

Advanced Lead Carbon Batteries for Partial State of Charge Operation in Stationary Applications

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Abstract

Traditional lead-acid batteries are limited in their ability to operate in environments where reliable power is not available or regular discharges occur without a subsequent recharge. These incomplete cycles left Lithium-Ion as one of the only viable options for many applications. New advanced lead carbon battery technology makes partial state of charge (PSoC) operation possible, increasing battery life and cycle counts for lead based batteries. An analysis of the economic benefits of advanced lead-carbon battery technology is summarized in addition to operational guidance to achieve these benefits.

Introduction

Lead carbon batteries and lead carbon technology are generic terms for multiple variants of technologies which integrate carbon materials into traditional lead acid battery designs. Lead carbon refers primarily to the use of carbon materials in conjunction with, or as a replacement for, the negative active material. A number of variations on the concept of a lead carbon battery are currently being utilized within the industry (Fig 1):

- Integrated lead/carbon electrodes, from carbon enhanced active materials, to mostly carbon formulations of the negative active material or carbon current collectors in conjunction with typical active material formulations.
- True asymmetrical super capacitors utilizing full carbon electrodes (carbon on a conductive substrate) and not a Pb/PbSO₄ system for the negative active material.
- Dual electrode systems with Pb faraday electrodes and carbon capacitor electrodes used in parallel against the PbO₂ electrode.

The focus of this paper will be on the first variant, the integrated lead carbon electrode. The use of specific carbon materials, at higher than traditional concentrations in the negative electrode, can significantly improve the performance of the battery. As an example, for the integrated carbon electrode, newly available materials can dramatically change the negative active material structure and surface area, effectively changing the electrochemical behavior of the electrode. By targeting specific material properties of these additives, in combination with normal active material formulations, engineering the final electrode structure, surface area, electrochemical behavior and by extension the battery's performance is possible.

Increasing or maintaining the conductivity of the battery in a discharged state (Fig 2), adding capacitance to the electrodes and increasing roundtrip charge efficiency in the application have been attributed to the engineering of the active materials in the electrodes [1].

In addition to the performance enhancements of the electrodes for PSoC performance, consideration for material processing, battery manufacturing and balancing the final electrode properties can maintain a robust battery design that is still capable of operating under typical stationary power application conditions.

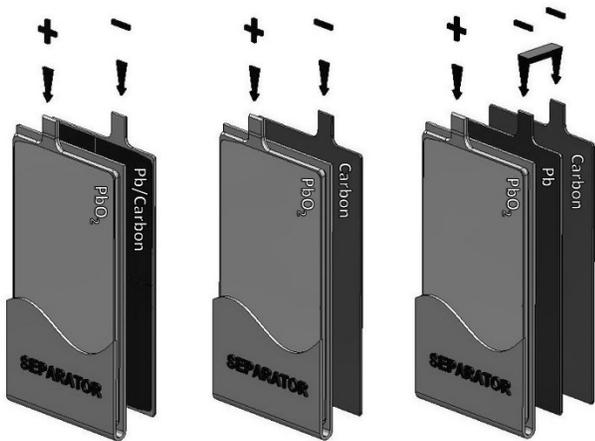


Figure 1 – Representation of lead carbon electrode configurations. Left to Right – Integrated Lead Carbon, Asymmetrical Super Capacitor, Dual Electrode

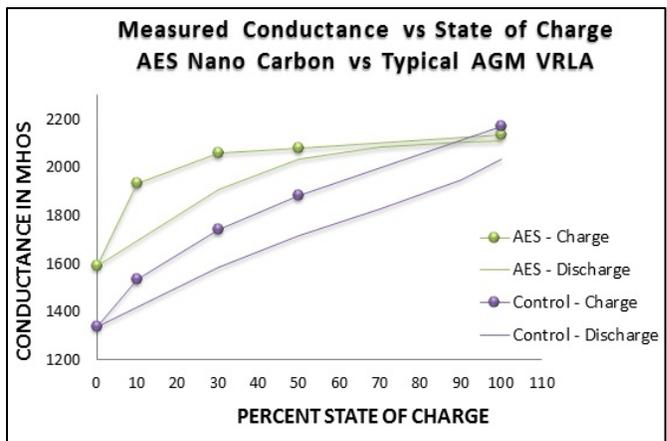


Figure 2 – C&D 12V AGM VRLA battery conductivity study. Conductivity vs SoC comparison between batteries with and without carbon materials. C/3 Charge/Discharge Rate. Measurements taken following 24 hour OCV stand.

Cycling Application Failure Modes

Lead carbon technology alone does not singularly guarantee the batteries cycle performance. Regardless of the state of charge at which the battery is operated, during cycling the degradation of the positive active material quickly becomes the limiting element of the battery. Therefore, it is necessary that the technology accompanies a robust cycle battery design which can provide a synergistic effect when utilized properly with lead carbon technology. Fig 3 illustrates this with the cycle life difference between standard valve regulated lead acid(VRLA) battery technology and deep cycle VRLA (C&D DCS) technology.

In VRLA batteries, all three components: positive electrode, negative electrode and electrolyte, experience degradation during cycling. Charging corrodes the positive current collector, causes hydrolysis of the water in the electrolyte and oxidizes the lignosulfonates in the negative electrode. Discharging degrades the positive active material, degrades the expander due to the increased solubility of the lignosulfonates at the end of discharge and consumes the sulfate in the electrolyte (stratification and sulfation). As charge and discharge degrade the components at different rates, the effects can have varying impact on the service life of the battery depending on the application conditions [4, 5].

Fig 3 further illustrates the failure modes of a VRLA battery in a cycling application, as a function of depth of discharge (DoD). For deeper discharge applications, the failure mode is primarily the softening of the positive active material. For shallower discharge cycles the overcharge of the cell, which is required to bring it to a full state of charge (SoC) following each discharge cycle, becomes the primary cause of degradation to the cell.

These limitations of the system define the shape of the cycle life graph (capacity versus cycles) for a cell. The typical capacity curve versus cycles for a deeper discharge is fairly linear as the active material is degraded. However, the curve for a shallow cycle life graph is more similar to an accelerated life test with a rapid decline in capacity as the battery nears end of life. This is especially true for batteries cycled at high (>1C) discharge rates as the degradation of the positive current collector becomes the dominant factor in the failure. At moderate DoD(30-50%), both failure modes are present and the capacity fade is a function of degradation of both the grid and the active materials.

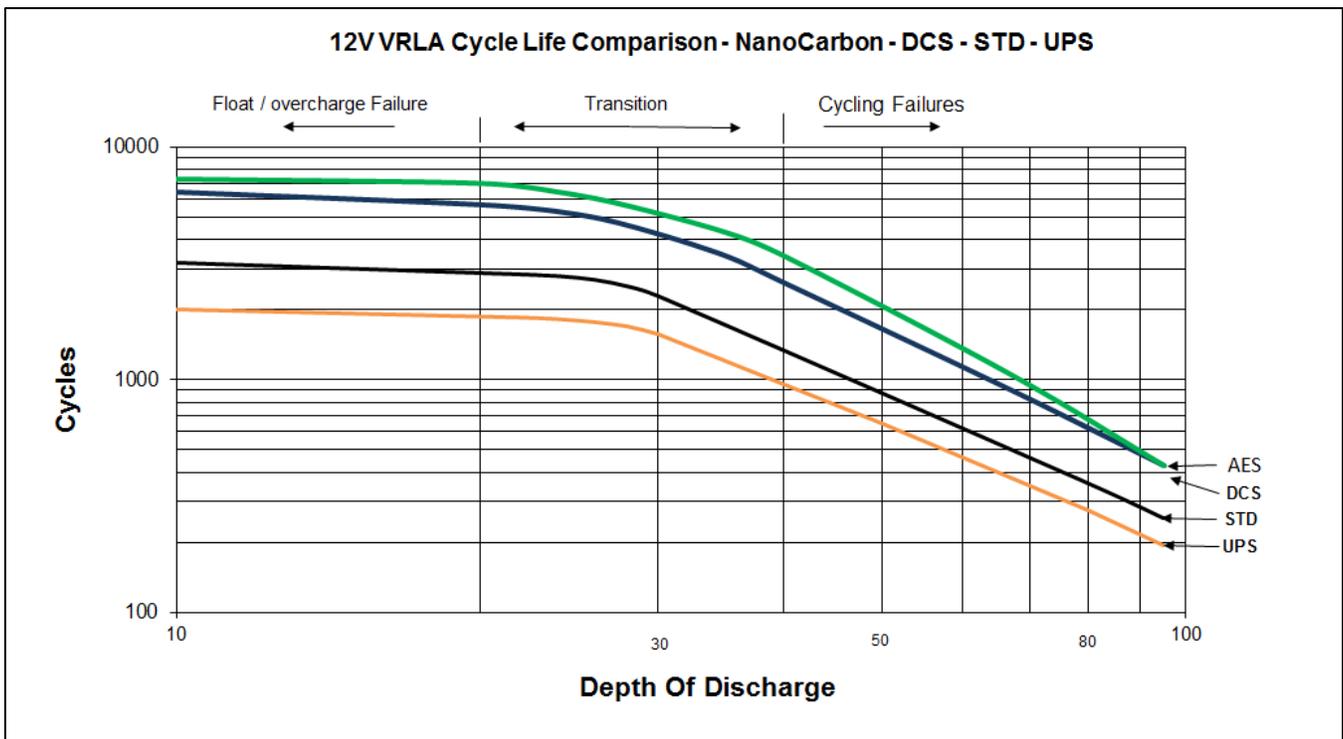


Figure 3 – Cycle Life Comparisons – C&D AES (Nano Carbon), Deep Cycle (DCS) and industry published AGM cycle life comparisons by technology. Illustrates the transition between cycle failure and overcharge/float failure as a function of DoD.

Influence of Carbon on the Negative Electrode

Figure 4 demonstrates the PSoC performance of a battery with carbon in the negative electrode. The stabilizing effect of the lead carbon negative is significant and provides for only a negligible capacity loss over the duration of the test (~4000 cycles). Furthermore, the charge efficiency for each PSoC is >99.9%.

- PSoC Cycle Life Operated between 80%-50% SoC
- Over 4000 cycles
- Continuous cycle duty up to 12 cycles per day
- Charge/Discharge Rates: C/3 with a 2.4VPC limit
- From 80% SoC: C/3 Discharge for 0.9 hour (30% DoD)
- C/3 Charge to 100% Ah Removed (14.4V Limit)

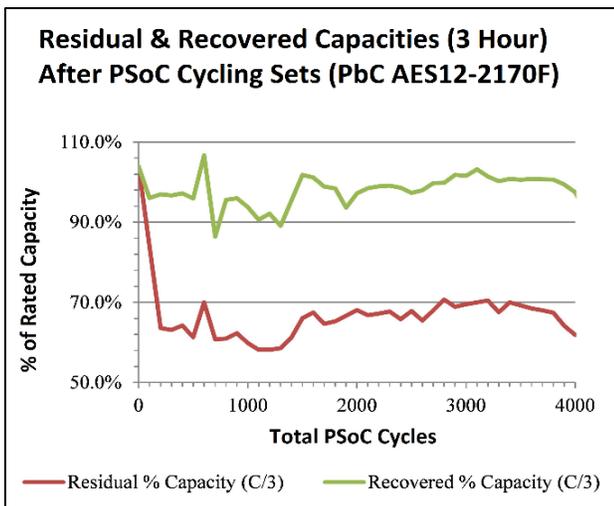


Figure 4 – PSoC Cycle Test – C/3 Capacity measured every 100 cycles. PSoC 80% - 50% SoC C/3 Discharge 2.4VPC charge to 100% of removed Ah

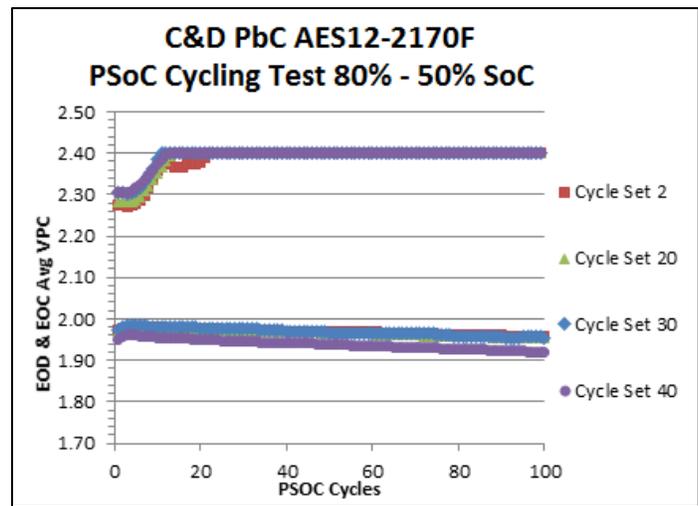


Figure 5 – PSoC Cycle Test – End of discharge and charge voltage for cycle sets. Each cycle set is 100 PSoC cycles (30% DoD)

Application Benefits and Considerations

One of the major advantages of lithium ion technologies over lead acid has been its ability to operate in a partial state of charge condition. With the addition of carbon materials, lead based batteries are able to achieve this method of charge operation.

Benefit

There are two primary benefits from operating the battery in a PSoC condition. First, the charge efficiency of the electrode is optimized. The Coulombic charge efficiency of a VRLA battery is nearly unity (~99.9%) up until approximately 90% SoC. However, from 90% to 100% SoC, the charge efficiency drops from nearly 100% to nearly 0%. True round trip charge efficiency of the lead carbon system (Ohmic efficiency Fig 5) is ~91-94% below 90% SoC and this can be maintained throughout the life of the system when it is operated in a PSoC with a proper charge algorithm.

The second advantage is the elimination of overcharge. The inefficiency of the charge process results in the degradation of the system, as previously explained. By eliminating overcharge, the degradation of the components is significantly reduced, resulting in an increase in the overall cycle life of the battery. Furthermore, reducing the mechanism leading to positive grid corrosion greatly increases the reliability and predictability of the battery. The mechanism of corrosion in VRLA positive electrodes is intergranular corrosion which is a non-linear form of corrosion and difficult to accurately assess in situ. Shifting the failure mode away from corrosion towards more linear decay mechanisms result in a more predictable service life.

Considerations

The principal consideration for a system operating in a PSoC condition is the charge algorithm and the charge termination requirement. Fig 6 depicts equivalent cycle tests with a difference in charge termination from a constant current charge of 100% of the removed Ah's versus the same charge amount of returned capacity with a 2.4VPC limit at the end of charge. The impact to the cycle life as measured by the capacity is significant, with an almost 30% difference in capacity after 4000 cycles. Similar results were found under actual application conditions with regards to the frequency, magnitude and duration of equalization charging. In which, a greater frequency and duration of equalization resulted in reduced cycle life and lower capacity during service life.

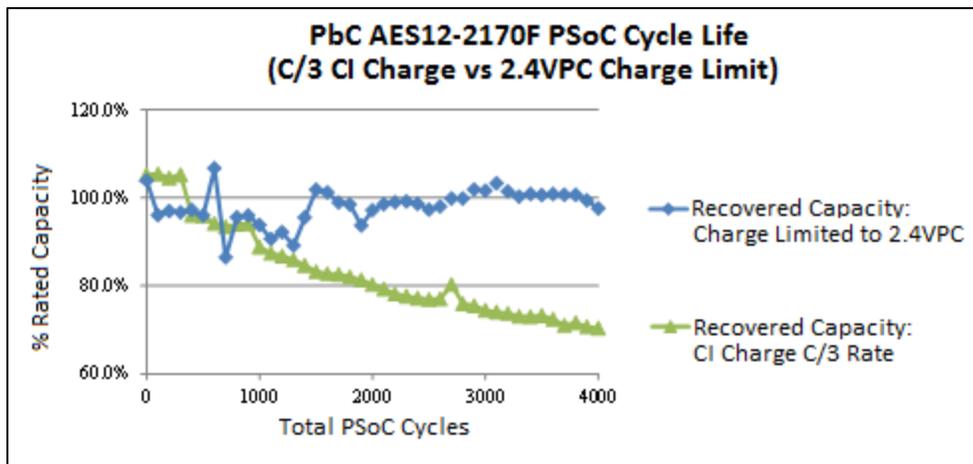


Figure 6 – PSoC Cycle Test – C/3 Capacity (80-50% SoC) Charge CI to 100% removed Ah vs 2.4VPC to 100% of removed Ah

Therefore, the principle concern for operating a battery under PSoC should be the minimization of over charge and equalization beyond what is required to offset charge inefficiencies, ancillary or parasitic system loads and the occasional requirement to recalibrate the SoC and state of health (SoH) determination of the system.

Economics

In numerous case studies, with proper sizing, the economic benefits of using lead carbon batteries has been demonstrated to be comparable or better in cost and performance with other battery technologies, such as, lithium ion. In addition, the benefits of using field tested and proven designs can limit the risk associated with using newer battery technologies and unproven system designs in mission critical applications.

The lead carbon battery system continues to rely on field proven mechanical and electrical design features and manufacturing methods of VRLA batteries, which in some cases have decades of proven service history. The benefit of this history is a well understood and predictable service life for the batteries which is critical in determining the economic benefits of a system.

Table 1 demonstrates economics of using lead carbon technology versus standard VRLA batteries, lithium ion batteries and the molten salt systems. Normalizing the systems based on depth of discharge (DoD), initial capital cost and calculating the cost per cycle used, in terms of \$/kWh, the lead carbon technology can provide a significantly lower cost solution than lithium ion (NCM) in terms of both initial capital cost and on a continuing cost of ownership basis. Furthermore, the end of life value of the lead carbon batteries can be up to 20% of the replacement cost of the battery, or in more practical terms, offset removal and replacement cost of the battery including shipping and labor expenses. Whereas, the recyclability and value, or possibly cost of, disposing newer battery technologies can be a significant concern when decommissioning a system.

Table 1 – Economics of Energy Storage – Comparison for cycling applications.

Battery Type	VRLA Deep Cycle 12V	Lead Carbon 12V	Lithium Ion (NCM)	Sodium Nickel Chloride
Description	48V 140Ah	48V 140Ah	48V 100 – 200Ah	48V 200 – 220 Ah
Battery Cost	\$1,000 - \$1,250	\$1,250 - \$1,500	\$2,000 - \$6,000	\$9,600 - \$13,000
Battery Cost (\$/Wh)	\$0.15 - \$0.19	\$0.19 - \$0.22	\$0.42 - \$0.63	\$1.00 - \$1.23
Actual DoD Used	50%	50%	80%	80%
Cycle Life	1,800	2,600	4,500	2,500 – 3,000
Service Life Cost per Cycle (\$/kWh)	\$0.17 - \$0.21	\$0.14 - \$0.17	\$0.12 - \$0.17	\$0.50 - \$0.51
Relative Volume	3.7x	3.7x	1.0	1.5x
Relative Weight	6.5x	6.5x	1.0	1.2x

Conclusion

Lead carbon batteries are an advancement in lead based technologies that continue to win market share due to their performance versus cost. The proper use of specialty carbons in the negative active material can significantly increase the performance of the negative electrode and stabilize the electrode for use in a PSoC application. However, the overall cycle performance of a VRLA battery is still determined by the robustness of the overall design including the positive electrode and the positive active materials.

Utilizing the battery in a PSoC can reduce the requirement for overcharge and equalization charging, significantly reducing the degradation of the positive electrode, improving overall performance, and achieving operational benefits. In PSoC cycle tests, using a lead carbon negative in conjunction with a deep cycle (DCS) positive electrode, the following benefits have been achieved.

- High charge efficiency – Up to 99.9% Coulombic efficiency at charge rates up to 1C and Ohmic efficiencies of 91-94%
- Increased cycle life – >5000 cycles at 80%-50% SoC
- Predictable service life – Reducing overcharge and positive grid corrosion results in more stable cycle service in the 30-60% DoD range

To take full advantage of the stabilizing effect that carbons play in the negative electrode, there must be consideration given to the charge algorithm to reduce overcharge and the damaging effects it has on the active materials within the cell. As system designs have evolved and incorporated these changes, new advanced lead carbon battery technology makes partial state of charge operation possible, thereby increasing battery life, reducing regular maintenance costs and maximizing cycle counts for new applications.

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