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VOLTAGE-TEMPERATURE CHARGE VERIFICATION TESTING
OF 34 AMPERE-HOUR NICKEL-CADMIUM CELLS

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ABSTRACT

This testing was designed to evaluate various voltage-temperature (V-T) charge curves for use in low-earth-orbit (LEO) applications of nickel-cadmium battery cells. The trends established relating V-T level to utilizable capacity were unexpected. The trends toward lower capacity at higher V-T levels was predominant in this testing. This effect was a function of the V-T level, the temperature, and the cell history. This effect was attributed to changes occurring in the positive plate. The results imply that for some applications, the use of even lower V-T levels may be warranted. The need to limit overcharge, especially in the early phases of missions, is underlined by this test program.

INTRODUCTION

V-T compensated charge control is the primary method of battery charging in low-earth-orbit (LEO) spacecraft. The careful selection of V-T levels is crucial for mission longevity. The ability to change V-T levels during operation gives the necessary flexibility to adapt to changing cell electrical characteristics. To evaluate the three most likely curves available in this spacecraft, a matrix of nine V-T combinations was selected. For each of these points, a series of tests was performed. The test series allowed for the evaluation of utilizable capacity as well as cyclic parameters. Based upon the results of this testing, implications regarding cell and system operation can be made.

TEST ARTICLES

The testing was performed concurrently on two (2) separate six (6) cell-packs of thirty-four ampere-hour (34 AH) sealed nickel-cadmium cells. The two cell packs have different test histories, although both were manufactured from the same plate lot. The group referred to as the "new cells" had no previous testing aside from pre-ATP, ATP, and cell receiving and matching. The "old cells" had been in test for approximately one and one-half years prior to this testing. The testing performed on the old cells includes minimum trickle charge evaluation (1), various characterization cycles, and a small amount of hot case testing. In all, approximately sixty 100% depth-of-discharge (DOD) cycles were performed. Each of the cell-packs was mounted in a restraining fixture to provide physical support and electrical isolation. The cells are series wired. The cell-packs were instrumented for battery and cell voltages and skin temperature. All tests were performed in an environmental temperature chamber.

TEST OPERATIONS

Prior to the start of any test series, the cells were shorted with one-quarter (0.25) ohm resistors. The testing was performed at 0°C, 15°C, and 30°C. At each of these three temperatures, three V-T levels were evaluated. Each of the V-T levels was evaluated using the following sequence:

Initial Capacity Check

A capacity check is performed following temperature stabilization. This test is performed once per temperature for each cell pack. The test uses a C/20 charge rate (1.70 amperes) for forty (40) hours. Discharge is performed immediately, at a C/2 (-17.0 amperes) rate, until a pack voltage of 6.0 volts (1.0 volt/cell) is reached. The recorded discharge capacities are then interpolated to the exact voltage cut-off level. Cell shorts are then installed, bringing the cells to less than twenty millivolts (20 mV) before continuing.

Pre-Charge

The cells are then charged at a C/20 rate (1.70 amperes) for forty (40) hours.

V-T Cycling

Following the pre-charge test, the simulated LEO cycling was initiated. Each of the cycles is one-hundred and eight (108) minutes long, with a seventy-two (72) minute charge phase, and a thirty-six (36) minute discharge phase. The charge current is limited to fourteen amperes (14 A) and tapers

at the assigned voltage limit. The discharge current is a constant eight and one-half amperes (-8.5A). This results in a consistent fifteen percent (15%) DOD. Operation of the simulated LEO cycling is continued until the cyclic parameters have stabilized, as determined through the use of specialized software routines.

Upon stabilization of recharge fraction, end-of-charge current, and end-of-discharge voltage, the test is stopped. This test halt is executed at the end of the charge phase. The set-up and test start of the next test is performed immediately. See Figure 1 for the V-T levels tested.

Post-Cyclic Capacity Check

This discharge test is very similar to the last half of the capacity check. It uses the same C/2 discharge rate and cell short-down procedure. At this time the testing proceeds to the next V-T series. Either a temperature stabilization or a pre-charge is performed, depending upon whether a change in temperature is required.

TEST RESULTS

To preface the discussion of the effects of V-T levels on cell performance, it is important to first look at the constant current testing performed. Both of the cell-packs displayed normal performance, considering the respective histories. Figure 2 displays the results of the capacity check tests for both cell packs at a range of temperatures. As would be expected, the old cells showed marginally lower capacities, with extreme temperatures perturbing the difference. The general shape of the curves fits very well with classical capacity curves (2). Figure 3 depicts the maximum charge voltage for the respective cell-pack as a function of temperature. The effect of test history on the old cells manifests itself again as higher charge voltage. This effect is most pronounced at low temperature. The formation of large crystals of active material, and the resulting reduction in the oxygen recombination rate is considered the primary cause of this phenomenon (2, 3, 4).

The cyclic testing can be evaluated by a number of electrical parameters. The parameters of greatest interest in this testing are recharge fraction, end-of-charge current (EOCI), end-of-discharge voltage (EODV) and temperature. The raw data from these parameters would constitute a large volume. For this reason, only the most representative data was presented. Figures 4 and 5 depict the data presented in Table 1. Figure 4 depicts the effect of V-T level on the EOIC of the two cell-packs as function of temperature. Figure 5 depicts the effect of V-T level on the recharge fraction of the two cell-packs as a function of temperature. This data represents values for the cycling just prior to the discharge.

The strong correlation between Figures 4 and 5 would be anticipated. Note that the plots for adjacent V-T levels of different cell-packs are very similar. This is another indicator of the general state of health of the respective cell-packs. The trends shown toward higher values at higher temperatures and/or V-T levels is normal. The fact that the new cells have consistently higher values is witness to the inherently lower charge voltages, as seen earlier.

The data presented thus far fit well into the expected trend for LEO applications of sealed nickel-cadmium battery cells. The results of the post-cyclic capacity checks do not fall into the range of anticipated values. Figures 6 and 7 present the ampere-hour capacities for the two cell-packs, as functions of the V-T level and the temperature. The most notable trend in these figures is that of decreased capacity with increased V-T level. Note also that this effect is a function of temperature as well. There are notable exceptions to this trend, as seen in Figure 6, "Effect of V-T Levels on Capacities of New Cells." While the 30°C data show clear and consistent trends, the 15°C and 0°C regions are less clear. The differences in the values at 15°C are quite minimal, considering the range of capacities recorded. The unexpected low value for the 0°C measurement for V-T curve number two can be attributed to an excessive number of cycles needed to achieve stabilization.

Figure 8 represents the general trends for capacities achieved by the new cells. The curves generated are interpretations of the data in Figure 6. Modification to the trends are based upon aforementioned factors.

Figure 7, "Effect of V-T Levels on Capacities of Old Cells", gave clear values for the 0°C and 30°C regions, with the 15°C region showing an excessively low capacity for V-T curve 2. This resulted from improper charge control and an excessive number of cycles being performed. Figure 9 is an expression of the trends established in Figure 7.

There are two major differences between Figures 8 and 9. First is the reversal in the general trend for the old cells at low temperature. An increase in discharged capacity correlated with increased V-T level for this one case. The exact temperature at which the crossover in trend occurs is beyond the scope of this testing. This testing lacks the necessary precision to identify that point. Second is the smaller reduction in utilizable capacity in the old cells. The presence of this reduction in utilizable capacity, and the magnitude of this effect, can be related to the data presented earlier in this paper.

DISCUSSION

The results of this testing represent a deviation from the traditional effects ascribed to V-T levels with respect to capacities. This paper does not, however, contradict reports which show increases in capacity with increased V-T level where only one cycle was performed (4). Earlier reports showed instances of phenomenon similar to that seen here (5). The presence of such an effect was attributed to a high self-discharge rate, as a result of elevated plate temperatures. This explanation is not feasible in light of the test method used in this testing. The self discharge rate would have to be in the C rate range (-34 A) for this to be the cause, based on maximum residual capacity and the average set-up time for the post-cyclic discharge test.

The phenomenon of lower capacities upon discharge can be attributed to many causes. A simple approach is to look at the individual components and analyze them separately. First is the separator. Degradation and drying out of the separator are gradual and primarily irreversible trends (6). Since the effect observed in this report is reversible, the separator is not a likely cause. The negative plate is a likely candidate to have the effect ascribed to it. The trend toward a decrease in surface area, and thus effective excess negative active material, is well known. Reconditioning of cells increases the surface area by decreasing the cadmium crystal size. Thus, the effects of the negative electrode can be considered somewhat reversible, like the effect reported herein. The fact that the decrease in utilizable capacity was most dramatic in the new cells, as seen by comparing Figures 8 and 9, is an indication that the negative plate is not the cause. It has long been known that overcharging of nickel-hydroxide electrodes results in the formation of charged active material of higher valence states, gamma-nickel-oxy-hydroxide (NiOOH) (7). Additionally, it has been noted that electrodes with high concentrations of the Gamma-NiOOH experience poor efficiency upon discharge (8, 9). The capacity unavailable at high rate is referred to as the residual capacity. Further evidence and explanations of the residual capacity effect were presented in a recent study of charge and discharge efficiencies (10). This paper shows a significant inefficiency for discharging at states-of-charge less than twenty-five percent (25%). In addition, the level of inefficiency is related to both the charge and discharge profiles used. These parameters affect the existence of depletion and defect layers in the positive electrode.

These previous studies do not address all of the intricacies of the data reported here. One example is the variation in the magnitude of residual capacity for the cell-pack with different levels of degradation. This phenomenon is simply an artifact of the higher charge efficiency of the new cells, and the resulting overcharge level. Consistent with the above theories, the higher level of overcharge results in a lower charge utilization. It is, however, unanticipated that the C/2 rate would result in residual capacity of the magnitudes seen. Another example is the lack of the manifestation of the residual capacity loss at low temperatures for the old

cells. It is common knowledge that cold temperature oxygen recombination, especially in cells with an extensive history, can be a problem, due to the morphological changes in the negative plate. A simple explanation would be to attribute the rise in capacity with V-T level to the increase in temperature of the electrodes. Another possible influence may be the effect of intra-cell oxygen pressure upon the equilibrium of the cell reactions. The effect of a reduction of charged excess negative active material may also play a role in this phenomenon.

CONCLUSIONS

This report presents data which supports the most modern theories on charge and discharge efficiencies and the related cell electro-chemistry. In addition it gives indications of the conditions under which the residual capacity effect will manifest itself. Applying these principles to system operation, several things become apparent. Primarily, the adverse effect of overcharging cells is highlighted. At the other extreme, the lower threshold for V-T charge effectiveness was not firmly established. These test results do indicate that effective charging at low temperature can be accomplished with extremely low recharge fractions. It becomes apparent that to some extent lower V-T curves are better for most cases. In conclusion, an approach of maintaining a minimum recharge fraction is a good approach toward monitoring the state-of-charge of a spacecraft electrical power system. Maximum life and higher operating efficiency may be obtained at recharge fractions lower than currently being used. In addition, the use of non-linear V-T curves might give more accurate charge control, especially in highly variable thermal environments.

BIBLIOGRAPHY

1. P. Timmerman, "Minimum Trickle Charge Testing of 34 Ampere-Hour Nickel-Cadmium Cells", 1984 GSFC Battery Workshop Proceedings, 1984, pp. 369-386.
2. W. R. Scott and D. W. Rusta, "Sealed Cell Nickel-Cadmium Battery Applications Manual", NASA NAS5-23514, Ref. Publ. 1052, 1979, p. 96.
3. "Nickel-Cadmium Battery Application Engineering Manual", Second Edition, Ed. by J. C. Grant, General Electric Company Publication Number GET-3148A, 1975, para. 6.5.5.
4. W. R. Scott and D. W. Rusta, Ibid, p. 94.
5. W. R. Scott and D. W. Rusta, Ibid, p. 97.
6. W. R. Scott and D. W. Rusta, Ibid, p. 213.
7. S. U. Falk and A. J. Salkind, "Alkaline Storage Batteries", John Wiley and Sons, Inc., New York, NY, 1969, p. 50.
8. R. Banard, G. T. Crickmore, J. A. Lee and F. L. Tye, "The Cause of Residual Capacity in Nickel Oxyhydroxide Electrodes", Journal of Applied Electro-Chemistry, 10-1, January, 1980, pp. 61-70.
9. R. Banard and C. F. Randall, "Studies Concerning Charged Nickel-Hydroxide Electrodes. VIII. The Relative Potentials of the Beta-Nickel-Oxyhydroxide Reduction Process", The Journal of Applied Electro-Chemistry, 12-1, January, 1982, p. 121.
10. A. H. Zimmerman and P. K. Effa, "Charge Efficiency and Charge Utilization in the Sealed Nickel-Cadmium Cell", Report SD-TR-82-91, The Aerospace Corporation, 20 December 1982.

Table 1. DISCHARGE CAPACITIES

Test Temperature	Baseline Capacity Test, Ah	V-T Level One, Ah	V-T Level Two, Ah	V-T Level Three, Ah
0°C	(41.18, 40.93)	1.45 (V/Cell) (37.73, 38.03)	1.47 (V/Cell) (34.82, 38.40)	1.49 (V/Cell) (35.10, 39.01)
15°C	(41.83, 41.72)	1.42 (V/Cell) (38.37, 38.77)	1.44 (V/Cell) (38.90, 36.73)	1.46 (V/Cell) (37.58, 38.73)
30°C	(40.03, 39.21)	1.38 (V/Cell) (37.39, 37.46)	1.40 (V/Cell) (35.73, 34.71)	1.42 (V/Cell) (33.06, 36.20)
Note: All Capacities are given as new cells & old cells.				

Table 2. CYCLIC DATA MATRIX

Test Temperature	Cell Pack	0 °C			15 °C			30 °C		
		Recharge Fraction	EOD Voltage	EOC Current	Recharge Fraction	EOD Voltage	EOC Current	Recharge Fraction	EOD Voltage	EOC Current
(Units)		N/A	Volts	Amps	N/A	Volts	Amps	N/A	Volts	Amps
V-T Level 1	New	1.003	1.257	0.44	1.055	1.252	0.69	1.078	1.235	0.74
	Old	1.005	1.248	0.46	1.035	1.259	0.5	1.045	1.238	0.60
V-T Level 2	New	1.025	1.254	0.57	1.162	1.256	1.264	1.230	1.244	1.67
	Old	1.015	1.265	0.52	1.086	1.251	0.711	1.12	1.247	1.00
V-T Level 3	New	1.03	1.259	0.60	1.464	1.248	1.461	1.562	1.231	3.50
	Old	1.04	1.265	0.56	1.18	1.248	1.16	1.31	1.251	1.42

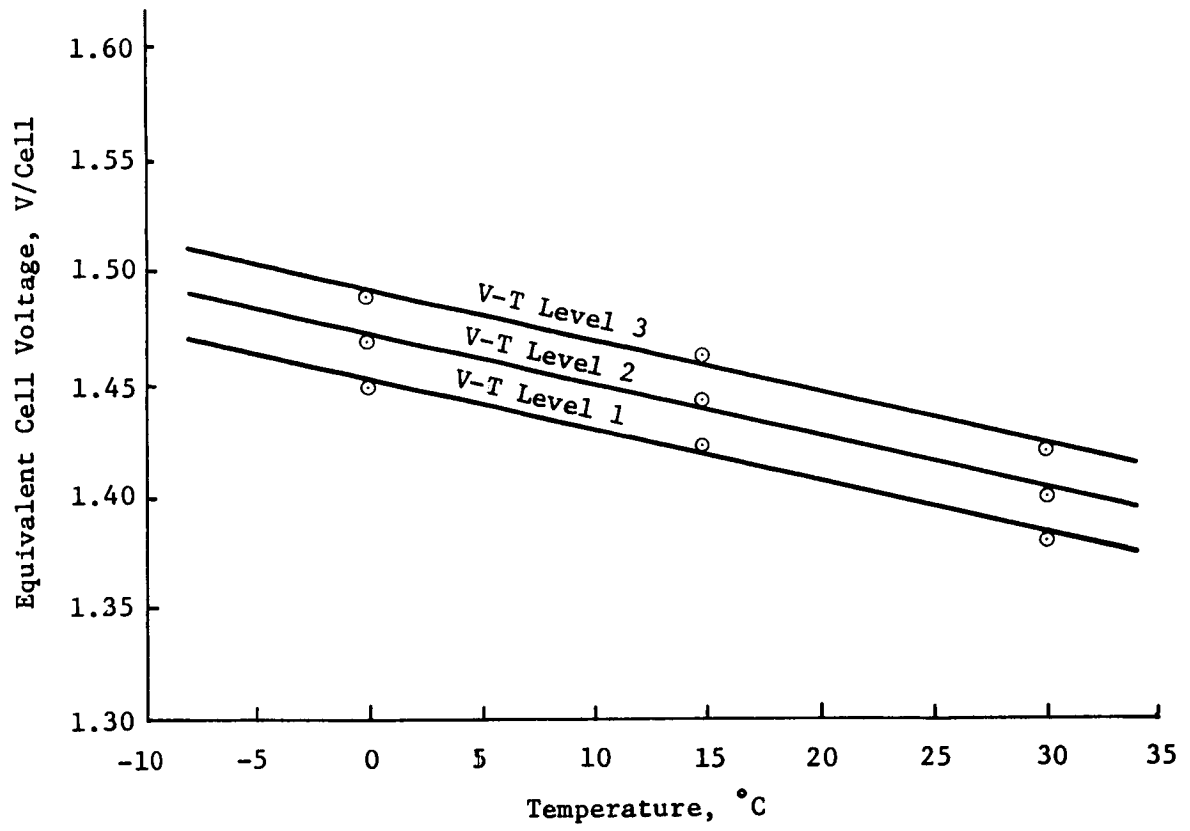


Figure 1. V-T LEVELS TESTED

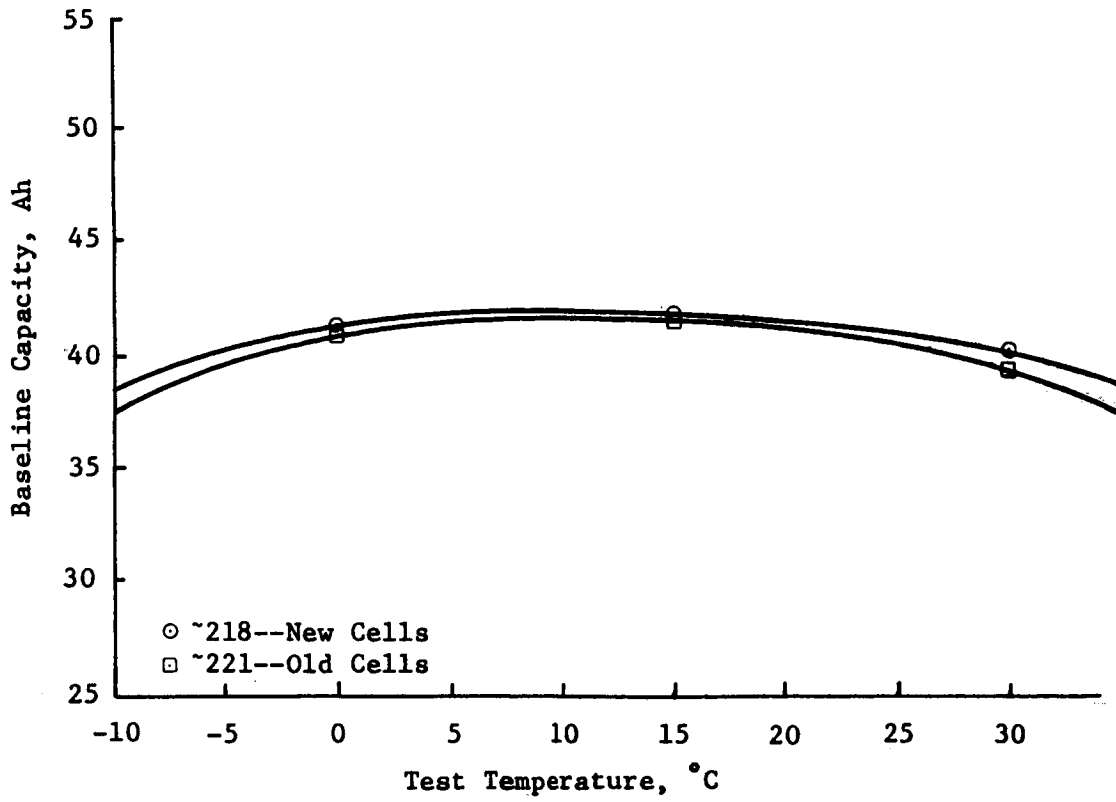


Figure 2. BASELINE CAPACITIES VERSUS TEMPERATURE

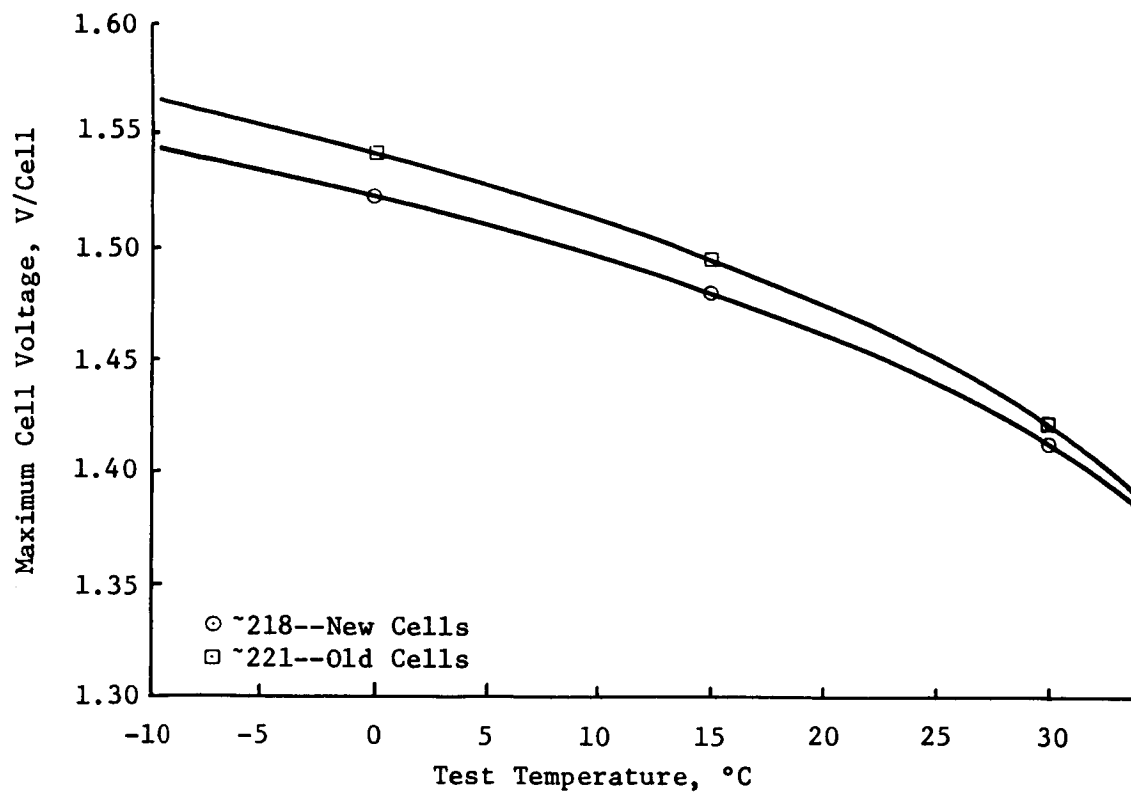


Figure 3. MAXIMUM CELL VOLTAGE FOR C/20 CHARGE RATE

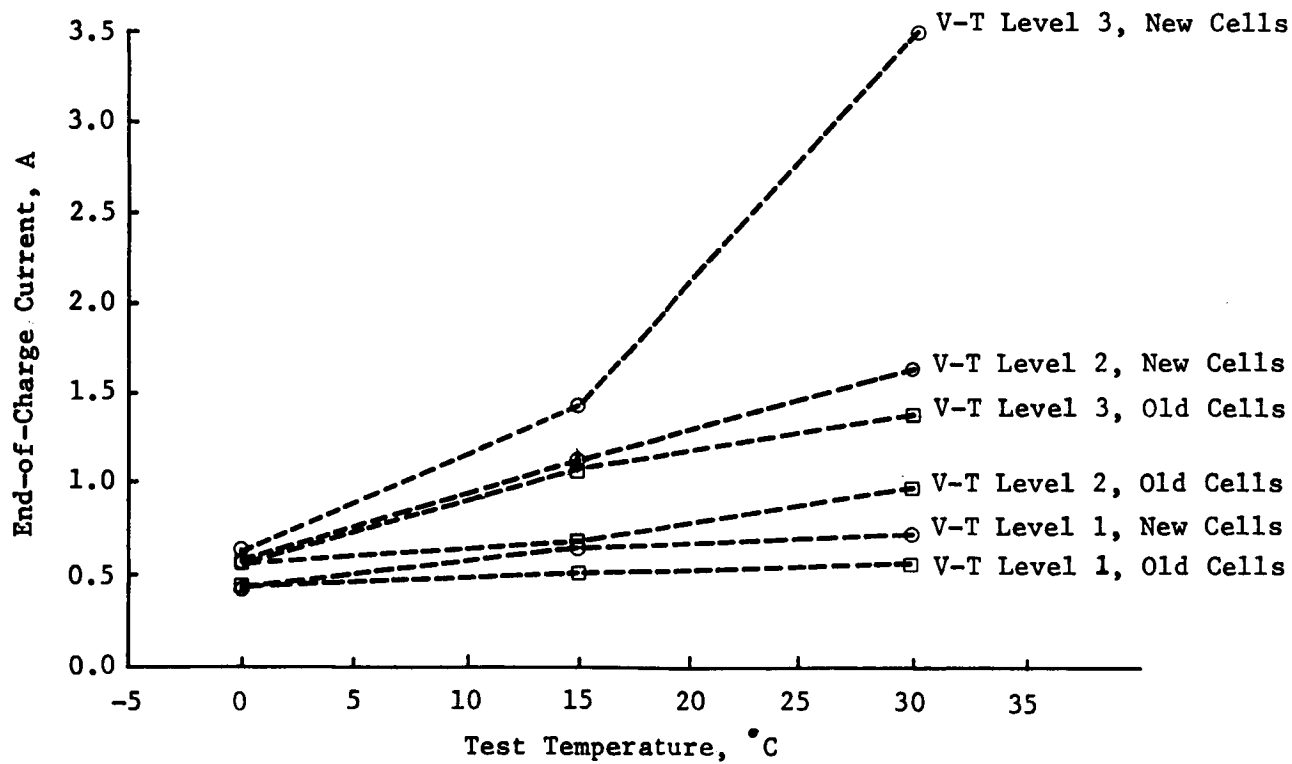


Figure 4. EFFECT OF V-T LEVEL ON END-OF-CHARGE CURRENT (EOCI)

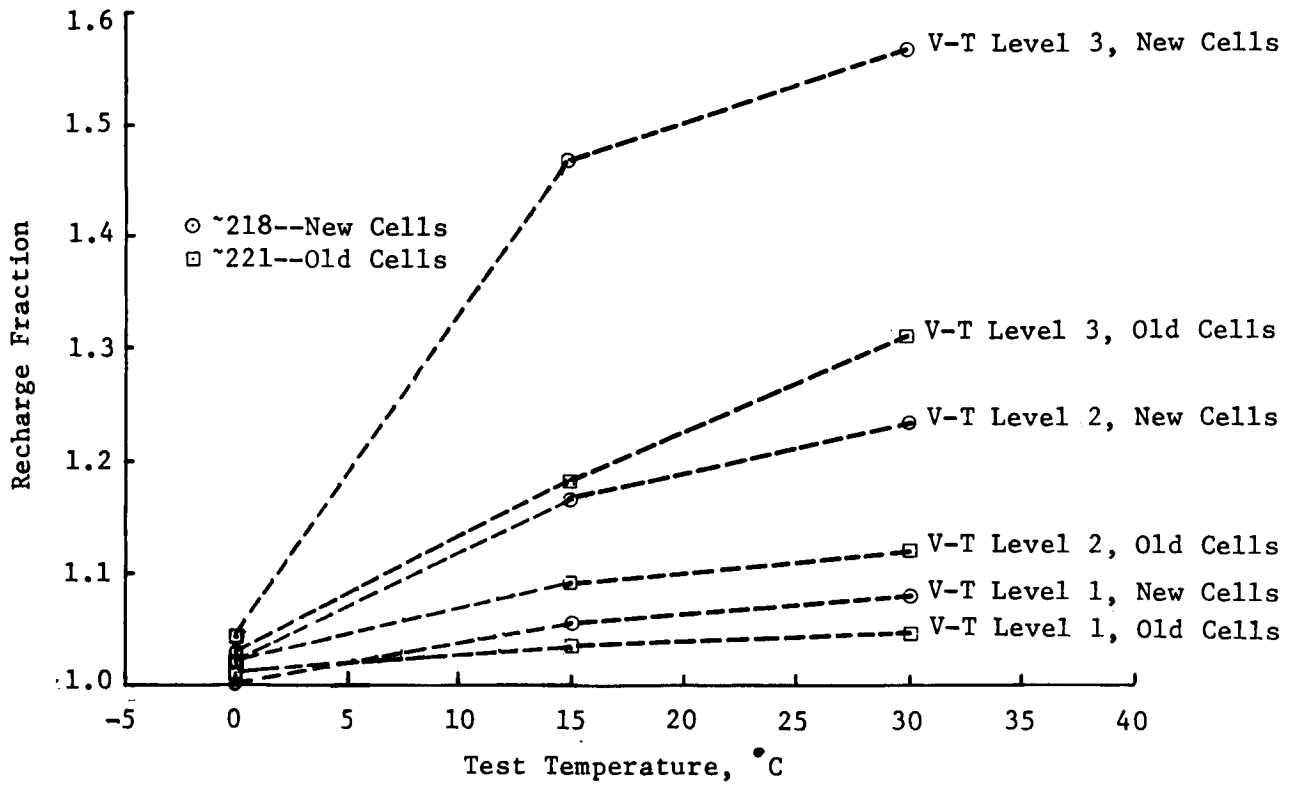


Figure 5. EFFECT OF V-T LEVEL ON RECHARGE FRACTION (RF)

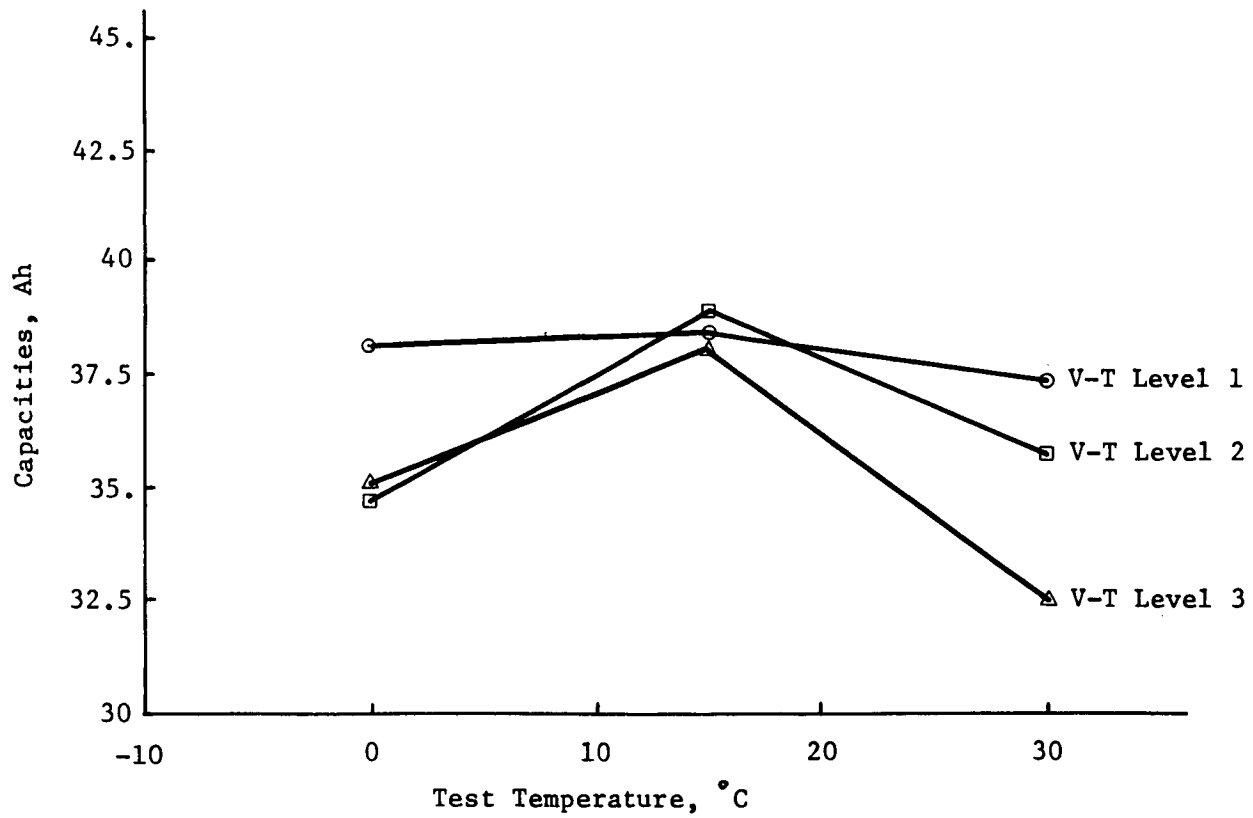


Figure 6. EFFECT OF V-T LEVELS ON CAPACITIES OF NEW CELLS

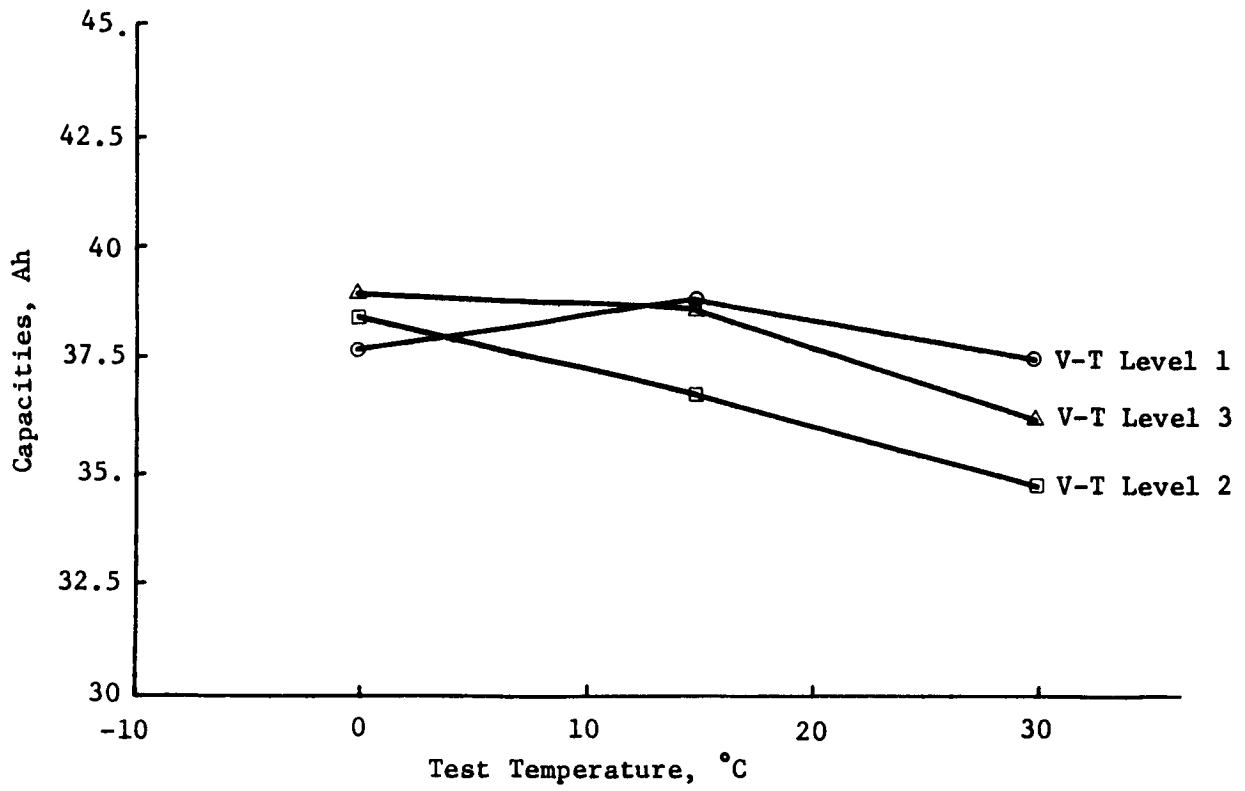


Figure 7. EFFECT OF V-T LEVELS ON CAPACITIES OF OLD CELLS

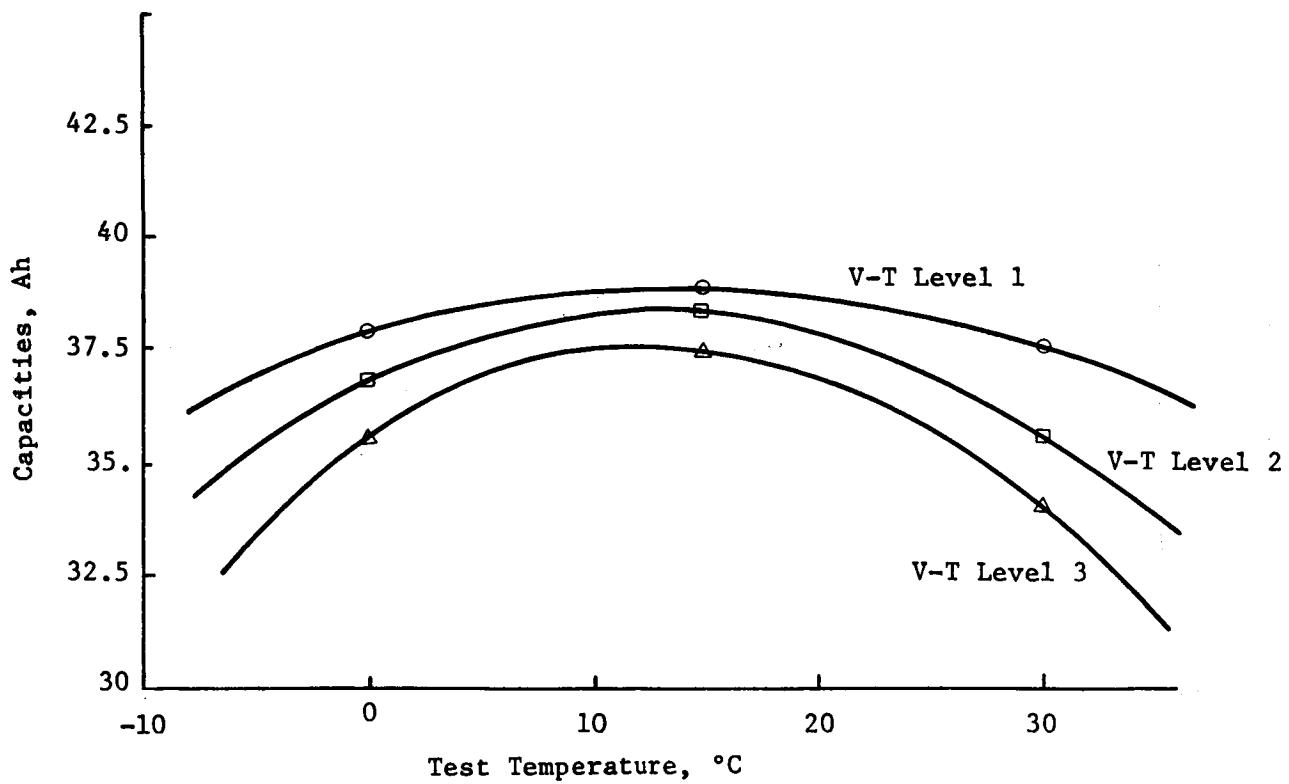


Figure 8. EFFECT OF V-T LEVELS ON CAPACITIES OF CELLS NEAR BEGINNING-OF-LIFE

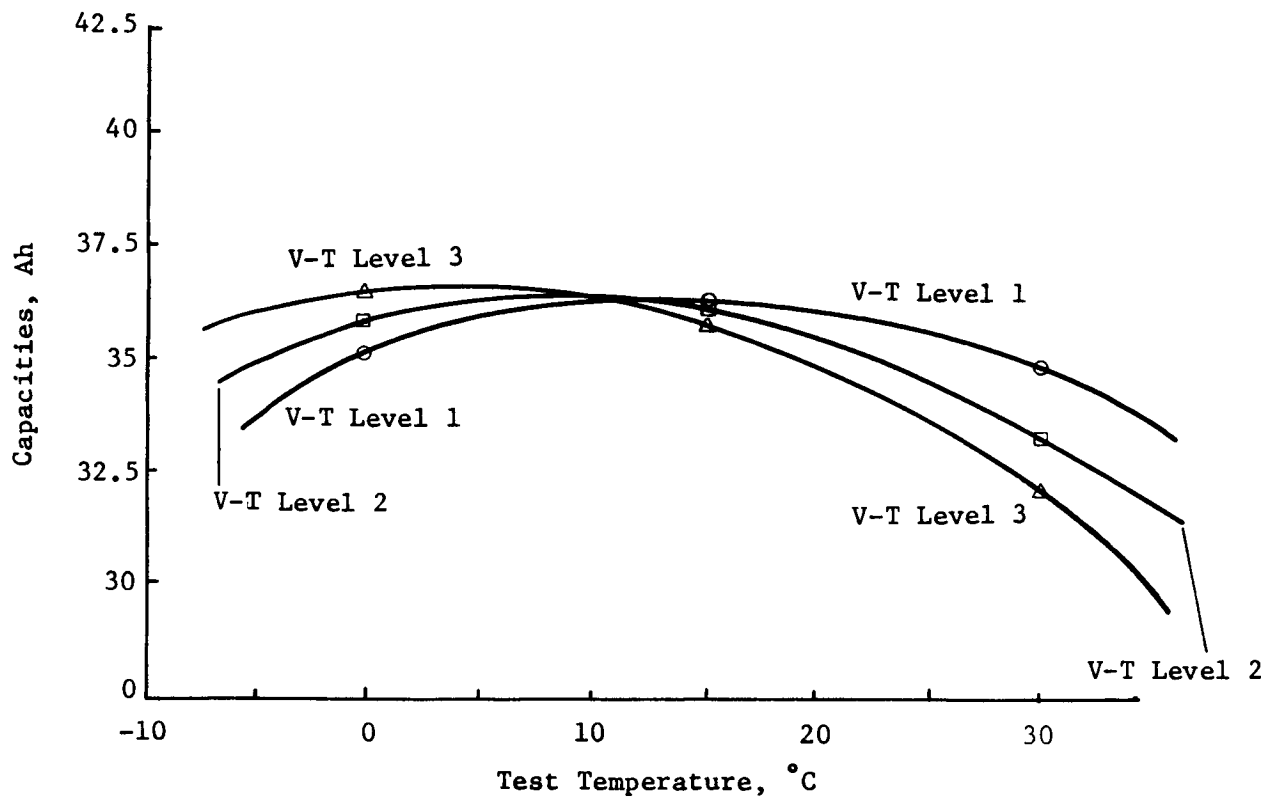


Figure 9. EFFECT OF V-T LEVELS ON CAPACITIES OF CELLS NEAR MIDDLE-OF-LIFE