Charging Algorithms for Increasing Lead Acid Battery Cycle Life for Electric Vehicles

Matthew A. Keyser
Ahmad Pesaran
Mark M. Mihalic
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401
E-mail: mkeyser@nrel.gov

Bob Nelson
Recombination Technologies
909 Santa Fe Drive
Denver, CO 80204
E-mail: nelson7402@aol.com

Presented at the
17th Electric Vehicle Symposium
Montreal, CANADA
October 16-18, 2000

Abstract

Some factors that make batteries suitable for commercially viable electric vehicles (EVs) are battery performance, cost, and life. Although valve-regulated lead acid (VRLA) batteries are low cost, their cycle life has been limited for EV applications. Improving the cycle life of VRLAs by a factor of 3–4 could make lead acid EVs competitive with other types of batteries. With funding from the Advanced Lead-Acid Battery Consortium, the National Renewable Energy Laboratory has worked with Recombination Technologies and Optima Batteries Inc., to improve the cycle life of VRLA batteries, which is strongly influenced by the way they are charged over their lifetime. The purpose of the project was to develop charge algorithms specifically aimed at improving the cycle life of VRLA batteries to 1000 deep discharges for electric vehicle applications. The motivation for the project was based on the hypothesis that VRLA batteries reach end-of-life prematurely with the "normal" constant voltage charge because of insufficient recharge at the negative plate and the "oxygen cycle" or recombination reactions interfering with recharge of the negative plate. During Phase 1 of this project, we developed zero delta voltage and current interrupt charging algorithms and strategies that improved the cycle life of VRLA modules from 150–200 deep discharge cycles to 300–350 deep discharge cycles. During Phase 2, we implemented a current interrupt charge algorithm on a 24-module battery pack that resulted in 700 deep discharge cycles. We found no correlation between operating temperature and failure when batteries stayed below the manufacturer's recommended temperature limit of 60°C. However, warmer modules appear to have longer lives.

Background

Valve regulated lead acid (VRLA) batteries have been developed primarily by companies that also manufacture flooded lead acid batteries. Thus, the VRLA products are charged similarly to those traditionally developed for flooded lead acid technology. The dominant charging method used is current-limited constant voltage (CV). Some manufacturers recommend two-step constant current (CC) or some combination of CV and CC (e.g., the European IUI approach). All these approaches are characterized by their use of some fixed overcharge level, usually 10%–20%, that can act as a secondary charge-termination limit in conjunction with a fixed termination method throughout cycle life (e.g., time or voltage). Charge times are generally quite long (8–16 hours), mostly because of the low current levels toward the end of the charge for either CV or two-step CC. Also, overcharge levels early in cycle life are generally low and show a gradual increase up to some point of fairly rapid rise. This rapid rise is often not noticeable because charge is limited by the 10%–20% overcharge limit. After careful inspection of cycle/capacity graphs for lead acid batteries, voltages during charge and overcharge currents will often show that discharge capacity begins to diminish at precisely the point in the cycle life where the overcharge limit is reached.

If the overcharge limit is removed, the capacity fade improves temporarily, but in many cases the resultant high overcharge amounts increase exponentially and the massive Ah inputs lead to premature failure caused by positive-plate degradation, dry-out, and/or grid corrosion. Regardless of how VRLA batteries are charged in electric vehicle (EV)-type duty cycles, the life to 80% of initial capacity is usually 200–300 cycles. This is probably due to the lack of compensation for the changing role of the oxygen-recombination cycle in the ways most VRLA batteries are charged.

Recent work in the Advanced Lead Acid Battery Consortia (ALABC) program by Tomantschger et al. (1) has shown that fast charging, particularly using partial-state-of-charge (PSOC) algorithms, can lead to enhanced lifetimes. However, the cycling profiles are variable and somewhat complex and the PSOC approach returns only about 60% of a battery’s full rated capacity on discharge—a serious limitation for a technology that has relatively poor specific energy to begin with (effectively, 50 Wh/kg is reduced to 20 Wh/kg). Fast charging is facilitated by the use of pulsed-charging. However, in the algorithms used the finishing currents are relatively low and various fixed overcharge limits are imposed on the batteries.

Beyond the obvious differences in plate chemistries, the charging characteristics of VRLA may be closer to those of sealed nickel-cadmium (NiCd) products than to flooded lead acid. Both VRLA and NiCd operate on oxygen-recombination to minimize water loss, whereas flooded lead acid does not. The extreme depolarizing effect of the oxygen cycle must be taken into account in developing charging strategies or the negative plate will fail early because of sulfation. NiCds are charged almost exclusively with CC methods and typically have overcharge levels of 40%–50% at room temperature. Their termination strategies are linked to sensing cell parameters (temperature, voltage/time changes) and not to a fixed time or overcharge level. This is easier to do with NiCd because overcharge is less harmful than for VRLA. NiCd cells cannot be charged using CV or even low-level CC because much of the finishing current is consumed by the oxygen-recombination cycle. The oxygen-recombination efficiency (ORE) is much greater for NiCd than for VRLA because of differences in the basic designs, but for flooded lead-acid the ORE is basically zero. A major key to understanding how to properly charge VRLA batteries in cyclic applications is that, in terms of charging behavior, they are more like NiCds than flooded lead acid. Therefore, looking at how and why NiCds are charged is useful.

Another key is to acknowledge that, unlike flooded lead acid or even NiCd products, VRLA batteries experience significant changes in electrolyte distribution as they age in deep-cycling applications such as EV duty. Early in life, they are almost flooded, and could probably be charged like a flooded product. However, as a VRLA battery ages it loses water because gases are vented and water vapor is transported through the plastic case. Also, water is consumed in the grid-corrosion process and electrolyte redistributes from the separator in the plate pores. These factors contribute to an increase in void space in the glass-mat separator that results in an ever-increasing ORE, which has an enormous impact on charging. In traditional CV and CC charging approaches, this increase in the role of oxygen recombination is not taken into account. Thus, another key to properly charging VRLA batteries is to either modify the charging/termination algorithm throughout the cycle life or charge them in such a way that these changes occur more slowly.

If such a modified algorithm is not used, a VRLA battery will invariably reach a point in cycle life where the oxygen-recombination cycle consumes most or all of the overcharge current allowed by the charge. Thus, a proper finishing charge for the battery cannot be delivered. As the battery ages and the ORE increases this becomes more and more pronounced. The result is a “walk-down” of capacity when the allowable overcharge amount (e.g., 10%–20%) cannot support the oxygen cycle. Atlung and Zachau-Christiansen (2) have presented data to demonstrate this and have developed a model that predicts ever-increasing difficulty in properly recharging the negative plate as the ORE becomes more and more dominant. Apparently this phenomenon must be compensated for, or the plate must be charged, so the difficulty is minimized during cycling. The battery can thus achieve a higher cycle life before failure occurs. A growing body of literature demonstrates that, initially, VRLA batteries in deep-cycling applications are positive-plate limited by the negative-plate capacity (3). Beyond this point, capacity diminishes gradually as the negative plate loses its activity.

Given these findings, and work already carried out in the ALABC program (3), we feel that a proper charging algorithm for VRLA batteries involves the following:

- High inrush currents to promote nucleation, thus maintaining a fine, open pore structure.
- No limitation on the percent overcharge (although, with proper charging and termination, this should never exceed ~20%).
- A modest-to-high rate of charging to provide current to the battery fairly rapidly, particularly at the beginning and end of charge.
- High finishing currents to provide enough charge for the recombination cycle and still have some available to finish charging the active materials.
- An effective charging termination point that completely recharge the active materials with minimal overcharge and compensates over the battery lifetime for the increasing influence of oxygen recombination.

The high finishing currents and the termination method differ from what has been done previously for VRLA. Both techniques are used routinely in NiCd technology and were applied to VRLA technologies. However, some critical differences between VRLA and NiCd must be recognized and compensated for to achieve proper charging. Particularly early in life, the ORE is much poorer for VRLA than for NiCd; in fact most VRLA products are in an almost flooded condition initially. Also, for VRLA there is the danger that the separator void space will increase dramatically through the cycle life; thus, some adjustments in charging are required to account for this and avoid either undercharging (as with overcharge limitation) or excessive overcharge. Allowing unlimited overcharge levels can be successful for small numbers of cycles, but it greatly accelerates failure because the positive active material softens, dries out, or corrodes. The purpose of this paper is to present the results of our work on improving the cycle life of modules using a zero delta voltage (ZDV) approach on a module and using current interrupt (CI) on a 24-module battery pack.

Setup for Zero Delta Voltage Test

NREL tested an Optima yellow top battery (nominally rated at 12 volts and 50 Ah) with the ZDV technique. The battery was tested with AeroVironment's ABC-150 cycle tester. Figure 1 shows the setup used to test it. The battery was placed in a Plexiglas enclosure and two muffin fans were used to circulate ambient air through the enclosure. Each fan has a volumetric airflow of 10 ± 1 ft^3/min. During testing, the battery voltage and temperature were monitored with AeroVironment's Remote Operating Software (ROS) through National Instrument's data acquisition board integrated with the ROS software. A middle cell temperature was monitored for the duration of the test. The thermocouple, type K, was placed on the interior wall of one of the center cells.

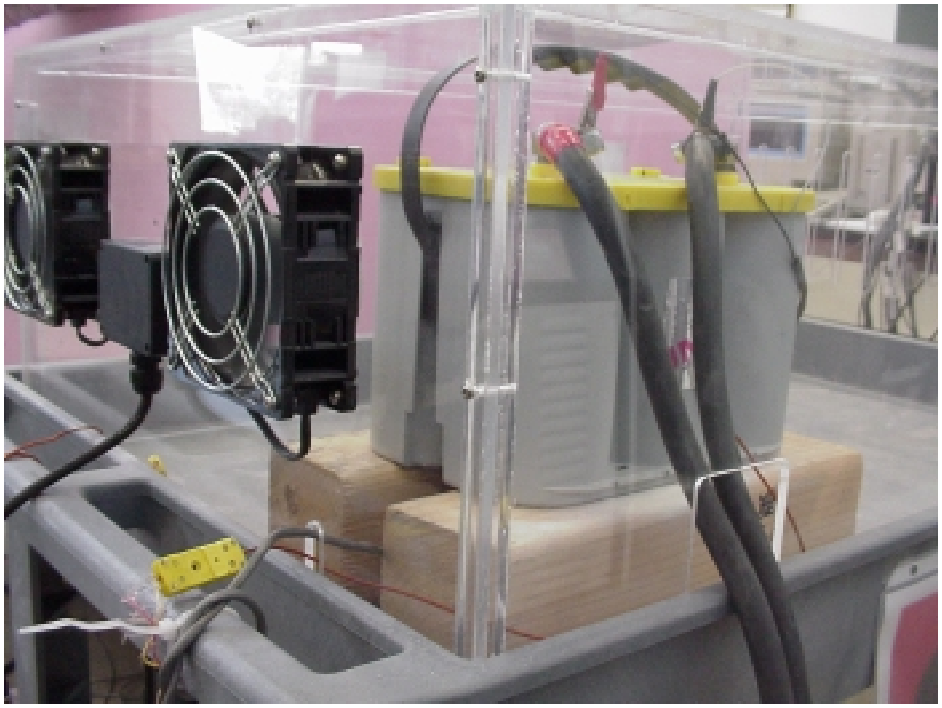

Figure 1
Optima 50 Ah, 12 Volt Module under Cycle Life Test

The battery was discharged at 25 amps (nominally C/2 rate) until the voltage of the battery went below 10.5 volts. This would be equivalent to 100% depth of discharge (DOD) or 1.75 volts per cell (VPC). The battery was then charged at 50 amps until 70% of the previous discharged Amp-hours was returned to the battery. The battery was then charged with 10 amps until ZDV was reached. During the ZDV charging, the battery voltage was sampled once every second for 30 seconds. The 30 readings were then averaged, and the average was subtracted from the previous 30-second average and then compared to a limit. The limit for this particular test was 15 mV. The limit chosen depends on the number of cycles placed on the battery. The 15-mV limit was used through cycle 295 and then lowered to below 10 mV after cycle 295. The final test for ZDV is when the limit is not exceeded 5 consecutive times. In other words, the difference between successive 30-second average readings needs to be below the assigned limit five consecutive times. Finally, the battery was overcharged at 5 amps according to the following table:

Cycle Number (#)	Fixed Overcharge Amount at 5.0 Amps (Ah)
0-295	3.0
296-340	10.0
341-356	6.0-7.0

The test ran continuously except when the battery was removed every 100 cycles to measure the mass, open circuit voltage (OCV), and impedance.

Results and Discussion for Zero Delta Voltage Test

Figure 2 shows the cycle/capacity curve for the Optima battery under test. The battery is above 80% of its initial discharge capacity until cycle 280. Following the Optima suggested CV charge algorithm, a typical Optima yellow top battery falls below 80% of its initial discharge capacity at approximately cycle 140—an improvement of 100% using the ZDV technique for charging the battery. After cycle 295, the amount of overcharge increased to 10 Ah. Increasing the overcharge increased the discharge capacity of the battery as expected but also increased the temperature. The battery was temperature limited at 60^{o}C for all cycling performed on the battery. Once the battery reached 60^{o}C, the battery was placed into discharge. This resulted in a varying amount of overcharge between cycles 341 and 356.

Figure 3 shows the difference in Amp-hours between charge return and discharge capacity. Between cycles 1 and 70, the battery receives less than 3 Ah in overcharge. The algorithm sensed ZDV before 100% charge return and did not sense ZDV at 100% charge return until approximately cycle 70. Between cycles 1 and 295, the 5 amp constant overcharge was held at 3.0 Ah from the point at which ZDV was sensed. The overcharge varied according to when ZDV was sensed. Thus, using an "intelligent" charging technique increased the overcharge as the battery aged.

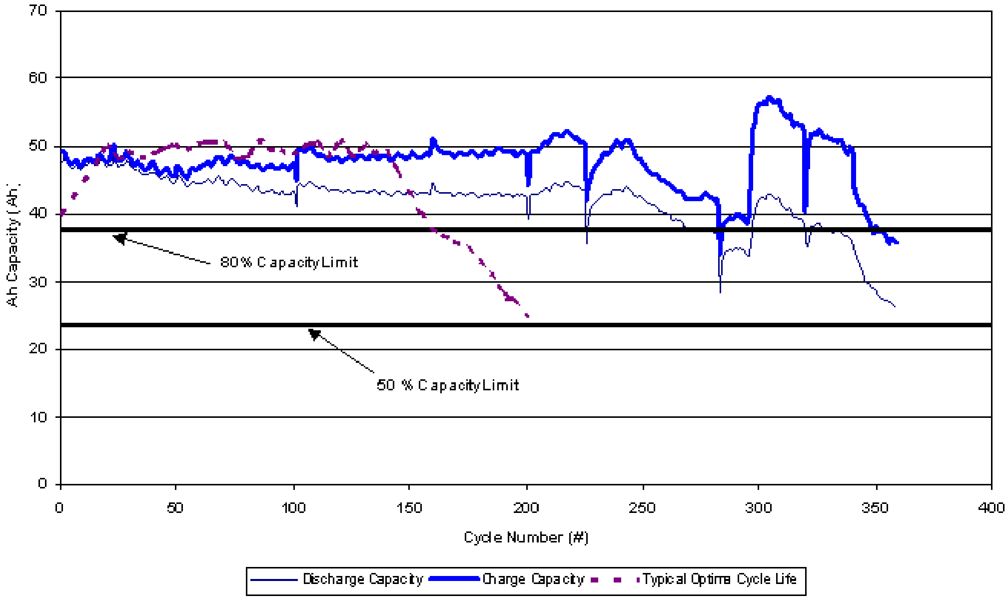

Figure 2
Optima ZDV Cycle Life Test

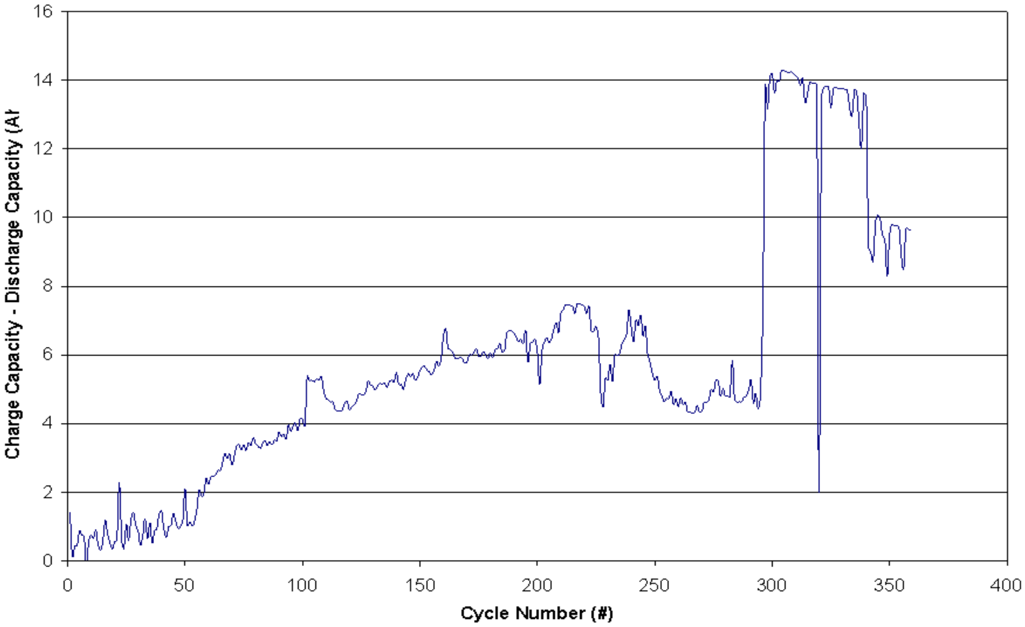

Figure 3
Overcharge of Optima Battery under ZDV Cycle Life Test

Table 1 shows the physical data for the battery under test. Weight losses were very low, on the order of 120 grams after 356 cycles, suggesting that "dry-out" is not a failure mode. The small differences between initial and final OCVs and impedances indicated that negative-plate sulfation was not severe.

Table 1
Physical Properties of Optima Yellow Top Battery under ZDV Test

Cycle (#)	Mass (kg)	Open Circuit Voltage (Volts)	Impedance (mOhms)
0	19.659	13.256	3.05
100	19.625	13.455	3.18
200	19.583	13.642	3.32
356	19.548	12.584	3.95

Figure 4 shows a charge curve for cycles 50 and 250. The beginning of the 10-amp ZDV charge is relatively flat, which can cause problems with sensing ZDV too early. A large voltage change between the start of the ZDV cycle and the end of the ZDV cycle helps determine when to sense ZDV, but comparing cycles 50 and 250 shows that the difference between the initial and final voltage changes as the battery ages. During cycle 50, the battery went into recombination during the 5-amp overcharge as evidenced by the drop in voltage. The battery received only 1.3 Ah of overcharge during cycle 50, but even this was more than adequate.

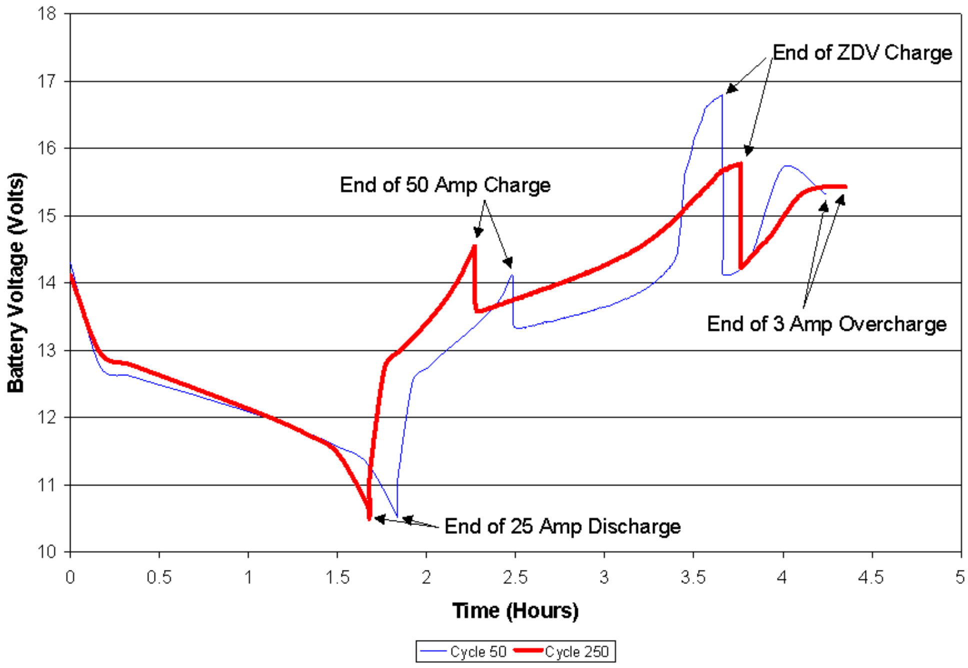

Figure 4
Optima ZDV Cycle Life Test—Cycles 50 and 250

Figure 5 shows the temperature of the battery at the end of the overcharge and at the end of the discharge cycle for the ZDV cycle life test. The highest battery temperature was observed during overcharge and the lowest at the end of discharge. The temperature of the battery stays below 50°C for discharge and charge during most of the test. The battery hits the 60°C limit around cycle 335 because of the 10 Ah overcharge. Figure 6 shows an infrared (IR) thermal image of the battery during the 5-amp overcharge for cycle 38. The battery temperature varies from 26°C to 33°C. The center cell is slightly hotter because of the decreased amount of surface area available to convect heat. Figure 7 shows an IR thermal image of the battery during the 5 amp overcharge for cycle 350. The battery temperature varies from 32°C to 48°C. The higher temperature, compared to cycle 38, is due in part to the higher amount of overcharge, 10 Ah instead of 5 Ah. The right cell shows signs of heating near its top, possibly because an internal short developed over the cycle life test.

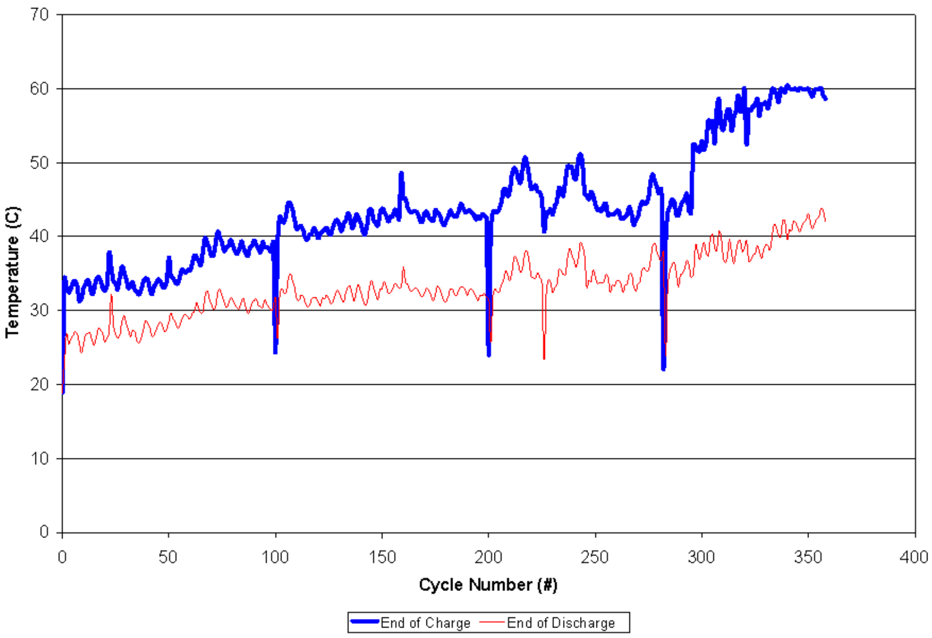

Figure 5
Temperature Data for Optima ZDV Cycle Life Test

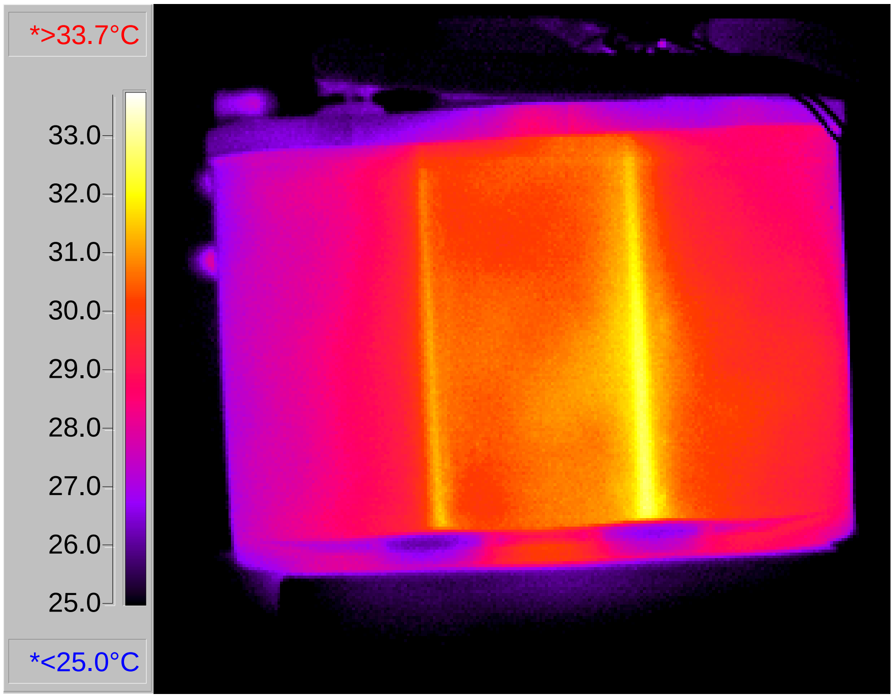

Figure 6
IR Thermal Image of Optima Battery during ZDV Cycle Life Test—Cycle 38.

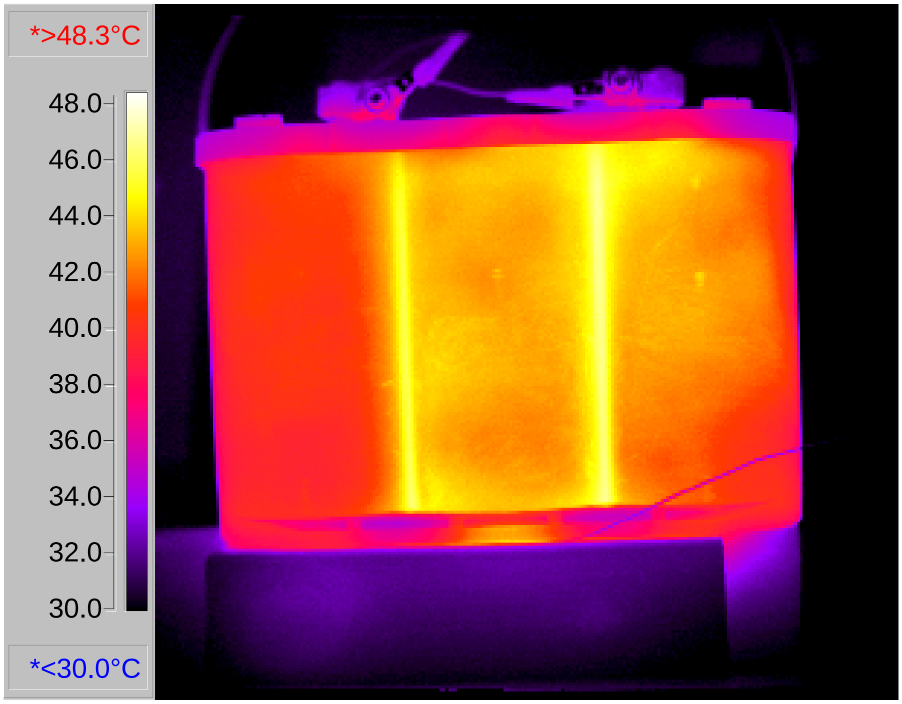

Figure 7
IR Thermal Image of Optima Battery during ZDV Cycle Life Test—Cycle 350

Battery Pack Cycle Life Test Setup and Charging Technique

The cycle life test was performed on a pack containing 24 Optima yellow top batteries. Each battery is nominally rated at 12 Volts and 50 Ah. The batteries were connected in series resulting in a nominal pack voltage of 288 volts. Figure 8 shows the arrangement of the batteries. Each battery was instrumented with a thermocouple and voltage tap. The battery temperatures and voltages were recorded with an independent Hewlett Packard data acquisition system. The battery pack was cycled with AeroVironment's ABC-150, which monitored and controlled the current through the battery pack and the overall voltage. The battery pack was further enclosed in a blown foam insulation box with an air plenum integrated in it to cool the batteries. The total airflow through the air plenum was approximately 470 ft^3/min and the inlet air was cooled to an average temperature of 13^{o}C.

Figure 8
Optima Battery Pack Used to Test Cycle Life

The battery pack was discharged at 25 amps (nominally C/2 rate) until the voltage of a single module went below 10.5 volts. This would be equivalent to 100% DOD or 1.75 VPC for a single module, but was approximately equivalent to 80% DOD for the non-limiting modules. The battery pack was then charged at 100 amps until 60% charge return, 50 amps until 80%

charge return, and 15 amps until 100% charge return. It was then overcharged with a current interrupt (CI) technique instead of ZDV because there was no battery monitoring system. The typical CI technique used was to apply 5 amps to the battery pack for 15 seconds and then no current for 20 seconds. This was repeated until 3 Ah of overcharge was provided to the battery pack. The CI charge/rest and the amount of overcharge varied depending on the age of the battery. Further details will be given in the results and discussion.

What is a CI technique?

- A pulsed-charge technique with on-off times of 5-30 seconds, which are adjustable so negative-plate polarization is achieved during charge, and heat dissipation is effected during rest.
- It is used with thin plate batteries for the finishing charge step, particularly late in life.
- No voltage limit is imposed during the charge steps (but gassing appears to be minimal or nonexistent).
- Little polarization during charge and rest voltages below 14.0 volts are used as criteria to trigger an increase in the pulsed-current amplitude.
- Late in life pulsed-current levels of 2C–4C may be necessary to achieve 100% recharge.

A CC charge and CI technique were used to charge the battery pack for several reasons.

- A CC charge allows for fast recharge and use of the voltage/time curves for predictive purposes.
- Overcharge at continuous high currents causes thermal problems, particularly as the battery ages when the oxygen cycle dominates.
- Current interrupt allows use of high currents with rest periods to maximize recharge efficiency, minimize overcharge, and reduce overall pack temperature.
- The charge/rest rate and current for a multi-step CI must be optimized for long cycle life for high discharge capacities.

Battery Pack Cycle Life Test Results and Discussions

Figure 9 shows the cycle/capacity curve for the Optima battery pack. The discharge capacity is relatively constant at 40 Ah over the 700 cycles. Below cycle 600, modules were replaced with new modules when a single module was limiting the overall capacity of the pack. For instance, a single module's voltage was at 10.5 volts, signaling the end of discharge but the other modules in the pack were at 11.2 volts. The vertical lines on Figure 9 indicate when a module was replaced in the battery pack. For instance, the first module replaced was at cycle 36. This particular module had a low capacity and short cycle life. It had apparently been struck with an object, possibly during shipping, causing a short in the layers of one of the spiral wound cells. Figure 10 shows a thermal image of the battery showing a hot spot on the module resulting from the internal short. After cycle 600, the modules limiting the capacity of the pack were bypassed rather than replaced. Table 2 shows the OCV, mass, and impedance of the modules when they were replaced. Weight losses were very low, on the order of 100–150 grams, suggesting "dry-out" is not a failure mode. The small differences between initial and final OCVs and impedances indicated that negative-plate sulfation was not severe.

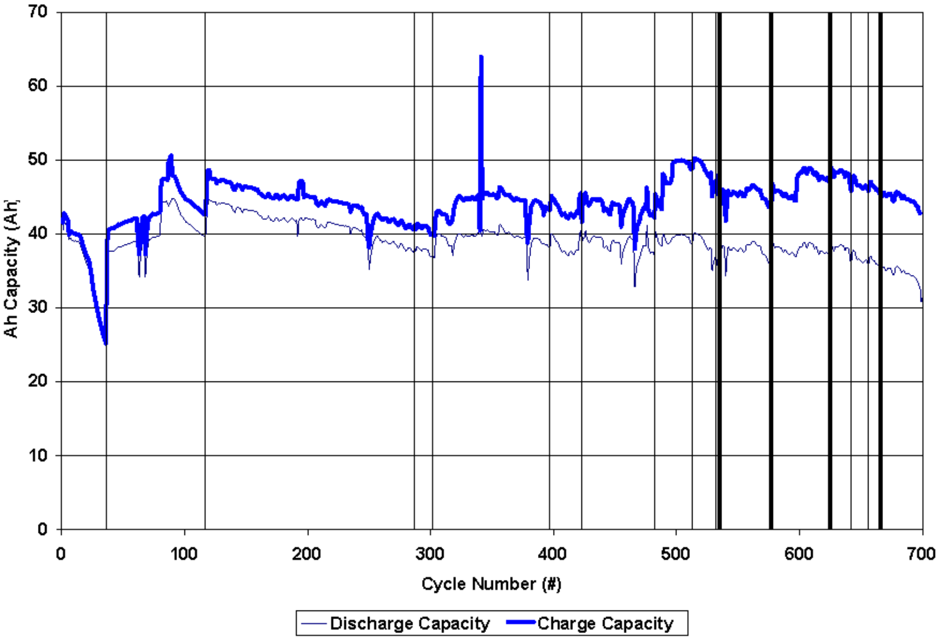

Figure 9
Cycle Life Test of Optima Battery Pack

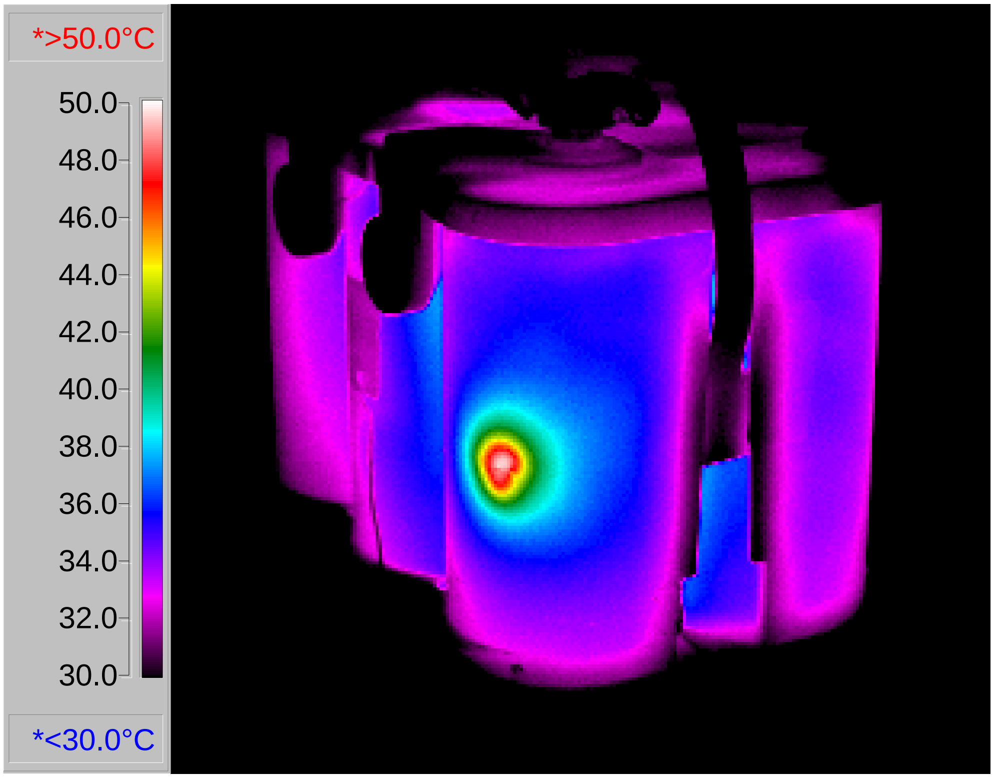

Figure 10
Thermal Image of module #14 with Shorted Layers

Table 2
Mass, Impedance, and OCV Data of the Modules Used in Optima Battery Pack

Battery Number	Serial Number	Date Replaced	Cycle Number	Initial Mass (kg)	Final Mass (kg)	Initial OCV (Volts)	Final OCV (Volts)	Initial Imp. (mOhms)	Final Imp. (mOhms)
14	9067210209	11/08/99	36	19.944	19.924	13.34	13.04	3.90	2.69
11	9062210257	11/21/99	117	20.494	20.456	13.36	13.19	4.20	5.00
23	9060210140	12/27/99	287	20.108	20.050	13.41	13.39	4.30	2.85
6	9062210485	1/3/00	302	20.424	20.320	13.44	13.17	4.00	3.00
18	9061230609	1/21/00	397	20.408	20.295	13.39	13.41	4.00	2.90
2	9062220068	1/26/00	423	19.977	19.803	13.46	13.51	4.40	3.25
18 (Old 23)	9060210140	1/21/00	482	20.050	19.964	13.39	13.44	2.85	3.20
3	9063220041	2/18/00	513	20.142	19.991	13.44	13.32	4.10	3.00
24	9062230133	2/18/00	513	20.284	20.119	13.42	13.36	4.30	3.10
14	8120220453	2/23/00	532	19.971	19.886	13.37	13.13	2.76	3.10
1	9067210632	2/24/00	535	19.813	19.667	13.42	13.14	4.10	3.20
16	9062220351	2/24/00	535	20.494	20.326	13.38	13.07	3.50	2.90
13	9064210100	03/03/00	577	19.911	19.772	13.44	13.27	3.85	2.79
17	9067210371	03/03/00	577	19.995	19.853	13.43	13.26	3.6	2.85
21	9012210159	03/13/00	625	19.853	19.748	13.37	7.31	4.1	19.5
12	9012239420	03/13/00	625	20.279	20.196	13.25	7.53	3.9	21.0
19	9012230381	03/17/00	642	20.158	20.014	13.27	12.34	4.1	3.7
20	9008230539	03/20/00	656	20.306	20.165	13.29	13.23	3.7	3.18
4	9060210138	03/22/00	666	20.400	20.210	13.41	13.07	4.0	3.45
8	9011220367	03/22/00	666	19.426	19.321	13.32	13.02	4.3	3.5
7	9012230419	03/24/00	677	20.305	20.219	13.25	12.94	3.9	3.2

Figure 11 shows the amount of overcharge as a function of cycle number for the pack. The maximum amount of overcharge used during the cycle life test of the battery pack was 10 Ah. Below cycle 500, the amount of overcharge was 5 Ah or less. As noted earlier, the CI pulses changed during the cycle life test. Table 3 shows the current used and the rest periods as functions of cycle number.

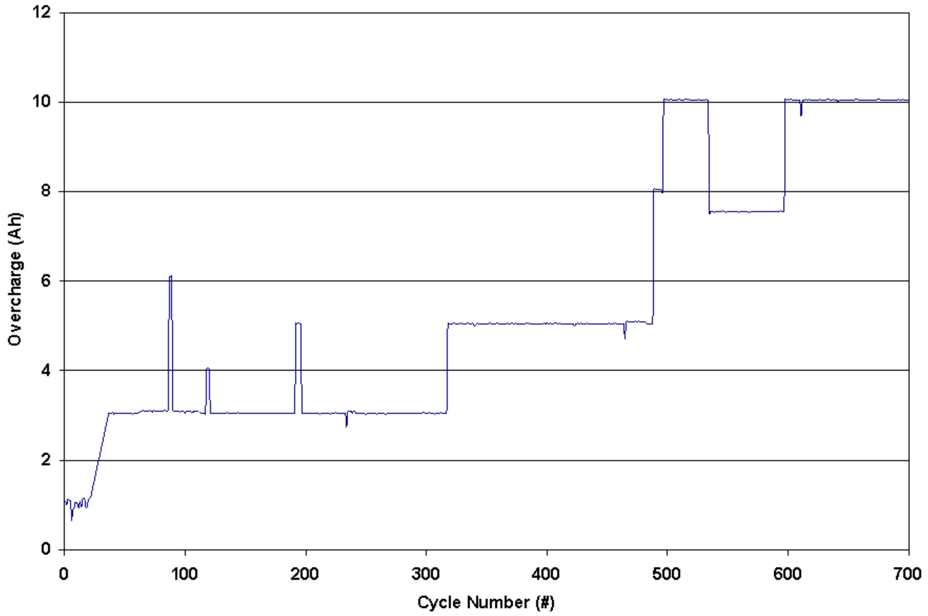

Figure 11
Overcharge Used with Optima Battery Pack Cycle Life Test

Table 3
CI Used during Battery Pack Cycle Life Test

Cycle Number (#)	Current (Amps)	Time Current Applied (seconds)	Rest Time (seconds)
1-355	5	15	20
356-400	10	15	20
401-454	5	15	20
455-656	7.5	5	5
657-670	15	5	15

Figure 12 shows how the temperature of a module is affected by the magnitude of the current used for CI and the amount of overcharge placed on the battery pack. For instance, the discharge and charge temperature of module #21 increased when the current was increased from 5 amps to 10 amps at cycle 356. The temperature of module #21, however, is quite reasonable over the 700 cycles shown. The maximum Optima suggested operating temperature for this module is 60^{o}C. Over the entire test, there appears to be no clear correlation between operating temperatures and failure; however, warmer modules appear to have longer lifetimes.

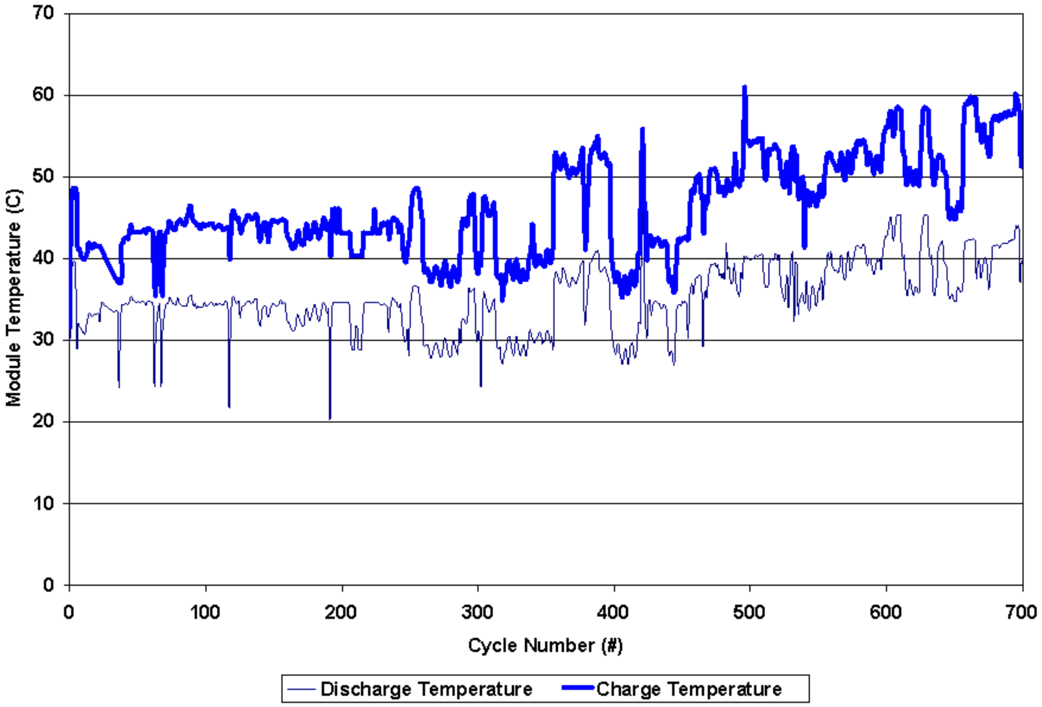

Figure 12
Temperature Data for Module #21 in Optima Battery Pack

Figure 13 shows the voltage/time curve for cycle 200 and Figure 14 shows the voltage/time curve for cycle 300. The shape of the CI charge pulse curve and the rest voltage values indicated the effectiveness of the charge process. During the CI of cycle 300, the peak charge voltages “bend over” and start to show a drop. Cycle 200 does not show this because oxygen recombination becomes more pronounced. Also, how high the voltages go during the CI pulses indicates whether the battery is polarizing properly. When the peak voltage values drop below approximately 15.5 volts, an increase in recombination occurs within the battery. Accompanying this, the rest voltages during the CI pulse do not rise as easily and will tend to stay below approximately 14 volts. When these events occur, the Ahs and the pulse amplitude of the CI need to be increased. Thus, the increase in the CI Ahs at cycle 320 and the increase in the current at cycle 356.

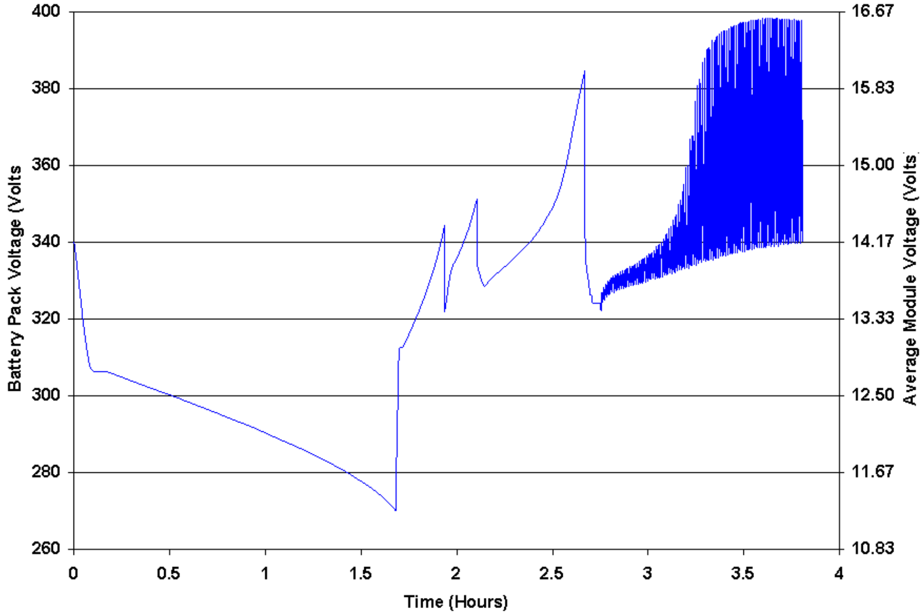

Figure 13
Pack Voltage for Cycle 200 of Optima Battery Pack Cycle Life Test

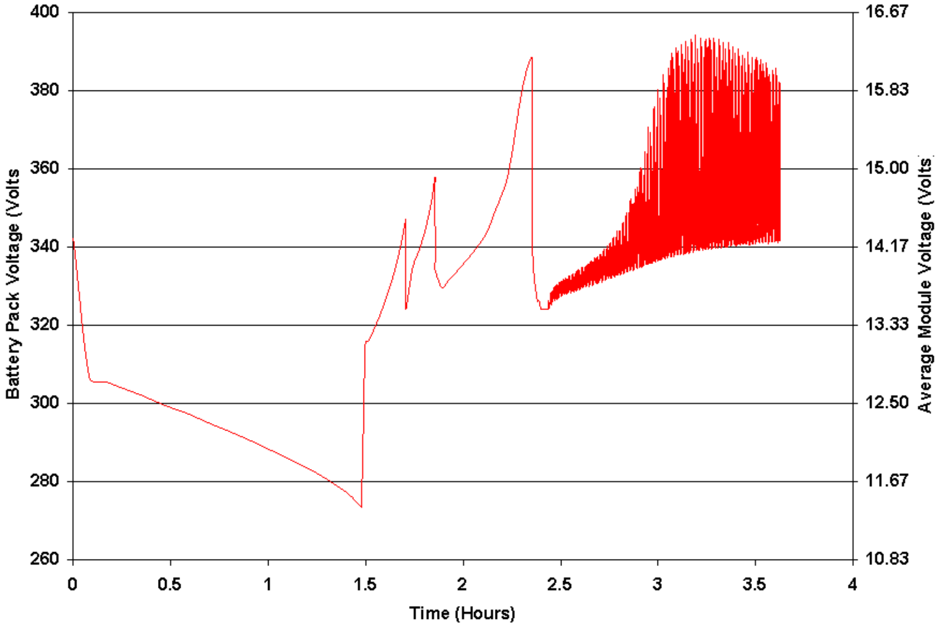

Figure 14
Pack Voltage for Cycle 300 of Optima Battery Pack Cycle Life Test

Conclusions and Summary

Conclusions for the Zero Delta Voltage (ZDV) charging technique on Optima VRLA battery are:

- Applying a ZDV technique similar to the one used for NiCd batteries, we were able to increase the cycle life of the Optima VRLA by a factor of 2.
- As VRLA batteries age, increasingly higher finishing currents are drawn because of the oxygen cycle; the charge/termination algorithm must be adjustable to respond to this. A fixed, monotonic algorithm will result in overcharge early in life and undercharge later in life.

Conclusions from the 24-module battery pack cycling using a current interrupt technique are:

- Applying the multi-step CC/CI charge algorithm without battery management results in excellent pack cycle lifetime for the Optima product.
- Insufficient recharge of 12V modules in a large pack appears to be amplified relative to single-module cycling.
- Weight losses are very low, on the order of 100–150 grams, suggesting that “dry-out” is not a failure mode.
- The small differences between initial and final OCVs and impedances indicate that negative-plate sulfation is not severe.
- There appears to be no clear correlation between operating temperature and failure; however, warmer modules appear to have longer lifetimes.

Using these types of charging algorithms can apparently increase the life of VRLA batteries for EV applications by a factor of at least 3. This will make lead acid batteries more attractive for EVs compared to more expensive but longer life batteries.

Acknowledgments

We would like to thank Dr. Pat Moseley and ALABC for funding the research for this program. Optima Batteries Inc. provided batteries and technical insight for the research. We would also like to express our appreciation to Bob Kost, DOE HEV program Manager, and terry Penney, NREL HEV Technology Manager, for permission to use DOE/NREL equipment for execution of this research program.

References

1. K. Tomantschger, et al., “Laboratory and Field Evaluation of Optima VRLA Batteries Utilizing Rapid Charging,” IEEE 98TH8299, in *Proceedings of the 13th Annual Battery Conference on Applications and Advances,* Long Beach, California, January 13-16, 1998, 173-178.
2. S. Atlung and B. Zachau-Christiansen, *J. Power Sources* 52 (1994), 201-209.
3. E. Sexton, “Improved Charge Algorithms for Valve Regulated Lead Acid Batteries,” IEEE 00TH8490, in *Proceedings of the 15th Annual Battery Conference on Applications and Advances,* Long Beach, California, January 11-14, 1999, 211-216.