In such devices, a standard ultracapacitor electrode comprising high-surface-area carbon is combined with a modified battery electrode, together with an appropriate combination of separators and electrolyte. The first version of this technology, using a  $\text{C}|\text{NiOOH}|\text{KOH}$  construction, was reported in 1997 [38] and is now commercially available. This was followed by a  $\text{C}|\text{PbO}_2|\text{H}_2\text{SO}_4$  design that was patented in 2001 [39]. Due to well-established battery materials and manufacturing technologies, these ultracapacitor-batteries are lower in cost and higher in specific energy relative to standard carbon–carbon ultracapacitors. Provided that the relative sizings and loadings of the battery and ultracapacitor plates are

optimized, they can also have excellent power characteristics [40,41].

The design of these lead–acid HES devices involves a standard high-surface-area carbon negative electrode that stores and provides capacitive energy. The positive electrode, which stores and provides Faradaic energy, is of a standard grid/ $\text{PbO}_2$  type, heavily overbuilt by a factor of 3–10 to provide longer cycle life and a stable voltage [39]. An absorptive glass mat (AGM) separator, a starved-electrolyte configuration and a valve-regulated design can also be employed, as the carbon negative is very efficient for operation of the oxygen-recombination cycle. The stability of the positive electrode voltage results in a higher operating voltage for the cell as a whole and a greater utilization of the negative-electrode capacitance; combined, these create a 16-fold energy output enhancement, in principle, for HES cells compared with equivalent carbon–carbon ultracapacitors [42].

Lead–acid based HES devices may be useful in a range of applications, from load levelling to UPS to HRPSoC operation in HEVs. They may be particularly attractive for the latter, as the charge–discharge processes do not require the formation of lead sulfate at the negative plate, which, as discussed earlier, is a key issue in the suitability of lead–acid for this type of application. For operation in long strings, they may be more appropriate than standard VRLA cells due to the absence of negative-plate self-discharge issues on float charge [43,44]. In fact, charging in general may be more efficient with HES devices, but more research is required to validate these speculative claims.

In suggesting that a carbon|lead–acid HES device could offer improved performance over a standard VRLA battery, partly because of the replacement of the lead negative electrode with one of carbon, it should be noted that there is evidence that the carbon electrode progressively takes up lead during the course of usage. Russian workers [45], who have conducted the bulk of development work on this device, have reported that the carbon ultracapacitor electrode collects between 200 and 600 mg Pb per square centimeter of electrode. It is implied that this electroplating of lead occurs fairly rapidly during the early part of service. The uptake of lead by the carbon electrode is associated with an increase in specific capacitance of that electrode from 130 to  $430 \text{ F g}^{-1}$  [45]. Based on the observation that the shape of the discharge voltage curve of the electrode does not change appreciably (just its slope), it appears that the increase in capacitance is due predominantly to an increase in area-specific capacitance ( $\text{F cm}^{-2}$ ) that is associated with metal surfaces, compared with those of carbon. While typical (minimum) values for metals can be as high as  $40\text{--}60 \text{ F cm}^{-2}$ , those for different types of carbon are generally lower and can be well under  $10 \text{ F cm}^{-2}$  [46].

The substantial improvement in performance of the carbon|lead–acid HES device, due to the incorporation of lead into the carbon electrode, clearly makes it a stronger development proposition. The presence of lead in the negative plate raises questions, however, over the long-term durability of this system. On the other hand, the development of optimized loadings of plate material, combined with judicious choice of charg-

ing and discharging voltages may be able to control any adverse secondary issues.

## 7. Conclusions and ultimate prospects

It seems fair to say that carbon, in various forms, has the potential to make a surprisingly wide-ranging contribution to the evolution of state-of-the-art VRLA technology. In some areas, such as positive plate preparation, examination of its largely transient effects has pointed to promising new areas of research, such as developing additives to harness the benefits of electro-osmosis. In negative-plate technology, there are strong prospects that greatly elevated levels of carbon will soon take a permanent place in industry standard procedures. Initially, this is being driven by the clear benefits that have been shown in negative-plate performance when VRLA batteries are operated under HRPSoc duty cycles. Given, however, the importance of negative-plate characteristics (particularly the stability of the electrode's potential during charging) in determining the suitability of VRLA batteries for a range of other applications, it is easy to see how high-carbon negative plates may soon become the default choice for VRLA products, across all applications. This seems more likely when it is remembered that a thorough understanding of the precise role(s) of carbon in the negative plate is still emerging and optimization has not yet been completed. In particular, a great deal remains to be learned about the relative importance of the increased conductivity and/or surface area (electrochemical or overall) that is conferred by raising the concentration of carbon to somewhere in the region of several weight percent. Further, only speculation is available as to whether other attributes of the added carbon, such as surface functionality and pore size distribution, contribute to the overall benefit on plate performance that has been observed to date.

Finally, it is exciting to note that the research that has uncovered the benefits of carbon in negative plates is now leading to what is really an extension of VRLA technology, in the form of the carbon|lead–acid hybrid energy storage device. Even at their very early stage of development, these devices have already demonstrated levels of specific power and energy that rival significantly more expensive technologies. Ultimately, such a device may offer all the benefits of present VRLA products together with a range of improvements (e.g., reduced weight, minimization/elimination of sulfation problems, etc.) that are associated with the use of a negative electrode containing high-surface-area carbon.

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