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Understanding the Function and Performance of Carbon-enhanced Lead-acid Batteries

**Milestone Report for the DOE Energy Storage Systems Program
(FY11 Quarter 1: September through December 2010)**

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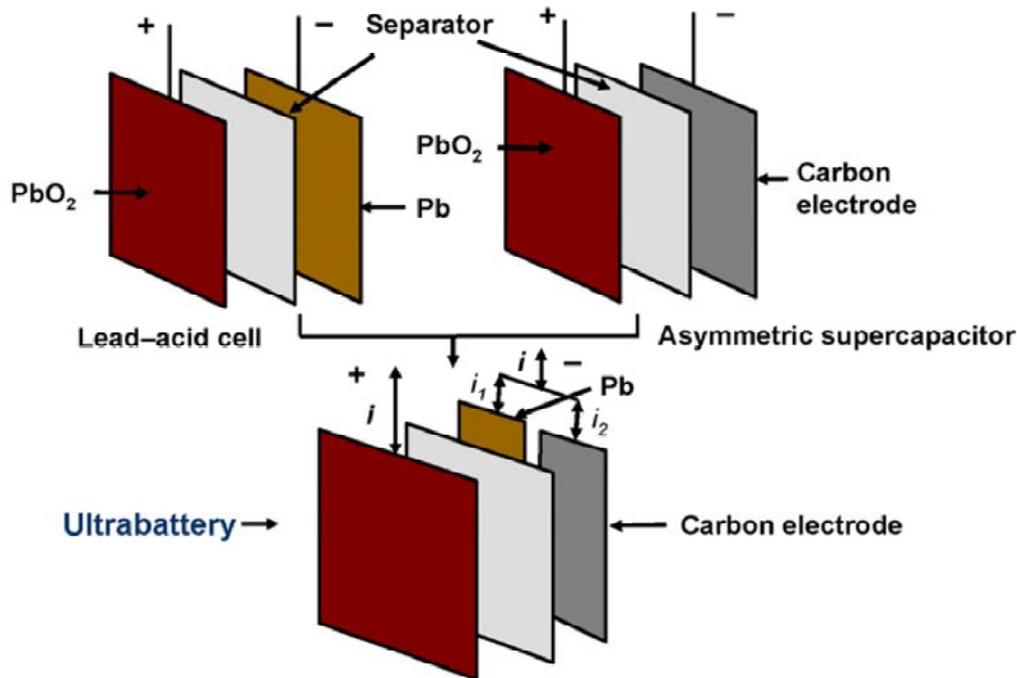
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Abstract

This report describes the status of research being performed under CRADA No. SC10/01771.00 (Lead/Carbon Functionality in VRLA Batteries) between Sandia National Laboratories and East Penn Manufacturing, conducted for the U.S. Department of Energy's Energy Storage Systems Program. The Quarter 1 Milestone was completed on time. The milestone entails conducting a thorough literature review to establish the current level of understanding of the mechanisms through which carbon additions to the negative active material improve valve-regulated lead-acid (VRLA) batteries. Most studies have entailed phenomenological research observing that the carbon additions prevent/reduce sulfation of the negative electrode; however, no understanding is available to provide insight into why certain carbons are successful while others are not. Impurities were implicated in one recent review of the electrochemical behavior of carbon additions. Four carbon samples have been received from East Penn Manufacturing and impurity contents have been analyzed.

Project Description

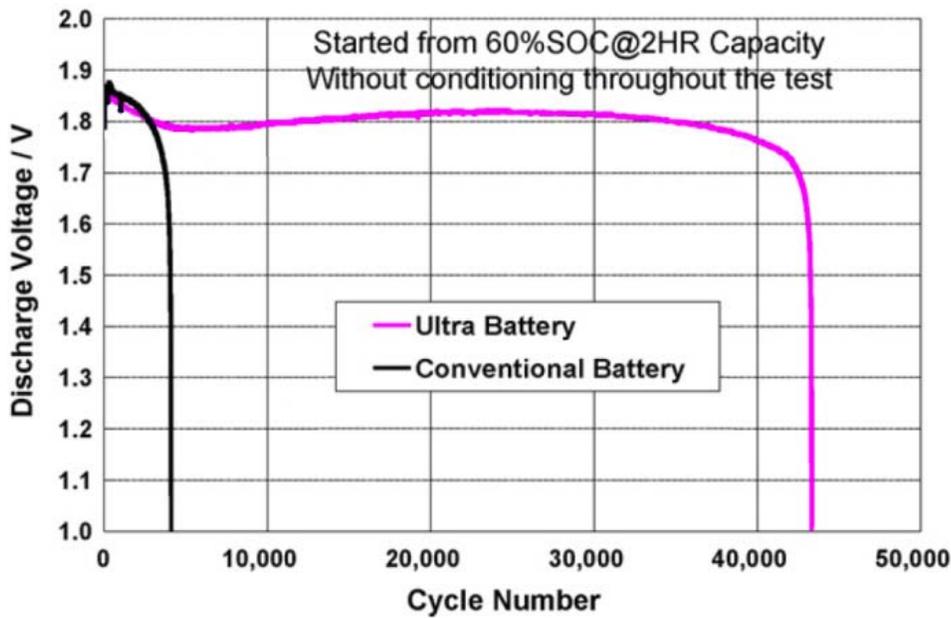
Carbon has been explored as an addition to lead-acid battery electrodes in a number of ways. Perhaps the most notable to date has been the hybrid “Ultrabattery” developed by CSIRO where an asymmetric carbon-based electrochemical capacitor is combined with a lead-acid battery into a single cell, dramatically improving high-rate partial-state-of-charge (HRPSoC) operation.¹ As illustrated below, the “Ultrabattery” is a hybrid device constructed using a traditional lead-acid battery positive plate (*i.e.*, PbO_2) and a negative electrode consisting of a carbon electrode in parallel with a lead-acid negative plate:



Schematic representation of a single cell from the Ultrabattery (after Lam et al. 2009)

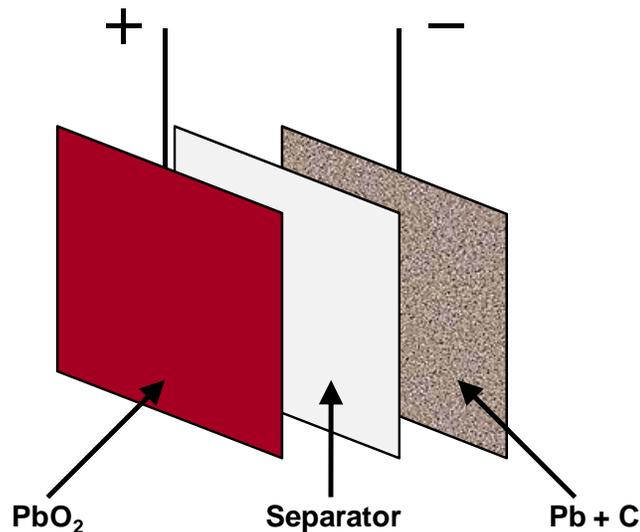
This device exhibits a dramatically improved cycle life over traditional VRLA batteries, as well as increased charge power and charge acceptance. The “Ultrabattery” has been produced successfully by both The Furukawa Battery Co. and East Penn Manufacturing. An example illustrating the dramatic improvement in cycle life of the Ultrabattery over a conventional VRLA battery is shown in the graph below:

¹ L.T. Lam, R. Louey, N.P. Haigh, O.V. Lim, D.G. Vella, C.G. Phyland, L.H. Vu, J. Furukawa, T. Takada, D. Monma, T. Kano, “Production and test of hybrid VRLA Ultrabattery designed specifically for high-rate partial-state-of-charge operation”, ALABC Project DP 1.1, Final report, April 2007.



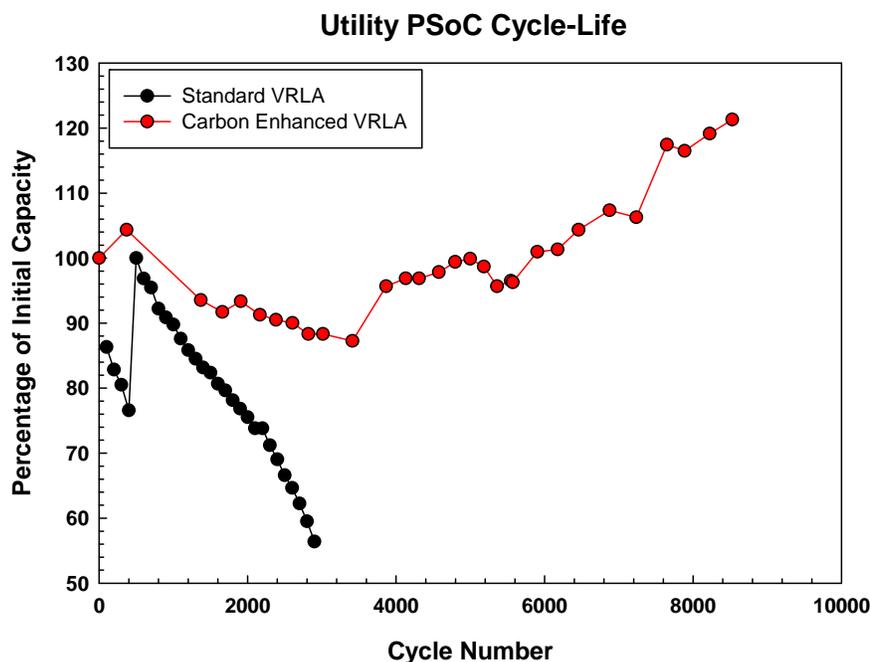
*Discharge voltage as a function of number of cycles under the EUCAR cycle life test.
Lam, et al., 2009.*

In addition to the aforementioned hybrid device, carbon has also been added directly to traditional VRLA batteries as an admixture in both the positive and negative plates, the latter of which has been found to result in similar improvements to battery performance under high-rate partial-state-of-charge (HRPSoC) operation. It is this latter construction, where carbon is added directly to the negative active material (NAM) that is the specific incarnation being evaluated through this program. Thus, the carbon-modified (or Pb-C) battery (termed the “Advanced” VRLA battery by East Penn Manufacturing) is a traditional VRLA battery where an additional component has been added to the negative electrode during production of the negative plate.



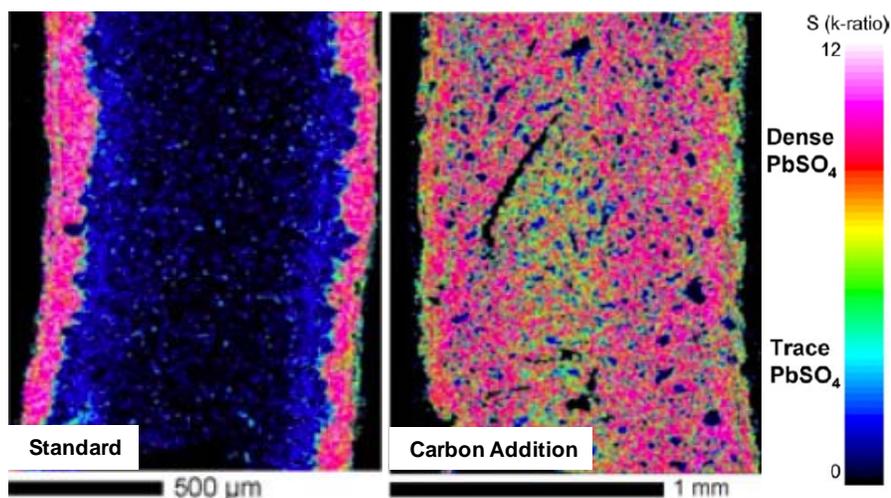
Schematic representation of a single cell from a carbon-modified or “Advanced” VRLA battery.

The addition of select carbon materials to the NAM of VRLA batteries has been demonstrated to increase cycle life by an order of magnitude or more under (HRPSoC) operation. Additionally, battery capacity increases on cycling and, in fact, exceeds the performance of the batteries when new.



Capacity as a function of cycle life for a commercially available, conventional VRLA, and a carbon-modified VRLA battery where carbon has been added to the NAM.

Physically, the mechanism by which carbon extends battery life is generally accepted to be through reduction/elimination of sulfation of the negative electrode. Sulfation is a process that results in the formation of lead sulfate (PbSO_4) crystals that are electrically isolated from the lead in the electrode, and thus are unable to be electrochemically reduced through the recharging process. These PbSO_4 crystals eventually block the surface, dramatically reducing the capacity of the negative plate. It is not clear why some carbons accomplish this effect and others do not.



Elimination of hard sulfation by carbon additions, allowing more complete usage of the battery (both images are from cells at end of life). Fernandez et al., 2010.

The underlying mechanism responsible for improving capacity on cycling is not known. Developing an understanding of the fundamental physical, chemical, and electrochemical mechanisms underlying both aspects of enhanced performance offers the possibility of significantly improving VRLA batteries by intentionally designing and fabricating electrode structures with superior performance. Furthermore, once understood at a fundamental level, it may be possible to extend this approach to other battery chemistries. In this collaborative effort with East Penn Manufacturing, we will

investigate the fundamental physicochemical basis and structure-activity relationships underlying carbon-enhanced VRLA batteries.

This program focuses on 1) developing a fundamental physical, chemical, and electrochemical understanding of the mechanism of enhanced performance of carbon-enhanced VRLA batteries; 2) demonstrating this understanding by fabricating batteries exhibiting optimum performance; and 3) determining to what extent this approach can be applied to other battery chemistries.

Engineering the enhanced performance of PbC batteries will ultimately lead to reduced life-cycle cost, which is an enabling factor for many stationary applications including utility ancillary regulation services, wind farm energy smoothing, and solar photovoltaic energy smoothing.

FY11 Quarterly Milestones

First Quarter—*Review relevant literature to establish the current level of understanding of the mechanisms through which carbon additions to the NAM improve VRLA battery performance.* This review will identify proposed mechanistic explanations that can be evaluated, built upon, or disproved through the course of the experimental portion of the program. ***This milestone has been completed.***

Second Quarter—*Characterize the carbon materials that will be used by East Penn Manufacturing to construct carbon-enhanced VRLA batteries that will be evaluated both physically and electrochemically by Sandia National Laboratories.* Key physical and electrochemical features of each material will be documented and later combined with the results of complete battery testing in an effort to identify the critical characteristics of the carbon additions required to enhance VRLA battery performance.

Third Quarter—*Characterize the raw and formed negative plates containing the four carbon materials characterized in the second quarter.* The physical and electrochemical activities of the carbon-enhanced negative plates will be documented and then combined first with the knowledge gained in the second quarter on the properties of the carbon raw material, and then with the results of complete battery testing in order to determine if there are any critical features or properties of the raw or formed negative plates that can be correlated with the performance characteristics of a VRLA battery that contains them.

Fourth Quarter—*Conduct initial cycle testing (i.e., low cycle count), combined with dissection and analysis of tested positive and negative plates for both carbon-enhanced and conventional VRLA batteries to establish their relative performance and physical characteristics.* In addition to quantifying the raw performance of the various batteries (and hence, carbon additions), an effort will be made to establish what, if any, chemical or structural changes occur early in the life of the carbon-enhanced VRLA batteries. These observations may provide valuable insight into the mechanism through which carbon additions to the NAM enhance the battery capacity and reduce the development of hard sulfation that ultimately leads to battery failure, as well as the degradation mechanisms that dictate the longevity of the carbon additions in the NAM.

FY11 Quarter 1 Project Status Summary

Literature review

Much of the research presented in the literature that discusses the effect of carbon additions to the NAM focuses primarily on the phenomenological observations (*i.e.*, cycle life increases, resistance to hard sulfation increases) rather than postulating/exploring potential mechanisms through which the effect is achieved. A summary of recent work from groups attempting to establish the mechanisms through which carbon enhances the performance of VRLA batteries is presented below.

Looking first to the work of Shiomi, *et al.*² where the beneficial effect of carbon added to the NAM was first reported, it was proposed that carbon forms a conductive network between PbSO₄ crystals, leading to an enhancement in the rechargability of the negative plate. Ohmae, *et al.* expressed a similar view, in that a highly conductive carbon was a necessary addition to the NAM in order to retard the sulfation process.³ In other words, the carbon served as a conductor, hindering the formation of PbSO₄ crystals that were electrically isolated from the lead within the plate, and thus not able to be reduced during the recharging process. While Shiomi and Ohmae believe that the electrical conductivity of the carbon addition is the critical aspect, other researchers, such as Spence, *et al.*⁴, have found that neither electrical conductivity nor surface reactivity were important in determining the effect of a carbon addition to the NAM.

Spence, *et al.*⁵, argued instead that the beneficial impact of the carbon was due to the alteration of the pore structure of the NAM, enabling electrolyte to be banked within the pore structure, and thus available within the NAM, rather than having to diffuse from the surface. They concluded that any addition, not just carbon, that modified the pore structure in such a manner would result in an improvement in performance. This theory is supported by Calebeck and Micka, *et al.*^{6,7,8} where both titania (TiO₂) and alumina (Al₂O₃) were found to provide improvements similar to those obtained by carbon, though their argument was that, in addition to obstructing large pores in the NAM, the additions hindered growth of PbSO₄ crystals, preventing the formation of the large crystallites associated with sulfation. Valenciano, *et al.*⁹ also observed a beneficial effect of an inert addition, in their case glass fibers, though the resulting improvement appeared to depend on the manner in which the battery itself was assembled.

As with Shiomi, Boden, *et al.*¹⁰ observed that the cycle life was increased by eliminating surface buildup of PbSO₄ on the negative electrode (*i.e.*, hard sulfation), and also hypothesized that the increased capacity of the carbon-modified battery was due to the increased electrochemical efficiency of the NAM brought about by the more thorough use of the electrode. Boden also reported that metallic lead clusters were observed on the surface of carbon particle, indicating that the soluble lead ions were electrochemically reduced on the carbon surface in the same way as they are on lead surfaces. A number of other researchers have presented results that support the theory that carbon acts as a nucleation site for the recharging process, improving utilization of the NAM. Kozawa, *et al.*¹¹ explored the addition of colloidal carbon to the electrolyte of a sulfated battery, where they observed

² M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota "Effects of Carbon in Negative Plates on Cycle-life Performance of Calve-regulated Lead/Acid Batteries." *Journal of Power Sources*, 64 (1997). pp. 147-152.

³ T. Ohmae, T. Hayashi, N. Inoue "Development of 36-V Valve Regulated Lead-acid Battery." *Journal of Power Sources*, 116 (2003), pp.105-109.

⁴ M. A. Spence, D. P. Boden, T. D. Wojcinski, "Identification of the Optimum Specification for Carbon to be Included in the Negative Active Material of a Valve-Regulated Battery in Order to Avoid Accumulation of Lead Sulfate During High-Rate Partial-State-of-Charge Operation." ALABC Research Project Designation C1.1/2.1A, Progress Report 2, May 2008.

⁵ M. A. Spence, D. P. Boden, T. D. Wojcinski, "Identification of the Optimum Specification for Carbon to be Included in the Negative Active Material of a Valve-Regulated Battery in Order to Avoid Accumulation of Lead Sulfate During High-Rate Partial-State-of-Charge Operation." ALABC Research Project Designation C1.1/2.1A, Progress Report 4, October 2009.

⁶ M. Calábek, K. Micka, P. Krivák, P. Bača, R. Bilko, R. Lábus "Significance Of Carbon Additive In Negative lead-Acid Battery Electrodes." ALABC Project No. C 2.2, Final Report, April 2008.

⁷ K. Micka, M. Calábek, P. Bača, P. Krivák, R. Lábus, R. Bilko "Studies of Doped Negative Valve-regulated Lead-acid Battery Electrodes." *Journal of Power Sources*, 191 (2009). pp.154-158.

⁸ M. Calebek, K. Micka, P. Krivak, P. Baca "Significance of Carbon Additive in Negative Lead-acid Battery Electrodes." *Journal of Power Sources*, 158 (2006). pp. 864-867.

⁹ J. Valenciano, A. Sanchez, F. Trinidad, A.F. Hollenkamp "Graphite and Fiberglass Additives for Improving High-rate Partial-state-of-charge Cycle Life of Valve-regulated Lead-acid Batteries." *Journal of Power Sources*, 158 (2006). 851-863.

¹⁰ D.P. Boden, D.V. Loosemore, M.A. Spence, T.D. Wojcinski "Optimization Studies of Carbon Additives to Negative Active Materials for the Purpose of Extending the Life of VRLA Batteries in High-rate Partial-state-of-charge Operation." *Journal of Power Sources*, 195 (2010). pp. 4470-4493.

¹¹ A.Kozawa, H. Oho, M. Sano, D. Brodd, R. Brodd "Beneficial Effect of Carbon-PVA Colloid Additives for Lead-acid Batteries." *Journal of Power Sources*, 80 (1999). pp.12-16.

that the battery could be electrochemically recovered, with the carbon adsorbing onto the NAM and acting as a nucleation site for Pb deposition during charge. Pavlov, *et al.*¹² also expressed that carbon was electrochemically active in the NAM, providing additional surface area upon which charge/discharge reactions could take place. Finally, Boden reported that Brunauer-Emmett-Teller (BET) surface area measurements indicated that the surface area decreased with cycle life, suggesting that the carbon is becoming progressively buried under lead and PbSO₄ reaction products and, consequently, losing its beneficial effects. The theory that the carbon serves as an additional electroactive material in the NAM is in contrast to the results reported above by Spence *et al.*, where surface reactivity did not appear to be important.

In a recent review of the effects of carbon on the electrochemical behavior of the negative active mass in a lead-acid battery, Moseley offered a number of potential mechanisms through which the performance could be increased.^{13,14} First, he suggested that the carbon may increase the electrical conductivity of the NAM, facilitating the recharging process (*i.e.*, easing reduction of PbSO₄ in the NAM). Another potential mechanism would be the restriction of PbSO₄ crystal growth, which constrains the size of PbSO₄ crystals and enhances their dissolution rate during recharge, again facilitating the reduction of PbSO₄ during recharge. The latter effect has been demonstrated for a series of inert materials, such as titanium oxide (TiO₂) as discussed above. A potential mechanism for the increase in capacity that Moseley put forward was that the carbon could be acting as a capacitive component, much like in electrochemical capacitors, adding a capacitive energy storage component to the battery. The addition of a capacitive component was also presented by Fernandez, *et al.*¹⁵ who attributed the dramatic improvement they observed in charge acceptance to the capacitive effect. Moseley also indicated a potential detrimental effect of carbon additions—if their impurity level is high, the impurities may facilitate detrimental side reactions (*e.g.*, such as water reduction) resulting in a loss of capacity.

Pavlov's group has also conducted significant research in this area.¹⁶ Their overall theory is similar to that put forth by Boden, where during recharge two parallel processes take place with lead being reduced both on lead surfaces within the NAM as well as on carbon surfaces within the NAM. Thus, the effect of the carbon is to increase the overall electrochemically active surface area within the negative plate, thereby increasing its capacity and facilitating more complete recharge. Pavlov also found that carbon acted to reduce the pore size within the NAM, and that once the pores were reduced to below approximately 1.5 μm the diffusion of sulfuric acid (H₂SO₄) into the pores was impeded, and lead oxide (PbO), not PbSO₄, formed during operation.

In addition to the number of theories concerning how carbon affects the electrochemical behavior of a VRLA battery, there are a similar number of views as to what the appropriate form of the carbon is. Researchers have found that various forms of graphitic carbon, carbon black, and activated carbon have worked, although the results between researchers appear to vary. For example, Spence, *et al.* found that the best performance was observed for flake graphite, while Valenciano, *et al.* determined that flake graphite was detrimental to performance. Seemingly in support of the results of Spence,

¹² D. Pavlov, P. Nikolov, T. Rogachev "Influence of Expander Components on the Processes at the Negative Plates of Lead-acid Cells on High-rate Partial-state-of-charge Cycling. Part II. Effect of Carbon Additives on the Processes of Charge and Discharge of Negative Plates." *Journal of Power Sources*, 195 (2010). pp.4444-4457.

¹³ P.T. Moseley, R.F. Nelson, A.F. Hollenkamp "The Role of Carbon in Valve-regulated Lead-acid Battery Technology." *Journal of Power Sources*, 157 (2006). pp.3-10.

¹⁴ P.T. Moseley "Consequences of Including Carbon in the Negative Plates of Valve-regulated Lead-acid Batteries Exposed to High-rate Partial-state-of-charge Operation." *Journal of Power Sources*, 191 (2009). pp. 134-138.

¹⁵ M. Fernandez, J. Valenciano, F. Trinidad, N. Munoz "The Use of Activated Carbon and Graphite for the Development of Lead-acid Batteries for Hybrid Vehicle Applications." *Journal of Power Sources*, 195 (2010). pp. 4458-4469.

¹⁶ D. Pavlov, T. Rogachev, P. Nikolov, G. Petkova "Mechanism of Action of Electrochemically Active Carbons on Processes that Take Place at The Negative Plates of Lead Acid Batteries." *Journal of Power Sources*, 191 (2009). pp. 58-75.

Sawai, *et al.*¹⁷ explored the use of carbon particulate and fiber, finding that the larger fibrous material was not able to provide an increase in performance. Further, there have been comprehensive studies where numerous forms of carbon were evaluated, such as that reported by Walmet,¹⁸ where none of the materials (a series of flake graphites, expanded graphites, carbon blacks, or activated carbons) were able to provide an appreciable increase in performance, and in many cases, reduced performance relative to an unmodified control.

Clearly, there is considerable variation from researcher to researcher in terms of both which carbons appear to work and the mechanism by which any beneficial effect that is observed has been achieved. This variability suggests that there may be other factors, such as how the battery was produced (*e.g.*, negative electrode paste formulation, plate production, battery activation, *etc.*), that play a major role in determining not only which carbons are beneficial, but also the role that they play in the battery's electrochemistry.

Material Evaluation

In this program, four different battery designs are to be evaluated—a control and three different carbon-modified batteries. The carbon containing batteries consist of an acetylene black carbon (Denka Black), an activated carbon (Mead-Westvaco E-105), and a combination of carbon black (Cabot Black Pearls 430) and a graphitic carbon (Superior Graphite Grade 2939 APH). Batteries demonstrating the desired enhanced performance have been built in the past by East Penn Manufacturing for both the activated carbon and the carbon black/graphite combination. The acetylene black carbon is an electrically conductive material that, based upon theories within the literature, should have a similar beneficial effect. Analysis of the chemical and structural properties of the carbons is in progress. Batteries of each composition have been manufactured; their testing/analysis is in progress.

¹⁷ K. Sawai, T. Funato, M. Watanabe, H. Wada, K. Nakamura, M. Shiomi, S. Osumi “Development of Additives in Negative Active-material to Suppress Sulfation during High-rate, Partial-state-of-charge Operation of Lead-acid Batteries.” *Journal of Power Sources*, 158 (2006). pp.1084-1090.

¹⁸ P.S. Walmet. *Evaluation of Lead/Carbon Devices for Utility Applications*. SAND2009-5537 (June 2009).

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