



Carbon-Enhanced VRLA Batteries

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Introduction

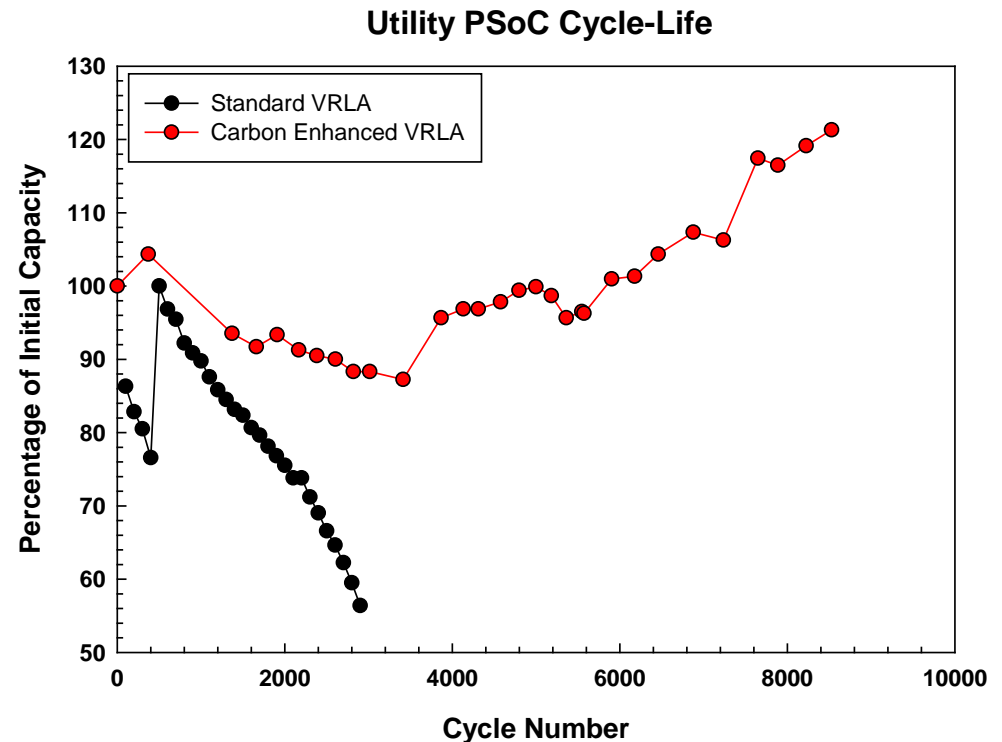
- **The addition of certain forms of carbon to the negative plate in valve regulated lead acid (VRLA) batteries has been demonstrated to increase the cycle life of such batteries by an order of magnitude or more under high-rate, partial-state-of-charge operation. Such performance will provide a significant impact, and in some cases it will be an enabling feature for applications including hybrid electric vehicles, utility ancillary regulation services, wind farm energy smoothing, and solar photovoltaic energy smoothing**
- **There is a critical need to understand how the carbon interacts with the negative plate and achieves the aforementioned benefits at a fundamental level. Such an understanding will not only enable the performance of such batteries to be optimized, but also to explore the feasibility of applying this technology to other battery chemistries**
- **In partnership with East Penn Manufacturing , Sandia will investigate the electrochemical function of the carbon and possibly identify improvements to its anti-sulfation properties**
- ***New Program* – CRADA between Sandia National Laboratories and East Penn Manufacturing, initiated August, 2010.**



Why add carbon to the NAM?

- **Shiomi, et al. (1997)* discovered that the addition of carbon to the negative active material (NAM) substantially reduced PbSO_4 accumulation in high rate, partial state of charge (HRPSoC) cycling applications**

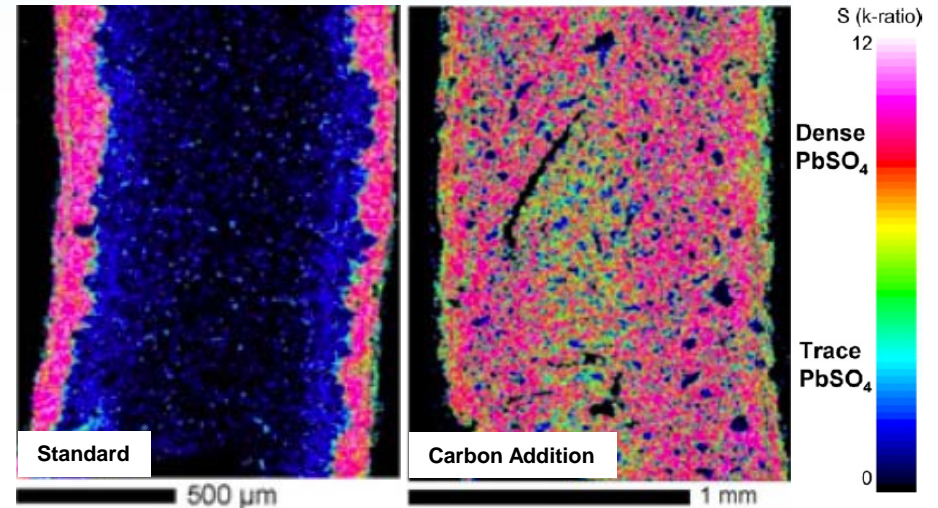
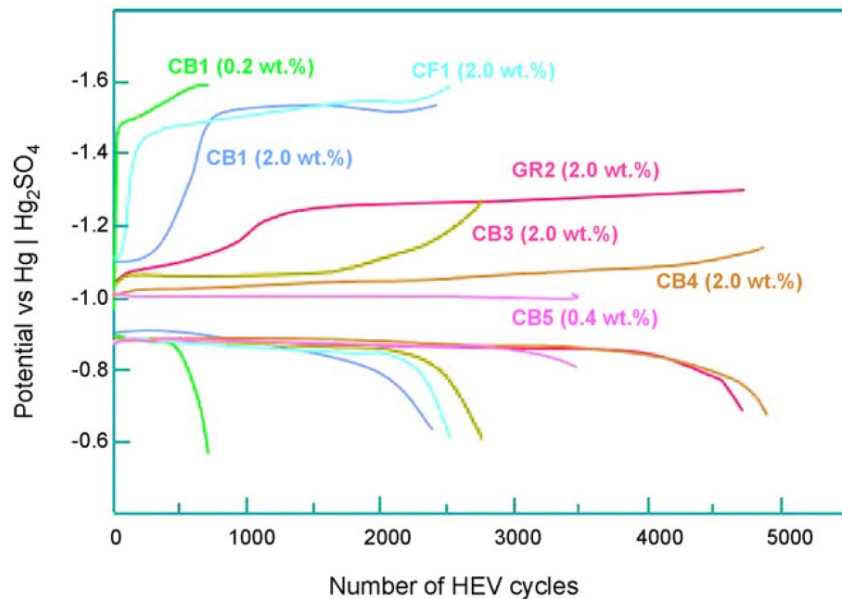
- Improved performance with a minimal cost
- Cycling applications that were uneconomical for traditional VRLA batteries are viable for the carbon enhanced VRLA



Impact of carbon on performance

- Sulfation process is significantly altered by the carbon additions

➤ Fernandez, 2010*



- Different results are achieved with different carbon additions (quantity and type)

➤ Moseley, 2009**

*M.Fernandez, J.Valenciano, F.Trinidad, N. Munoz, Journal of Power Sources, Vol. 195 (2010), pp. 4458-4469.

**P.T. Moseley, Journal of Power Sources, Vol. 191 (2009), pp.134-138.

How does carbon impact battery performance?

- **Previous work by Pavlov et al. (2010)*, Boden et al. (2010)** and others, funded by the ALABC arrived at a series of preliminary conclusions:**
 - Not all carbon additions provide beneficial effects.
 - Carbon appears to enhance nucleation and retard recrystallization of lead sulfate
 - Smaller crystallite size -> increased Pb^{2+} concentration
 - Increased Pb^{2+} enhances the charging process within the NAM.
 - Carbon particles adsorb onto the lead crystallites within the NAM
 - Carbon exposed to electrolyte (rather than buried in the electrode) .
 - The carbon increases the electrochemically active surface area of the NAM.
 - The increased specific surface area of the NAM
 - Lower current density on the electrode as it is being charged
 - Lower polarization experienced by the electrode for a given charging current
 - Enhanced charge acceptance/efficiency.

*D. Pavlov, P. Nikolov, T. Rogachev, Journal of Power Sources, Vol. 195 (2010), pp. 4444-4457.

**D.P. Boden, D.V. Loosemore, M.A. Spence, T.D. Wojcinski, Journal of Power Sources, Vol 195 (2010), pp. 4470-4493.



Limitations

- **Limitations of the work performed to date**
 - Some data obtained from laboratory constructed cells and mock electrodes – rarely indicative/representative of production battery performance
 - Limited data set – many of the assertions do not have a substantial technical basis



Research Goals

- **The overall goal of this work is to quantitatively define the role that carbon plays in the electrochemistry of a VRLA battery.**
 - What reactions/changes take place on the surface of the carbon particles?
 - What processes govern the increase and then eventual decrease in capacity with increasing # of cycles?
 - Are the kinetics of the charge/discharge process different when carbon is present vs. when it is not?
 - Why are some carbons effective additions while others are not? Are there any distinguishing characteristics of effective additions? Is the effectiveness controlled by aspects of the plate production method? etc.



Constituent Material Analysis

- **Given the limited understanding of what characteristics yield an effective carbon addition, a broad spectrum approach is being taken to quantify the carbon particle properties.**
 - Particle size and size distribution
 - Effective surface area (BET)
 - Structure/composition (XRD)
 - Acid soluble contaminant concentration
 - Surface electrochemical activity (Boehm)



Battery Performance Testing

- **Performance characteristics of carbon enhanced cells will be compared to those of a standard cell of nominally identical construction.**
 - Mass measurement of all batteries prior to cycling
 - Initial capacity testing
 - Initial DC ohmic resistance
 - Cell float current test
 - Hybrid pulse power charge test (HPPC)
 - ALABC Hybrid cycle test (0, 1k, 10k, 50k, 100k cycles plus to end of life)
 - Electrochemical Impedance Spectroscopy at key cycles
 - Mass measurement of all batteries upon completion of cycling (water loss)



Battery Materials Evaluation

- **Characterize the chemical and structural properties of the positive and negative plates as a function of cycle life.**
 - NAM Visual assessment
 - NAM Structure (SEM)
 - NAM porosity (Hg porosimetry)
 - NAM Surface area (BET)
 - NAM Carbon content and distribution/uniformity (cross sectioning + backscatter SEM)
 - NAM Sulfation (XRF)
 - PAM Visual assessment



Summary/Conclusions

- **Historically, carbon additions to the negative active mass of VRLA batteries has yielded substantial improvements in the resistance to hard sulfation, dramatically enhancing cycle life.**
- **Not all carbons yield the same effect.**
- **A CRADA has been initiated with East Penn Manufacturing and Sandia National Laboratories, the goal of which is to develop a more complete understanding of how the carbon interacts with the negative plate and achieves the performance improvements that have been reported.**



Future Work

- **Battery production**
- **Chemical and physical evaluation of carbon additions and uncycled negative plates (both raw and formed)**
- **Battery cycle testing and plate evaluation**

