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REVIEW

Applications of carbon in lead-acid batteries: a review

Jakub Lach[1] · Kamil Wróbel[1] · Justyna Wróbel[2] · Piotr Podsadni[3] · Andrzej Czerwiński[1,4]

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Abstract

A review presents applications of different forms of elemental carbon in lead-acid batteries. Carbon materials are widely used as an additive to the negative active mass, as they improve the cycle life and charge acceptance of batteries, especially in high-rate partial state of charge (HRPSoC) conditions, which are relevant to hybrid and electric vehicles. Carbon nanostructures and composite materials can also play such a role. The positive active mass additions are generally less beneficial than the negative ones. Carbon can also be applied as a material for reticulated current collectors for both negative and positive plates. This modern technology allows to increase the battery specific energy and active mass utilization. Batteries with such collectors can show improved cycle life, owing to a better active mass mechanical support. Other recent use of carbon in secondary batteries is as supercapacitor electrodes. They can replace the negative plate or be connected in parallel with such a lead plate. These solutions increase the specific power and HRPSoC performance. Presented new carbon-based technologies in a construction of lead-acid batteries can significantly improve their performance and allow a further successful competition with other battery systems.

Keywords Lead-acid batteries · Carbon · Additives · Battery paste · Reticulated current collectors

Introduction

Several types of carbon find various uses in many types of electrochemical power sources. In this article, we focus on implementations of its elemental forms in presently used lead-acid batteries, as well as potential future improvements to their construction that carbon can bring. Unique properties of carbon and a variety of its allotropes allow it to find a use in different parts of lead-acid battery, namely in its negative or positive active mass, a part of the electrode or current collectors.

A lead-acid battery was invented in 1859 by Gaston Planté, and nowadays, it is one of the oldest chemical systems allowing an electrical energy storage. In the last 160 years, many applications have been found and they are still in a widespread use, e.g., as car batteries or a backup power. The lead-acid battery is a secondary cell, where during a discharge, it produces lead(II) sulfate(IV) from a metallic lead (on the negative electrode) and from lead(IV) oxide (on the positive electrode). Both mentioned processes involve the electrolyte, i.e., sulfuric(VI) acid. The overall discharge reaction is as follows:

$$Pb + PbO_2 + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O \qquad (1)$$

The main advantages of this type of battery are its low cost, simple and well-known technological process, almost 100% effective recycling, long operation in floating charge conditions, and low self-discharge. The disadvantages include a high mass caused by a low specific energy in relation to newer battery types, a limited number of full charge/discharge cycles and a need of storing in charged condition.

The lead-acid battery construction has changed noticeably since its invention. First, cells were made from spiral-wound lead sheets separated with strips of cloth or rubber. The cells were enclosed in a glass container filled with sulfuric acid. These containers were connected in a series or paralleled and placed in a wooden rack, which was later exchanged by

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✉ Andrzej Czerwiński
aczerw@chem.uw.edu.pl

[1] Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

[2] Division of Elastomers and Rubber Technology, Institute for Engineering of Polymer Materials and Dies, Harcerska 30, 05-820 Piastów, Poland

[3] Department of Drug Technology and Pharmaceutical Biotechnology, Medical University of Warsaw, Banacha 1, 02-097 Warsaw, Poland

[4] Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

an ebonite. Today, both the cases and separators are mainly made of plastics, like polypropylene or polyethylene. Most plates are currently composed of the lead alloy current collector and active mass (negative or positive) pasted into it. The electrochemical processes of lead oxidation or reduction occur in this paste during the battery operation. Figure 1 presents the comparison between the first batteries and the current ones. The evolution of the lead-acid battery technology is, however, still ongoing, and it can be improved in many ways. Carbon is an important part of these advancements.

An introduction of carbon to the negative paste was one of the main changes in the accumulators. Contemporary active masses contain not only lead paste but also additives, which improve their properties during the battery operation. One of the most widely used additives to negative mass is carbon in different forms, such as graphite or carbon black. It can also be used in positive pastes, but with lesser beneficial effects. Besides being an active mass component, carbon can have many additional uses in currently developed lead-acid batteries. Its different forms can improve the properties of these accumulators as a new type of the current collector material or as a capacitor quickly storing additional energy. These applications are discussed in detail in further sections of this article.

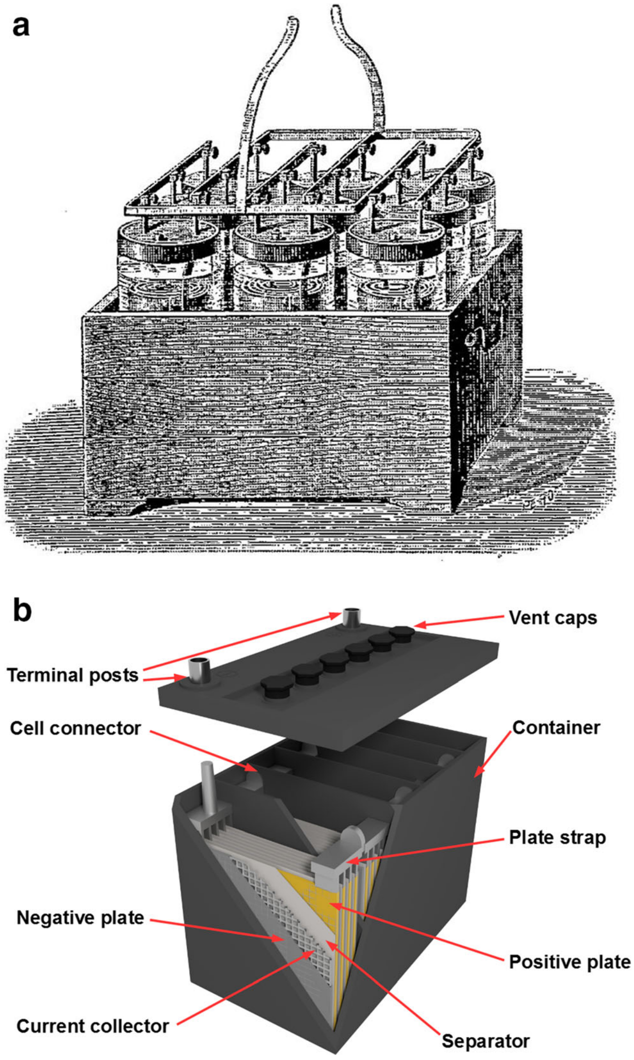


Fig. 1 Construction of the first (**a**) [1] and present (**b**) lead-acid batteries

Carbon as an additive to negative active mass

Additives to negative active mass (NAM), the so-called expanders, were introduced after the World War II [2]. Their three main components were lignosulfonates, barium sulfate, and active carbon. They were used to prevent formation of a passive lead(II) sulfate layer, increase fraction of the active mass involved in electrochemical reactions, and improve current conductivity when the plate is discharged and is composed mainly of the isolating sulfate. Nowadays, many types of carbon are employed in this role, e.g., active carbon, graphite, acetylene black, or carbon black.

The effects of carbon additive are positive. It greatly improves the cycle life of batteries and the charge acceptance during an operation. The significant rise of the durability and the number of battery discharge/charge cycles allow the lead-acid battery to become competitive in relation to other more expensive types of electrochemical power sources, e.g., Ni-Cd cells. Figure 2 shows the marked improvement in the cycle life of 12 V lead-acid batteries with a standard design and an addition of carbon black, where they complete twice as much cycles as a battery without the additive.

The addition of carbon has a very moderate effect on the cost of the battery. Typical expanders are added to lead oxide at 1–2 wt.% and cost around 3–10$ per kilogram, which amounts to less than 1% of the price of the complete battery. The carbon additive represents less than a quarter of the mass of the expander. The benefits of such additive are especially important when using a high-rate partial state of charge (HRPSoC) regime. The increase in the number of charge/discharge cycles for different types of carbon additives is shown in Fig. 3. The cycling conditions were as follows: First, the cells were discharged to the SoC of 50% by 0.5C current. Then, the HRPSoC cycles consisted of charge and discharge with 1C current for 25 s, each separated by a rest for 5 s.

The HRPSoC conditions are relevant to hybrid vehicles, as during travels their batteries are discharged only partially and charged using short current pulses with high intensity (e.g., during braking). The SoC of the battery cannot be below 30%, as it will not have enough power to start the engine; on the other hand, too high SoC lowers the charge acceptance during braking [5]. Additionally, charging with the high current favors hydrogen generation, which further lowers the charge acceptance. The other problem more pronounced during HRPSoC operation is the so-called negative plate sulfation,

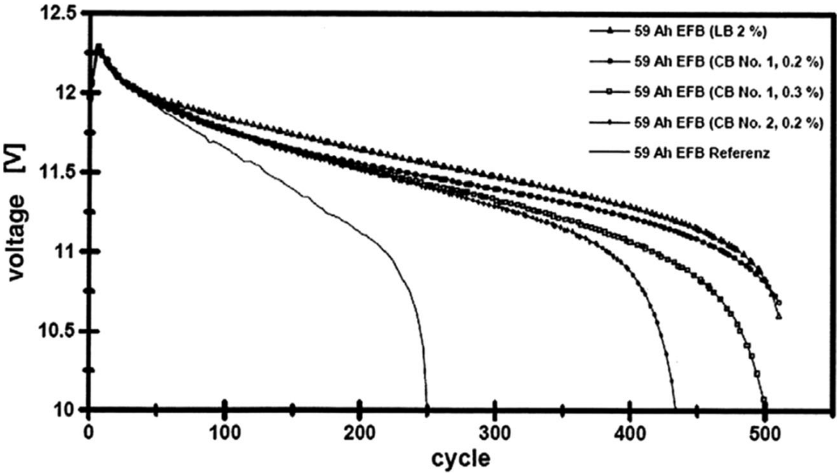


Fig. 2 The final charging voltage of 17.5% depth of discharge cycle test of 12 V lead-acid batteries with carbon black (CB) and lamp black (LB) additives. The tested batteries were first discharged to the state of charge (SoC) of 50% and then cycled at 17.5% depth of discharge using 0.35C current, according to the regime described in the reference [3]. Reprinted from [3] with permission from Elsevier

as these operating conditions allow for an easier generation of big lead sulfate crystals. Bigger crystals have a lower surface area relatively to their volume and are more difficult to reduce during the recharge of the battery. This leads to a drop in its capacity. The positive plates do not undergo sulfation in these conditions owing to their much higher specific surface area and lower pore size, preventing uneven distribution of the sulfate, which would cause difficulties in its full oxidation [6, 7]. In addition, the series of reactions in the volume of the PbO_2-hydrated zones leading to their reduction is detrimental to the formation of big $PbSO_4$ crystals [8]. The addition of carbon to the negative plates improves the uniformity of the sulfate distribution. This fact can be observed on scanning electron microscope (SEM) images registered after 100,000 PSoC micro-cycles [9]. Big lead sulfate crystals can be found on images of a standard cell after cycling (Fig. 4a); on the other hand, the cell with a paste with a higher carbon content is not sulfated (Fig. 4b).

Pavlov and Nikolov argued that the dominating process determining electrical parameters of cells depends on the current pulse duration [10]. When discharge/charge cycles are shorter than 5 s, a non-Faradaic process (connected with the electrical

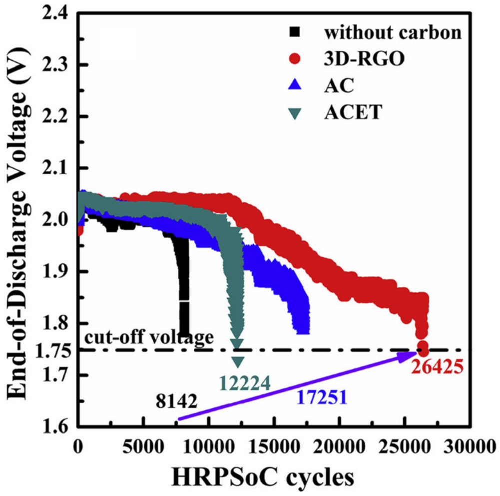


Fig. 3 Number of HRPSoC cycles for cells with different active mass carbon additives. 3D-RGO, three-dimensional reduced graphene oxide; AC, activated carbon; ACET, acetylene black. The HRPSoC cycles were conducted at 50% SoC with 1C current. Reprinted from [4] with permission from Elsevier

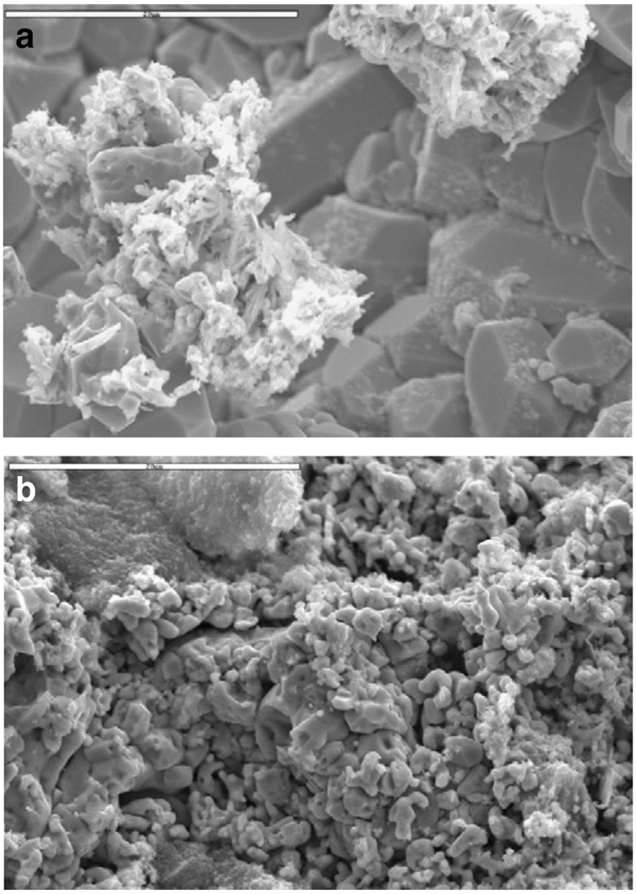


Fig. 4 SEM image of the negative plate after 100,000 PSoC cycles with 0.1% addition of carbon (**a**) and with 2% addition (**b**). Reprinted from [9] with permission from Elsevier

double layer capacity) dominates. On the other hand, for 30–50-s second cycles, a Faradic process of lead electrochemical reactions was the main contribution. To improve the life cycle during HRPSoC operation, it is recommended to increase the contribution of the capacitance processes and hinder Faradaic processes using, for example, suitable carbon additives. Besides influencing HRPSoC operation carbon increases the available voltage of the battery during the last parts of the discharge and prevents a sulfate accumulation at the bottom parts of the plates resulting from the acid stratification [9, 11].

There are however some negative effects. Carbon lowers the initial capacity and hydrogen overpotential; so, in large amounts, it leads to a higher NAM self-discharge and a lower charge efficiency [12]. Additionally, the reactions between lead oxides and carbon during the charging and discharging are possible, especially with the rise of the temperature of the electrode due to the ohmic resistance. In the case of valve-regulated lead-acid batteries (VRLA), carbon can be oxidized by oxygen transported from positive plates, which prevents recombination of this gas with hydrogen and increases the loss of water [13] and additionally lowers the beneficial effect of this additive on the charge acceptance [14].

The exact way of how carbon influences the active mass is not fully explained, and many scientists proposed different mechanisms. Today, three main mechanisms are assumed to be responsible for the beneficial effects of carbon addition [15]. Firstly, carbon additives can increase the electroactive surface of an electrode and increase the rate of the electrochemical processes. Secondly, the additives can physically restrict the growth of the sulfate crystals and facilitate the formation of small, isolated crystals. Finally, carbon can increase the amount of the energy that can be stored in the electrical double layer.

The first mechanism is related to one of the earliest proposed explanations: an increase in the conductivity of the negative active mass. Carbon particles can form a conductive skeleton in the lead sulfate layer, which makes the battery recharge easier and improves its lifespan [11, 16]. The CSIRO Energy Technology team investigated the influence of the added carbon black amount on the cured paste conductivity [17]. When the addition of carbon black is over 1 wt.%, there is a sudden increase in the conductivity, corresponding to the amount of the additive needed to improve the cycle life of a battery. The addition of carbon increases the electroactive surface, which also improves the battery behavior during a cyclic work with high currents and a charge acceptance during the charging. The research of Pavlov et al. showed that Pb^{2+} ions are reduced also on the carbon surface [18]. The reduction of the Pb^{2+} ions to Pb on carbon improves the reversibility of the process and the speed of recharging, as the surface of carbon is larger than that of lead. A described effect takes place when carbon particles have a good contact with the active mass and the current collector, which happens when they show a high affinity to lead and become incorporated in a lead skeleton [7]. The addition of different forms of carbon also changes the structure of the active mass. It can, for example, change its porosity, which facilitates the access of the electrolyte.

The second mechanism assumes that carbon restricts the growth of sulfate crystals by constituting a phase physically separating the growing crystals [6]. Carbon materials can accumulate in big pores of NAM [19] or modify the porosity of the whole mass [10] which limits the growth of big crystals. On the other hand, too small pore sizes (below micrometer) impede the transport of the SO_4^{2-} ions in NAM, which causes PbO formation during the discharge, hindering the battery operation [10]. This physical growth restriction is confirmed by an improved charge acceptance after adding a poorly conducting titanium dioxide to the active mass. Such additives were investigated by Krivik and co-workers [20]. During charging, the addition of both carbon and titanium dioxide lowered the voltage of the cell, decreased the pore size in NAM, and improved the charge acceptance. A cell with titanium dioxide addition completed a similar number of partial state of charge (PSoC) cycles as the one with carbon. A physical restriction of the crystal growth does not require the use of highly conductive carbon types, but their particles should not be too small.

The third explanation of the beneficial carbon effect is that it can work as a capacitor. Carbon forms with large specific surface area, and microporous structure can act as supercapacitors after filling their pores with an aqueous medium. Water and H^+ ions penetrate pores, and during charging, the electric charge is concentrated in carbon particles, which then can be redistributed along the lead skeleton [14]. The ability to rapidly store protons in the electrical double layer prevents a hydrogen generation appearing when the lead electrode reaction is unable to cope due to the high current. This effect increases the efficiency of charging process and can also help during the battery discharge, when the double layer can be discharged during the reduction of lead sulfate [6]. Fernández et al. showed that the discharge current and charge acceptation rise during the microcycles when adding the carbon additive with the highly developed surface [21]. During charging, the current peak related to the charge accepting by the capacitor was more pronounced when state of charge of the battery was low, which corresponded to a situation when electrochemical reactions of lead should have lower contribution. The described results show that the tested carbon additives work like a capacitor. Additives with a good electrical contact with the collector and larger specific surface area facilitate a higher charge acceptance. The pore size is also important as they have to be big enough to allow an access of ions. Large percentage of big pores in the material additionally allows such capacitor to achieve a higher power; however, they can store less total energy.

There are also other processes previously used to explain the carbon additives' influence [7]. For graphite, it could be caused by intercalation with different chemical species, e.g., hydrogen or HSO_4^-, which can improve the conductivity. Carbon can also contain impurities, changing the hydrogen overvoltage, which can improve or worsen the charging efficiency and additionally explain the differences between various forms of this element. Carbon can also react with oxygen produced at the positive plate, which prevents the diffusion of this gas to the negative plates and subsequent oxidation of lead to its sulfate. In this case, however, the beneficial effect would be of limited duration, as carbon would be depleted relatively fast.

The differences in results reported in this area show that the beneficial carbon additive effect is probably a combination of a few mentioned mechanisms and is mainly dependent on a form of carbon and its physical properties. The best results are obtained for materials with a good electrical conductivity, large specific surface area, and easily incorporated into the lead structure.

Currently, new types of carbon additives are still being proposed. One of the novel solutions is the use of carbon nanostructures, like nanotubes or fullerens. Logeshkumar and Manoharan compared several additive types, like multi-walled carbon nanotubes (MWCNT), graphene, VulcanXC-72 carbon, lead oxide nanorods, and ball-milled lead oxide nanospheres. They concluded that MWCNT showed the best improvement [22]. Other teams also reported a beneficial effect of this additive [23, 24]. Carbon nanotubes have a large surface area and good conductivity and can integrate into NAM and create a conductive skeleton, which improves the cycle life of the battery to a great extent. Other types of carbon additives are also examined. Long et al. used a three-dimensional reduced graphene oxide as their additive, characterized by a porous structure and high conductivity [4]. It was prepared from graphene oxide synthesized by Hummer's method and reduced by hydrothermal method. This 3D-reduced graphene oxide greatly increased the number of completed HRPSoC cycles, and it also improved the initial discharge capacity. Zhao et al. reported the possibility of the chemically activated carbon prepared from a plastic [25]. It was made from polyethylene bags calcinated under nitrogen atmosphere and activated with phosphoric(V) acid, nitric(V) acid, or zinc chloride.

Carbon can also be a part of a composite additive. Jiang et al. proposed a combination of mesoporous carbon and bismuth sulfide (C/Bi_2S_3) in NAM [26]. A negative plate prepared with this additive completed over 19,000 HRPSoC microcycles and displayed a high efficiency in low temperatures. This effect was explained by a high affinity between the carbon additive and active mass, its large specific surface area, and good electrical conductivity, as well as a reduced hydrogen evolution on the negative plate through addition of Bi_2S_3. There are also other materials that can be used to reduce the hydrogen evolution, which typically rises as a result of carbon additives. Wang et al. proposed a combination of graphite and mesoporous carbon doped with lead in its pores [27]. This additive reduced the growth of $PbSO_4$ crystals in 2 V cells and improved the reversibility of the $Pb/PbSO_4$ reaction, simultaneously reducing the hydrogen evolution on carbon. Batteries with such additives completed 3 to 5 times more HRPSoC microcycles, compared to batteries without carbon. Yang et al. used a composite of polypyrrole and graphene oxide, which reduced the sulfation of plates, and the polypyrol additive prevented the increase of hydrogen generation caused by adding only graphene oxide [28]. Hong et al. studied an active carbon doped with nano-lead [29]. Lead adsorbed into carbon pores reduced hydrogen evolution to levels comparable to a battery without carbon additives. Other parameters of the cell with additive were also improved, which was explained as a result of a greater porosity, allowing a faster diffusion of ions. Carbon doping using heteroatoms, like phosphorus [30] or nitrogen [31], can also decrease the hydrogen evolution through creating electron-deficient carbon atoms and weakening its bonding with hydrogen ions. Activated carbon can be doped by phosphorus by, first, pretreatment in 80 °C in nitric acid, then pretreatment in 80–90 °C in phosphoric acid, and finally calcination in 400–500 °C under argon [30]. Doping with nitrogen can be achieved by refluxing activated carbon in 80 °C in a mixture of diethylenetriamine and anhydrous ethyl alcohol. The carbon material isolated after filtering and drying had nitrogen atoms embedded in its structure [31].

Carbon as an additive to positive active mass

The positive active mass (PAM) additives are not in widespread use and are less researched, as they had not shown positive influence as in the case of the negative mass. There are, however, some reports of its beneficial effects.

Tokunaga et al. observed that the 0.1–2% addition of anisotropic graphite to PAM improves the capacity and cycle life explained by increased porosity of PAM caused by graphite expansion during oxidation [32]. This allows for a better access of sulfuric acid to the active mass. The sulfate layer formed in these conditions is more uniformly distributed on the electrode. The positive effect is more pronounced for bigger carbon particles. This is in opposite to findings for the negative mass. Baker et al. proposed other probable explanations of this effect: improved wetting of the plates and the electro-osmotic pump [33]. The electrolyte can move relative to the surface charged by the HSO_4^- ion intercalation into graphite. This process would provide a better access of the sulfuric acid to the pores of the active mass.

Dietz et al. reported that a 0.2–1% addition of carbon black was beneficial for the formation process and increased the mass porosity [34]. During the formation with carbon black, a bigger fraction of PbO underwent oxidation to α-PbO_2 than to β-PbO_2. This effect is a result of a greater surface of the electrical contact available during the first stages of the formation. Additionally, carbon black assured a more uniform morphology of the active mass, composed of spherical agglomerates, which suggests that current densities and lead ion supersaturation were moderate during the formation process. However, this additive did not improve the cycle life, as it was quickly oxidized during the cell operation.

The additions of different synthetic fibers are known to improve the properties of PAM. Ball et al. used short carbon fibers in this role [35]. Ball's team studied both the mechanical properties of the paste and the electrochemical properties of the active mass. They added 0.25 wt.% of carbon fibers to a standard paste. Batteries using that paste had increased capacity during 1000 work cycles, especially for high currents. This performance was likely a result of the improved mechanical integrity, porosity, and conductivity of PAM.

Carbon nanostructures can also be added to PAM. Lead sulfate crystals forming during the cyclic work are smaller when cells employ a paste with the nanotube addition, which was explained by Marom et al.; a formation of local networks provides a more even current distribution in the active mass [24]. Banerjee et al. compared the use of single-wall carbon nanotubes (SWCNT) and multi-wall nanotubes (MWCNT) [36]. The addition of carbon nanotubes caused an increase in the cycle life and the initial capacity of the plates, the latter owing to greater amounts of β-PbO_2 present in PAM. Additionally, as the number of nanotubes in the unit volume is higher for SWCNT, the increase of the stability is greater for nanotube type. To further improve properties of the active mass, carbon nanotube surface can be additionally functionalized. For example, the functionalization with hydrophilic carboxyl groups improves the wetting and adhesion of the mass [24].

There was also limited research on the area of adding carbon directly to the electrolyte. In works of Kimura et al., the addition of carbon colloid increased a cyclic work capacity of tested batteries [37]. After the end of the measurements, carbon was present in the electrodes, which suggested that the improvements of cell parameters were the result of the same mechanisms, as for a direct carbon addition to the active mass.

In general, carbon additives in PAM can improve the current conductivity and form a skeleton-simplifying charge flow. They can also prevent the active mass shedding, improve their mechanical properties, and increase the porosity. The influence of carbon on the positive paste is greatly dependent on its form and its stability in conditions of the PAM operation. The positive effects are not as pronounced as for the negative mass, which prevented its widespread adoption.

Carbon in current collectors

Carbon can be used in batteries as a building material of reticulated current collectors. Replacement of heavy lead grids with carbon collectors reduces the weight of batteries resulting in the increased specific energy of the battery. There is a major difference between the theoretical specific energy of the lead-acid battery, which equals 168 Wh kg^{-1}, and typically acquired results in the 30–40 Wh kg^{-1} range. One of the reasons is ineffective utilization of lead, which comprises 67% of battery weight [38]. A lead grid is a heavy component, which functions only as a mechanical support and current collector, without participating in battery redox reactions. Despite that, it can be responsible for 33–50% of the weight of the plate and ca. 25% of the total mass of the battery. The utilization of the active mass is also relatively low, only 40–50% of lead and lead oxide transforms into sulfate during a discharge with 0.1C current [39]. Overall, 65–75% of the total mass of lead in the battery does not take part in electrochemical reactions generating current [39]. An improvement of these parameters is one of the challenges for battery manufacturers. Replacing metal grids with reticulated collectors allows also for a better active mass utilization. Typical values of the γ coefficient (which equals to the ratio of the mass of the paste and a collector surface area) are between 2 and 2.5 g cm^{-2} [40]. When using the new reticulated collectors, γ value can equal 0.25 g cm^{-2}, when comparing to similar plate sizes [41]. The lower value of the coefficient is related to lower densities of the flowing current, a high active mass utilization, and a high discharge capacity. Reticulated collectors also offer a better mechanical support for the active mass, which can improve a cycle life of a battery. For negative current collectors, carbon is a good choice because it is characterized by a high hydrogen evolution overpotential and is inert in electrochemical processes of NAM. In case of positive plates, the protection against oxidation is usually required as it can proceed quickly in operating conditions of this plate, when carbon is in contact with electrolyte. This protection can be achieved, e.g., by employing a protective, metallic, outer layer. At the same time, pasting of the plates can be more problematic for reticulated collectors, owing to their small pores and often higher thickness.

Reticulated vitreous carbon (RVC) [42] or conductive porous carbon (CPC) [43, 44] has a good perspective for use as reticulated current collectors. CPC is made from a polyurethane precursor with a proper pore size. The precursor is impregnated with a phenol-formaldehyde or furfural resin or their mixture. The used resin preferably should not graphitize during the later carbonization. Additives, like metallic salts or graphite can be used. This process can be modified by using volatile additives (e.g., chloroalkanes with short carbon chain) in substrates. During curing, these additives evaporate, creating pores and puffing out the whole mass. Afterwards, the impregnated precursor is carbonized in vacuum, under inert (nitrogen, argon) or reducing (carbon(II) oxide) atmosphere. During the carbonization process, the organic compounds are transformed into an amorphic glassy carbon. The finished product losses some mass, but its initial structure and shape are preserved, with some volume compression (about 40–70%). The impregnation and carbonization can be repeated a few times, using a new resin portion on the carbonizate each time.

Porous carbon materials show interesting properties. For RVC, empty spaces comprise 90–97% of its volume, which ensures its high surface to volume ratio. This material also has a good electrical conductivity. The first research concerning the use of RVC in lead-acid batteries was conducted by Czerwinski's group, which resulted in a patent submission in 1995 [45]. Their early research focused on properties of RVC covered with lead using galvanic baths. Electrodes composed of metallic lead, RVC covered with lead, RVC covered with platinum, and then lead were compared [46]. In another work, lead(IV) oxide deposited on RVC was examined [47]. Overall, conducted experiments did not show significant disparities in the behavior of Pb and Pb/RVC electrodes and showed that RVC can be used as a material of a new collector in a lead-acid battery.

During further work, Czerwiński's group built complete cells with collectors based on RVC [48, 49]. Plates with the RVC collector look similar to typical plates, but they are thicker (ca. 5 mm), as shown in Fig. 5. Two types of negative plates were used during the described research: with collectors made of the bare RVC and made of the RVC covered with 10–15 μm of lead. Positive plates were taken from a standard battery. These cells achieved good capacity, about 135–155 Ah per kilogram of NAM. Obtained Peukert coefficients were comparable to values reached by commercial batteries. A discharge using currents in the 0.05–1C range did not show significant differences between two types of negative collectors. However, depositing lead on the collector improves its resistance to mechanical damage. During tests, both types of cells completed about 50 charge/discharge cycles with a stable capacity [49]. A negative plate can also be modified with a copper layer or lead deposited on top of the copper layer [50]. Experiments showed that both types of copper collectors are stable during the negative plate operation. The main benefit of using the copper layer in this type of collectors is an increase in the electrical conductivity, which lowers the polarization of the battery, especially during final stages of charging.

Positive plates made from RVC coated with lead were also prepared [51, 52]. They employed lead coatings with thickness of 20–140 μm, which protected RVC from oxidation in H_2SO_4 environment. During discharge with 0.05C current, obtained capacities (around 120–165 Ah per kilogram of active mass) were higher than for standard batteries, although the results were worse for high currents. Positive plates had a very favorable ratio of the collector mass to the total plate mass, equal to 8% for 20 μm lead layer and 22% for 100 μm layer, compared to 40% for typical plates [52]. The thickness of the lead layer has also a very large influence on a cycle life. The capacity of the cell with positive collectors with 20 μm coating quickly decreased after only around 15 cycles; on the other hand, a cell with 60 μm coating completed about 45 cycles without a significant capacity loss.

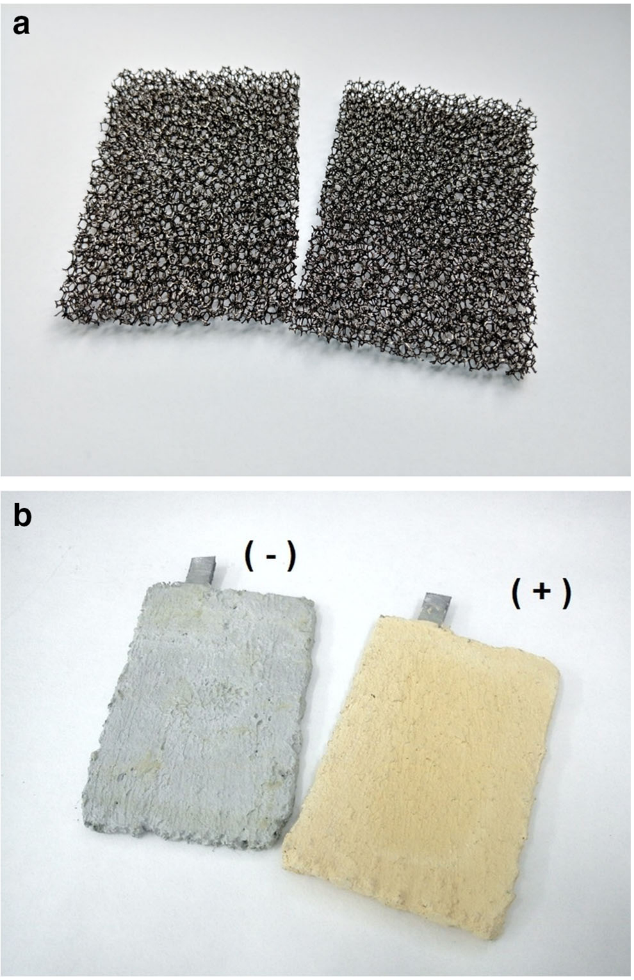
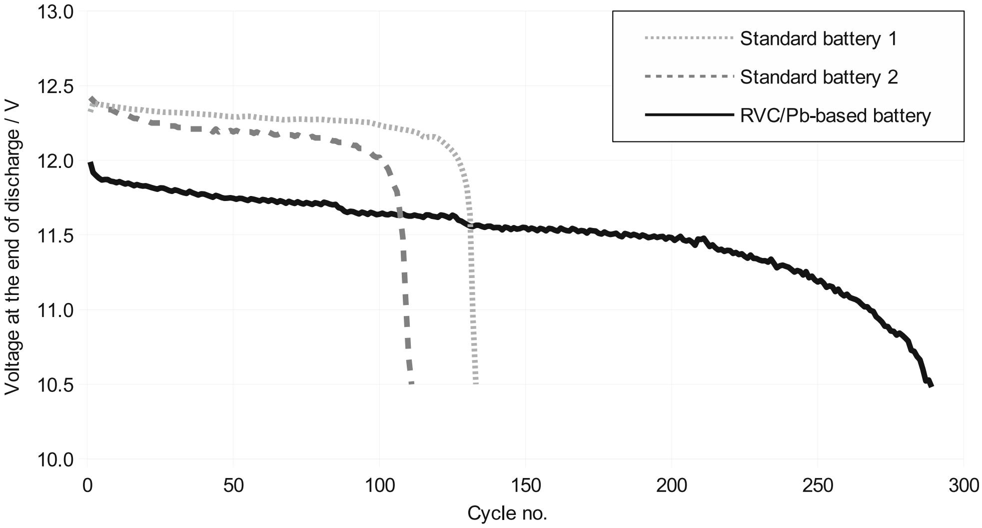


Fig. 5 RVC matrices (**a**) and negative and positive plates (**b**) based on RVC current collectors

During later research, both negative and positive reticulated collectors were successfully implemented in cells. A further optimization of the production process allowed improvements in both cycle life and high current performance. A RVC-based cell completed almost 200 full charge/discharge cycles before failure [41]. A complete 12 V battery was also prepared, which finished 300 partial charge/discharge cycles; two commercial batteries compared in the same tests finished only about 100 cycles, as shown in Fig. 6. A 2 V cell with similar reticulated collectors was also characterized by a very low self-discharge, at about 2% per month. Cells with collectors based on CPC (a material with higher conductivity)

Fig. 6 Voltage at the end of the discharge step during incomplete charge/discharge cycles for 2 standard 12 V batteries and a 12 V battery with RVC-based collectors [41]



obtained high capacities even during discharge with high current, competitive with standard batteries [41].

The replacement of a standard grid in a lead-acid battery with a RVC or CPC carbon foam matrix leads to the reduction of battery weight and lead consumption of about 20%. Additionally, a spatially (3D) cross-linked matrix collector with small distances (5 mm or lower) between the ribs increases the efficiency of the charge collection from the active mass introduced into the pores. This increases its electrical capacity by more than 20%, which further reduces the amount of lead used. Considering the difference in the materials and the production costs of classic grids and modified carbon matrix, the production of carbon lead-acid battery (CLAB) leads to a decrease in costs. These savings will be equivalent to the reduction of the used lead corresponding to around 30% of the total weight of a standard battery. For example, the weight of CLAB with the 75 Ah capacity is about 16 kg, when a comparable standard battery with the same capacity weighs up to 23 kg. Assuming the current lead price ca. 2 USD per kilogram, the saving for CLAB will be almost 15 USD. Additionally, this type of battery is more environment-friendly and has better electrochemical parameters [41].

Good results achieved by reticulated collectors were met with high interest among different research teams. In the USA and Canada, Gyenge [53], Jung [54], and Kelley [55] filled patents for reticulated collectors. Gyenge coated RVC with a 1% PbSn alloy, by electrodeposition of 200–300-μm-thick layer on positive collectors and 80–120-μm-thick on negative ones [56]. Cells comprised from one positive plate between two negative ones were prepared. They reached a 48% PAM utilization for 0.33C current and 29% for 1C. Such a cell completed over 500 cycles with 1.33C current and 21% nominal active mass utilization. A high thickness of the metallic coating meant a long cycle life, but also a higher mass and lower specific energy. Today, Firefly Energy's OASIS battery with negative plates based on the reticulated carbon collectors is available on the market in the USA. The specific energy value of this OASIS battery has reached ca. 41 Wh kg^{-1} with very good performance parameters.

Researchers also investigated reticulated collectors made of different carbon materials. Chen's team explored the possibility of use of the carbon foam based on a carbonized, pitch-impregnated polyurethane foam [40, 57–59]. In 2008, they prepared the negative plate current collectors from a small piece of the foam with positive collectors made of a punched lead sheet [57]. In comparison to a typical cell, the modified construction achieved a higher capacity by about 13% during 0.05C discharge. During work, in the PSoC regime, smaller lead sulfate crystals were formed and the battery with new collectors completed more cycles. Better properties of the modified cell were explained by a higher area of the electric contact for the active mass, providing more equal distribution of the current density [57]. The NAM utilization coefficient of 57% was calculated for a similar system, which was 14% better than for a standard lead grid [58]. EIS measurements showed also that the carbon foam has a worse conductivity than lead grids. Chen's team conducted further research where they constructed a cell with foam collectors also in the positive plate [59]. However, in comparison to a standard cell, it was characterized by a higher oxygen evolution, lower charge acceptance during charging, and lower voltage. Additionally, after cycling, its positive mass was very loose and easily shed from the plate. They also investigated positive and negative plate foam collectors with a lead coating of about 50 μm [40]. Prepared plates had a high γ coefficient and large specific surface area, which enabled good utilization of the active mass and small current densities. As a result, better capacities were reached during cycling. It was also ascertained that the structure of formed PbO_2 provided a better adhesion and electrical contact, which facilitates the reduction process. Three-dimensional collector also prevents a positive active mass shedding during work, as it provides good mechanical support. A cell with coated positive and bare negative foam collectors was also prepared. It showed good electrochemical properties, but needed further optimization.

Jang and coworkers were investigating the possibility of using graphite foams with graphene aligned along the pore walls as current collectors [60]. This material has 30 times better conductivity than RVC. However, the pasting of the plates was problematic, as the active mass poorly penetrates this material. Additionally, these collectors become intercalated with sulfate ions in positive potentials, which causes a shedding of carbon particles from the foam; so, the use of this material is not suitable for positive plates.

Hariprakash and Gaffor prepared positive and negative collectors using graphite sheets with holes cut out for the paste, coated with lead and then the polyaniline layer [61]. They reached satisfactory capacities during a high current discharge and a specific energy around 40 Wh kg^{-1}; however, the paste content in their plates was low compared to volume of the collector. After 30 work cycles, the active mass shedding was observed.

Kirchev et al. proposed the use of the composite "honeycomb" structures as collectors [39, 62, 63]. They were made from a cellulose-based material impregnated with a phenolic resin and are carbonized after heating in inert atmosphere. The surrounding frame and a current collecting tab are also made from carbon. The final stage of the production is the electrodeposition of the metal on the whole grid. The advantages of this solution are higher active mass utilization, low γ coefficient, and efficient use of the compression in VRLA batteries, as the pressure is applied to the mass itself, not the collector. The basis for the composite is a corrugated paperboard soaked with phenolic aldehyde resin and ethanol in a mold, which was next heated. The block was then cut into slices, dried, and finally carbonized in a nitrogen atmosphere. They were later coated with a 100 μm layer of a PbSn 2% alloy. The tab at the top of the plate was coated with copper. The appearance of such collectors is presented in Fig. 7 [39]. The paste pasted into the grid comprised only 50% of the mass of the plate. A cell with a positive collector prepared in this way reached a higher than standard PAM utilization of 58% [39]. According to EIS measurements, PAM behaved as in typical batteries during the cyclic work. The cell showed a good cyclic behavior; it completed 191 full cycles and retained 1/3 of the initial capacity. The composite lost some of its mechanical strength during work and broke into several pieces when removed from the cell. A high corrosion of the collector was explained by too aggressive charging regime. The proposed collector was later used in a negative plate of a VRLA cell with an absorbent glass mat (AGM) [62]. During the experiments, the cell completed over 900 full charge/discharge cycles. The stability of the plate was explained by the presence of small pores in the collector structure, which reduced the active mass shedding, by a low γ coefficient and by use of the carbon fiber as a paste additive. In the next stage of research, a series of experimental 12 V batteries was made, with both positive and negative experimental collectors [63]. Four experimental batteries were successfully used as a power source for an electric scooter in place of a standard VRLA battery. The obtained results show that, in general, the proposed technology can be successfully used in the construction of the negative plates. On the other hand, in case of the positive plates, the use of these honeycomb collectors is limited because of the anodic corrosion of both the carbon matrix and PbSn alloy.

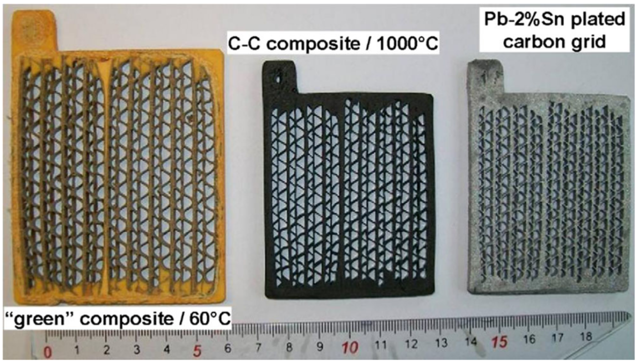


Fig. 7 Stages in preparation of the "honeycomb" collector. Reprinted from [39] with permission from Elsevier

Zhang et al. presented an experimental negative plate current collector based on polymer-graphite composite [64]. In this solution, the carbon matrix can be modified through chemical deposition of the $PbSO_4$ layer. Experiments showed that the $PbSO_4$ deposit reduces the hydrogen evolution and increases the affinity of the active mass to the collector. The stability of the described collector was confirmed during cyclic measurements, where a modified cell retained 85% of capacity after 100 deep cycles when discharged with 0.1C current.

ArcActive, a company from New Zealand, uses collectors made of the carbon fiber fabric activated in an electric arc under appropriate conditions [65]. This fell is soaked in the active mass and top parts of a few layers are connected with a lead lug. The batteries with negative plate collectors constructed this way showed good properties during the PSoC work.

Lannelounge et al. proposed a battery with negative collectors made from a very thin (0.25 mm) graphite foil electrochemically coated with lead [66]. Active masses used by them contained only a small portion of lead compounds or were even fully made from carbon materials, working as a capacitor. They proposed three mechanisms of the energy storage in their battery. The main one was a reversible storage of hydrogen generated during a hydrogen ion reduction in pores of the active carbon. The second mechanism was the electrochemical reactions of lead, and the third was the electrostatic energy storage in the electrical double layer. The described battery was limited by positive plates, and its special construction allowed it to complete over 3000 HRPSoC microcycles with a high energy efficiency.

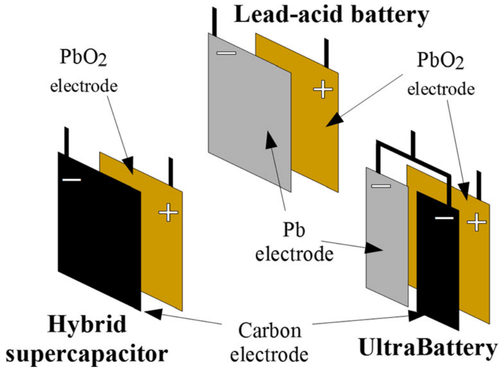


Fig. 8 Types of lead-acid batteries with a carbon electrode

Carbon as a capacitor

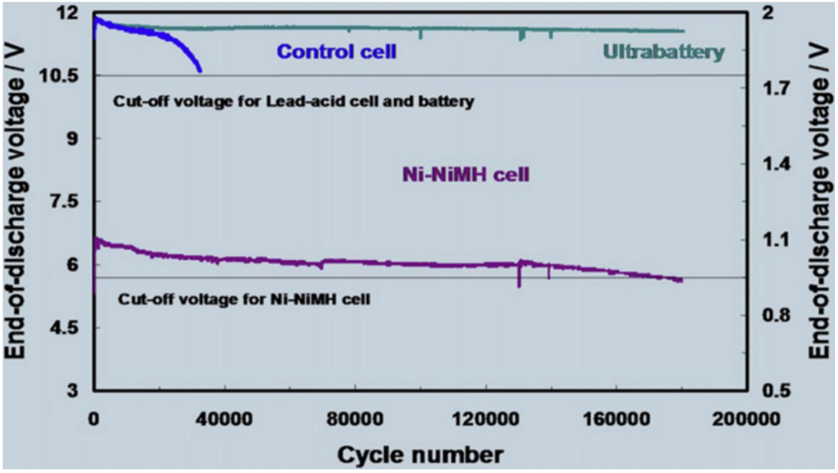
Carbon can be used in batteries as a capacitor, storing energy in its electrical double layer. This element is very popular in this application, as it is very versatile with a wide variety of forms. It has a high electrical conductivity, large specific surface area, low cost, and environmental impact [67]. The idea of the lead-acid battery with carbon capacitor electrode is applied in hybrid supercapacitors. They employ negative plates as capacitors, where lead in the active mass is replaced by carbon materials. In order to achieve a high capacity, the use of carbon forms with high specific area is required. A negative plate of this type is connected with a standard positive plate with a higher capacity, drawing the energy from electrochemical reactions of lead [68]. Hybrid supercapacitors have usually a rather low specific energy and can display fluctuations in their voltage, but they have a very good cyclic behavior and can be charged and discharged with high currents. Hybrid supercapacitors are manufactured for example by Axion Power in the USA.

The other proposed technological solution is the use of a capacitor connected in parallel with a standard negative plate. UltraBattery, developed by Australian Commonwealth Scientific and Industrial Research Organization, is an example of such an asymmetric battery with negative plate comprised of two parts: carbon capacitor and standard plate [69]. The disadvantages of the capacitor include a high price, low energy, and high fluctuations in the voltage, but it provides a very high power compared to typical batteries. Connecting a supercapacitor with a battery gives the possibility to minimize the flaws of both components. Schematics of the construction of described battery types containing capacitors are presented in Fig. 8.

UltraBattery-type solutions are not easy to construct, and the operational potentials of its components are very important. Simply placing a capacitor plate in a battery is not enough, as such a plate discharges in the lower potential than a standard negative lead plate. During discharge, the charge would firstly be drawn from the lead plate and the capacitor would be working only to a small extent. On the other hand, during charging, the capacitor would be initially charged, and a significant hydrogen evolution would appear. The capacitor construction needs to be properly modified to prevent described problems and enable a proper work of the battery. Requirements for the capacitor electrode in UltraBattery are as follows: similar working potential as the negative battery plate, low hydrogen evolution, high enough capacity to work at least 30 s together with the lead electrode, long cycle life, good mechanical strength, and low cost [5].

As mentioned before, batteries in hybrid electric vehicles typically are not working in a fully charged state, but at 30–70% SiC, which would result in a shorter life for a lead-acid battery. UltraBattery has better work characteristics in the described conditions: improved power, lifespan, high-rate charge acceptance, and minimized unfavorable sulfation [70]. Lam and Louey reported higher capacities for an electrode with supercapacitor than for a standard electrode; it could reach values even 10 times higher for high current densities [5]. They also tested complete cells, which had 50% higher power than standard batteries and showed a better performance during cycle life, where it completed 3–4 times

Fig. 9 UltraBattery cycling under the EUCAR power-assist profile. Reprinted from [70] with permission from Elsevier



more cycles. The UltraBattery pack was fitted in a hybrid electric car in place of a NiMH battery. It completed a road test simulation cycle for 100,000 miles without battery problems [70]. Figure 9 shows that under the EUCAR power-assist profile, a 12 V UltraBattery completed more than five times the number of cycles done by a control VRLA battery [70]. The EUCAR testing profile was simulating medium hybrid electric vehicle driving conditions.

Currently, there are some commercially available batteries using the UltraBattery technology. Manufacturers of these accumulator types are, e.g., East Penn Manufacturing Company and Furukawa Battery. Their website (http://www.ultrabattery.com) claims around fifteen times longer cycle life in PSoC operation and high rate charge acceptance three times higher than standard VRLA batteries. Additionally, when put through the PSoC cycles, it has 3–4 times lower lifetime cost per kilowatt hour than conventional VRLA batteries.

Summary

Nowadays, carbon finds use in lead-acid batteries mostly as an additive to the negative active mass to improve its electrochemical properties. This additive works mainly in the following three ways: increasing the portion of the active mass where electrochemical reactions of lead can proceed, storing the energy in the electrical double layer as a capacitor, and physically restricting the growth of the large and hard to reduce lead sulfate crystals. The use of carbon gives a real possibility of the lead-acid battery implementation in hybrid vehicles, as it improves cycle life and reduces the negative plate sulfation occurring during the operation in such vehicles. The most effective carbon additives have a large specific surface area, good conductivity, and high lead affinity. In recent years, investigations of carbon nanostructures or composite materials for this role have started. Carbon has also the potential to be the next breakthrough in lead-acid battery technology in the near future. Its use in current collectors can lead to improvement in the weakest point of lead-acid batteries, namely their low specific energy. Reticulated carbon collectors ensure a lower weight, better active mass utilization, and mechanical support. The improvement of lead-acid batteries parameters can allow them to better compete with newer battery types, like lithium-ion, in different areas (e.g., in energy storage, hybrid vehicles). Carbon can also be used in the battery construction as a capacitor electrode allowing them to achieve a higher power density. Spread of mentioned carbon-based improvements in the lead-acid battery construction can lead to many further years of the economically feasible use of this type of batteries. Despite their long history, lead-acid batteries do not seem to lose their current standing and can even reach new implementations in the future.

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