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

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Summary

A test program 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 were 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

Voltage–temperature compensated charge control (V–T) 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 LEO 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 separate six-cell-packs of 34 A h, sealed nickel–cadmium cells. The two 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 (Acceptance Test Procedures), and cell receiving and matching The "old cells" had been in test for approximately one and one-half years

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prior to the current program. The testing that had been performed on the old cells included minimum trickle charge evaluation [1], various characterization cycles, and a small amount of high temperature testing. In all, approximately sixty 100% depth-of-discharge (DOD) cycles had been performed. Each of the cell-packs was mounted in a restraining fixture to provide physical support and electrical isolation. The cells were 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 0.25 Ω 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 using the following sequence

Initial capacity check

A capacity check was performed following temperature stabilization. This test was performed once per temperature for each cell pack. The test used a *C*/20 charge rate (1 70 A) for 40 h Discharge was performed immediately, at a *C*/2 (17 0 A) rate, until a pack voltage of 6.0 V (1.0 V/cell) was reached The recorded discharge capacities were then interpolated to the exact voltage cut-off level. Cell shorts were then installed, until the individual cells were less than 20 mV before continuing

Pre-charge

The cells were then charged at a *C*/20 rate (1.70 A) for 40 h.

V–T cycling

Following the pre-charge, the simulated LEO cycling was initiated Each of the cycles is 108 min long, with a 72 min charge phase, and a 36 min discharge phase The charge current is limited to 14 A and tapers at the assigned voltage limit The discharge current was a constant This resulted in a consistent 15% DOD Operation of the simulated LEO cycling was continued until the cyclic parameters were stabilized as determined through the use of specialized software routines.

Upon stabilization of the recharge fraction, end-of-charge current, and end-of-discharge voltage, the test was stopped This test halt was executed at the end of the charge phase The set-up and start of the next test was performed immediately Figure 1 indicates the *V–T* levels tested (Data from Table 1.)

Post-cyclic capacity check

This discharge test is very similar to the last half of the capacity check. It used the same *C*/2 discharge rate and cell short-down procedure. At this time the testing proceeded to the next *V–T* series Either a temperature

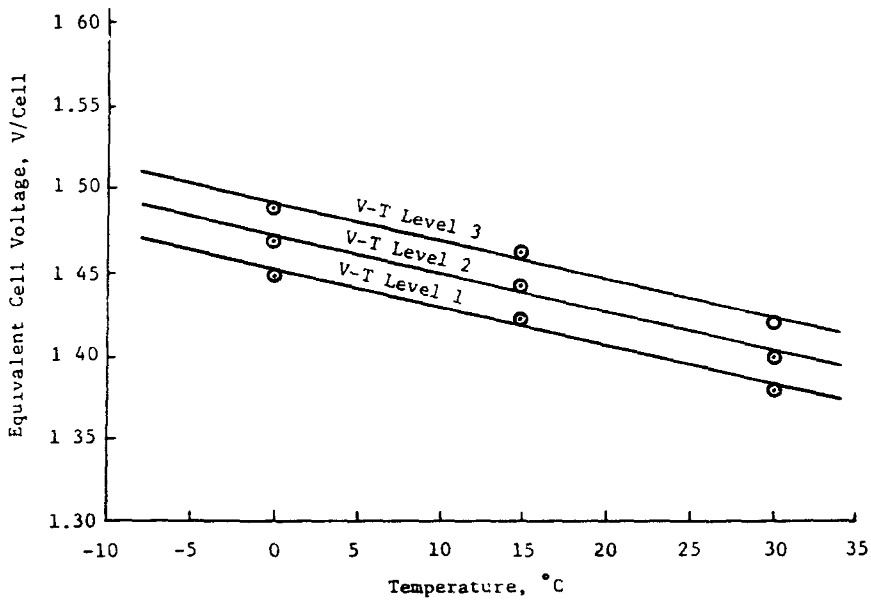

Fig 1 *V–T* levels tested
V–T level 1 (V/cell) 0 °C, 1 45, 15 °C, 1 42, 30 °C, 1 38
V–T level 2 (V/cell) 0 °C, 1 47, 15 °C, 1 44, 30 °C, 1.40
V–T level 3 (V/cell) 0 °C, 1 49, 15 °C, 1 46, 30 °C, 1 42

stabilization or a pre-charge was performed, depending upon whether or not a change in temperature was 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 cell-packs 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 increased difficulty in oxygen recombination are considered to be the primary causes of this phenomenon [2 - 4].

The cyclic testing can be evaluated by a number of electrical parameters. The parameters of greatest interest 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

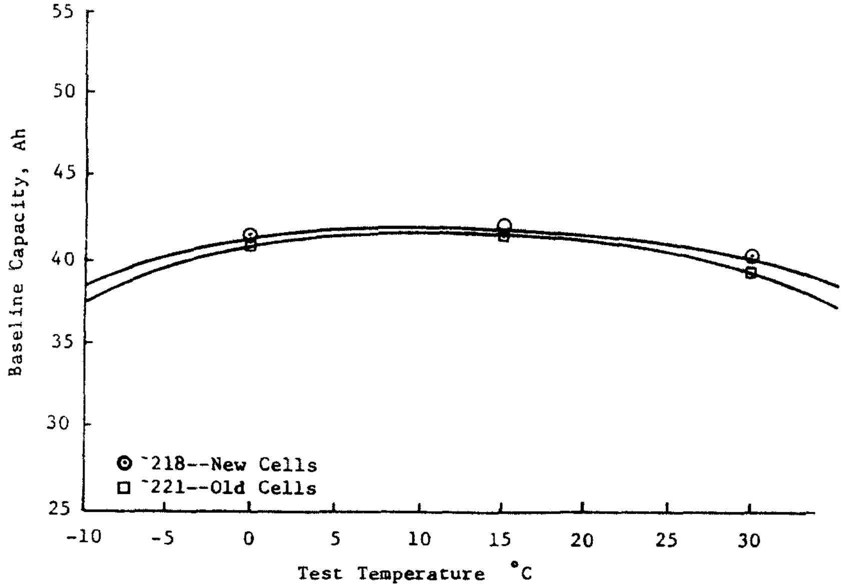

Fig 2 Baseline capacities *vs* temperature (Data from Table 1)
New cells (A h) 0 °C, 41 18, 15 °C, 41 83, 30 °C, 40 03
Old cells (A h) 0 °C, 40 93, 15 °C, 41 72, 30 °C, 39 21

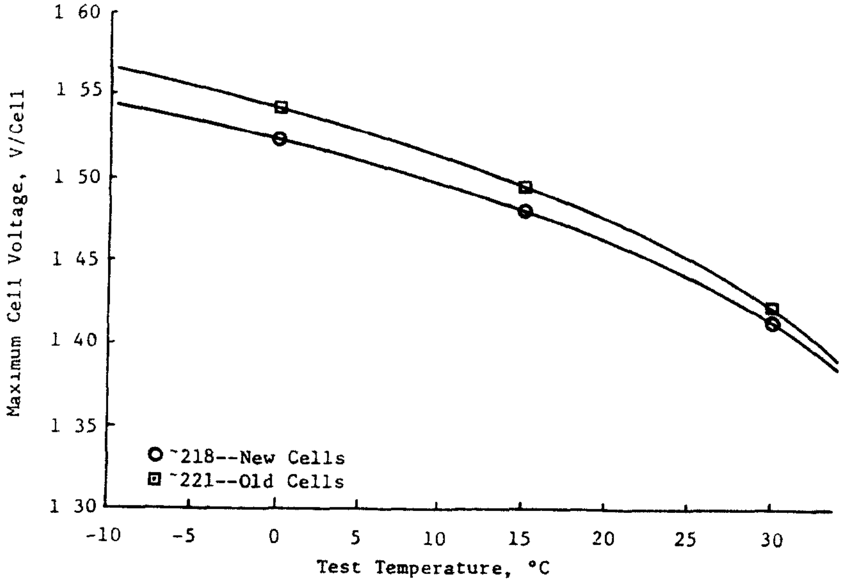

Fig 3 Maximum cell voltage for $C/20$ charge rate ○, new cells, □, old cells

this reason, only the most representative data are presented. Figures 4 and 5 depict the data presented in Table 2. Figure 4 depicts the effect of V–T level on the EOCI of the two cell-packs as a function of temperature. Figure

TABLE 2

Cyclic data matrix

Test temperature		Cell pack	0 °C			15 °C			30 °C		
Test parameter			Recharge fraction	EOD voltage	EOC current	Recharge fraction	EOD voltage	EOC current	Recharge fraction	EOD voltage	EOC current
	V/cell		N/A	(V)	(A)	N/A	(V)	(A)	N/A	(V)	(A)
V–T	0 °C = 1 45	New	1 003	1 257	0 44	1 055	1 252	0 69	1 078	1 235	0.74
Level	15 °C = 1 42										
1	30 °C = 1 38	Old	1 005	1 248	0 46	1 035	1 259	0 5	1 045	1 238	0 60
V–T	0 °C = 1 47	New	1 025	1 254	0 57	1 162	1 256	1 264	1 230	1 244	1.67
Level	15 °C = 1 44										
2	30 °C = 1 40	Old	1 015	1 265	0 52	1 086	1 251	0 711	1 12	1 247	1 00
V–T	0 °C = 1 49	New	1 03	1 259	0.60	1 464	1 248	1 461	1 562	1 231	3 50
Level	15 °C = 1 46										
3	30 °C = 1 42	Old	1 04	1 265	0 56	1 18	1 248	1 16	1 31	1 251	1 42

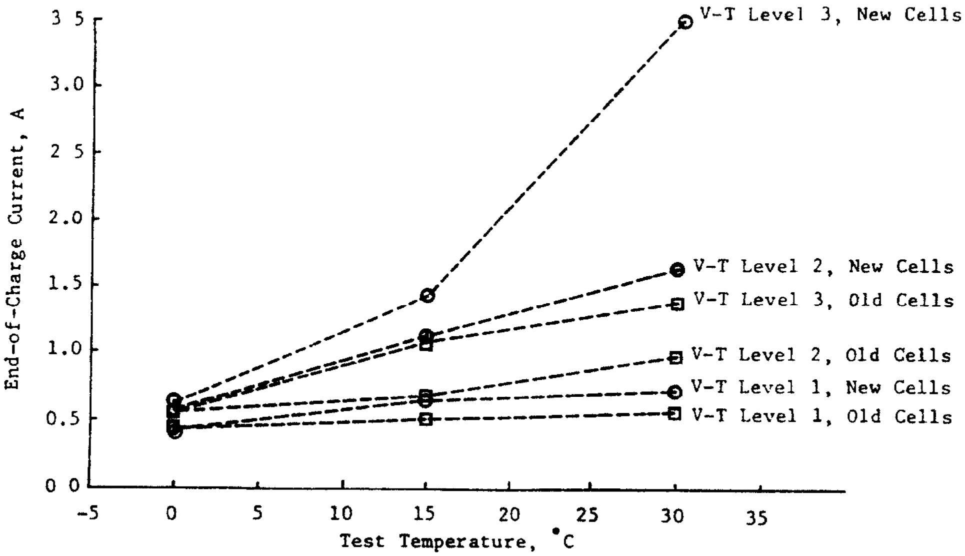

Fig 4 Effect of *V–T* level on End of Charge Current (EOCI)

V–T level 1, new cells (A) 0 °C, 0 44, 15 °C, 0 69, 30 °C, 0 74
old cells (A) 0 °C, 0 46, 15 °C, 0 5, 30 °C, 0 60
V–T level 2, new cells (A) 0 °C, 0 57, 15 °C, 1 264, 30 °C, 1 67
old cells (A) 0 °C, 0 52, 15 °C, 0 711, 30 °C, 1 00
V–T level 3, new cells (A) 0 °C, 0 60, 15 °C, 1 461, 30 °C, 3 50
old cells (A) 0 °C, 0 56, 15 °C, 1 16, 30 °C, 1 42

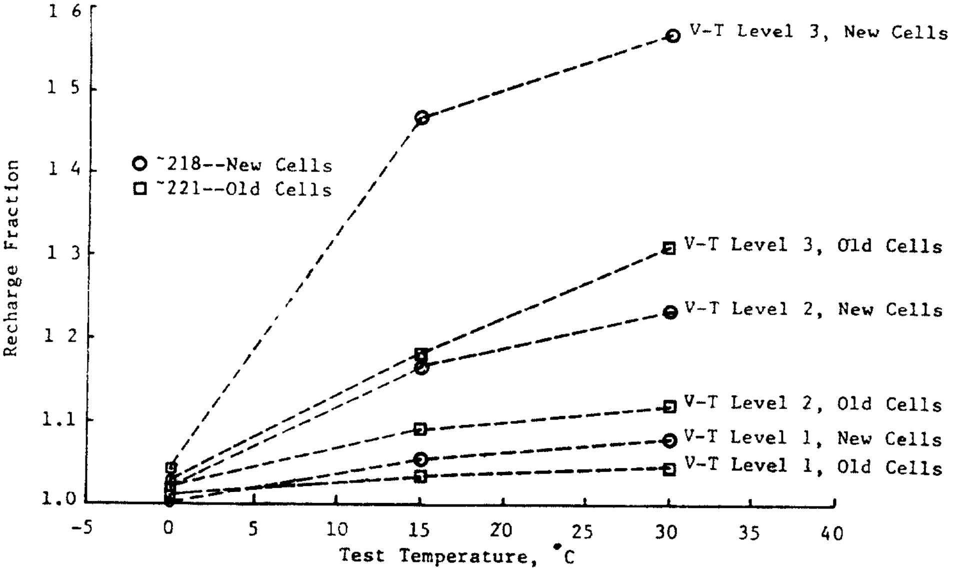

Fig 5 Effect of *V–T* level on Recharge Fraction (RF)

V–T level 1, new cells 0 °C, 1 003, 15 °C, 1 055, 30 °C, 1 078
old cells 0 °C, 1 005, 15 °C, 1 035, 30 °C, 1 045
V–T level 2, new cells 0 °C, 1 025, 15 °C, 1 162, 30 °C, 1 230
old cells 0 °C, 1 015, 15 °C, 1 086, 30 °C, 1 12
V–T level 3, new cells 0 °C, 1 03, 15 °C, 1 464, 30 °C, 1 562
old cells 0 °C, 1 04, 15 °C, 1 18, 30 °C, 1 31

TABLE 1

Discharge capacities

Temperature (°C)	Test			
	Baseline capacity test (A h)	V–T level 1 (A h)	V–T level 2 (A h)	V–T level 3 (A h)
0		1 45 (V/cell)	1 47 (V/cell)	1 49 (V/cell)
	(41 18, 40 93)	(37 73, 38 03)	(34 82, 38 40)	(35 10, 39 01)
15		1 42 (V/cell)	1 44 (V/cell)	1 46 (V/cell)
	(41 83, 41 72)	(38 37, 38 77)	(38 90, 36 73)	(37.58, 38 73)
30		1 38 (V/cell)	1 40 (V/cell)	1 42 (V/cell)
	(40 03, 39 21)	(37 39, 37 46)	(35 73, 34 71)	(33 06, 36 20)

Note All capacities are given as new cells and old cells

5 depicts the effect of V–T level on the recharge fraction of the two cell-packs as a function of temperature. These data represent values for the cycling just prior to the discharge.

The strong correlation between Figs. 4 and 5 is 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 post-cycling 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 Fig. 6. 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 2 can be attributed to an excessive number of cycles needed to achieve stabilization

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

Figure 7 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 interpretation of the expected trends shown in Fig. 7.

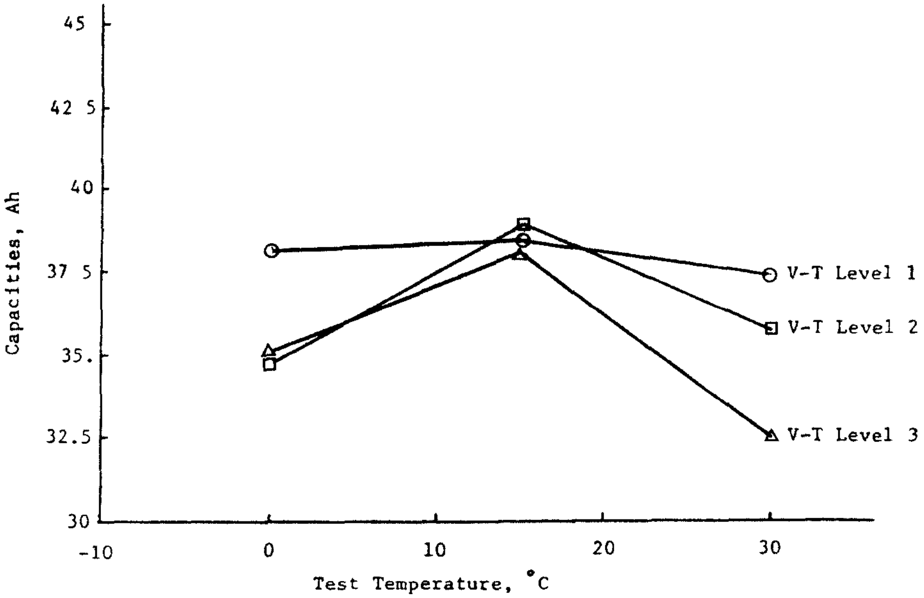

Fig 6 Effect of *V–T* levels on capacities of new cells
V–T level 1 (A h) 0 °C, 37 73, 15 °C, 38 37, 30 °C, 37 39
V–T level 2 (A h) 0 °C, 34 82, 15 °C, 38 90, 30 °C, 35 73
V–T level 3 (A h) 0 °C, 35 10, 15 °C, 37 58, 30 °C, 33 06

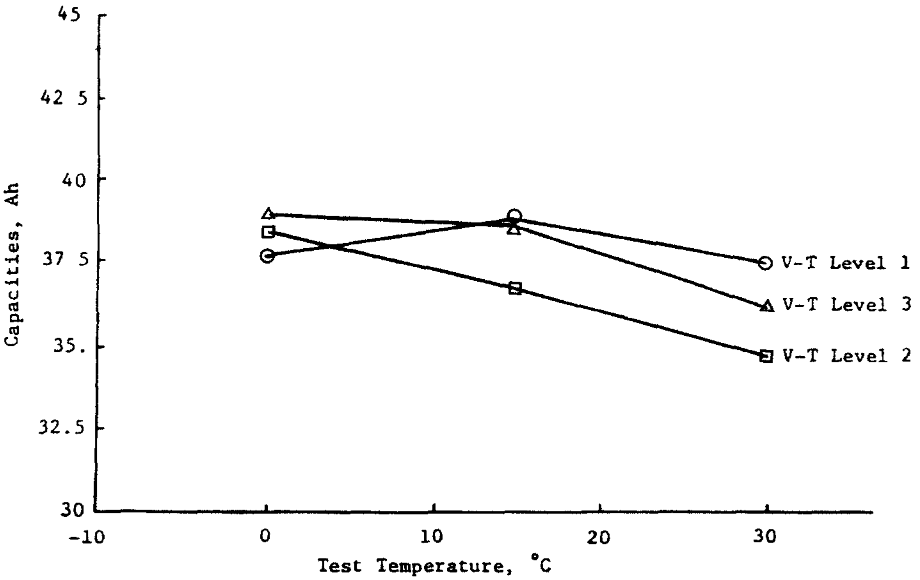

Fig 7 Effect of *V–T* levels on capacities of old cells
V–T level 1 (A h) 0 °C, 38.03, 15 °C, 38 77, 30 °C, 37 46
V–T level 2 (A h) 0 °C, 38 40, 15 °C, 36 73, 30 °C, 34 71
V–T level 3 (A h) 0 °C, 39 01, 15 °C, 38 73, 30 °C, 36 20

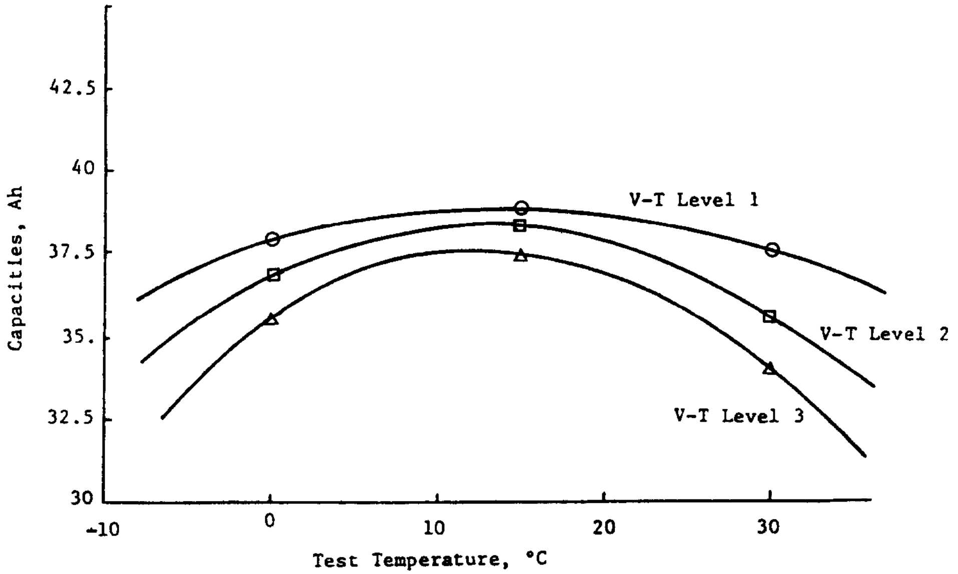

Fig 8. Effect of *V–T* levels on capacities of cells near beginning of life Expected general trends for capacities achieved by the new cells from interpretation of data in Fig 6

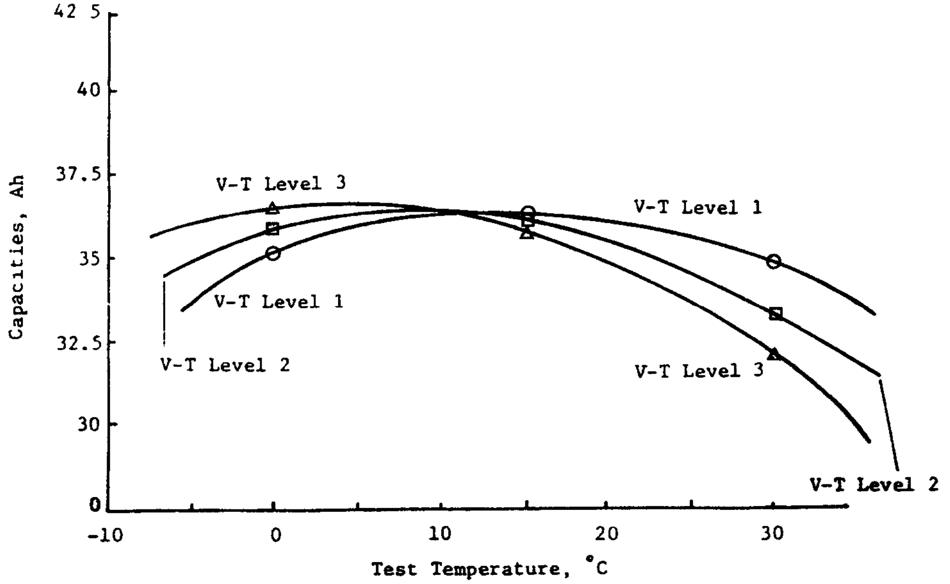

Fig 9 Effect of *V–T* levels on capacities of cells near middle-of-life Interpretation of the expected trends shown in Fig 7

There are two major differences between Figs. 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 investigation which 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, 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 is performed [4]. Earlier reports showed instances of a 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 elavated plate temperatures. This explanation is not valid in the light of the 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 a decrease in 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 Figs. 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, γ-nickel oxyhydroxide (NiOOH) [7] Additionally, it has been noted that electrodes with high concentrations of γ-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] which showed a significant inefficiency for discharging at states-of-charge less than 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-packs 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, not anticipated 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 if 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 support 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 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, 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.

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