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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 3: April through June 2011)

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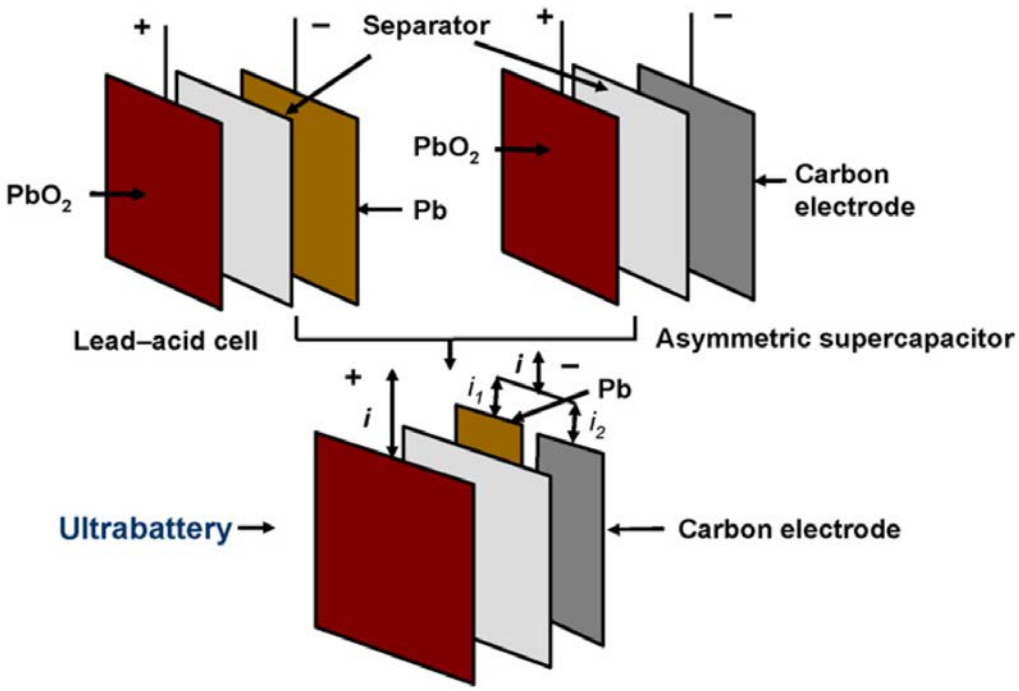
Abstract

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 3 Milestone was completed on time. The milestone entails an *ex situ* analysis of a control as well as three carbon-containing negative plates in the raw, as cast form as well as after formation. The morphology, porosity, and porosity distribution within each plate was evaluated. In addition, baseline electrochemical measurements were performed on each battery to establish their initial performance. These measurements included capacity, internal resistance, and float current. The results obtained for the electrochemical testing were in agreement with previous evaluations performed at East Penn manufacturing. Cycling on a subset of the received East Penn cells containing different carbons (and a control) has been initiated.

Project Description

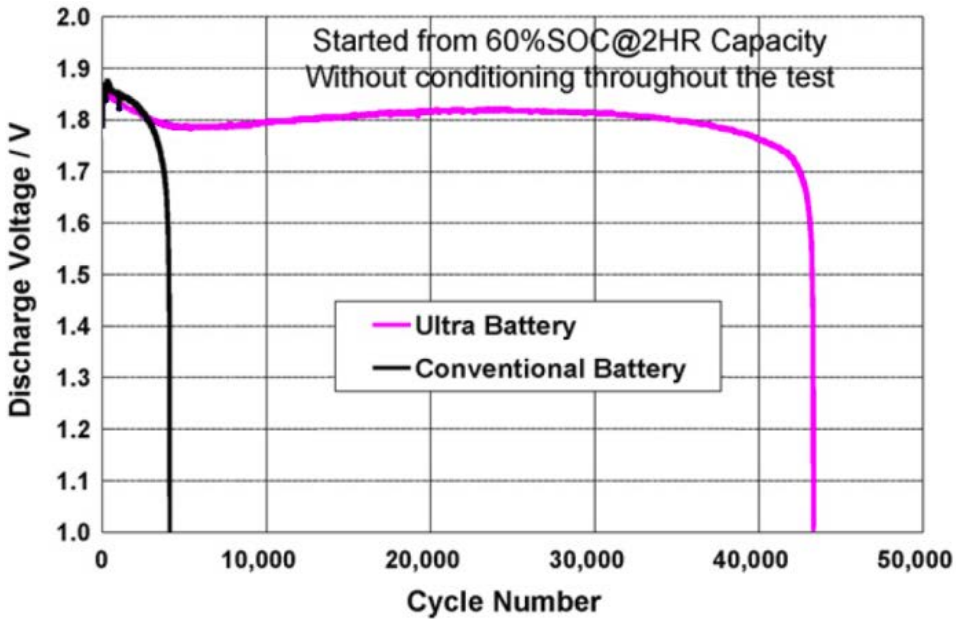
Carbon has been explored as an addition to lead-acid battery electrodes in a number of ways. Perhaps the most notable to date has been the hybrid "Ultrabattery" developed by CSIRO where an asymmetric carbon-based electrochemical capacitor is combined with a lead-acid battery into a single cell, dramatically 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. 2007)

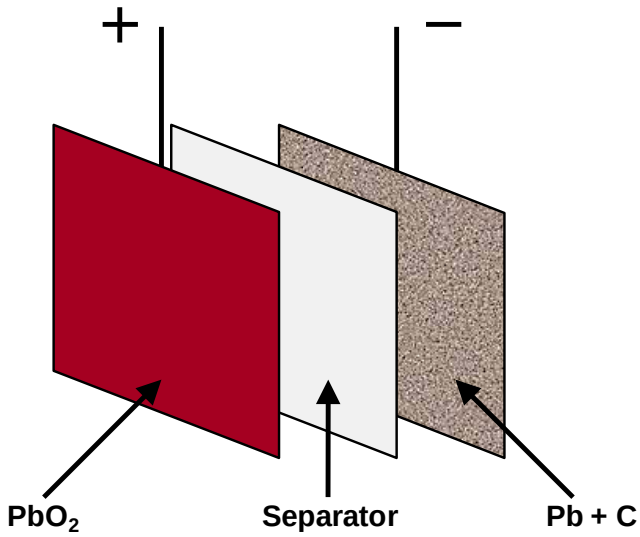
This device exhibits a dramatically improved cycle life over traditional VRLA batteries, as well as increased charge power and charge acceptance. The "Ultrabattery" has been produced successfully by both The Furukawa Battery Co. and East Penn Manufacturing. An example illustrating the dramatic improvement 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.



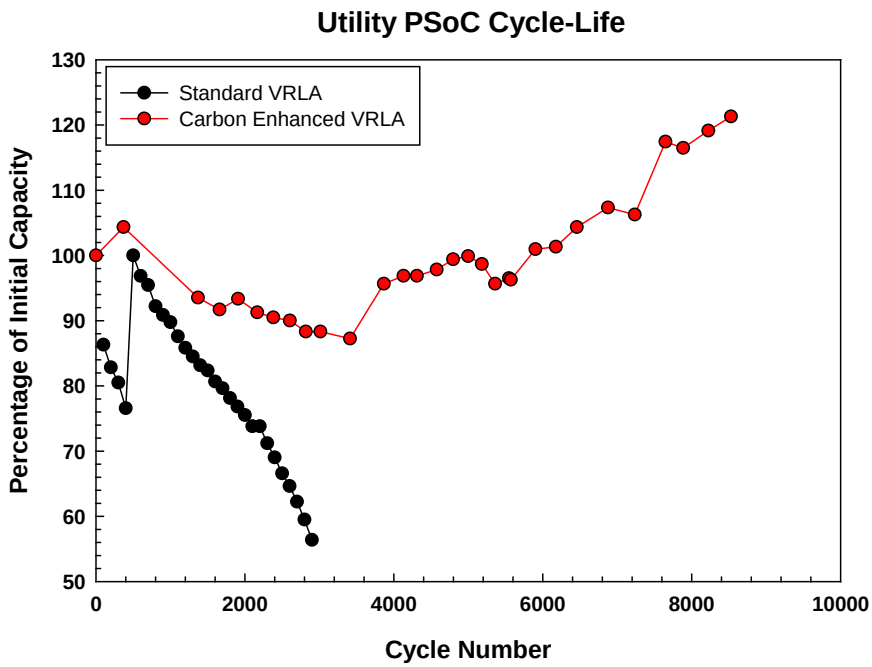
Discharge voltage as a function of number of cycles under the EUCAR cycle life test. Lam, et al., *2007.*

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.



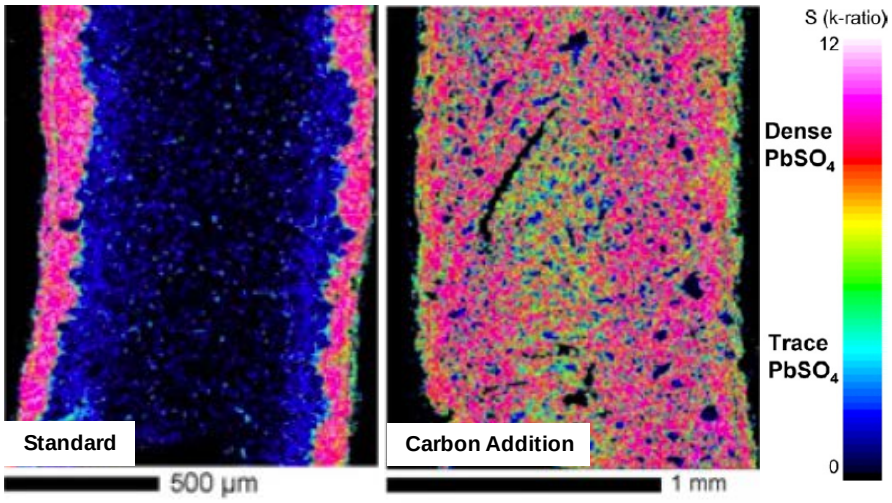
Schematic representation of a single cell from a carbon-modified or "Advanced" VRLA battery.

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 usege 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. ***This milestone has been completed.***

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. ***This milestone has been completed.***

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 $PbSO_4$ 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 $PbSO_4$ 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 (TiO_2) and alumina (Al_2O_3) 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 $PbSO_4$ 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 $PbSO_4$ on the negative electrode (*i.e.*, hard sulfation), and also hypothesized that the

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[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. Křivák, 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. Křivák, 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.

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 that the battery could be electrochemically recovered, with the carbon adsorbing onto the NAM and acting as a nucleation side 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 $PbSO_4$ 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 $PbSO_4$ in the NAM). Another potential mechanism would be the restriction of $PbSO_4$ crystal growth, which constrains the size of $PbSO_4$ crystals and enhances their dissolution rate during recharge, again facilitating the reduction of $PbSO_4$ during recharge. The latter effect has been demonstrated for a series of inert materials, such as titanium oxide (TiO_2) 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 (H_2SO_4) into the pores was impeded, and lead oxide (PbO), not $PbSO_4$, formed during operation.

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[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.

[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.

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, 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, an activated carbon, and a combination of carbon black and a graphitic carbon. 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.

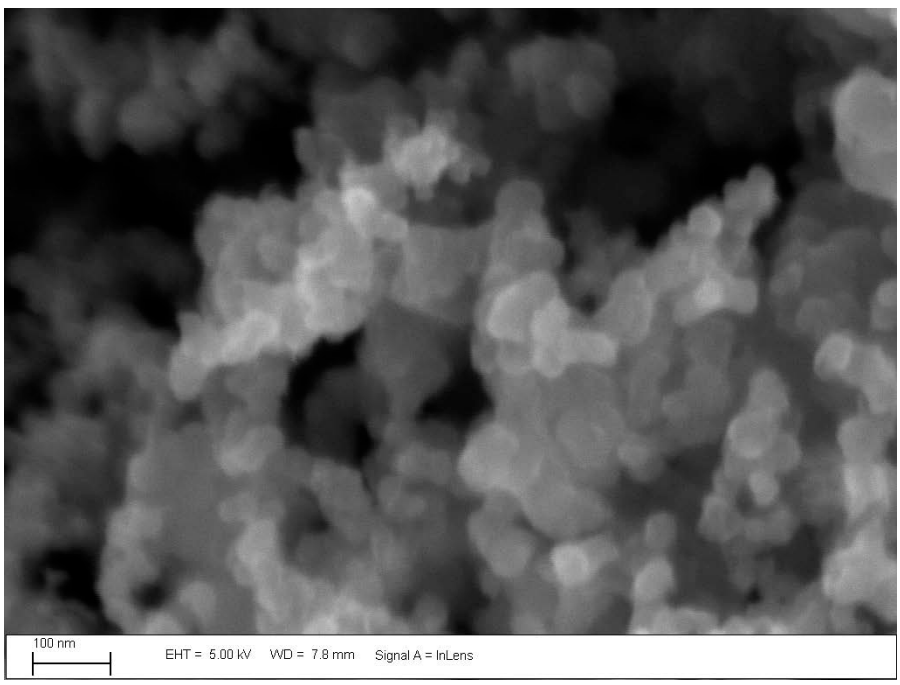
[18] P.S. Walmet. *Evaluation of Lead/Carbon Devices for Utility Applications.* SAND2009-5537 (June 2009).

FY11 Quarter 2 Project Status Summary

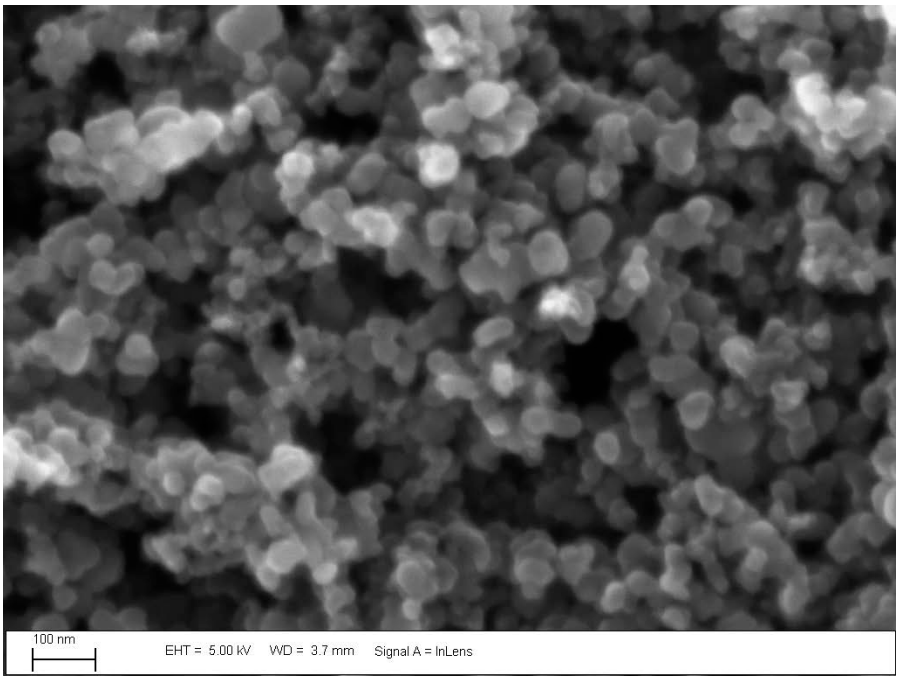
In this program, four different battery designs are to be evaluated – these include a control along with three different carbon modified batteries. The carbon containing batteries consist of an acetylene black carbon, an activated carbon, and a combination of carbon black and a graphitic carbon. Batteries demonstrating the desired enhanced performance have been built in the past by East Penn Manufacturing for both the activated carbon and combination of carbon black and graphite. The acetylene black carbon is an electrically conductive material that, based upon theories within the literature, should have a similar beneficial effect. As it is unclear which characteristics of the carbon might be beneficial, a complete characterization of each material was performed.

Structural Analysis of Carbons

Physically, the acetylene black and carbon black pearls are very similar. Both consist of agglomerations of extremely small particulate (approximately 20-30 nm in size), as illustrated below. The graphitic carbon is very different than the carbon black and acetylene black materials, consisting of numerous platelets of graphite with a particle size on the order of tens of microns. The activated carbon consisted of larger, blocky particles and has a glassy appearance to it (in terms of the fracture surfaces/edges of the particles).

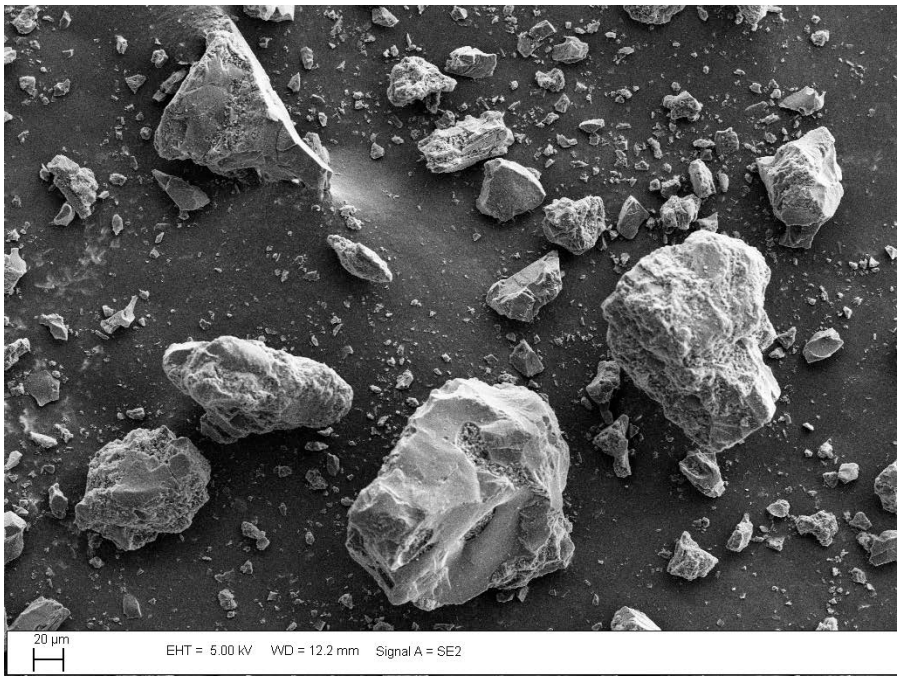


SEM image of the acetylene black material. The material consists of agglomerations of small (20-30nm) particles



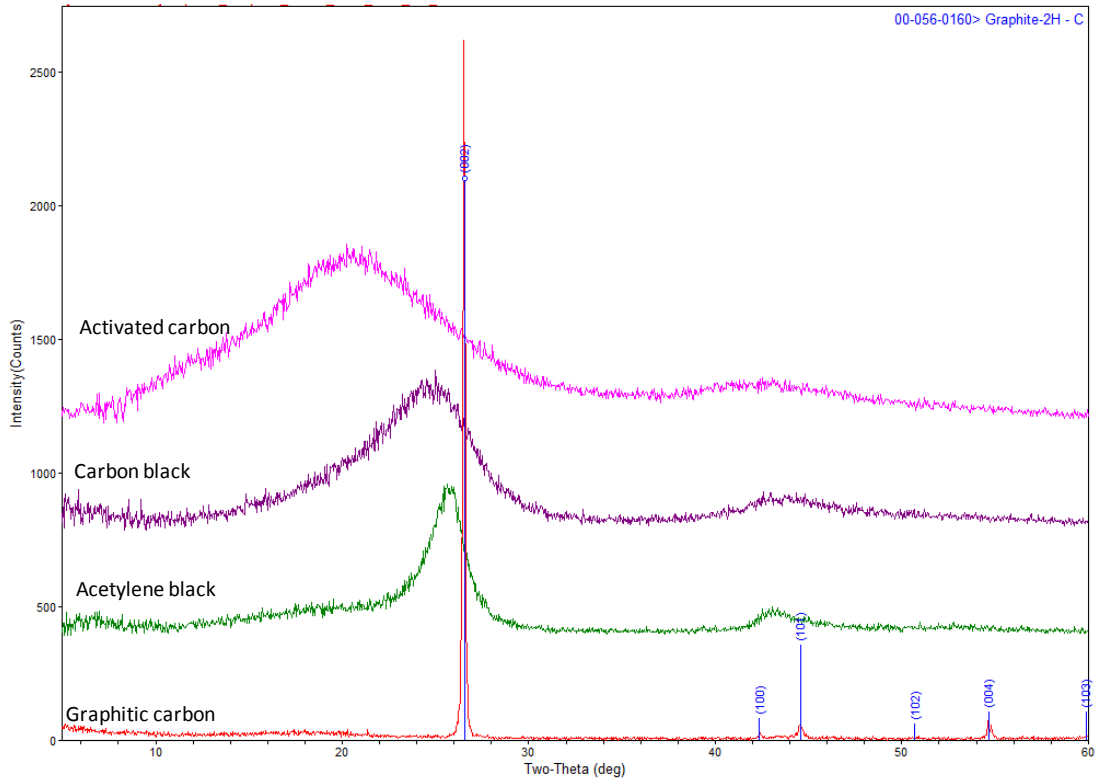
SEM image of the carbon black material. The material consists of agglomerations of small (20-30nm) particles, similar in appearance to the acetylene black.

SEM image of the natural graphitic material. The material consists of numerous plates of graphitic carbon, as expected for such materials.



SEM image of the activated carbon material. This material consists of a variety of large and small particles, and has an amorphous appearance to it (based upon the fracture surfaces particularly visible on the larger particles).

X-ray diffraction was used to probe the crystalline structure of each of the materials. X-ray diffraction analyses were performed by Mark Rodriguez of Sandia National Labs. The graphitic carbon had well-ordered hexagonal graphite (type 2H) diffraction data, as anticipated for this highly crystalline material. The activated carbon exhibited a diffraction pattern consistent with amorphous material, further supporting the physical observation of a glassy-appearing material. The acetylene black and carbon black had diffraction patterns that were similar to graphite, with the main diffraction peak shifted to larger d-spacings. The shift in spacings and considerable peak broadening suggest that they have a very fine crystallite size. Both of these materials exhibit evidence of a mixture of nano-crystalline as well as amorphous type peaks. This was more easily observed in the carbon black sample which had two distinctly different peak profiles (one sharper, one broader). The acetylene black peak profile fitting resolved two discrete peaks, but the broadness of the peaks made clear distinction of peak location and degree of peak broadening determination difficult.



Comparison of the x-ray diffraction data from the four carbon materials, illustrating the crystalline structure (or lack thereof) for each material.

Sample	Main peak - pseudo (002) peak					Broad peak – amorphous signature				
	2θ (°)	d-spacing (Å)	FWHM (°)	Xtal size* (Å)	Relative Peak Area	2θ (°)	d-spacing (Å)	FWHM (°)	Xtal size* (Å)	Relative Peak Area
Graphite	26.538(1)	3.3560(1)	0.095(2)	>1000	100	18.1(2)	4.9(1)	5.7(5)	14(2)	17.1
Acetylene Black	25.84(4)	3.45(1)	2.26(6)	37(2)	100	19.3(7)	4.6(3)	10.7(8)	8(2)	56.3
Carbon Black	24.8(1)	3.59(4)	5.3(1)	16(1)	100	19.7(6)	4.5(3)	6.6(6)	12(2)	35.8
Activated Carbon						20.5(1)	4.33(1)	11.3(2)	7(1)	100
*Crystallite size estimates are based on Scherrer equation – values less than 10 Å strongly suggests amorphous characteristics										

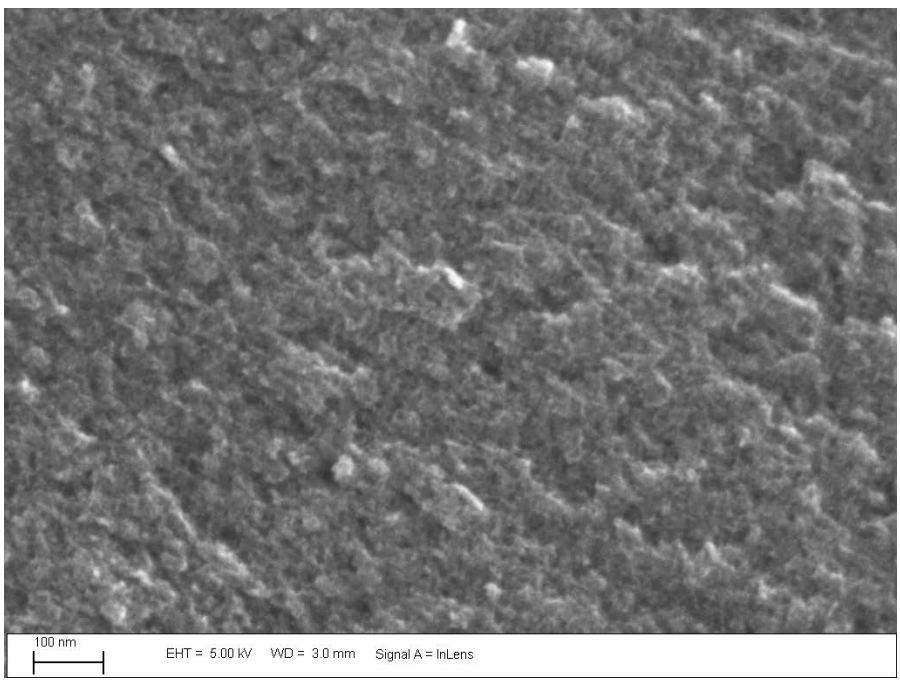
Based upon the x-ray diffraction data, the degree of crystalline order of the four materials is ranked as follows (from most crystalline to least crystalline (amorphous))

1. Graphitic carbon
2. Acetylene black carbon
3. Carbon black
4. Activated carbon

In addition to the basic geometry and phase structure of the carbons, the Brunauer, Emmet, and Teller (BET) surface area (i.e., the specific surface area of the materials per unit mass of material determined via gas adsorption) was analyzed. With one exception, the results are as one might predict from the shape/size of the individual particulate in each material.

	Activated Carbon	Carbon Black	Acetylene Black	Graphitic Carbon
sample 1	2077.9754 ± 7.9393 m²/g	74.2100 ± 0.2129 m²/g	75.0488 ± 0.4638 m²/g	6.5482 ± 0.0289 m²/g
sample 2	2052.7406 ± 9.1734 m²/g	73.2207 ± 0.2193 m²/g	74.6294 ± 0.4196 m²/g	7.2968 ± 0.0478 m²/g
sample 3	2048.5571 ± 6.5117 m²/g	73.7229 ± 0.1845 m²/g	75.3409 ± 0.4351 m²/g	6.6581 ± 0.0182 m²/g

The carbon black and acetylene black, being similarly sized particles, are expected to have the same basic surface area per unit mass, as confirmed via BET measurements. The graphitic carbon, having larger particles/plates, would be expected to have a considerably lower surface area than the carbon black, and BET measurements demonstrated that there is nearly an order of magnitude difference. However, the activated carbon, which had the largest particles, would be expected to have (based upon their size) the smallest surface area, however, it has the largest – more than 25 times that of the carbon black. The reason for this large difference is the microscopic structure of the activated carbon. Being derived from wood, it is highly porous, and thus the actual surface area (which includes the walls of the pores) is vastly larger than the macroscopic surface area based solely on particle size. This porous nature is illustrated in the figure below which, while it does not allow individual pores to be physically resolved, does illustrate the lattice-like structure of the material.



High resolution SEM image of the surface of an activated carbon particle. Being derived from wood, the material is extremely porous, and thus has a very high surface area per unit mass.

Presently, it is not clear which structure will be most effective as a battery addition. Clearly, the nature of the carbon surfaces (chemical reactivity and surface area) will be important if the material is electrochemically active within the NAM, as suggested by Pavlov (2010). However, if the carbon instead acts to increase the electrical conductivity of the NAM, then the ability of the carbon particles to provide a conductive network may be more important, in which case smaller particulates such as the carbon black or acetylene black may be more beneficial.

Chemical Analysis of Carbons

In addition to the structure of the carbon additions, the nature of any soluble contaminant species which they might contribute to the electrolyte within the battery may have an impact on the performance of the system. Specifically, detrimental species such as iron may act to poison the electrochemical reactions which take place within the battery as it functions.

Samples of all four carbon materials were also analyzed for their acid soluble contaminant species, as well as the accompanying anions. The results of these experiments are presented below in Tables 1 and 2. Each table entry represents the average and standard deviation obtained from three runs of each material. Acid soluble contaminants were extracted in 6N HCl and then analyzed via ICP-MS. Anions were extracted by sonicating the carbon specimens in water and then analyzing the leachate via ion chromatography.

Table 1: Acid Soluble Contaminants in Carbon Samples (ppm by weight)

	Al	B	Ba	Ce	Fe	K	La	Mg	Mn	Mo
Carbon Black	10.5 ± 0.6	--	--	--	6.24 ± 0.79	123 ± 8	2.48 ± 0.19	287 ± 12	0.57 ± 0.09	--
Acetylene Black	--	--	--	--	--	0.96 ± 1.07	--	--	--	--
Activated Carbon	28.3 ± 0.8	2.35 ± 1.21	1.03 ± 0.03	--	91.6 ± 5.8	13.4 ± 2.5	--	12.5 ± 0.3	1.83 ± 0.15	--
Graphite	--	--	--	0.85 ± 0.03	--	--	--	--	--	0.95 ± 0.08

	Na	Ni	Pb	Sr	Ti	Zn	Zr
Carbon Black	89.9 ± 5.7	--	--	--	0.51 ± 0.09	--	--
Acetylene Black	--	--	--	--	--	--	--
Activated Carbon	2450 ± 30	1.65 ± 0.62	--	1.04 ± 0.14	15.2 ± 0.7	2.54 ± 1.00	--
Graphite	--	--	2.96 ± 1.02	--	7.3 ± 0.31	--	3.04 ± 0.21

Table 2: Water Soluble Anions in Carbon Samples (ppm by weight)

	Sulfate	Nitrate	Phosphate	Chloride	Fluoride
Carbon Black	3920	trace	--	trace	trace
Acetylene Black	--	--	--	--	--
Activated Carbon	94.1	71.1	11929	--	--
Graphite	--	--	--	--	--

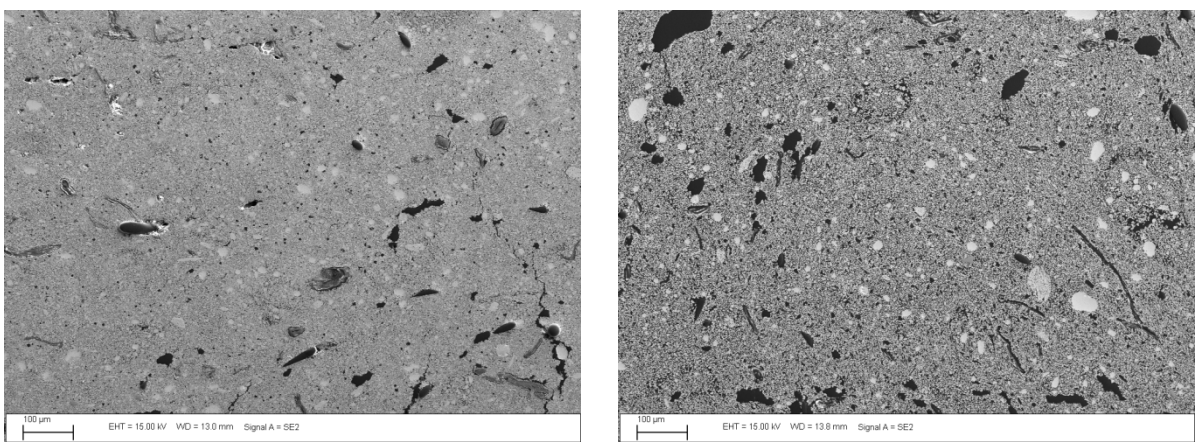
All of the observed values were in line with past data, and consistent with the type of material being analyzed. As expected, the acetylene black material was very clean, followed by the natural graphite. The activated carbon contained significant contaminants, including nearly 100ppm Fe.

FY11 Quarter 3 Project Status Summary

Four different battery formulations are being evaluated in this study. These include a control along with three different carbon modified batteries. The carbon containing batteries consist of a battery where the negative active mass contains either acetylene black carbon, activated carbon, or a combination of carbon black and graphitic carbon. The physical structure of the plates used to construct each battery type was assessed in both the as-cast and formed condition. In addition, the baseline electrochemical properties of the different formulations have been assessed. Plates were evaluated both in the raw (i.e., as cast and cured) and formed condition. Through the forming process, the as cast material, which is a combination of lead oxide, lead sulfate, metallic lead, and various other additions (expanders, the carbon, etc.), is electrochemically transformed to predominantly metallic lead such that it can effectively function within the battery.

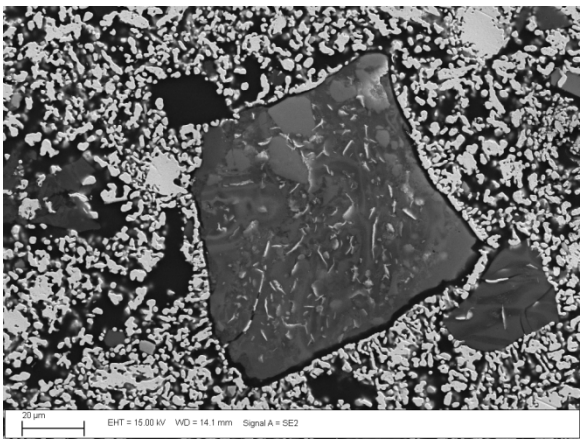
Cross Sectional Analysis of Negative Active Material

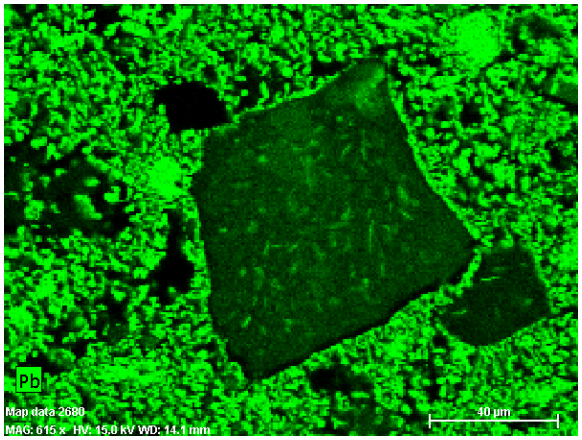
Samples of the raw and formed negative plates for each battery type were cross sectioned metallographically, then documented within the SEM. The figures below contain representative images from each plate type. Several features were observed which were common to all of the plate types. These were generally related to the binder and other materials which make up the general formula for the negative active material. In some cases, such as with the acetylene black and carbon black, small regions were visible within the plate that were far more porous than the surrounding material. While the origin of these regions is unclear, they may be the result of large agglomerates of the two carbon materials which were visible when evaluating the carbon prior to being placed within the battery. In all cases, the carbon appeared to be well dispersed through the thickness of the plate. In addition, in the case of the activated carbon, a chemistry previously explored by East Penn Manufacturing, there is strong evidence that the carbon is itself electrochemically active, allowing for the formation of metallic lead throughout the material during the forming process.



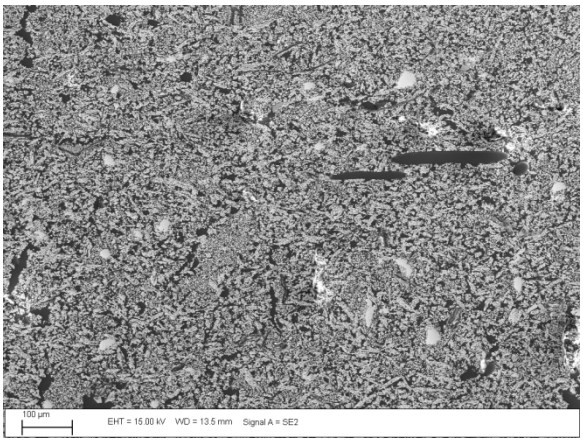
Control battery – raw (left side) and formed (right side). Cylindrical/fibrous materials are the binder used in the standard formulation of the negative active material, and can be seen in the carbon containing cells as well.

Activated carbon containing battery – raw (left side) and formed (right side). Carbon particles are well dispersed and clearly visible in the matrix.

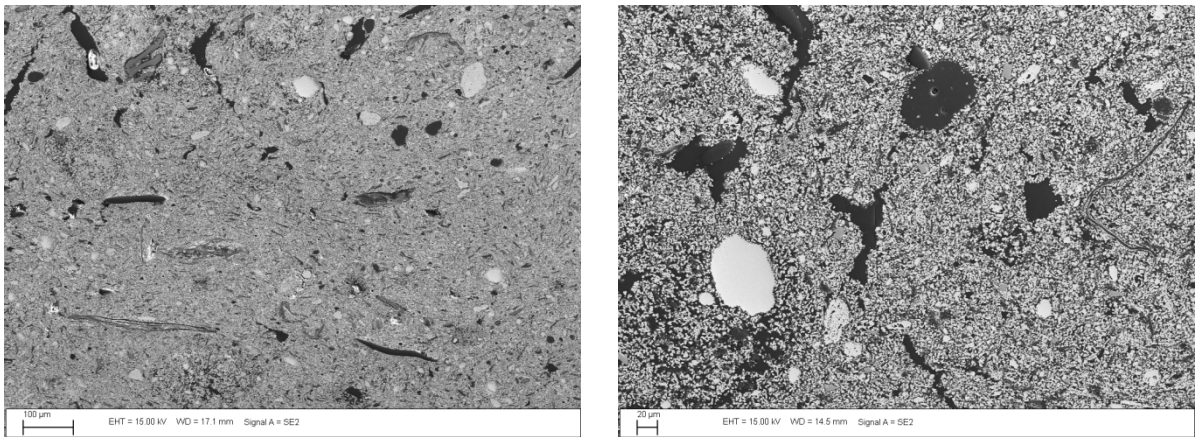




Activated carbon particle from a formed plate, illustrating that metallic lead can be found throughout the fissures/pores within the carbon. Image on right side is a compositional map, with green indicating presence of lead, confirming that the material within the carbon particle is indeed lead. This observation strongly suggests that this carbon specie is electrochemically active.



Acetylene black containing battery plate – raw (left side) and formed (right side). Carbon particles are well distributed and not generally visible within the structure. There are some regions which appeared more porous, which may be the result of large agglomerates of carbon particles, as illustrated previously for the carbon itself prior to incorporation in the negative active material.



Carbon black and graphitic carbon containing plates – raw (left side) and formed (right side). Both materials appear to be well dispersed through the plate, but only the graphitic carbon is visible. As with the acetylene black material, regions which appeared more porous are visible throughout the plate, potentially due to large agglomerates of the carbon black material.

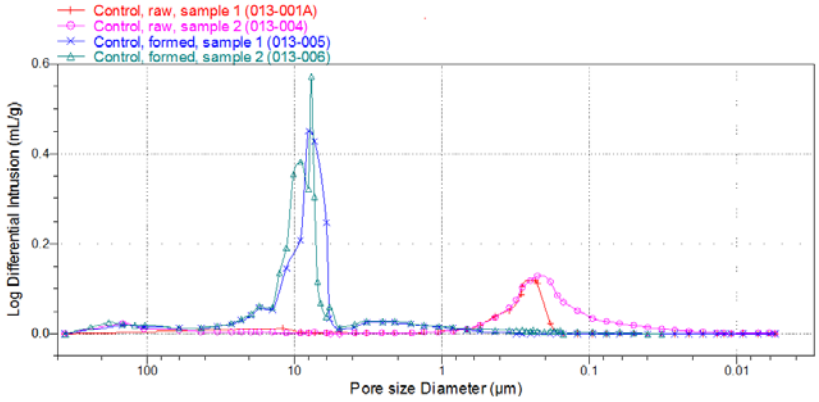
Microscopic Plate Porosity

In order to effectively utilize the entire negative active material within the plate, the battery relies on pores within its structure to allow solution to penetrate through the thickness of the plate and maximize the surface area of metallic lead available for reaction. Mercury porosimetry was utilized to explore the overall porosity of each carbon containing negative plate as well as the control. As can be seen in the table below, the degree of porosity was similar when comparing the various materials. The degree of porosity is a variable which will be monitored as a function of time for the batteries which will be cycled later this FY.

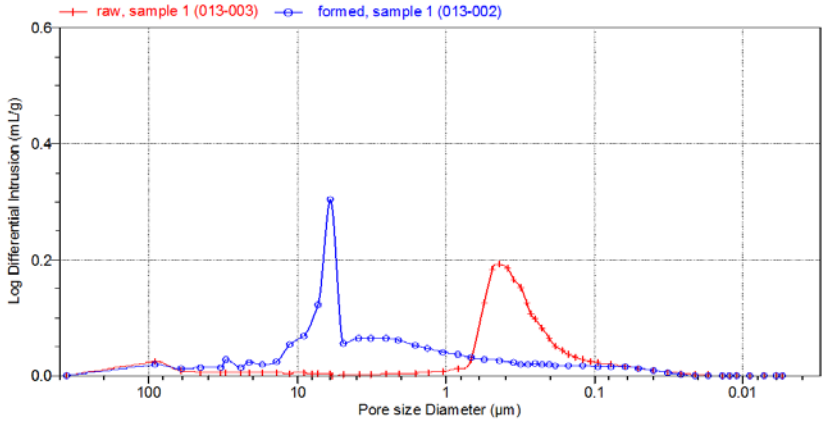
	% Porosity	
	Raw	**Formed**
Control	39.7	59.2
Acetylene black	44.8	55.8
Graphitic carbon + carbon black	45.7	59.5
Activated carbon	37.1	55.8

In addition to the overall degree of porosity, the distribution of pore sizes can also be extracted from the mercury porosimetry data. As can be seen in the figures below, in all cases, while the overall pore volume increases as the plates are formed, the size of the pores decreases. Comparing the different materials, the distribution of pore sizes is shifted to larger values when the carbon is present. This is particularly true for the plates containing activated carbon or a combination of activated carbon and carbon black. It is likely that the large particle size found with the activated carbon and the graphitic carbon result in an increase in the typical pore size, whereas for the acetylene black containing plates, the carbon particles do not result in a modification of the pore structure of the negative active material. The pore distribution will also be monitored as a function of time as the batteries are cycled later this FY.

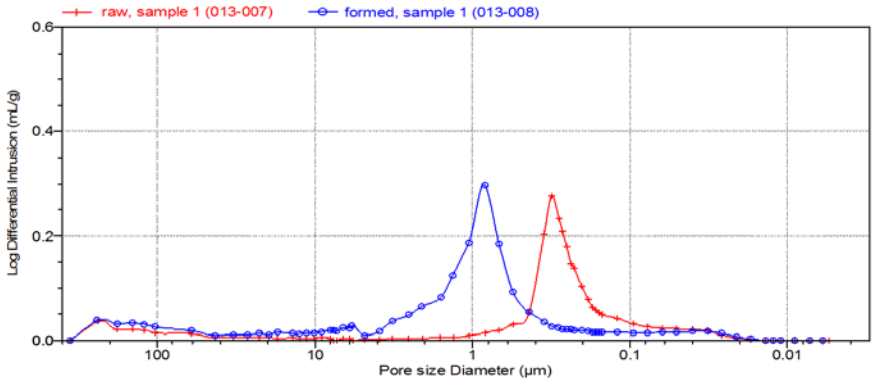
Control

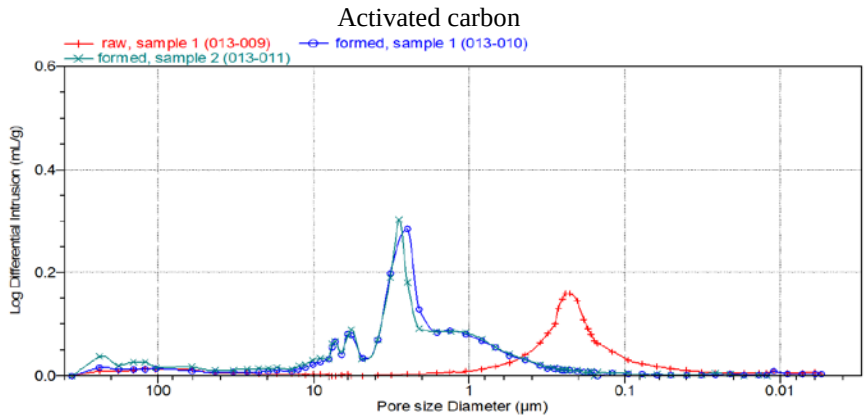


Acetylene Black



Carbon black + graphitic carbon





Intrusion rate as a function of pore size diameter, illustrating the distribution of pores found in each formulation.

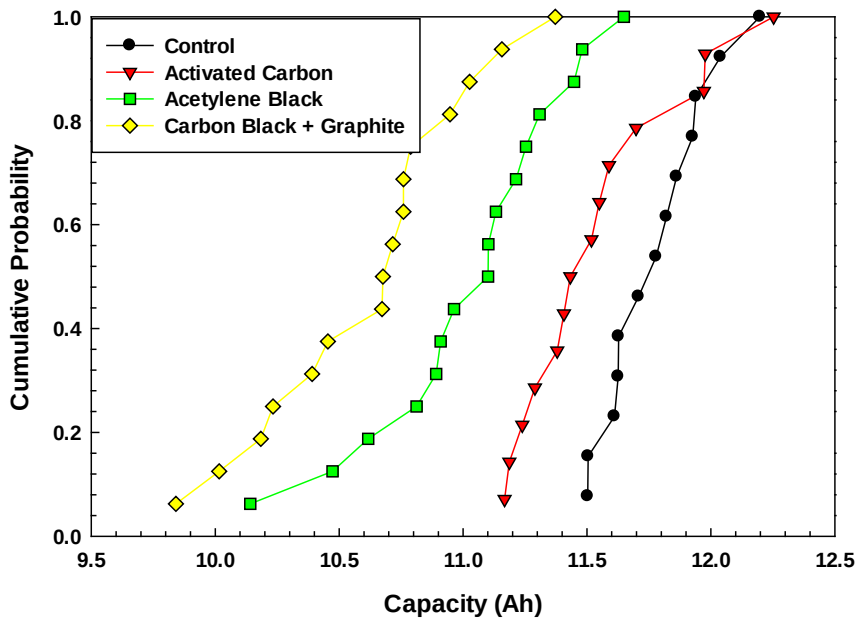
Baseline Electrochemical Performance Data

The baseline electrochemical performance of each battery type was evaluated. This information will form the initial data point to which the batteries will be compared as they are cycled. The batteries themselves are based upon an existing case design produced by East Penn Manufacturing. The plate count within each cell was reduced such that the overall capacity would be on the order of 10 Ah. While the entire 6 cell battery was populated with positive and negative plates, only a single cell was filled with electrolyte and activated. As such, all of the electrochemical results are reported for a single cell, rather than multiple cells in series.

The open circuit potential and internal impedance of each battery was measured. As illustrated in the table below, the open circuit voltage was nominally identical for all of the cells. Since the basic electrochemical reactions which occur within a VRLA battery remain unchanged by the addition of carbon, this result was expected. The internal impedance of the batteries was also measured, and was also nominally identical for the four battery types. Both of these factors will also be monitored as batteries of each formulation are cycled later this FY.

	Weight (Kg)	V_{oc} (V)	R (micro-ohm)
Control	9.429 ± 0.034	2.147 ± 0.002	1997 ± 30
Activated Carbon	9.450 ± 0.025	2.158 ± 0.003	2038 ± 36
Acetylene Carbon	9.422 ± 0.033	2.141 ± 0.008	2015 ± 36
Carbon Black	9.455 ± 0.029	2.146 ± 0.005	2114 ± 20

A charging protocol was developed to assess the initial capacity of the different batteries. Each battery (single cell) was charged at 2.3 V (with a maximum current equal to the 1C rate) until the charging current fell to below 75 mA, then allowed to stand at open circuit for one hour. Next, the cell was discharged fully at a 1C rate to a final voltage of 1.75 V, and the total charge passed during the discharge process was recorded. After standing for an hour at open circuit, the cell was then recharged to 108% of the previously recorded discharge capacity (with the maximum current clamped at the 1C rate). Finally, after another hour at open circuit, each cell was discharged at a 1C rate to 1.75 V, and the total charge passed during the discharge process recorded. This second discharge capacity was logged as the cell capacity. The distribution of capacities, along with the average capacity and standard deviation are presented in the figure and table below.



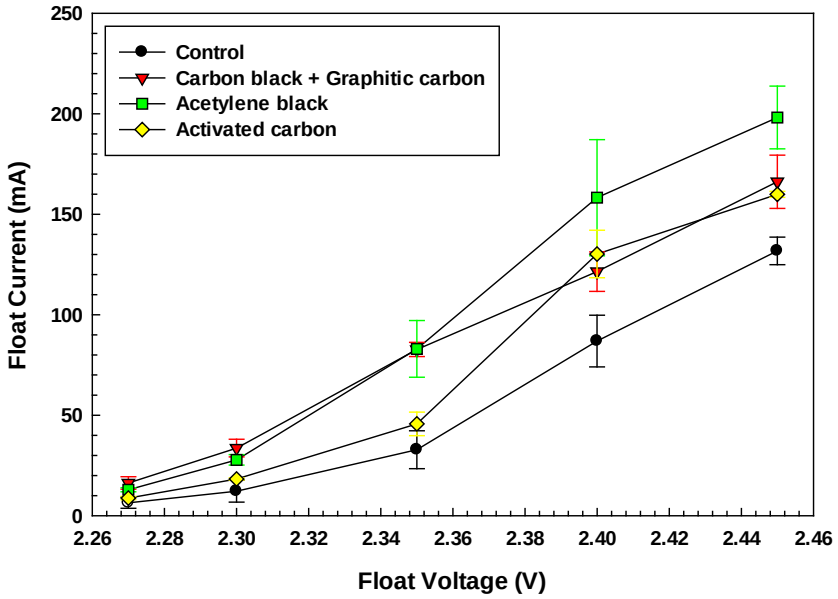
Capacity distribution for each of the battery types evaluated. Note that the "battery" consists of a single cell.

	Capacity (Ah)
Control	11.78 ± 0.21
Activated Carbon	11.55 ± 0.33
Acetylene Black	11.03 ± 0.39
Carbon Black + Graphitic Carbon	10.63 ± 0.42

As expected, the control cells, which are based upon a highly optimized production process, have the tightest distribution of capacities. The carbon containing batteries had a more substantial distribution, as well as a lower overall capacity. The reduced initial capacity for the carbon containing batteries was not unexpected as the carbon has displaced some of the active material (i.e., a certain percentage of the negative active material has been replaced with carbon), resulting in a lower quantity of material available for reaction within the cell. It should be noted, though, that these batteries typically increase in capacity with cycling, as has been noted in past work performed at Sandia as well as other laboratories.

Once the capacities were determined utilizing the procedure described above, the batteries were then recharged following the same procedure (i.e., charge to 108% of the previously measured discharge capacity). Three examples of each battery type were then set aside to evaluate the degree of self discharge which occurs over a 6 month period.

The float current for each battery type was measured at a series of five voltages. Three examples of each material were evaluated. Float current measurements were carried out by first charging each battery at a fixed potential of 2.45 V for 24 h. The batteries were then allowed to rest for 48 h. Next, each battery was held at a fixed potential of 2.27 V for ten days, and the final current (the float current at that voltage) measured. This process was repeated by holding each battery at a potential of 2.30 V, 2.35 V, 2.40 V and 2.45 V for periods of 72 h, 24 h, 12 h and 6 h respectively. The resulting float currents are presented in the figure below.



Float current as a function of applied potential for each of the battery types evaluated. In all cases, the float current is increased by the presence of carbon when compared to the control.

The float current is a measure of the rate of reactions which occur during the overcharge of the battery (i.e., each cell is being held at a potential greater than the open circuit potential of a fully charged cell). These reactions include oxygen evolution and potentially grid corrosion at the positive electrode, along with hydrogen evolution (and oxygen reduction) at the negative plate. In all cases, the float current was observed to increase when carbon was added to the negative active material. While the precise explanation for this increase has not yet been determined, it would be reasonable to assume that the increase was the result of more effective water reduction on the carbon surface.

Distribution
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