RELATION OF CONDUCTANCE TO CAPACITY OVER THE LIFE OF LARGE FORMAT VRLA PRODUCTS

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INTRODUCTION

A recent Google search on VRLA batteries and conductance showed more than 180 scholarly works on the relation of VRLA performance to conductance or impedance measurements. The degree of study on this topic shows the level of interest of battery manufacturers, equipment manufacturers and battery users on the use of conductance equipment to determine battery performance. The basic claim of conductance and impedance equipment manufacturers is that changes that cause capacity loss, and ultimately, failure in the internal conditions of VRLA batteries can be measured using AC impedance methods. Tracking conductance or impedance therefore will detect capacity loss and failing cells.

Recently, what had been a matter of testing and debate has taken on a significant economic overtones. Several large battery users have demanded that conductance measurements be used as the basis for warranty replacement, and have written this requirement into purchasing contracts. Given the cost of replacing VRLA products, and the cost of unanticipated outages for battery users, errors in setting the parameters for "good" and "bad" ohmic readings can have a significant impact on both battery producers and customers.

Generally, battery manufacturers are responsible for determining the conductance/impedance behavior for their products and communicating these to the users. Accelerated life testing methods must be used for new products (or for new measuring techniques) to determine whether there is a valid correlation of impedance or conductance behavior with capacity data over the expected life of the product. If a valid correlation is found, the use of internal impedance measures may be used to estimate battery behavior. If no correlation exists – or if the behavior changes as the cells age – manufacturers and users may be exposed to significant risks when impedance or conductance measurements ***alone*** are used as a judge of cell performance.

This paper looks at the conductance behavior of several brands of VRLA products during accelerated life testing. Typical conductance calculations (comparison to absolute conductance limit, percent change from original reading, regression of capacity data to conductance data) are used to estimate if product failure is impending, and these results are compared to actual capacity results.

EXPERIMENTAL

A total of four different battery brands were selected for the test program. The brands are identified as follows:

Brand A: VRLA – 700 AH, sample size 6 cells
Brand B: VRLA – 665 AH, sample size 6 cells
Brand C: VRLA – 460 AH, sample size 6 cells
Brand D: Lithium Ion, 90 AH, sample size 6 cells

All cells were received into the testing facility as production quality product, shipped as ready for customer use. A standard set of characterization tests were performed on receipt. These included:

- Open Circuit Voltage
- Cell Weights

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- Conductance Measurements (using a Midtronics CTM-100 meter)
- Float voltage spread and current measurement at room temperature
- Capacity at the published C/8 discharge rate to 1.75 VPC. (C rate for the Li-Ion cells)

Accelerated Testing: The testing program for the VRLA products was based on the SR-4228[1] protocols. The accelerated test environment was 71°C and 20% rH. The products were charged at the manufacturers recommended voltages while at temperature. Cells were removed from the environmental chambers at intervals of approximately 30 days, simulating approximately 2 years of life at 25°C for the VRLA products. Test conditions for the Li-Ion cells are described in the results section for Brand D, page 9.

On removal from the test chamber the cells were allowed to cool to room temperature while still on constant voltage charge for a minimum of 24 hours. Float current was measured once the cells cooled and stabilized. Capacity testing was repeated at the C/8 rate, with percent capacity determined for each cell as the cell passed 1.75 VPC. Cell recharge was performed at constant voltage charge for a minimum of 72 hours. The cells were then weighed, conductance values measured using the Midtronics device, and if the capacity was > 80%, the system was reassembled and put back into the test chamber for additional aging. Teardowns were performed on any cells failing to reach 80% capacity or that were otherwise incapable of continuing the test. The teardowns recorded the gross condition of the cell, degree of corrosion in any components, paste and plate conditions, and specific gravity of the electrolyte.

RESULTS AND DISCUSSION

Results were obtained from each of the battery brands tested. The data obtained were reviewed to determine if it was possible to use the conductance and capacity data gathered to predict cell or system failure. For two of the brands classic capacity failure was found – system run time <80% along with individual cell failures. One brand did not show capacity failure during the testing, but did succumb when the container system failed. The lithium ion product "system" was accelerated to below 80% capacity, however, no estimate of product life can be obtained until data from further testing at lower temperature become available. Following are the results and discussion for each of the different models.

Brand A: Capacity results vs. time are shown on Table 1. At the 163 day mark capacity for five cells were limited to 81% due to one cell running 68.7%. Two cells were removed from the test due to high current demand (the demand pushed the charging system into current limit). On the subsequent test the system failed catastrophically, with system voltage going to zero on application of current. Two cells were found to have open circuit response to load current, a third had less than 50% capacity, and only one cell retained useful life. Teardown of the system showed failure due to corrosion and detachment of the positive straps from the plate lugs, combined with dryout and positive plate corrosion.

TABLE 1. BRAND A CAPACITY AND CONDUCTANCE DATA

Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	mho	Cap	mho	Cap	Mho	Cap	mho	Cap	mho	Cap	mho
0	103.2	3168	100.1	3014	103.2	3037	101.1	2917	103.2	3181	103.2	3207
34	106.6	2849	102.1	2696	106.6	2764	104.4	2688	106.6	2998	106.6	2934
60	98.1	1958	94.6	2184	99.3	2198	93.3	2070	99.3	2066	99.3	2225
91	94.7	1806	94.4	2038	96.9	1838	89.9	1774	89.2	1758	96	1873
120	96.2	1860	93.7	1879	94.4	2406	91.6	1827	89.2	1717	96.4	1902
142	96.6	1717	94.2	1738	96	1722	93.6	1789	87.5	1643	96.8	1816
163	81.7	1282	81.7	1630	81.7	1622	81.7	1565	68.7	1117	81.7	1463
193	Removed		81.3	1323	43.5	790	0	360	Removed		0	39

A chart of the average capacity and conductance values is shown on Figure 1. The useful portion of the batteries life was 163 days-before the thermal runaway effects in cells 1 and 5 swamped the charger output. Total capacity drop during the useful portion of the battery life was roughly 25%, the average conductance drop was 50%. The conductance drop occurred at two times during the test, a 35% drop between test start and 90 days, and then a 15% drop between 140 days and 163 days. The capacity also had an initial drop, plateau, and final drop. The first capacity drop between 0 and 90 days was about 11% on average. The second capacity drop was more pronounced totaling 14% between 140 and 163 days.

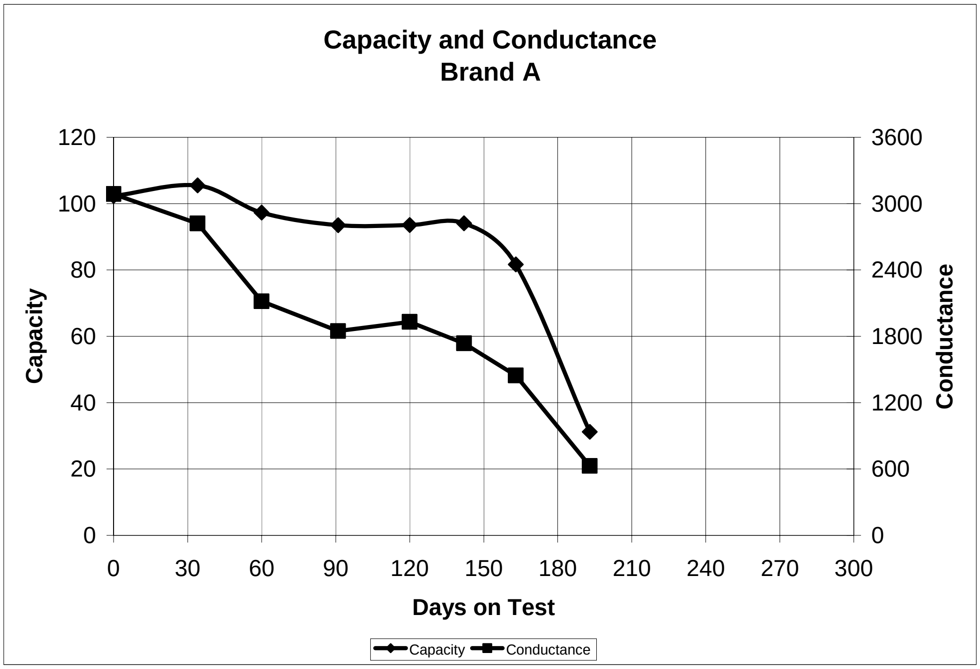

Figure 1

As noted in the introduction, some customers are replacing capacity testing with conductance readings as the basis for determining battery performance. A natural question is whether the conductance readings taken during the test could be used predict the capacity of the product. One method is to compare the change in conductance to capacity. Table 2 shows the cell capacities for Brand A with the ratio of test conductance to as new conductance.

TABLE 2 BRAND A CAPACITY AND CONDUCTANCE RATIO												
Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn
0	103.2	100%	100.1	100%	103.2	100%	101.1	100%	103.2	100%	103.2	100%
34	106.6	90%	102.1	89%	106.6	91%	104.4	92%	106.6	94%	106.6	91%
60	98.1	62%	94.6	72%	99.3	72%	93.3	71%	99.3	65%	99.3	69%
91	94.7	57%	94.4	68%	96.9	61%	89.9	61%	89.2	55%	96	58%
120	96.2	59%	93.7	62%	94.4	79%	91.6	63%	89.2	54%	96.4	59%
142	96.6	54%	94.2	58%	96	57%	93.6	61%	87.5	52%	96.8	57%
163	81.7	40%	81.7	54%	81.7	53%	81.7	54%	68.7	35%	81.7	46%
193	Removed		81.3	44%	43.5	26%	0	12%	Removed		0	1%
Ct=Conductance at capacity test Cn=conductance when new												

Previous studies[2] have suggested using an 80% limit on conductance drop. This clearly would have resulted in the rejection/replacement of cells well before the end of their useful life – the average conductance reached 80% of its initial value in 45 days, barely a quarter of the useful time in the field. The same study also suggested possibly using a 50% limit – with the caveat that the customer would be exposed to additional risk. The data indicate that this approach may be more useful – the cells on average reached 50% of their initial conductance at approximately the same time (160 days) that the string capacity reached 80%. This approach would not, however, detect the high float current issue that ultimately caused the cells to be removed from the string.

In the same work regression analysis was used to determine if there was a statistically significant relationship between conductance and capacity. This could point towards a more suitable figure for use in determining good and bad cells. A capacity vs. conductance scatter plot is shown on Figure 2. The best fitting linear relationship has an R^2 of 67%, meaning that the change in conductance explains roughly 67% of the change in capacity for all of the life test cells. The best fit line predicts that the capacity will fail below 80% when the cell conductance falls below 1631 mho, about 52% of the original average conductance. As shown on the scatter plot there were six points below the conductance limit, but above the capacity limit. These would represent the risk of removing cells that are still defined as "good". Referring back to Table 1, however, these cells would have been at the end of life.

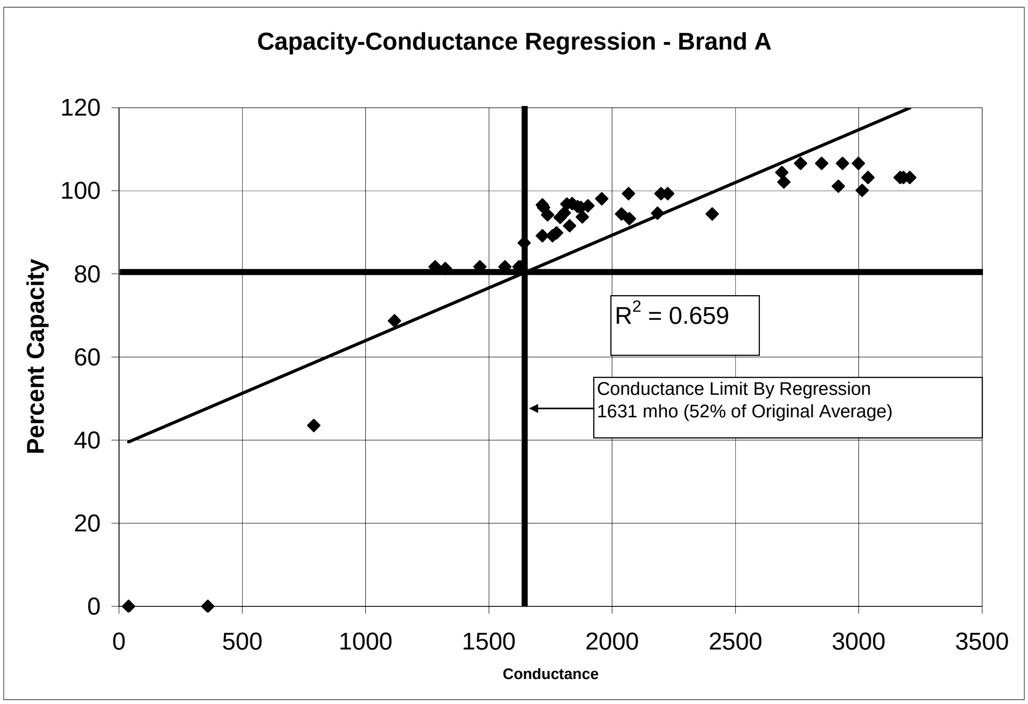

Figure 2

Brand B: The capacity and conductance readings for Brand B are shown on Table 3. This system ran 179 days with good capacity. Testing at 208 days showed a sharp drop in capacity to 49%. After returning the system to the test chamber less the failed cell, two additional cells showed failure at 238 days. Teardowns showed that cause of failure was dry out and sulfation, compounded by two dropped outside negative plates in one cell. The sulfation on the negative plate and strap probably contributed to the dropped plates. In contrast to Brand A the system never went to zero capacity – a far better result for a customer than the catastrophic failure found at 193 days in Brand A. During the course of the test there were two non-conformities. The first was a unexplained drop in capacity at 150 days, followed by a rebound at 179 days, and the second was a missed conductance reading on a failed cell at 208 days.

TABLE 3. BRAND A CAPACITY AND CONDUCTANCE DATA												
Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	mho	Cap	mho	Cap	mho	Cap	mho	Cap	mho	Cap	mho
0	104.2	3417	104.2	3331	104.2	3224	102.4	3410	102.7	3419	104.1	3369
32	96.3	3216	96.3	3287	96.3	3168	95.1	3148	93.4	3224	95.7	3233
60	101.2	3242	101.2	3216	101.2	3202	99.9	3061	97.0	3233	101.2	3331
90	103.3	3164	102.7	3126	103.3	3037	102.8	2823	98.3	3025	103.3	3369
120	100.1	3498	97.4	3325	100.1	3250	100.1	3207	96.0	3269	100.1	3400
150	82.8	3516	82.8	3181	82.8	3359	82.8	3126	81.2	2654	82.8	3429
179	102.9	3427	98.5	3379	103.1	3260	102.5	3287	87.3	2678	102.5	3379
208	49.7	3298	49.7	3250	49.7	3199	49.7	3224	49.0	N/R	49.7	3014
238	50.6	2737	49.4	2487	50.6	2749	50.6	2587	Removed		50.6	2806

The chart of average capacity and conductance is shown on Figure 1. The system had a useful life of ~200 days, about 25% longer than Brand B, and there was no sudden loss of capacity as experienced with Brand A. The conductance behavior of this model was also much different than Brand A. The profile with time was relatively flat until the end of its useful life.

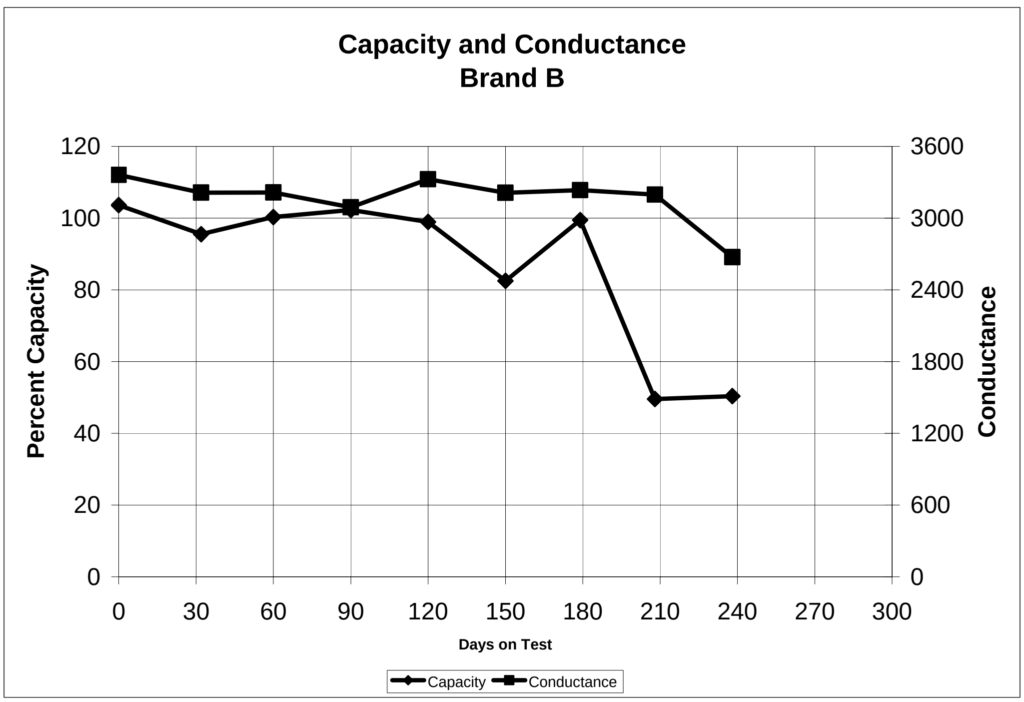

Figure 3

Table 4 shows the capacity and percent conductance drop for Brand B. The cells that limited the system capacity are shaded. There was relatively little change in conductance with capacity during the life of the product for individual cells. Cell 4 showed the greatest degree of variation in the test, dropping to 83% of its initial conductance at 90 days, and then dropping to 76% of its original conductance at the end of the 238 day test.

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TABLE 4 BRAND B CAPACITY AND CONDUCTANCE RATIO												
Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn
0	104.2	100%	104.2	100%	104.2	100%	102.4	100%	102.7	100%	104.1	100%
32	96.3	94%	96.3	99%	96.3	98%	95.1	92%	93.4	94%	95.7	96%
60	101.2	95%	101.2	97%	101.2	99%	99.9	90%	97	95%	101.2	99%
90	103.3	93%	102.7	94%	103.3	94%	102.8	83%	98.3	88%	103.3	100%
120	100.1	102%	97.4	100%	100.1	101%	100.1	94%	96	96%	100.1	101%
150	82.8	103%	82.8	95%	82.8	104%	82.8	92%	81.2	78%	82.8	102%
179	102.9	100%	98.5	101%	103.1	101%	102.5	96%	87.3	78%	102.5	100%
208	49.7	97%	49.7	98%	49.7	99%	49.7	95%	49	NR	49.7	89%
238	50.6	80%	49.4	75%	50.6	85%	50.6	76%	Removed		50.6	83%

Setting conductance limits for this type of behavior introduces more uncertainty than even Brand A. Setting the limit to 80% of its value would catch the cells ultimately responsible for limiting the system capacity; however, it would also have removed Cell 5 at 150 days, well before the end of its useful life.

Regression analysis was also performed on Brand B, again in an attempt to get a more refined limit on conductance values. The results are shown in Figure 3. The R^2 value was very low at 0.269. The model gave a conductance limit of 2978 mho, or 89% of the original value, a higher value than any published in the literature. Using this method would have both alpha and beta type risks – good cells removed for no reason, and cells with less than 80% capacity left in the system.

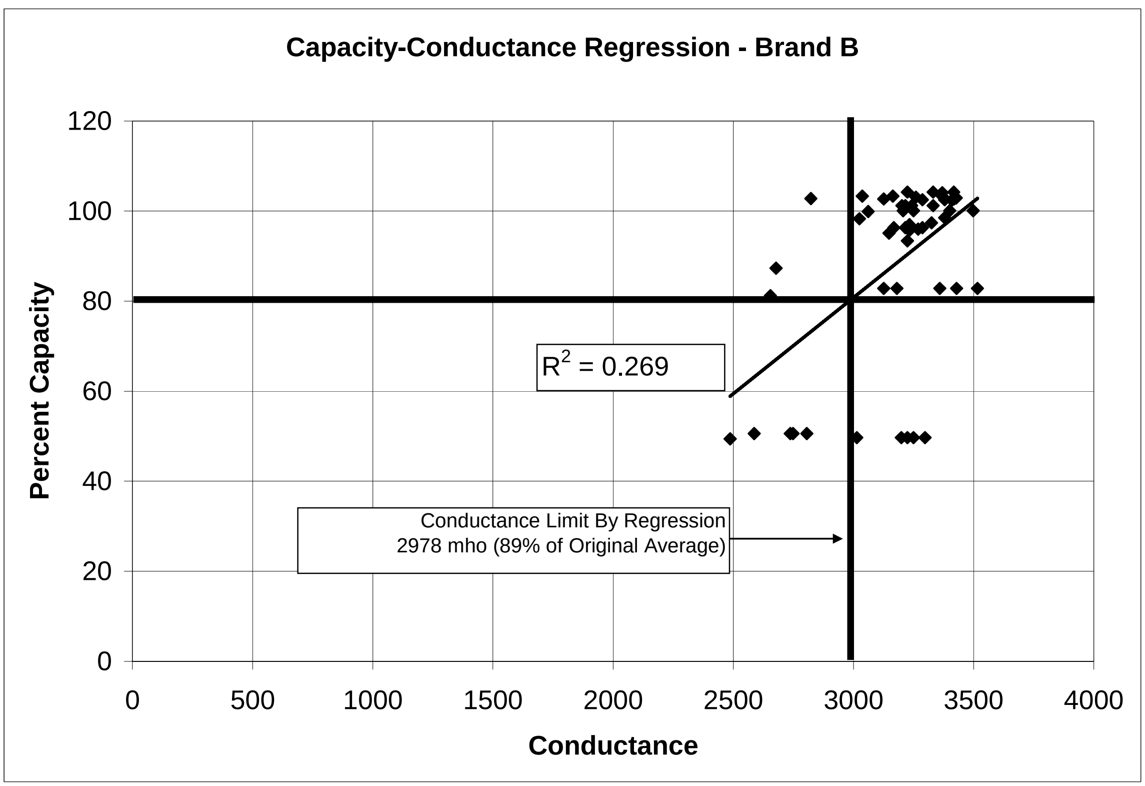

Figure 4

Brand C: The capacity and conductance behavior for Brand C are shown in Table 5. The system ran 299 days with good capacity. At the 299 day point the plastic on several jars, brittle due to the high test temperatures, failed when the cells were being weighed. Teardowns on the cells showed slight indications of cell dryout, positive plate sulfation, and some positive grid corrosion. These conditions were consistent with the 95%+ capacity of the cells at teardown.

TABLE 5. BRAND C CAPACITY AND CONDUCTANCE DATA

Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	mho	Cap	mho	Cap	mho	Cap	mho	Cap	mho	Cap	mho
0	109.9	2737	110.9	2230	111.0	2920	109.7	2547	112.4	2684	108.8	2797
29	111.0	2777	106.3	2089	112.7	2681	109.7	2666	110.1	2121	NO READING	
59	96.2	2452	108.0	2644	106.1	2353	108.2	2393	108.7	2615	105.5	2454
90	110.8	1921	117.3	2420	113.0	2414	111.3	1998	117.4	2463	114.4	2465
121	100.9	3007	108.1	2504	97.4	2775	106.9	2074	108.1	2288	108.1	2334
150	102.0	3099	111.8	2468	106.8	2106	110.2	2198	111.8	2156	108.2	2244
180	106.8	2626	106.8	2273	98.8	2269	106.8	2124	103.6	1978	104.5	2088
210	112.9	2313	109.6	2214	103.5	2066	111.0	2156	112.9	2140	105.6	2103
242	108.1	2202	104.3	2103	101.2	2080	107.2	2095	108.2	2106	102.9	2080
272	102.4	1850	102.0	1965	99.5	1958	108.1	2010	109.1	2066	105.1	2060
299	99.5	1727	96.0	1763	98.1	1674	102.9	1952	102.9	1934	101.4	1884

The average capacity and conductance for the test is shown on Figure 3. The pattern is different than either Brand A or Brand B. There was a significant drop in conductance – 31% from initial values to final, with a small drop in average capacity – 10% from the initial 110% to 100% at the end of the test. Most of the conductance drop occurred during the second half of the battery's life. At the 90 day point there was a negative correlation between capacity and conductance – a rise to 114% capacity with a drop in conductance of 8% from the previous test.

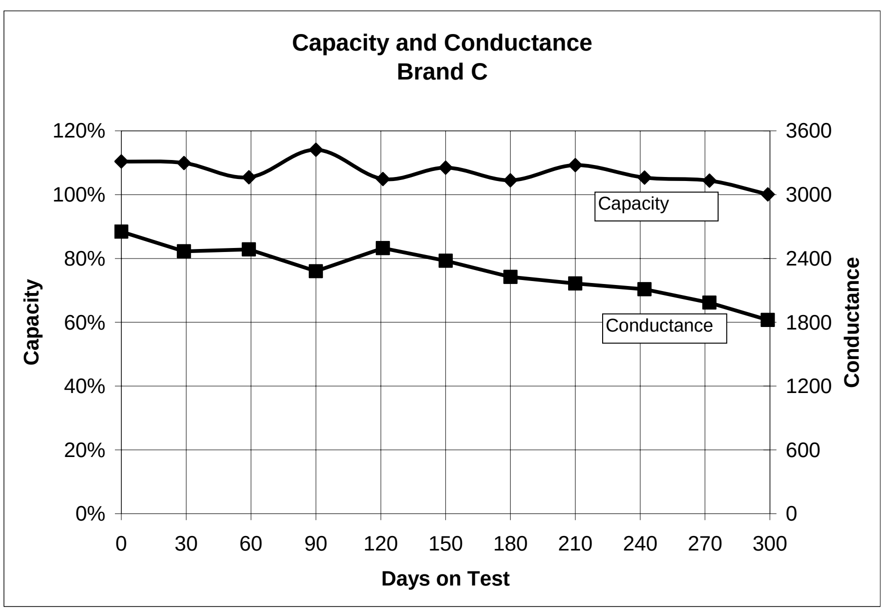

Figure 5

Table 6 shows the capacities and percent conductance drop for Brand C. Since there were no individual cell failures during the test conductance limits cannot be set. The 80% limit suggested in previous works would have caused replacement of nearly all cells while the cells still had 50% or more of their life remaining. A 50% limit would not have caused any replacements during the duration of this test.

TABLE 6 BRAND C CAPACITY AND CONDUCTANCE RATIO												
Days	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5		Cell 6	
	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn	Cap	Ct/Cn
0	109.9	100%	110.9	100%	111.0	100%	109.7	100%	112.4	100%	108.8	100%
29	111.0	101%	106.3	94%	112.7	92%	109.7	105%	110.1	79%		
59	96.2	90%	108.0	119%	106.1	81%	108.2	94%	108.7	97%	105.5	88%
90	110.8	70%	117.3	109%	113.0	83%	111.3	78%	117.4	92%	114.4	88%
121	100.9	110%	108.1	112%	97.4	95%	106.9	81%	108.1	85%	108.1	83%
150	102.0	113%	111.8	111%	106.8	72%	110.2	86%	111.8	80%	108.2	80%
180	106.8	96%	106.8	102%	98.8	78%	106.8	83%	103.6	74%	104.5	75%
210	112.9	85%	109.6	99%	103.5	71%	111.0	85%	112.9	80%	105.6	75%
242	108.1	80%	104.3	94%	101.2	71%	107.2	82%	108.2	78%	102.9	74%
272	102.4	68%	102.0	88%	99.5	67%	108.1	79%	109.1	77%	105.1	74%
299	99.5	63%	96.0	79%	98.1	57%	102.9	77%	102.9	72%	101.4	67%

Obtaining a limiting conductance value by regression (Figure 6) returned a meaningless result when the regression line was extrapolated to 80%. In addition, the correlation was worse than Brand A or B (R^2 = 0.097) suggesting that prediction even within the data set would be risky.

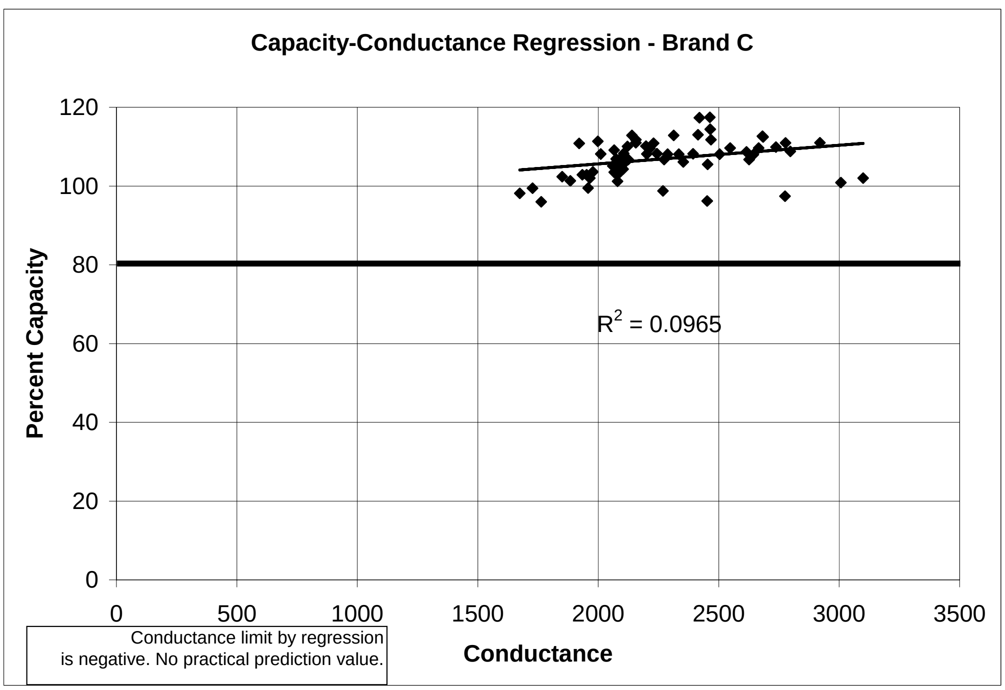

Figure 6

Brand D: Brand D was a lithium ion cell with 90 AH nameplate capacity. The goal of the on-going test is to develop an activation energy value for the accelerated aging of the cells. Due to safety concerns and equipment limits both the temperature and sample size were limited in the initial evaluation. Test temperatures chosen were 50°C (manufacturer's recommended limit), 40°C, and 25°C, sample size is two cells, and the cells are discharged at the one hour rate.

The test program for the Li-Ion cells is on-going, however, initial capacity and conductance measurements have been taken, and significant capacity loss has occurred in the highest temperature tests. Results for capacity and conductance at different temperatures are shown on Figure 4.

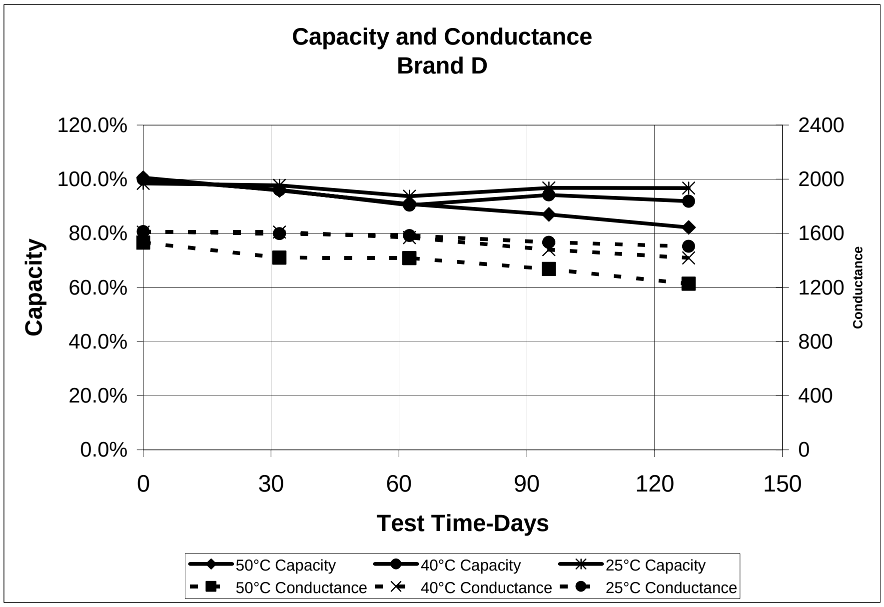

Figure 7

Regression analysis for all cells tested is presented in Figure 5.

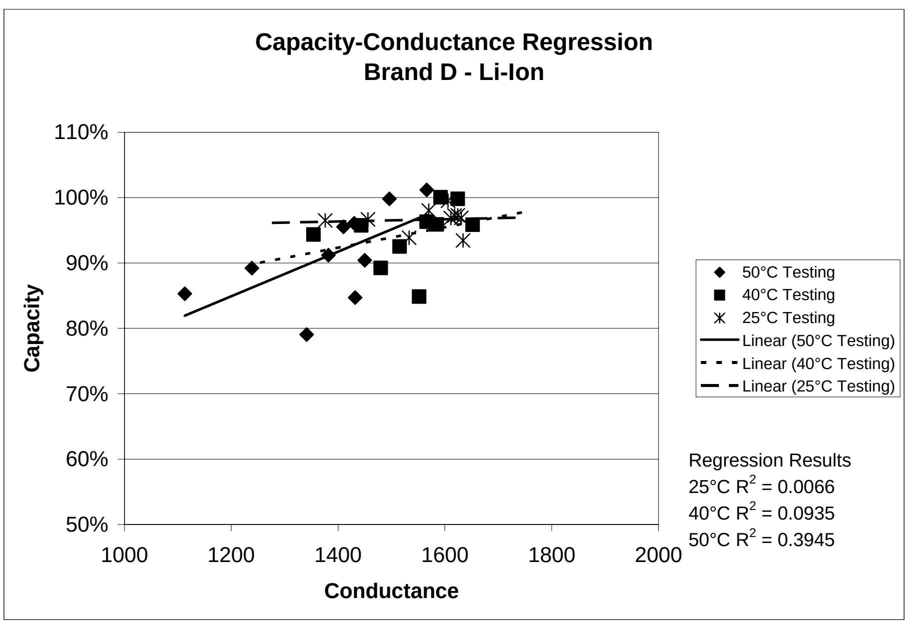

Figure 8

The R^2 for all the tests was 0.3385. As shown, most of the correlation is contributed by the higher temperature tests, (R^2 = 0.39), where the most separation has occurred in capacity and conductance. It appears that good correlation found in the average capacity vs. conductance graph breaks down when individual cells are considered. Additional samples and test results are needed to develop this study further, and tests with significantly larger sample sizes have been started.

CONCLUSIONS

Three general conclusions can be made from the analysis of the data generated by this study

1. The cell life (at least as measured using SR-4228 methods) all exceeded 10 years and reached 20 years for one brand. This behavior is quite different than previous experience with large format VRLA products, and points towards improvements in the design and construction of the products.

2. There were wide variations in the relationship between capacity and conductance between the different brands. The behavior ranged from a roughly linear response, to no change in conductance with wide changes in capacity, to wide changes in conductance with small changes in capacity. This shows, at a minimum, that results from one brand of battery cannot be generalized to other manufacturer's products. Using Brand B's conductance "rules" for Brand A or C would have caused significant replacements of good products, while using A's rules for B would have exposed the battery users to significant risk of battery failure.

3. The correlation between capacity and conductance within brand types was poor enough to place significant doubt on the practice of replacing capacity testing with conductance testing. The data simply do not show the R^2 values of 90 or 95% required to make economic decisions using regression data.

The authors are not intending to say that ohmic measurements do not have value in monitoring VRLA products. These devices are used effectively both in a laboratory and field environment. The data indicate, however, that these readings should not be used alone as an absolute judge of product performance, especially when there are no custom models developed for the type of battery being tested. Users and manufacturers need to use judgment and experience to analyze the data, and then supplement the data with additional measurements – including capacity testing - when deciding whether to replace products in the field.

The study does indicate that further work is needed developing better models based on additional measurements. Specific areas include:

- Expanding testing to short rate high power (UPS) applications. Ohmic readings may be much more highly correlated to capacities in the 5-60 minute range, as internal resistance would play a much more important role for these discharges than the telecommunication rates tested here.

- Correlating ohmic readings to specific failure modes. The study showed a more pronounced relationship in the cells that failed due to positive strap corrosion and grid growth than to the cells that failed due to plate sulfation. This can be expanded to studies involving established VRLA failure mechanisms – loss of compression, contamination, persistent under or over-charging, etc. By eliminating noise through careful experimental design it may be possible to develop ohmic testing as an effective in-process or field test for specific problems.

- Expanding the use of ohmic readings for other battery technologies. High energy density products like lithium ion cells can have failure modes that are far more disruptive to users than typical VRLA products. Using ohmic or other technologies to detect potential issues in these products would be at least as valuable as their use in VRLA products today.

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[1] Telcordia Technologies **SR-4228,** *VRLA Battery String Certification Levels Based on Requirements for Safety and Performance, Issue 1,* 1996

[2] D. Feder, M Hlavac, "*Analysis and Interpretation of Conductance Measurements used to Assess the State of Health of Valve Regulated Lead Acid Batteries – Part III: Analytical Techniques*" Intelec, 1994