Large Format Carbon Enhanced VRLA Battery Test Results

Tom Hund (Sandia National Laboratories*) — Albuquerque, New Mexico, USA — tdhund@sandia.gov
Wes Baca (Sandia)

A carbon enhanced East Penn AVR85-25 valve regulated lead-acid (VRLA) battery has been tested in a partial-state-of-charge (PSOC) cycling test and has demonstrated exceptional ability to cycle well beyond 8,529 PSOC cycles. The development and support for this new lead-acid battery technology was originally provided by the Advanced Lead-Acid Battery Consortium (ALABC) as a replacement for the more expensive NiMH batteries used in hybrid electric vehicles (HEV)[1,2,3,4]. The ALABC development work discovered that 2 to 4% carbon additions in the negative active material minimizes negative plate sulfation and enhances VRLA battery cycling performance in PSOC cycling applications. In addition to the carbon, the ALABC technology optimizes grid designs for high power performance. Traditional VRLA batteries will develop "hard" negative plate sulfation in PSOC cycling and thus quickly lose capacity. The negative plate sulfation can easily be identified when the end of charge battery voltage quickly increases to the voltage limit. There are a number of PSOC cycling applications that can include hybrid electric vehicles, utility ancillary regulation services, wind farm energy smoothing, and solar photovoltaic energy smoothing. East Penn Manufacturing was one of the first to manufacture a large format (1,048 Ah Cell at 8 hr rate) carbon enhanced battery designed for utility PSOC cycling (see Figure 1). Sandia National Labs purchased this battery to evaluate for wind farm energy smoothing and it has demonstrated its ability to PSOC cycle well in excess of 8,529 cycles. Our testing has included capacity, impedance, float current, and the Utility PSOC Cycle Test. The Utility PSOC Cycle Test spends most of the time between 40 and 50% state of charge (SOC) and full charges are only conducted as required when end of charge voltage exceeds the high voltage limit. The traditional VRLA battery failure modes are minimized because there are relatively few full charges, therefore water loss and grid corrosion are kept at a minimum. In addition to the extended PSOC cycle life of the ALABC technology, VRLA batteries are also very efficient cycling at a partial state of charge, thus energy losses are also kept at a minimum. This new VRLA technology is cost competitive because there are only small changes to the VRLA battery production line. As a result of the competitive cost and improved PSOC cycling performance, previously uneconomical cycling applications can now be much more economical.

Figure 1: East Penn Carbon Enhanced VRLA Battery.

This work was conducted as part of the Energy Storage Systems Program of the U.S. Department Of Energy (DOE/ESS) through Sandia National Laboratories (SNL). The DOE Energy Storage Program provides support to develop and evaluate integrated energy storage systems involving batteries, superconducting magnetic energy storage (SMES), flywheels, super capacitors and other advanced energy storage devices. In addition to energy storage devices, the DOE program supports improvements in multi-use power electronics, controls, and communications components.

*Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

This work was funded by the DOE Energy Storage Program.

1) **Capacity Test** – Establishes an initial and final capacity at 200 amps and measures initial capacity at 100, 250, and 375 amps. At currents over 400 amps the battery temperature would approach or exceed the temperature limit of 45°C.
2) **DC Ohmic Battery Resistance and Cell Impedance** – Establishes an initial and final resistance using a 200 amp DC discharge pulse on the battery and the Alber Cellcorder for cell impedance measurements on each cell. Usually as the battery approached end of life the impedance will increase from water loss, capacity loss or sulfation, and grid corrosion.
3) **Float Current** – Establishes the initial float current at 2.27 V per cell after a full charge and 24 hours at float voltage. Some carbon formulations can result in excessively high gassing currents and cycling can also increase the gassing current.
4) **Utility PSOC Cycle Test** – Measures the ability of the battery to PSOC cycle. Some important performance characteristics are the number of cycles before the high voltage limit is reached, capacity, cycling current, and cycling temperature. This test used a 200 or 400 amp 15 or 7.5 minute pulse to discharge and charge 10% of the battery Ah capacity at the 1 hour rate at near 50% state of charge (SOC). A 5 minute rest was included after every pulse and a battery recovery charge was initiated after 1,000 PSOC cycles, or after battery voltage reached 28.8 V (2.40 vpc), or if there is a low or high voltage cell. Traditional float service VRLA batteries will exhibit a steady increase in end-of-charge voltage resulting from partial state of charge cycling. This is caused by negative plate sulfation, which is a "hard", meaning not recoverable by conventional charging, layer of sulfate crystals on the surface of the negative plate. The addition of carbon in the negative active material inhibits the accumulation of "hard" sulfation, thus increasing the number of partial state of charge cycles before a recovery charge is required and minimizing capacity fade.

The capacity test results from the East Penn carbon enhanced VRLA battery are in Figure 2 and show a battery capacity that is about 91% of the identical VRLA battery without the carbon and grid enhancements at the 10 h rate. As the discharge approaches the 1 to 2 h rates, then the battery capacity approaches the conventional Unigy II VRLA battery without enhancements. This is a result of less active material from the carbon additions and the high rate grid design.

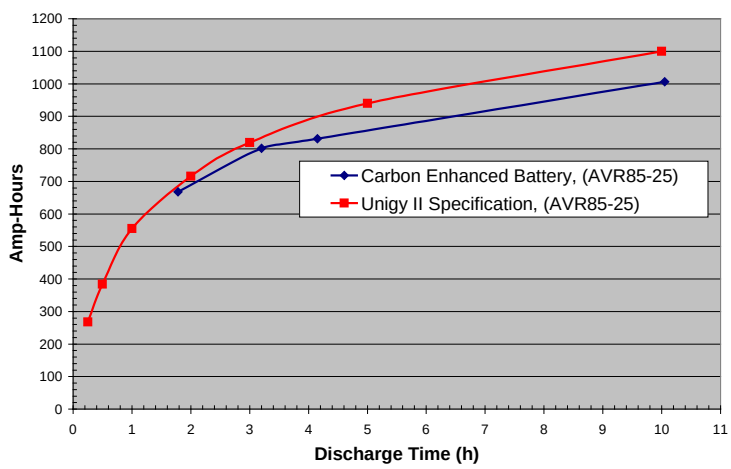

Figure 2: Carbon Enhanced Battery Capacity As A Function of Discharge Time.

In Figure 3 and 4 are the Alber Cellcorder cell impedance measurements and the DC discharge pulse ohmic resistance measurements on the 12 cell battery. The Cellcorder results in Figure 3 show a slight drop in impedance at 7,734 cycles, then a return to initial values at 8,529 cycles. In Figure 4 are two charts with the first chart on the left showing the voltage drop over a 2 ms time period from a 200A discharge pulse. All of the curves for this carbon enhanced battery were unique because of the steep voltage spike and recovery. This may be the Coup de fouet effect, but all other VRLA batteries tested to date have displayed a proportional voltage drop with respect to current. On the right side of Figure 4 are three plots of the voltage drop as a function of current. The DC discharge

resistance values on the right are measured by the average slope of the lines shown at about 2.4 milli-ohms. At zero amps the open circuit voltage at 7,734 cycles increases, then drops below the initial value at 8,529 cycles. The sum of all Cellcorder cell impedances values is between 2.2 to 2.7 milli-ohms, which does not include interconnect resistances. Based on the impedance and resistance measurements, the changes to battery performance appear to be minimal up to this point.

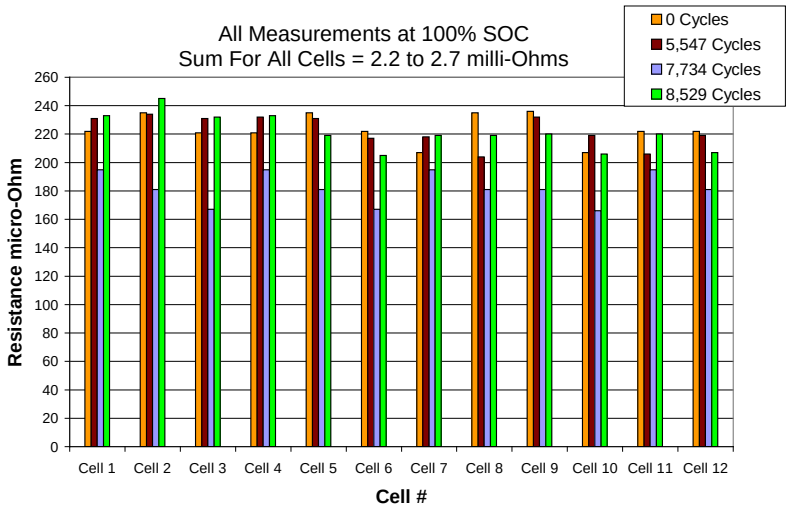

Figure 3: Alber Cellcorder Cell Impedance Measurements At 0, 5,547, 7,734, and 8,529 Cycles.

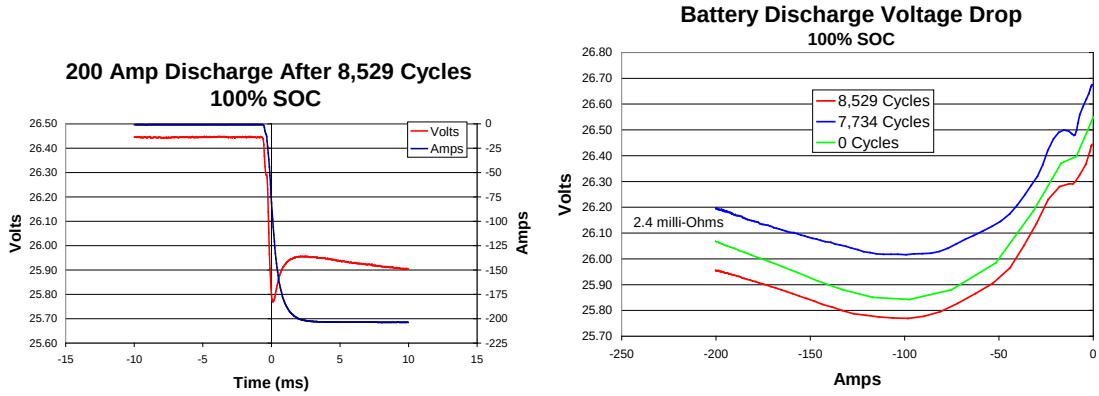

Figure 4: 200A DC Ohmic Resistance Discharge Pulse At 0, 7,734, and 8,529 Cycles.

In Figure 5 are the cell voltages and the charge and float current measurements for the carbon enhanced battery. The results show that after 12 h on finish charge at 2.40 V per cell the current is at 1.32 amps and was still tapering. The float current after 24 h at 2.27 vpc is at 0.176 amps and was also still tapering down. Both the charge and float current are within manufacturers specification for the Unigy II AVR85-25 battery. There was also no indication that the end of charge current was increasing after 8,529 cycles. Full charge termination on the 1,048 Ah battery was always maintained at 2.0 A without significant change in charge profile as shown in Figure 6. The cell voltages did begin to drift significantly as the battery approached 8,529 cycles and two cells #1 and #6 were high, approaching 2.55 V per cell, and none were low. The stabilized capacity in Figure 6 indicates that only a small increase in capacity occurred from 831 Ah at 0 cycles to 851 Ah at 8,529 Cycles. As seen from the curve only small changes occurred.

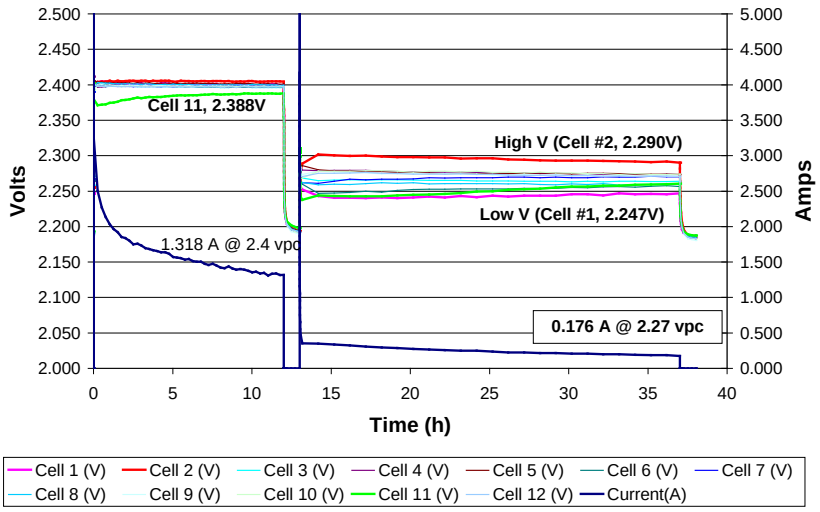

Figure 5: Charge and Float Current On the Carbon Enhance Battery.

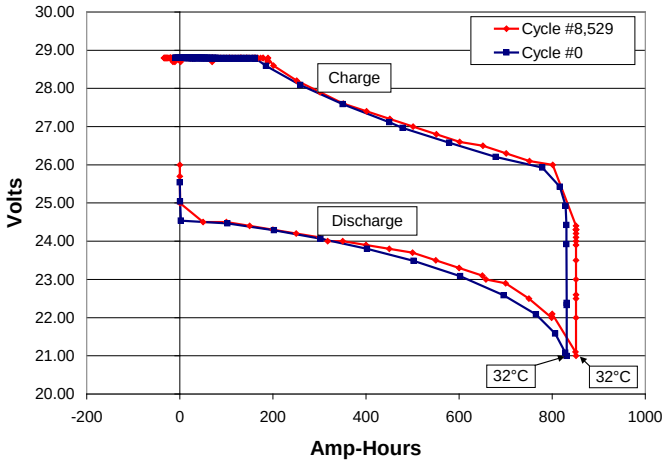

Figure 6: Initial And Final Capacity Test At 200A.

In Figure 7 and 8 are the initial and final Utility PSOC Cycle Test results at 200A and 400A. As seen in Figure 7, the number of PSOC cycles has decreased from 1,000 to 305 cycles after 8,529 cycles. The reason for the dramatic reduction in PSOC cycles is the rapid rise in end of charge voltage to 28.8V, which implies that the battery's negative plate is sulfating much more quickly than when the PSOC cycling was initiated. The operating temperature is also about 10°C higher, but this is predominately due to an ambient temperature that is about 7°C higher. The cycling temperature at 200A was initially 9°C above ambient and at the end of test the temperature was about 12°C above ambient. In Figure 8 are the initial and final Utility Cycle Tests at 400A. The results are similar except for the number of PSOC cycles achieved before the high voltage limit is reached. Initially there are 290 PSOC cycles after a total of 1,909 cycles and 186 PSOC cycles after a total of 5,547 cycles. The temperature for both tests is the same at about 40°C. The cycling temperature at 400A maintained a constant 15°C above ambient temperature.

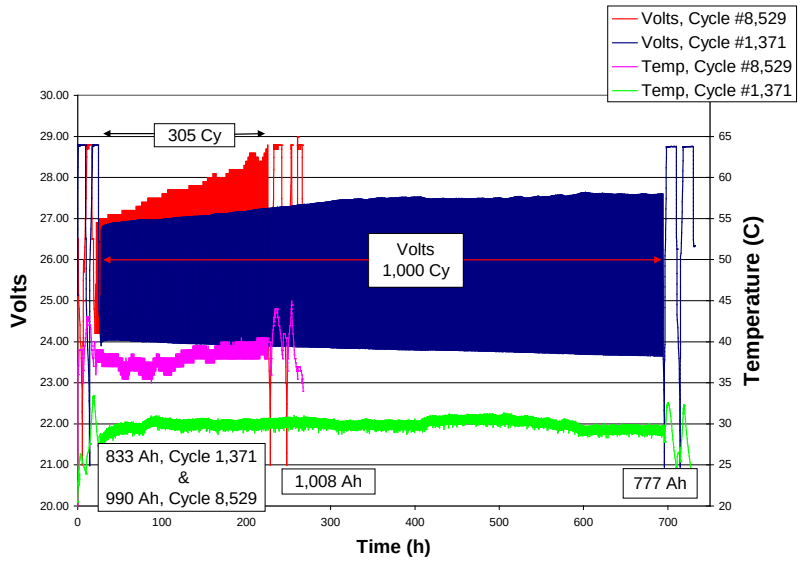

Figure 7: Utility PSOC Cycle Test 200A.

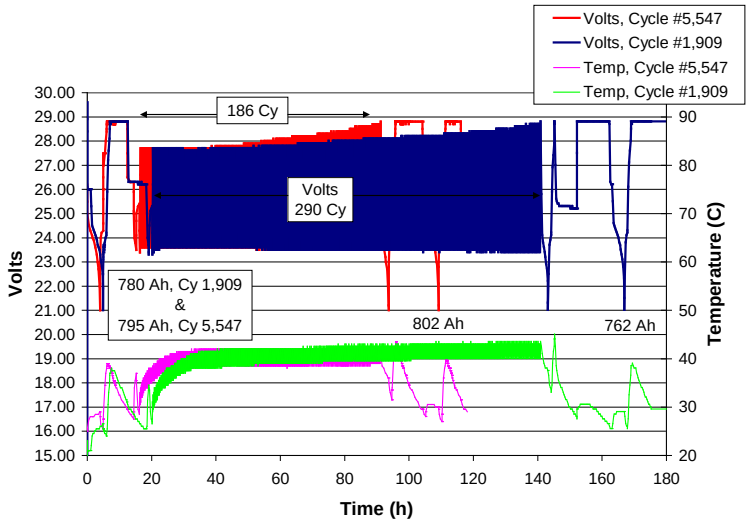

Figure 8: Utility PSOC Cycle Test 400A.

In Figure 9 is a plot of the operational capacity during the Utility PSOC Cycle Test. These capacity measurements were made after each PSOC cycling interval where a full recovery charge was provided before a full 200A discharge to 1.75 V per cell was conducted as the capacity measurement. The capacity initially follows a slow trend down, but this trend is reversed after about 3,400 cycles and continues to increase out to 8,529 PSOC cycles. It is not known why the operational capacity has increased in excess of the initial value, but this increase has been seen on other carbon enhanced batteries and may be a characteristic of the technology. In this case the operational battery capacity was initially measured at 831 Ah, then dropped to a low of 725 Ah at 3,400 cycles, and at 8,529 PSOC cycles capacity was measured at 1,008 Ah. A 21% increase from the initial capacity. It is apparent from Figure 6 vs. 7 and 8 that the capacity measured during a continuous cycling environment is higher than a one time capacity measurement after an extended rest. The capacity increase was clearly seen during the final 200A capacity measurements in Figure 6 where the first capacity was measured at 851 Ah @ 32°C, the second capacity was measured at 953 Ah @ 37°C, and third capacity was measured at 977 Ah @ 38°C. If capacity is temperature compensated at 1% per degree, then the temperature compensated capacity would be 851, 905, and 918 Ah. This is an 8% capacity increase just from two cycles.

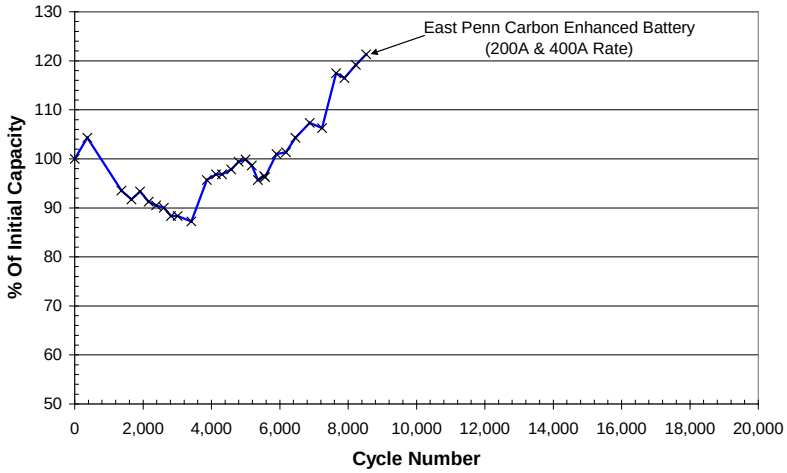

Figure 9: Utility PSOC Cycle Capacity Curve.

In summary, the East Penn ALABC carbon enhanced battery has proven to cycle well without capacity loss after 8,529 10% DOD PSOC cycles. Operational capacity was up from 831 to 1,008 Ah, a 21% increase in capacity and steady state capacity was also up from 831 to 851 Ah, a 2% increase in capacity. The operational capacity trend was initially down through 3,400 PSOC cycles, but this trend reversed and generally increased to 1,008 Ah at 8,529 PSOC cycles. At present the reason for this increase is not known, but similar increases have been seen on other carbon enhanced batteries.

The Utility Cycle Test did identify a number of areas where performance degradation did occur. These areas include the number of PSOC cycles before a recovery charge is required and the divergence of the cell voltages near the end of a PSOC cycle sequence. At a 200A cycle current the number of PSOC cycles decreased from over 1,000 to about 305 PSOC cycles and at a 400A cycle current the number of PSOC cycles decreased from 290 to 186 PSOC cycles. This is a 1/3 to 2/3 reduction in PSOC cycles as the battery aged. The other major area of performance loss is the cell voltage divergence toward the end of the PSOC cycle sequence. At the end of the Utility Cycle Test two cells were between 2.45 and 2.55 volts, while all the other cells were below 2.4 V per cell. In all cases the cell voltage did return to within specification after the recovery charge. There was just a slight increase in operational temperature at end of test from 9° to 12°C above ambient temperature. At present, it is not known if any of these degrading performance characteristics will limit the ultimate cycle-life of the battery.

1. Advanced Lead-Acid Battery Consortium, "Lead-Acid Breakthrough Could Propel Hybrid Electric Vehicle Market," News Release, http://www.csiro.au/news/UltraBattery.html, http://www.batterypoweronline.com/images/BPPTMA08.pdf 1/15/2008 .
2. L.T. Lam, et al., "VRLA Ultrabattery for high-rate partial-state-of-charge operation," Journal of Power Sources 174 (2007), pp.16-29.
3. Tom Hund, et al, "Testing of Energy Storage Devices", Energy Storage Systems Publications, Annual DOE PEER Review Meeting – 2008, http://www.sandia.gov/ess/Publications/pubs.html
4. Tom Hund, et al, "Ultrabattery Test Results for Utility Cycling Applications", The 18th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Dec. 8, 2008.