CONF-900801--20

CONF-900801--20

DE90 013649

LIFE EVALUATION OF VALVE REGULATED LEAD-ACID BATTERIES FOR CYCLING APPLICATIONS

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

Electrochemical Technology Program
Argonne National Laboratory
Argonne, IL 60439

Paper Number 900052

25th Intersociety Energy Conversion Engineering Conference
August 12 - 17, 1990
Reno, Nevada

LIFE EVALUATION OF VALVE REGULATED LEAD-ACID BATTERIES FOR CYCLING APPLICATIONS

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

Electrochemical Technology Program
Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

Argonne National Laboratory (ANL) 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 ~470 cycles. The GNB module operating to 80% DOD at 30°C has accrued ~600 cycles and retains ~92% 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 ~170 cycles; the 100% DOD module retains ~84% of its initial capacity, and the 80% DOD module retains ~89% of its initial 80% DOD capacity. Only one of the gelled-electrolyte JCI modules remains on test (30°C, 80% DOD). It retains ~86% of its initial 80% DOD capacity after >450 cycles. The other two JCI modules were removed from test because they reached end-of-life. Teardown analyses at JCI indicate that a manufacturing defect caused premature failure of one module. The second module is undergoing teardown analyses at ANL.

INTRODUCTION

Valve-regulated lead-acid (VRLA) batteries are primarily used in standby and uninterruptible power source applications at present. Insufficient data are available to determine their performance and life in repetitive cycling applications. Argonne National Laboratory (ANL) is conducting a life evaluation of VRLA batteries to determine their suitability and life in repetitive deep-discharge cycling applications. This work is sponsored by the Electric Power Research Institute (EPRI) and, in part, by 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 was 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 underwent teardown examination and analyses to identify the failure mode. End-of-life was 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 twelve 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 the DC-to-AC power conversion equipment has a specific minimum operating voltage level.

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 manu-

Table 1. VRLA Battery Test Matrix

Module Number	Test Temp., ^oC	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

Table 2. VRLA Battery Characteristics

Manufacturer	GNB	JCI
Model Number	85A25	LL12-70
Configuration	3 cells in series	15 modules in parallel
Electrolyte	absorbed	gelled
Positive Plate Alloy	Antimony	Calcium
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

factured 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%) delivered to ANL 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. Module capacity was 23% lower at the 3-h rate (272 A) than that measured at the 8-h rate (130 A); this decline is in close agreement with that specified by GNB (Table 2). The average capacity of the delivered 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-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 DCOV for the 80% DOD 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 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 limit) are performed about every 25 cycles to ensure that full capacity is maintained. The charge method and overcharge for each battery type were defined by the manufacturers and will be discussed in a later section.

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 >450 cycles. The 80% DOD module has accrued ~600 cycles and still retains ~92% 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% is needed to maintain full capacity.

In June 1989, the first GNB module was operated at 50°C, and soon after studies were initiated to establish a satisfactory high-temperature charge procedure. Plots of module capacity, temperature, and charge return vs.

cycles during this study are given in Fig. 2. About 30 cycles of acceptance and baseline performance tests were conducted at 100% DOD and 30°C. A capacity of ~1000-Ah was achieved prior to high temperature operation. With the start of 50°C operation (cycle #28), the capacity of the GNB module increased by ~13%, but rapidly declined with cycling (>1%/cycle). GNB was consulted and the charge procedures altered. Reducing the initial constant-current (CI) charge rate (300 ⇒ 150 A) had no effect, but increasing the charge return (105% ⇒ 110%) stopped the rapid decline in capacity (cycle #50) and recovered some of the loss. The operating temperature was returned to 30°C (cycle #53) and the capacity restored to almost its initial level by increasing the charge return from 105% to 110%. The temperature was then increased in 5°C increments and the overcharge increased as needed to prevent any loss in capacity. The results showed that a charge return of 115% and extended charge times (≥17 h) were needed to operate at 50°C.

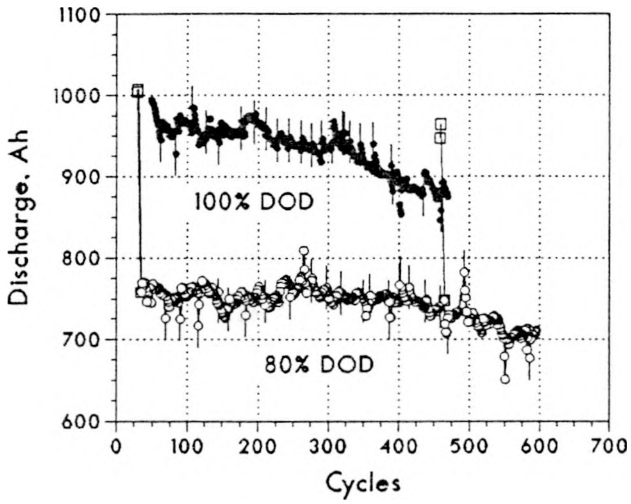

Fig. 1: Capacity History of Two GNB Modules Operating to 80% and 100% DOD at 30°C.

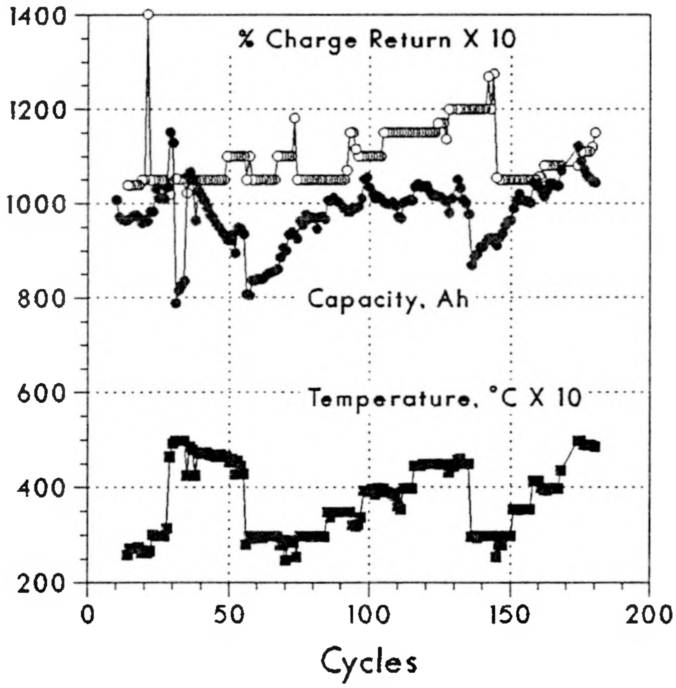

Fig. 2: Plots of GNB Module Capacity, Operating Temperature, and Charge Return with Cycling during Study to Establish a 50°C Charge Regime.

In September 1989, the first module was placed on 50°C, 100% DOD life evaluation after previously accumulating ~170 cycles. A second module was placed on 50°C, 80% DOD life evaluation (previously accrued ~55 cycles at 30°C). The capacity history of these modules at 50°C is given in Fig. 3. The second module also had an initial 30°C capacity of ~1000 Ah and exhibited a capacity increase of ~13% with temperature (30 ⇒ 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 increase in capacity with temperature of both modules was only temporary and rapidly declined with cycling to about the level exhibited with 30°C operation. VRLA battery performance appears to be electrolyte limited and therefore unable to attain the full benefit of high temperature operation. Both GNB modules have accrued ~170 cycles at 50°C. The 100% DOD module retains ~88% of its initial capacity (1000 Ah at 30°C), and the 80% DOD module retains ~86% of its initial 80% DOD capacity (800 Ah at 30°C).

Testing of the JCI gelled-electrolyte modules was started in May 1989. The capacity history of the two JCI modules operating at 30°C is given in Fig. 4. The module operating to 100% DOD had an initial capacity of 938 Ah (11.1 kWh) and attained a maximum capacity of 976 Ah

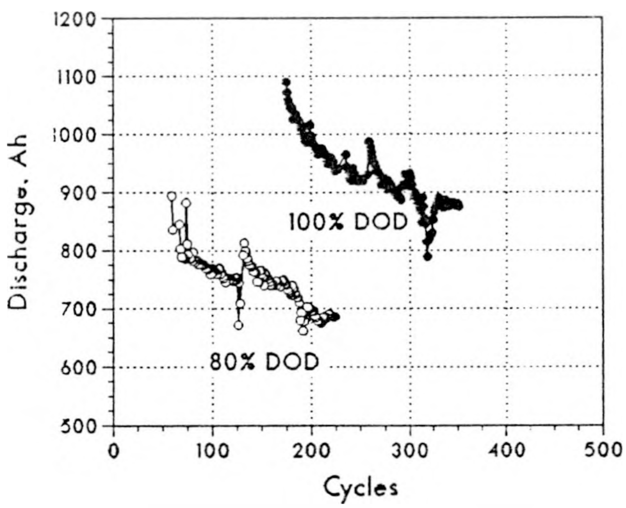

Fig. 3: Capacity History of Two GNB Modules Operating to 80% and 100% DOD at 50°C.

(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) 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 450 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, the module was near the end of its test life (module capacity <64% of rated). The charge return limit was then removed to use the full daily (8 h) and equalization (24 h) charge times. This has allowed higher charge returns (109%) and resulted in an increase in 80% DOD capacity by 10%.

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. Plots of module capacity, temperature, and charge return vs. cycles during the period at elevated temperatures are given in Fig. 5. 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 declined with cycling (>1%/cycle) as did the GNB modules. The capacity decline at 50°C was stopped by increasing the charge return to 110%, and the capacity loss that occurred at 50°C was restored with cycling at 30°C. The temperature was then increased in 5°C increments to determine the overcharge needed to prevent any losses in capacity. After ~85 cycles, the capacity started to decline at a rapid rate, and module capacity was <650 Ah after 105 cycles. After changing to CI/CV/CI charges and furnishing high overcharges, a capacity of 850 Ah was achieved at 30°C but could not be maintained. Module capacity decreased to less than 800 Ah at 30°C after 150 cycles. This module was returned to JCI for special testing and teardown analyses.

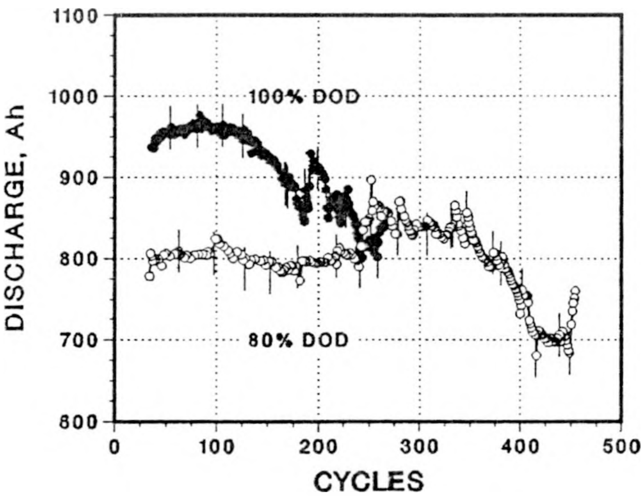

Fig. 4: Capacity History of Two JCI Modules Operating to 80% and 100% DOD at 30°C.

VRLA BATTERY CHARGING

The matrix operating conditions used in the life tests at ANL have revealed valuable insights on VRLA battery charging, including:

1. an adequate charge return (≥105%) is not achievable in 8 h with CI/CV charging because the immobilized electrolyte results in very low CV charge rates,
2. elevated operating temperatures reduce VRLA battery charge efficiency and require the application of higher charge returns (charge return increased ~0.5%/°C at ANL for stable capacity),
3. VRLA battery charge efficiency decreases with cycle life.

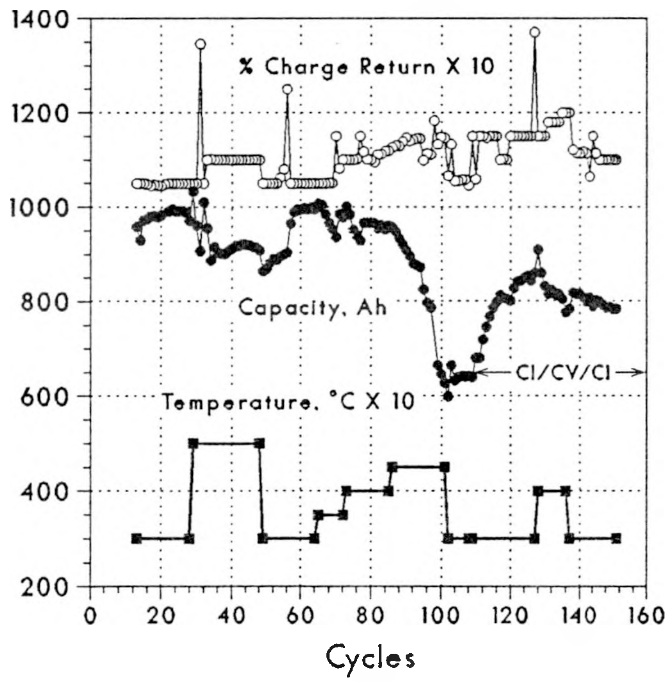

Fig. 5: Plots of JCI Module Capacity, Operating Temperature, and Charge Return with Cycling to Study Elevated Temperature Operation.

For the ANL tests, the only constraints on charging were that daily charges be limited to 8 h (30°C operation) and equalization charges be limited to 24 h. The 8-h time limit for daily charges was selected as representative of that in utility applications. The charge method, level of overcharge, and frequency of the equalization charges were defined by each manufacturer for its battery. Initially, CI/CV charges to a 105% return were 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. Increasing the CI charge rate to 300 A (~3-h rate) and the CV level to 2.40 V/cell achieved an 8-h charge return of only ~104%. These results were discussed with each manufacturer, and GNB requested that its 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 charge procedures defined and used at the start of life testing are given in Table 3.

Table 3. Charge Procedures for VRLA Battery Life Tests

	GNB 85A25	JCI LL12-70
DAILY CHARGES		
• Charge Method	CI/CV/CI	CI/CV
• Initial CI Rate, A	300	300
• CV Level @ 25°C, V/cell	2.40	2.35
• Final CI Rate, A	10	~0.2
• Termination	8-h or 105% Return	
EQUALIZATION CHARGES		
• Charge Method	CI/CV	CI/CV
• Initial CI Rate, A	300	300
• CV Level @ 25°C, V/cell	2.40	2.40
• Cycles/Equalization	~25	~25
• Termination	24 h or 110% Return	

Table 4. GNB Battery Charge Variation with Life at 30°C

Mod. DOD %	CI/CV/CI Daily Charge Cycle No.	Time h	Return %	Final V	CI/CV Equalization Cycle No.	Time h	Return %	Final A
100	45	8.0	104.7	7.48	82	24.0	108	0.98
100	327	7.7	105	7.08	320	21.2	110	2.69
80	38	7.0	105	7.47	68	24.0	109	1.71
80	412	5.2	105	7.07	414	10.6	110	4.40

The CI/CV/CI charges on the 100% DOD GNB module at 30°C initially provided a charge return of 104.7% in 8 h. The CV charge started after a return of ~60% and continued for ~4 h. At the end-of-charge (EOC) 10-A rate, a module voltage of 7.48 V was obtained (~2.49 V/cell). In comparison, the CI/CV charges provided the JCI modules an 8-h return of ~102% and the CV charge started after a return of about 90%. The variation in battery response with life to the initial charge regimes is summarized for the GNB modules operating at 30°C to 80 and 100% DOD in Table 4. Initially, the charges were terminated at the time limit, but were stopped at the charge return limit after 300 to 400 cycles. The time needed to provide the daily (105%) and equalization (110%) charge return decreased significantly with life because the average current during the CV charge period increased. The CI/CV charges had both a slower current taper and a higher EOC current with life. The CI/CV/CI charges had a lower EOC battery voltage with life for the same charge return. These changes indicate a decline in charge efficiency with life. Based on these data, the charge return limit was removed, and the full daily (8 h) and equalization (24 h) charge times are being used on all modules. This has increased the charge return for the 30°C GNB modules to 108% at 80% DOD and to 106% at 100% DOD. The remaining JCI module (80% DOD at 30°C) increased its return from 105 to 109%, and a 10% capacity increase resulted (Fig. 4).

CELL PRESSURE AND OUTGAS MEASUREMENTS

GNB has sponsored a study to analyze the VRLA cell outgas and provided ANL with a new three-cell module and special cell vents that allow measurement of the internal pressure and outgases from individual cells. The equipment for this study also made it possible to obtain outgas data on older EPRI cells under life test. The pressure and outgas data given in Table 5 were acquired on two of the cells in the new GNB module (100% DOD, 30°C) and three older cells (100% DOD, two at 30°C and one at 50°C). The same valve was used for measuring outgas in four of the cells; only new cell #1 used a second

Table 5. GNB Cell Pressure and Outgas Measurements

Module	New GNB		EPRI		EPRI
Temp., °C	30		30		50
Cell Number	1	3	1	3	1
Cycle Number	31	32	373	328	301
Charge Return, %	108	105	105	105	115
Max. Pressure, psi	4.5	3.5	3.9	3.5	3.4
Max. Flow Rate, cm^3/min	50	20	12	~1	8
Outgas Volume, L	12.4	3.9	1.4	~0	3.1

valve (releases at a higher pressure). Outgassing was observed at two points during charging. The first is at the end of the initial CI charge when the cell temperature is near maximal, and the second is near the end of charge when the cell voltage exceeds 2.4 V. The outgas flow rate and volume were highest on the new cells. This is due to (1) the presence of excess electrolyte installed during assembly, and (2) the higher EOC voltages attained (Table 4). At 30^{o}C, outgassing diminished with cycle life. However, cycling at higher temperatures (50^{o}C) resulted in a factor of two to three increase in outgas volume. The outgassing at 50^{o}C is not sufficient to cause cell dryout. It should also be noted that the valve pressure release point did not vary significantly between 30 and 50^{o}C operation.

POST-TEST ANALYSES

Johnson Controls completed a post-test teardown analyses of the JCI module that ANL operated to 100% DOD at elevated temperatures (30 to 50^{o}C). The module accrued 151 cycles, with ~70 cycles being performed at temperatures >30^{o}C. JCI individually cycled each of the fifteen 12-V batteries (monoblocks) in the module to measure its capacity; three monoblocks provided ~78 Ah for several cycles (~108% of 72-Ah rated capacity), nine increased from ~58 to ~65 Ah with cycling, and three improved from ~35 to 56 Ah. All 15 monoblocks were then inspected. Each of the three monoblocks at <80% rating 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 additional cycle life will be attained if the the manufacturing defect is eliminated.

Argonne has started a post-test analyses on the JCI module that was operated to 100% DOD at 30^{o}C for 266 cycles. The analyses involve both operational and teardown analyses. The operational analyses include (1) capacity measurement of each monoblock, (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. Capacity measurements on the 15 monoblocks in the module showed that ten provided ≥100% of their 72-Ah rating, four attained from 12 to 74% of rating, and one had a very high resistance. A monoblock was selected for further study, and reference electrodes measurements in its best and worst cells showed that the limiting electrode was the negative. Teardown analyses have been started to (1) visually inspect components from the best and worst cells and (2) analyze samples for electrode characterization and component degradation. Preliminary inspection shows that corrosion of the positive cast on strap and active material changes are present. This work is continuing and will be reported at a later date.

FUTURE ACTIVITIES

Life testing of the four GNB modules will be continued. A proposal is being reviewed to remove just the limiting cell at module end-of-life and continue operating the remaining cells to improve lifetime statistics and acquire more cell performance data. Individual cell performances are being examined to determine the present variation. The GNB modules under test at 50^{o}C are expected to reach end-of-life within the next several months and will then undergo post-test analyses at ANL. These modules are expected to provide valuable data regarding high-temperature and DOD failure mechanisms.

JCI delivered two new modules to ANL in April 1990 to replace the previous modules with the manufacturing defect. These modules will undergo life testing to 100% DOD at 30 and 50^{o}C. These operating conditions were selected to acquire life data in a minimal time period. ANL will also complete the post-test analyses of the JCI module operated at 30^{o}C and 100% DOD and compare the findings with those obtained by JCI on the 50^{o}C, 100% DOD module.

REFERENCES

1. W. H. DeLuca et al, "Accelerated Life Evaluation of Valve-Regulated Lead-Acid Batteries," Proc. Int. Lead/Zinc Research Organization (ILZRO) Lead-Acid Battery Seminar, May 1989, pp. 370-378

2. W. H. DeLuca et al, "Life Evaluation of Valve-Regulated Lead-Acid Batteries for Load-Leveling Applications," Proc. Second Int. Conf. on Batteries for Utility Energy Storage, July 1989, Session III, Paper 2

ACKNOWLEDGMENT

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