CoNF-9004196--2

STATUS OF ARGONNE LIFE EVALUATION OF VALVE REGULATED LEAD-ACID BATTERIES

W. H. DeLuca, R. L. Hogrefe, C. E. Webster, and A. F. Tummillo

Argonne National Laboratory
Chemical Technology Division
Argonne, Illinois

CONF-9004196--2

DE90 011098

Abstract

Argonne is conducting a life evaluation of valve-regulated lead-acid (VRLA) batteries for cycling applications. Two technologies are being evaluated: (1) gelled-electrolyte modules from Johnson Controls, Inc. (JCI) and (2) absorbed electrolyte modules from GNB, Inc. A matrix of operating temperature and depth-of-discharge (DOD) conditions is being used to accelerate the end-of-life for given modules. In May 1989, two modules from each manufacturer were placed on life test at 30°C (80 and 100% DOD), and a third module was placed on accelerated life testing at 50°C (100% DOD). The GNB module operating to 100% DOD at 30°C still retains ~87% of its initial capacity after >400 cycles. The GNB module operating to 80% DOD at 30°C has accrued >500 cycles and retains ~93% of its initial 80% DOD capacity. After a high-temperature charge procedure was established, a fourth GNB module was placed on test at 50°C (80% DOD) in September 1989. Both GNB modules tested at 50°C have accrued ~150 cycles; the 100% DOD module retains ~84% of its initial capacity, and the 80% DOD module retains ~89% of its initial 80% DOD capacity. The three gelled-electrolyte JCI modules were removed from test because they reached end-of-life. Preliminary teardown analyses indicate that a manufacturing defect caused premature failure of these modules.

STATUS OF ARGONNE LIFE EVALUATION OF VALVE REGULATED LEAD-ACID BATTERIES

W. H. DeLuca, R. L. Hogrefe, C. E. Webster, and A. F. Tummillo

Argonne National Laboratory
Chemical Technology Division
Argonne, Illinois

Introduction

Argonne is conducting a life evaluation of valve-regulated lead-acid (VRLA) batteries for cycling applications. This work is sponsored by the Electric Power Research Institute (EPRI) and the International Lead Zinc Research Organization (ILZRO). The objectives are (1) to determine VRLA battery life within a 2-3 year time period under conditions similar to those encountered in a utility operating environment and (2) to use accelerated testing techniques to obtain data within 6 months on VRLA battery life expectancy. The battery testing strategy was developed and finalized in 1988.[1] A matrix of operating conditions was selected to vary the stress of known failure modes and, thereby, accelerate the end-of-life for given modules. The primary failure mode is expected to be active material changes caused by charge-discharge cycling (i.e., microstructural and morphological changes, sulfation, mass isolation, loss of surface area, loss of porosity, etc.). After life testing, select cells are to undergo teardown examination and analyses to identify the failure mode. End-of-life is defined as the inability to furnish 80% and 64% of rated capacity for 100% and 80% depth-of-discharge (DOD) tests, respectively.

This paper describes the activities and status of the VRLA test program at ANL and presents the results of the first seven months of VRLA battery life testing.

Background

The test matrix formulated for use in this VRLA battery life evaluation is given in Table 1. Module operating temperature and DOD were used to vary the amount of active material utilized in four cycling regimes and thereby vary the approximate cycles to module failure. The 80% DOD test condition at 30°C (86°F) was selected as most representative of a utility environment. The operating temperature of 50°C (122°F) was selected to maximize active material utilization within the operational limits specified by the manufacturer. This temperature is also within the extreme limits found at certain utility locations. The acceleration factors in Table 1 are approximated based on available literature. The estimated test time assumes that 2 cycles/day is achievable and that ~50 cycles/month can be accrued on the average. The discharges to 80% and 100% DOD are terminated at predetermined voltages at each operating temperature. In this manner, only the specified degree of active material is continuously utilized to aid cycle-life analyses. Discharge voltage limiting is also consistent with those utility applications where electrical power conversion equipment has fixed minimum operating voltage levels.

Table 1. ACCELERATED LIFE TEST MATRIX FOR VRLA BATTERIES

Module Number	Test Temp., °C	DOD, %	Approx. Accel. Factor	Approx. Cycles to Failure	Estimated Test Time, months
1	30	80	1	1200	24
2	30	100	2	600	12
3	50	80	2	600	12
4	50	100	4	300	6

Two technologies are being evaluated: (1) 12-V modules manufactured by Johnson Controls, Inc. (JCI) that have a gelled electrolyte and (2) 6-V modules manufactured by GNB, Inc. with an absorbed electrolyte. A summary of manufacturer specifications for each VRLA module type is given in Table 2. The variation in weight among the GNB modules (1.6%) was a factor of four greater than that for the JCI modules (0.4%). However, the initial capacities of the GNB modules were matched to within 2% and were about 17% higher than their specified ratings at both the 8-h and 3-h discharge rate. A 23% decline in module capacity resulted with increased discharge rate (130 to 272 A); this decline is in close agreement with that specified by GNB. The average capacity of the JCI modules was within 1% of their ratings at both the 8-h and 3-h discharge rates. Their capacity decreased by only 12% as the discharge rate was increased from 135 to 318 A. However, individual module capacities at the 8-h rate varied (minimum to maximum) by ~7%. At the 3-h rate, the variation increased to ~12%. The module-

Table 2. SPECIFICATION SUMMARY OF VRLA BATTERY TYPES

Manufacturer	GNB	JCI
Model Number	85A25	LL12-70
Configuration	3 cells in series	15 modules in parallel
Electrolyte	absorbed	gelled
Voltage, V	6	12
Capacity, Ah		
8-h Rate	1040	1080
3-h Rate	816	954
Size, m^3	0.122	0.605
Weight, kg	240	570
Cooling	natural convection	100-cfm blower

to-module capacity variations were discussed with the manufacturer, who recommended that the weakest module be given a special 24-h charge with a constant-voltage (CV) level of 2.45 V. Following the special charge, the capacity of the weakest module increased by ~9%, and the variation between modules decreased to 7.4%. The manufacturer did not deem a 7% variation in module capacities to be excessive.

Life Evaluation Activities/Status

The GNB modules were received in November 1988 and the JCI modules were delivered in February 1989. Each module completed acceptance and baseline performance tests prior to life testing.[2] In May 1989, two modules from each manufacturer were placed on life test at 30°C (80 and 100% DOD), and a third module was placed on accelerated life testing at 50°C (100% DOD). After a high-temperature charge procedure was established, a fourth GNB module was placed on test at 50°C (80% DOD) in September 1989.

All life cycles are performed with 3-h rate discharges to a voltage limit. A discharge cut-off voltage (DCOV) of 1.75 V/cell is used on all 100% DOD modules at both 30 and 50°C. A DCOV of 5.64 and 5.66 V is used for 80% DOD on the GNB modules at 30 and 50°C, respectively. The 80% DOD DCOV for the JCI modules is 11.45 and 11.51 V at 30 and 50°C, respectively. A 3-h discharge rate was selected to maximize the total Ah per day of life testing. Daily charges are limited to 8 h or 105% return for 30°C operation. The 8-h time limit for daily charges was selected as representative of that in utility applications. Equalization charges (24 h or 110% return) are performed about every 25 cycles. The charge method and overcharge were to be defined by the manufacturers.

Initially, constant-current/constant-voltage (CI/CV) charging was recommended by both manufacturers (CV = 2.35 V/cell with -5 mV/°C temperature compensation at >25°C). The time needed to achieve the desired 105% charge return from 100% DOD was excessive for both the

GNB (~18 h) and JCI (~26 h) modules. These results were discussed with each manufacturer, and GNB requested that their charge procedure be changed to a CI/CV/CI method to ensure an 8-h daily charge return of 105%. JCI was satisfied with an 8-h charge return of ~103% and recommended the continued use of CI/CV charges with a CV of 2.35 V/cell.

The capacity history of the two GNB modules operating at 30°C is given in Fig. 1. The GNB module operating to 100% DOD still retains ~87% of its initial 1009-Ah (5885-Wh) capacity after >400 cycles. The 80% DOD module has accrued over 500 cycles and still retains ~93% of its initial 80% DOD capacity (770-Ah, 4583-Wh). After ~460 cycles, discharges to 100% DOD were performed on the module being life tested at 80% DOD. The results (given by open squares in Fig. 1) show that the 100% DOD capacity had declined by only 5% after more than 400 cycles of operation. Equalization charges (24 h or 110% return) are being performed about every 25 cycles (indicated by I symbol in Fig. 1). After 200 cycles, the 100% DOD GNB module developed a noticeable difference in discharge capacity for daily (105% return) and 24-h equalization (~108% return) charges. The equalization charge provides an increase in capacity that rapidly declines on the subsequent cycles with 8-h charges. The development of this sensitivity to overcharge and/or charge method indicates that the charging efficiency of the GNB module has declined with life and that a daily charge of >105% may be required.

Two GNB modules are undergoing accelerated life testing at 50°C. The first module started 50°C operation in June 1989 after completing ~30 cycles of acceptance and baseline performance testing at 100% DOD and 30°C. To operate at 50°C, a higher charge return (≥115%) and longer charge time (≥17 h) were needed. To acquire charge acceptance vs. temperature data and establish a satisfactory high-temperature charge procedure, ~170 cycles were accrued on this GNB module. In September 1989, the first module was placed on 50°C, 100% DOD life evaluation, and a second module was placed on 50°C, 80% DOD life

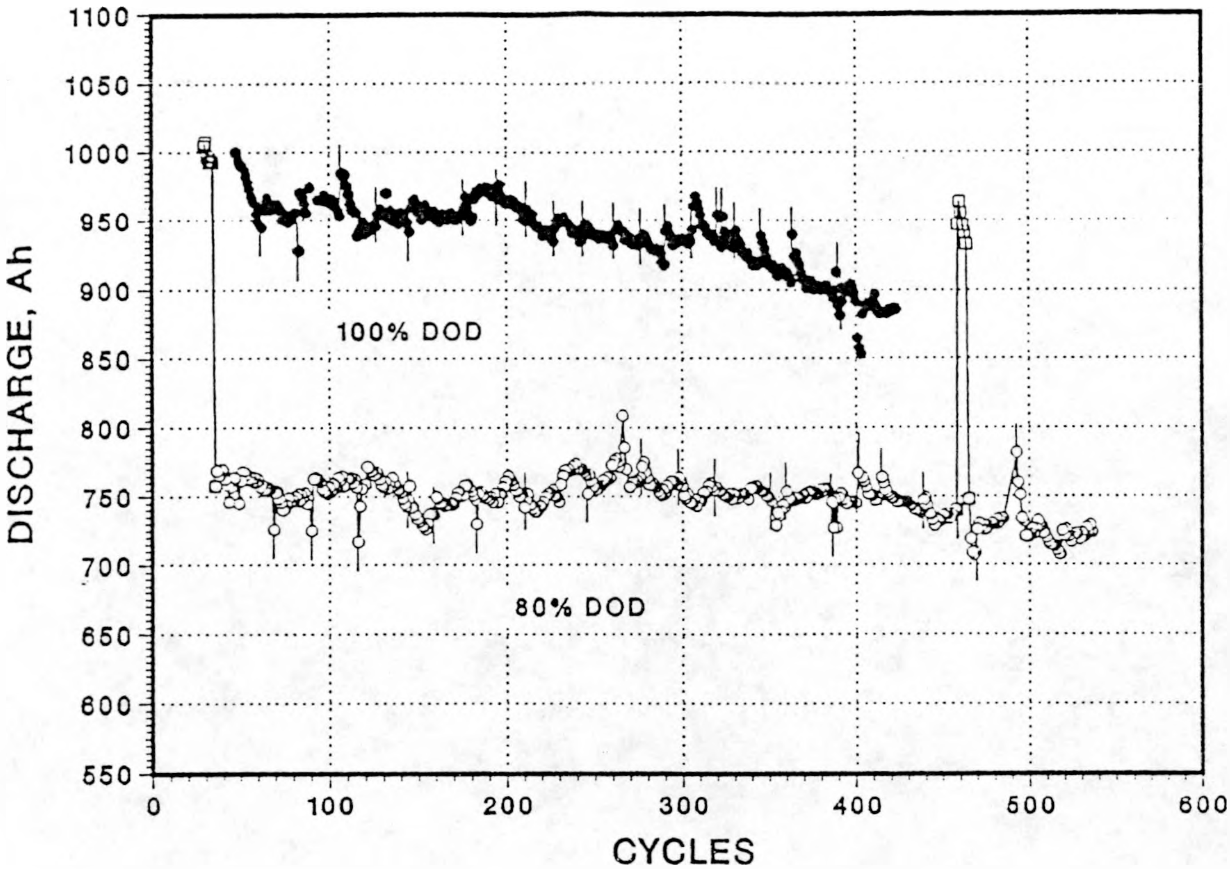

Fig. 1. Capacity History of Two GNB Modules Operating to 80% and 100% DOD at 30°C.

evaluation (previously accrued ~55 cycles at 30°C). The capacity history of these modules at 50°C is given in Fig. 2. Both modules had an initial 30°C capacity of ~1000 Ah prior to high temperature operation. The capacity of both GNB modules increased by ~13% when the temperature was increased from 30 to 50°C. This increase in capacity is less than that exhibited by flooded-electrolyte types of lead-acid batteries (>20% for 20°C increase). The VRLA batteries cannot attain the full benefit of high temperature operation because their performance appears to be electrolyte limited. It was also observed that the increase in GNB module capacity with temperature was only temporary and rapidly declined with cycling to about the level exhibited with 30°C operation. Both GNB modules have accrued ~150 cycles at 50°C. The 100% DOD module retains ~84% of its initial capacity and the 80% DOD module

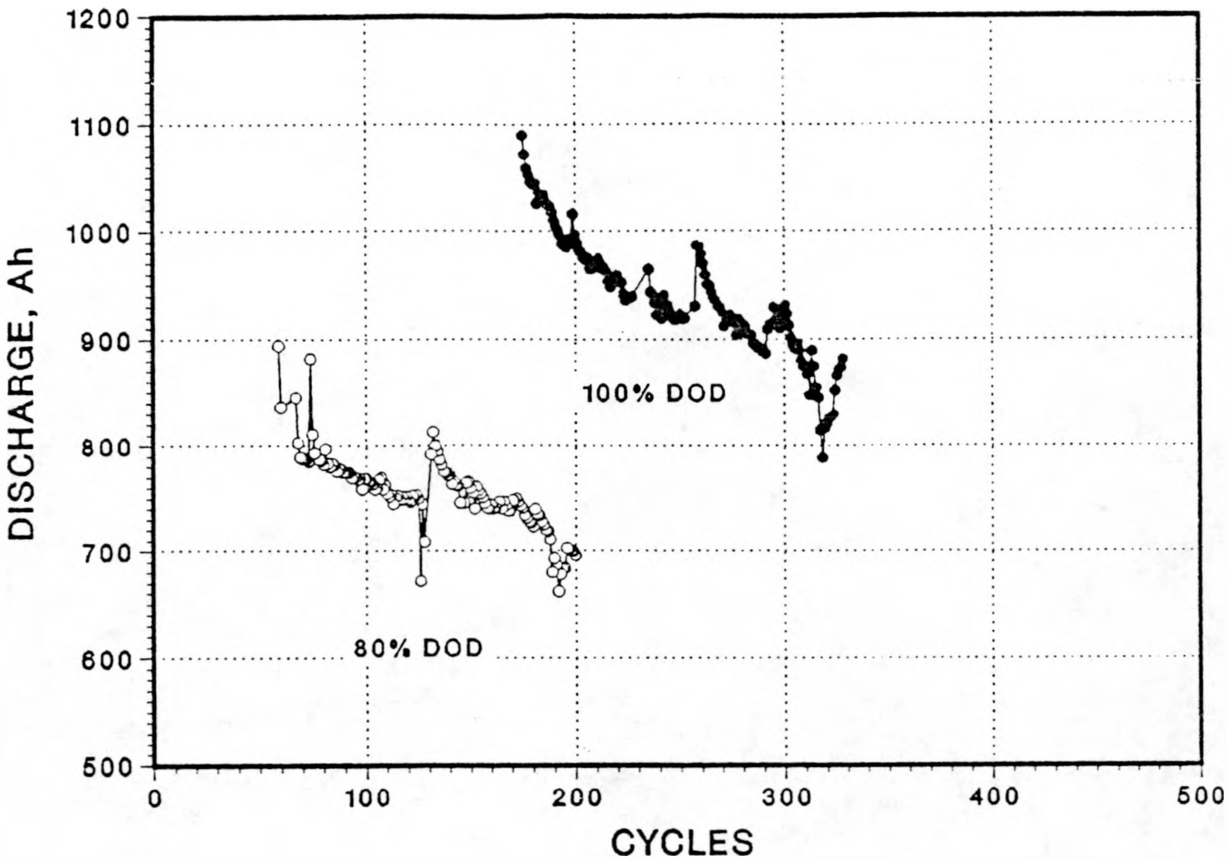

Fig. 2. Capacity History of Two GNB Modules Operating to 80% and 100% DOD at 50°C.

retains ~89% of its initial 80% DOD capacity.

Testing of the JCI gelled-electrolyte modules was also started in May 1989. The capacity history of the two JCI modules operating at 30°C is given in Fig. 3. The module operating to 100% DOD had an initial capacity of 938 Ah (11.1 kWh) and attained a maximum capacity of 976 Ah (11.5 kWh) after ~80 cycles. Equalization charges had no noticeable effect on the capacity of the JCI modules in that they yielded no noticeable increase in charge return for the increased charge time (8 ⇒ 24 h). After ~130 cycles, the capacity of the module cycling to 100% DOD started to decline at a rate of ~1.6 Ah/cycle. The manufacturer was consulted and various charge procedure revisions were recommended and applied in unsuccessful attempts to halt the capacity decline. The module reached end-of-life (module capacity <80% of rated)

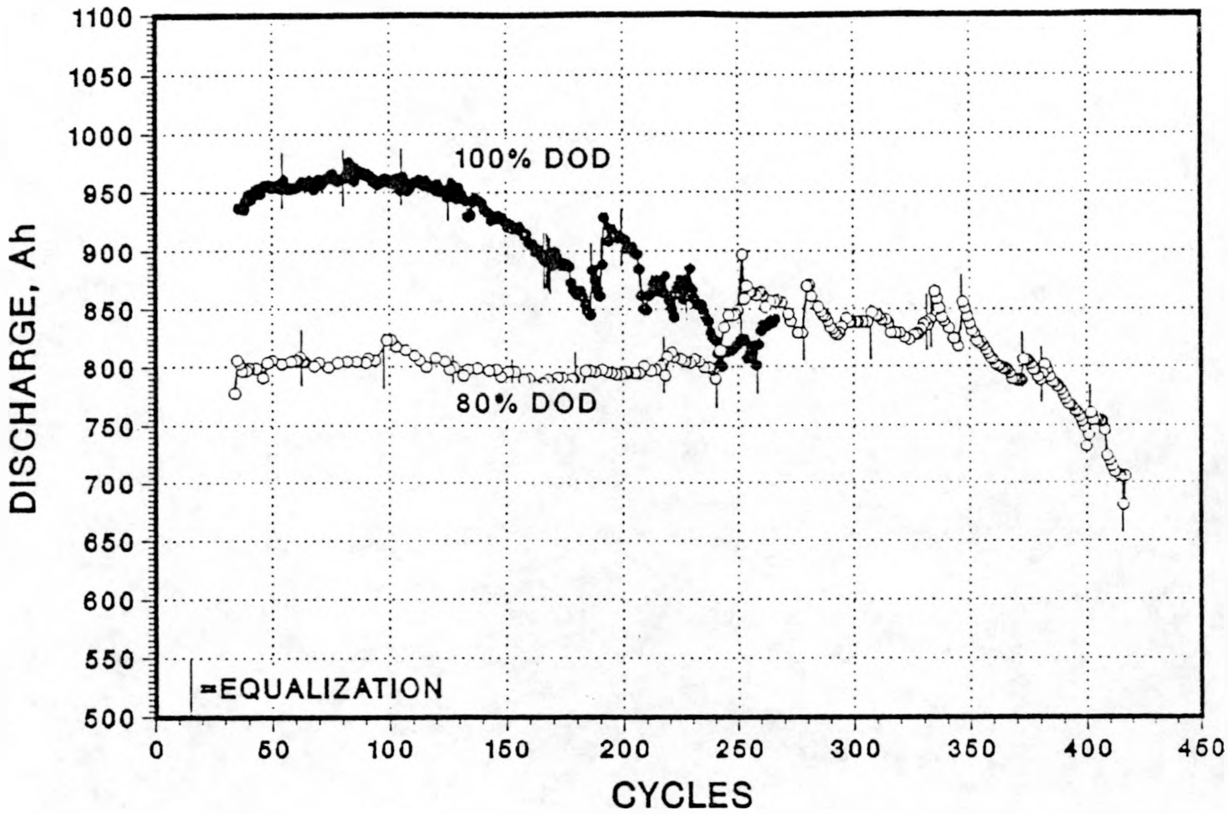

Fig. 3. Capacity History of Two JCI Modules Operating to 80% and 100% DOD at 30°C.

after 243 cycles. Excessive overcharging provided temporary improvements in capacity but the 100% DOD, 30°C life evaluation was halted after 266 cycles. This module is undergoing post-test teardown analyses at ANL.

The JCI module on 80% DOD, 30°C life test has completed over 400 cycles and retains about 65% of rated capacity. The module had an initial 80% DOD capacity of 806 Ah (9.74 kWh). After 240 cycles, its CI/CV charges were changed to CI/CV/CI charges to satisfy a JCI recommendation to increase the charge return from 102% to 105%. The CI/CV/CI charges resulted in a module capacity increase to ~840 Ah. After 415 cycles, however, the module is near the end of its test life (module capacity <64% of rated). Charge procedures are being reviewed in an attempt to improve the 80% DOD capacity.

A JCI module was placed on accelerated life evaluation at 50°C and 100% DOD in June 1989 after completing ~30 initial test cycles at 30°C. The module accrued 151 cycles before it was removed from testing due to low capacity. About 70 of its life cycles were conducted at temperatures above 30°C. With the start of 50°C operation, the capacity of the JCI module increased by only ~3%, as compared to the 13% for the GNB modules. Its capacity rapidly decline with cycling (>1%/cycle) as did the GNB modules. Various charging revisions were implemented in an attempt to avoid the capacity decline at different elevated temperatures. However, after 105 cycles, module capacity was <650 Ah. With special conditioning and high overcharges, a capacity of 850 Ah was achieved at 30°C but steadily decreased to less than 800 Ah after 150 cycles. This module was returned to JCI for special testing and teardown analyses.

Post-Test Analyses

Argonne has started a post-test analyses on the JCI module (#2) that was cycled to 100% DOD at 30°C and accrued 266 cycles. The analyses involve both operational and teardown analyses. The operational analyses include (1) measurement of the 15 individual 12-V battery (monoblock) capacities, (2) identification of the best and worst cells in the lowest performing monoblock by using cell voltage measurements, and (3) identification of the limiting electrode by using reference electrode measurements in the best and worst cells. The teardown analyses include (1) visual inspection of components from the best and worst cells and (2) preparation/analyses of samples from the best and worst cells for electrode characterization and component degradation analyses. This work will be reported at a later date.

JCI has completed a post-test teardown analyses of the module (#3) that ANL operated to 100% DOD at elevated temperatures (30 to 50°C). The module accrued 151 cycles, with ~70 cycles being performed at temperatures >30°C. JCI individually cycled each of the 12-V batteries (monoblocks) from module #3 to measure its capacity; 3 remained level at ~78 Ah (~108% of their 72 Ah rated capacity), 9 increased from ~58 to ~65 Ah with cycling, and 3 improved from ~35 to 56 Ah. All 15 batteries were then toredown for inspection. Each of the three low capacity batteries contained a bad cell that had a broken positive plate lug strap. The cause of failure was identified as corrosion of the positive cast on strap, and monoblock capacities were correlated with the degree of corrosion. The corrosion failure was attributed to a manufacturing defect caused by poor fusion of the plate lug to the positive cast on strap. This resulted in active crevice type corrosion that led to separation of the plate lugs and straps. The cell grids and plate paste remained in good condition, indicating that in the absence of the manufacturing defect, additional cycle life remained.

Future Activities

The four GNB modules undergoing life test will continue as defined in the original test plan. GNB and ANL are reviewing the acquired test data and discussing possible charge revisions to the discharge capacity following daily recharges. GNB is also sponsoring out-gas measurements and analyses of a fifth cell delivered to ANL. Out-gas measurements will also be acquired on the GNB modules operating at 30 and 50°C in the EPRI life evaluation.

JCI is to deliver two new modules in April 1990 to replace earlier modules having the previously described manufacturing defect. These modules will undergo life testing to 100% DOD at 30 and 50°C. These were selected to acquire life data in a minimal time period.

Argonne will also complete the post-test analyses of JCI module #2 to verify the JCI findings for module #3. The GNB modules under test at 50°C are expected to reach end-of-life within the next several months and will then undergo post-test analyses. These modules are expected to provide valuable data regarding high-temperature and DOD failure mechanisms.

References

1. Accelerated Life Evaluation of Valve-Regulated Lead-Acid Batteries
   W. H. DeLuca and J. F. Miller
   Proc. of the Int. Lead/Zinc Research Organization (ILZRO) Lead-Acid Battery Seminar, Orlando, FL, May 4-5, 1989, pp. 370-378 (1989)
2. Life Evaluation of Valve-Regulated Lead-Acid Batteries for Load-Leveling Applications
   W. H. DeLuca, J. F. Miller, C. E. Webster, and R. L. Hogrefe
   Proc. of the Second Int. Conf. on Batteries for Utility Energy Storage, Newport Beach, CA, July 24-28, 1989, Session III, Paper 2 (1989)

Acknowledgment

This research is sponsored by the Electric Power Research Institute (EPRI) and, in part, by the International Lead Zinc Research Organization (ILZRO).