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BEHAVIOR OF 2-CELL CPV NI-H_2 BATTERY DURING PULSE DISCHARGE

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ABSTRACT

A study was carried out to determine the transient voltage behavior of the 2-cell CPV nickel-hydrogen battery with the objective of using the results as a basis for mathematical modeling . The 2- cell CPV battery which is manufactured by Eagle Picher, Inc. for the GOES program yields 18.5 Ah at C/2 rate of discharge at 10°C with a mid-discharge voltage of 2.514 V. The capacity increased with decrease of temperature and a maximum capacity of 22 Ah was obtained at - 5°C. The pulse tests consisted of obtaining the voltage profile in the first 20 milliseconds of the one minute pulse discharge at 37 A and pulse discharge was repeated as a function of state- of- charge. The pulse test at 10°C and 20°C provided voltage profiles with the expected decrease in voltage as the pulse was applied. The end of pulse voltage decreased with the state-of-charge. The battery voltage was above 2V at the end of the one-minute pulse at 8 % state-of-charge at 10°C. The voltage profile during the 37 A pulse discharge consists of an initial drop in voltage which was independent of the state of charge. The invariability in the value for the initial drop in voltage with state of charge is a very important observation. The results show that towards the end of discharge the dominant resistance is not ohmic in nature. It could be hypothesized from the nature of the voltage transients that the dominant mechanism towards the end of discharge is proton diffusion. The study also shows that the dominant resistance in the voltage plateau during discharge is activation polarization.

INTRODUCTION

The 2-Cell CPV nickel-hydrogen battery manufactured by Eagle Picher is a variation of the aerospace individual pressure vessel cell (IPV) with the same elctrochemical performance features but with an operating voltage of 2.5 V and a specific energy of 58 Wh/Kg. The purpose of this work is to examine the characteristics of the 2-cell CPV battery including the behavior during pulse discharge. The purpose of the pulse test was to determine lowest state of charge at which the battery can sustain a 37 A pulse discharge with minimum voltage degradation and assess the effect of high burst currents on the usable capacity. Another objective is to analyze the transient voltage response to determine the dominant mechanism for the abrupt decrease in voltage at low states-of- charge.

CAPACITY AND SELF DISCHARGE

The capacity of the four 2-cell CPV batteries at 10°C was determined to be 18.5 Ah (to 2V) and the mid-discharge voltage to be 2.514 V. The capacity remaining after 72-hours of open-circuiting at 10°C was 86.7%. Thus, the self-discharge rate is similar to that of single cells. Figures 1 and 2 show the voltage profiles during charge and discharge, respectively and the features are such as voltage roll-over during charge and plateau region during discharge are identical to that of IPV cells. The mid-discharge voltage during discharge at C/2 after the 72-hour stand test was 2.485 as shown in Figure 3. Thus, the initial capacity tests indicate performance features of two properly connected cells in series.

RATE AND TEMPERATURE DEPENDENCY

The variation of capacity with the rate of charge and discharge and temperature was determined. The capacity was the highest with a value of 22 Ah at -5°C at a charge rate of C/10 and discharge rate of C/10. The capacity increased from 19.58 Ah to 20.35 Ah when the charge rate was increased from C/20 to C/2 at 10°C. The capacity at a charge rate of 0.8 C and discharge rate of 0.8 C was 20.05 Ah. The capacity increased with decrease of temperature and at -5 °C, a charge rate of C/2 yielded a capacity of 20.97 Ah. Figure 4 shows the voltage profiles at different rates of discharge at 10°C for one of the CPVs. As expected the mid-discharge voltage decreased with increase in the rate. The capacity decreased when the discharge rate was increased from 0.5 C to 0.8 C. Figure 5 shows the voltage profiles at C/2 rate of discharge at different temperatures. At -5°C the discharge voltage is high in the beginning and low towards the end. In the plateau region the mid-discharge voltage is almost the same at all temperatures studied. Figure 6 shows the voltage profiles at C/10 rate of discharge at different temperatures. The profiles at C/10 differ from that obtained at C/2 rate with respect to the appearance of a shift in the mid-discharge region and the observation of higher discharge voltages at -5°C towards the end of discharge. It is to be noted that the negative electrode polarization is higher at - 5°C and this characteristic results in a slightly lower discharge voltage at -5°C The reason for the higher voltage beyond the mid-discharge region at C/10 rate compared to C/2 is due to the overwhelming influence of the polarization at the nickel electrode. The variation of capacity with temperature when charged and discharged at 0.8 C was also determined as shown in Table 1. The mid-discharge voltage and capacity showed marginal changes with the temperature.

PULSE TEST

The pulse test was performed using a Hewlett-Packard 6050 A programmable electronic load which has a slew rate of 400,000 A/s to reach the pulse current of 37 A in <150 μs. The CPV battery voltage was measured using a Nicolet 460 storage oscilloscope. The procedure consisted of obtaining the transient voltage profile in the first 20 milliseconds of a one-minute pulse at 37 A. The application of the 37 A pulse was done by increasing the discharge rate from 9.3 A to 37 A during discharge at regular intervals such as 90% state-of -charge, 80%, 70 %, etc. The application of pulses were concluded when the voltage reached 2 V during the 9.3 A discharge. The pulse discharge was first done with the CPV battery stabilized at 10°C and then the test was repeated at 20°C.

Figure 7 shows the voltage transient obtained during the first 2 milliseconds of pulse discharge. The voltage of the battery decreases by 0.71 V in first few microseconds and then the voltage recovers to a value 200 mV less than that obtained during the 9.3 A discharge. This is an expected behavior and the initial drop of 710 mV translates to an ohmic resistance of 25.6 milliohms.

Figure 8 shows the variation of end of pulse battery voltage as a function of state-of -charge at 20°C. The features of the curve are similar to a discharge voltage profile with an initial decline, a plateau region and final decrease in voltage. Thus, the battery is able to sustain pulse discharges at states-of-charge as low as 12%. A very similar behavior was observed at 10°C and the lowest state-of-charge at which the battery would support a pulse current was 8 %.

Figure 9 shows the variation of initial drop in voltage with the state-of charge. The trend in the data showed that the initial drop was ~ 670 mV and it did not change with state-of-charge. The initial drop in voltage is related to the ohmic resistance at the nickel electrode surface. It is known that, the discharged active material, $Ni(OH)_2$ grows on the surface of the charged active material. The electronic conductivity is expected to decrease with the growth of the discharged active material on the nickel electrode with the consequent increase in polarization. The pulse behavior data indicates that the ohmic resistance calculated from the initial drop in voltage amounts to ~ 25.6 mohms and it does not increase with the accumulation of discharged active material.

DOMINANT RESISTANCE

During constant current discharge the reaction rates at the nickel and hydrogen electrode proceed at a constant rate, the reaction at the nickel electrode being the limiting factor. The hydrogen electrode functions with an average polarization loss of 25 mV at 15 mA/cm^2 at a discharge rate of C/2. Thus the shape of the voltage - time curve depends primarily on the reactions of $Ni(OH)_2$ which consists of processes like the diffusion of OH^- ions in the bulk electrolyte, diffusion of protons into the bulk of the solid phase, increase of OH^- concentration on the nickel electrode surface, and build-up of $Ni(OH)_2$ on the surface of NiOOH active material. The voltage of the nickel electrode and the cell is therefore governed by:[1]

- Concentration polarization due to a rise in the KOH concentration
- Activation polarization or charge transfer resistance of the nickel electrode reaction
- Diffusion polarization related to proton
- Ohmic effects: resistance polarization at the solid phase

The dominant resistance at different segments of the discharge curve is not known with certainty. The dominant resistance in the plateau region of the discharge curve is said to be activation polarization. The dominant resistance towards the end of discharge (knee of the curve) during constant current discharges is said to be ohmic in nature. The invariability in the initial voltage drop obtained in the pulse test indicates that the dominant resistance is not ohmic. The other possibilities such as concentration polarization and activation polarization can be excluded based on published information in the literature. The other alternative is polarization loss attributable slow proton diffusion. A previous study by Salkind et al[2] attributed the suppressed discharge voltages at 1C rate of discharge at 25% state of charge by sintered impregnated electrodes to a diffusion problem since an ohmic effect would have magnified the effect in a fiber mat electrode. The results of this study also suggests that the voltage drop is attributable diffusion and specifically proton diffusion. Weidner et al[3]. pointed out that the ohmic effect is not significant during a major portion of discharge and contributes very little to the overall polarization loss, but conductivity at the end of discharge causes significant polarization losses. The results obtained in our study are contrary to this and the reason for the large polarization loss towards the end of discharge is not ohmic in nature.

CONCLUSIONS

The results of this study suggest the following conclusions:

• The CPV battery yields a capacity of 22 Ah and retained 86.7% of the capacity in the 3-day open-circuit stand test.
• The battery can sustain a 3C rate pulse for one minute at low states-of-charge (8%). The initial decline in the voltage during the 3C rate pulse is about 670 mV and the voltage recovers in less than one millisecond.
• Analysis of the initial decline in voltage during the pulse test indicates that the resistance polarization is not significant and the polarization loss at very low states-of-charge is attributable to slow proton diffusion.

REFERENCES

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2. Salkind, A.J., Kelly, J.J., and Ockerman, J.B. Proc. Symp.on the Nickel Electrode, 176th Meeting of the Electrochemical Society, Hollywood, Fl, Pennington, N.J. Vol.90-4, pp247-260
3.J.W.Weidner, and P. Timmerman, J. Electrochem. Soc ,Vol 141,1994,p 346

FIGURE 1: VOLTAGE PROFILES DURING CHARGE AT C/10 AT 10°C

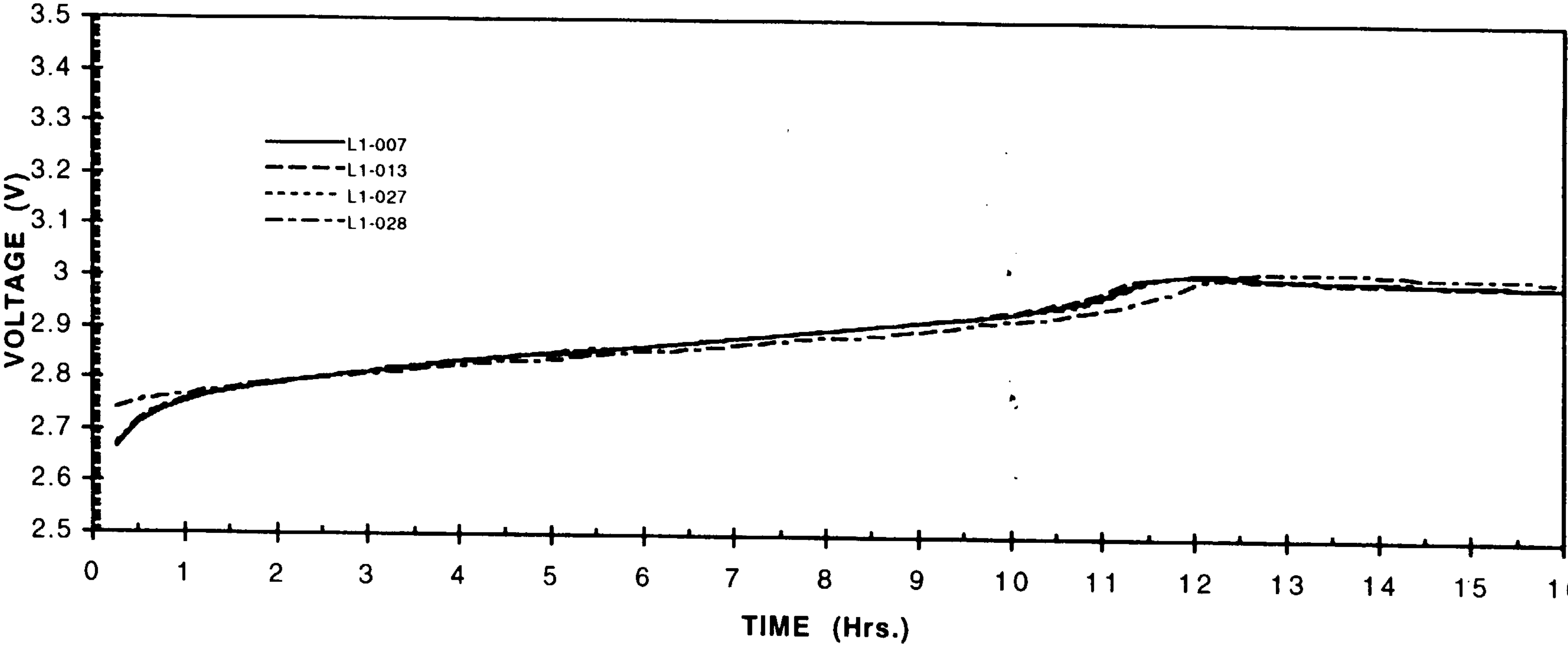

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FIGURE 2: VOLTAGE PROFILES DURING DISCHARGE AT C/2 AT 10°C

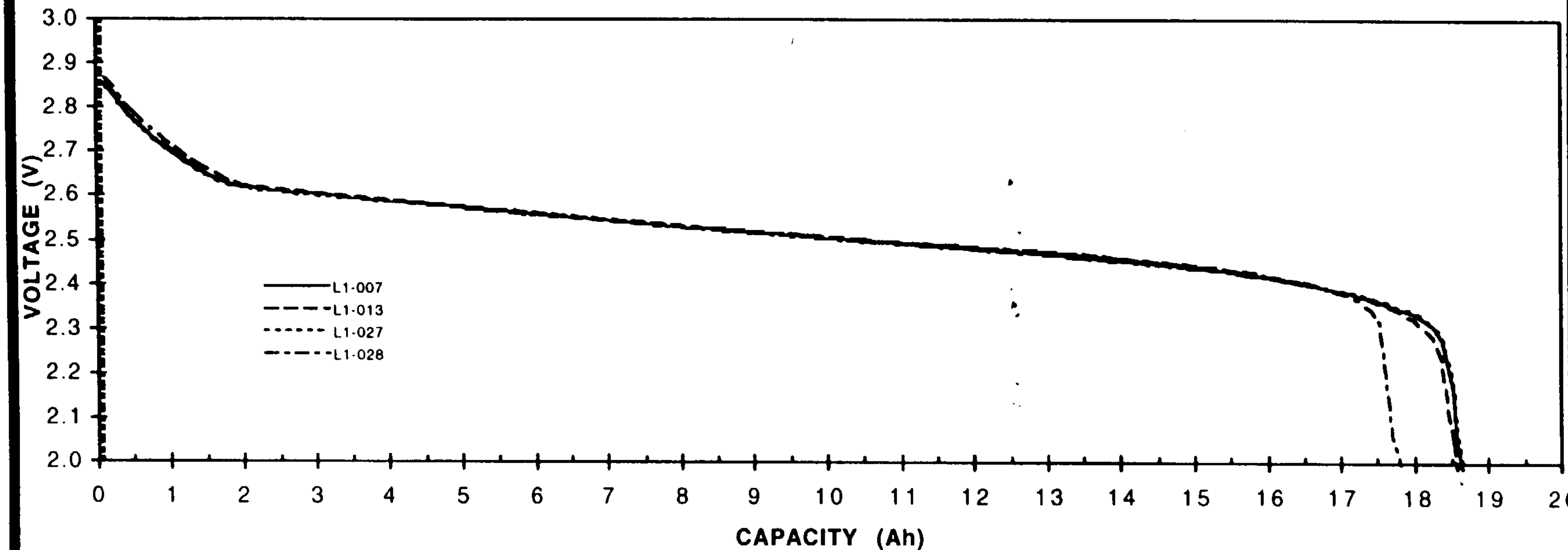

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FIGURE 3: VOLTAGE PROFILES AFTER OPEN-CIRCUIT STAND AT 10°C

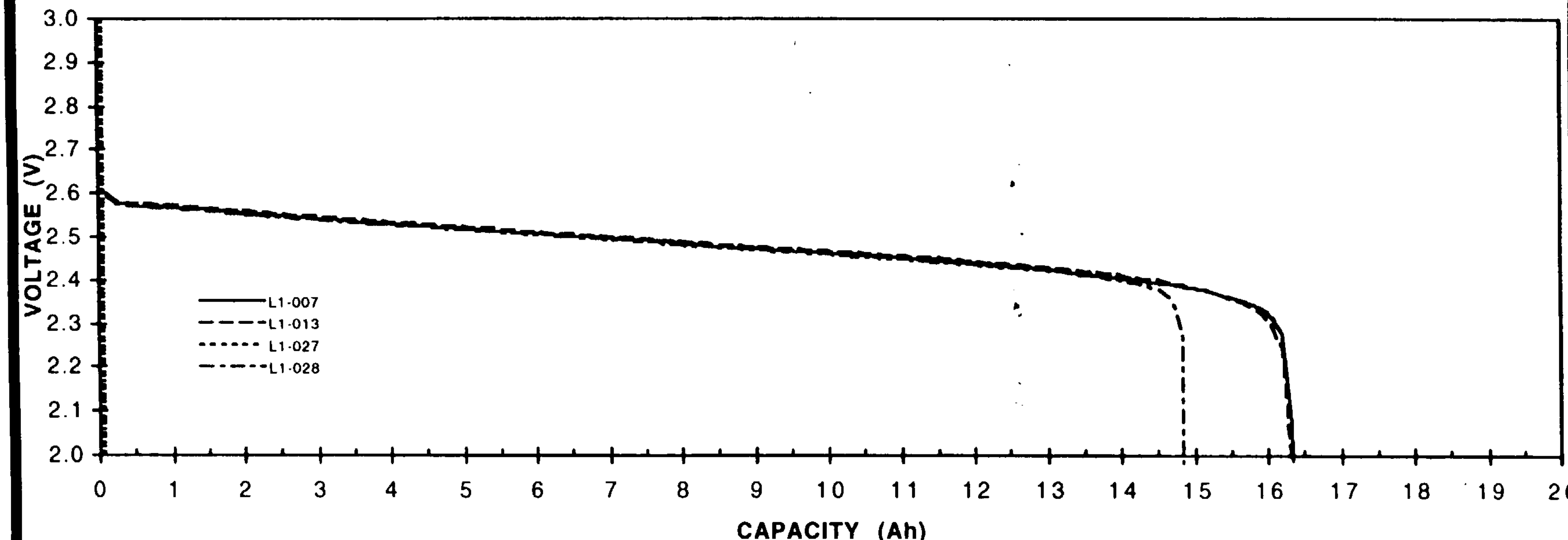

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FIGURE 4: VOLTAGE PROFILES AT DIFFERENT RATES OF DISCHARGE AT10°C

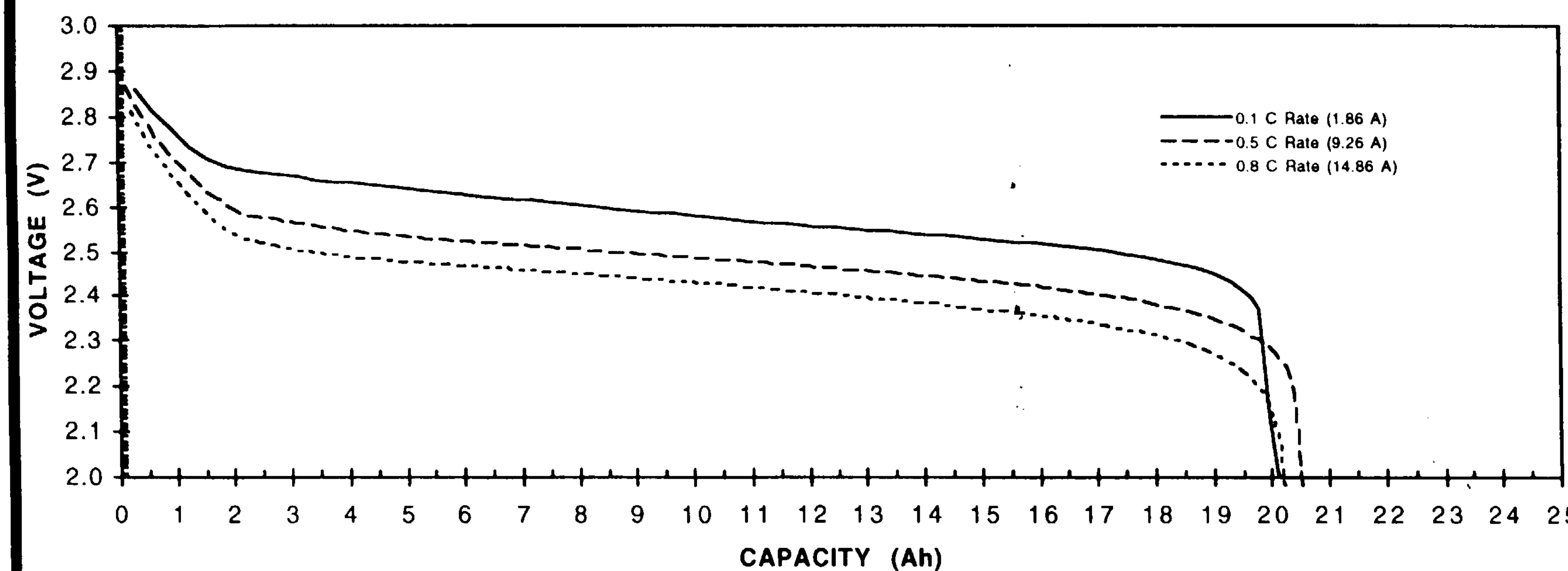

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FIGURE 5: VOLTAGE PROFILES AT DIFFERENT TEMPERATURES DURING DISCHARGE AT C/2

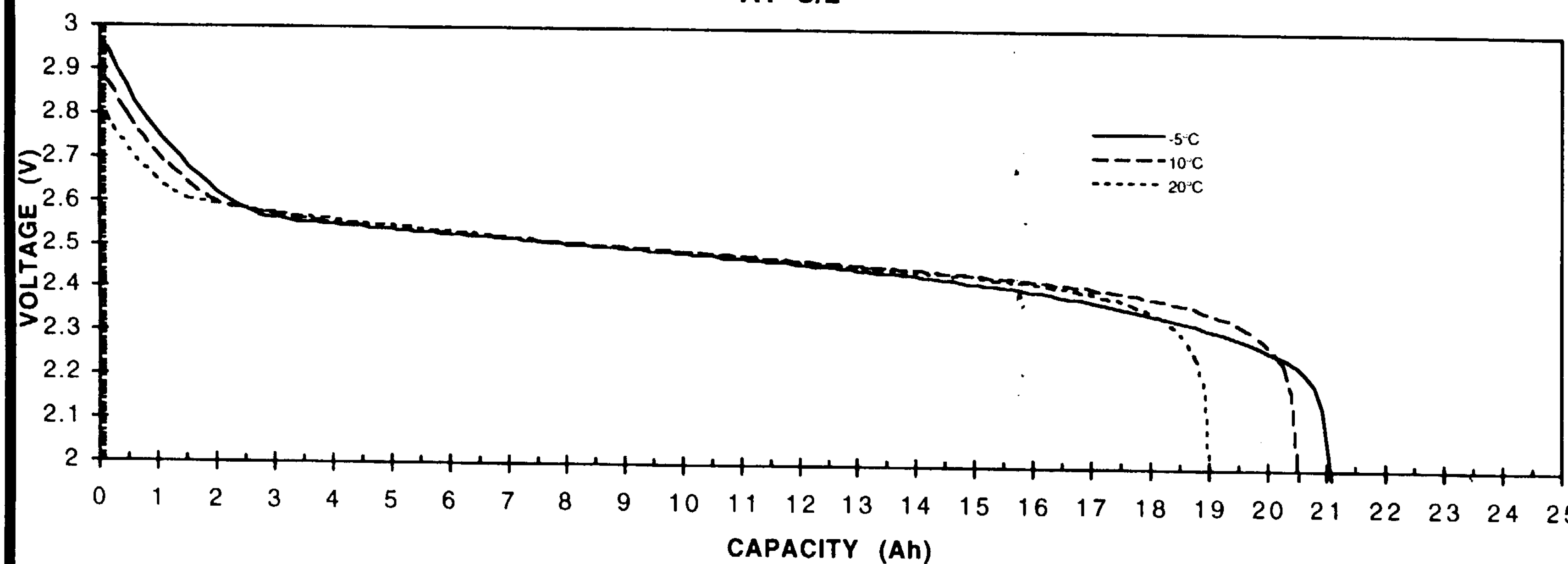

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FIGURE 6: VOLTAGE PROFILES DURING C/10 DISCHARGE AT DIFFERENT TEMPERATURES

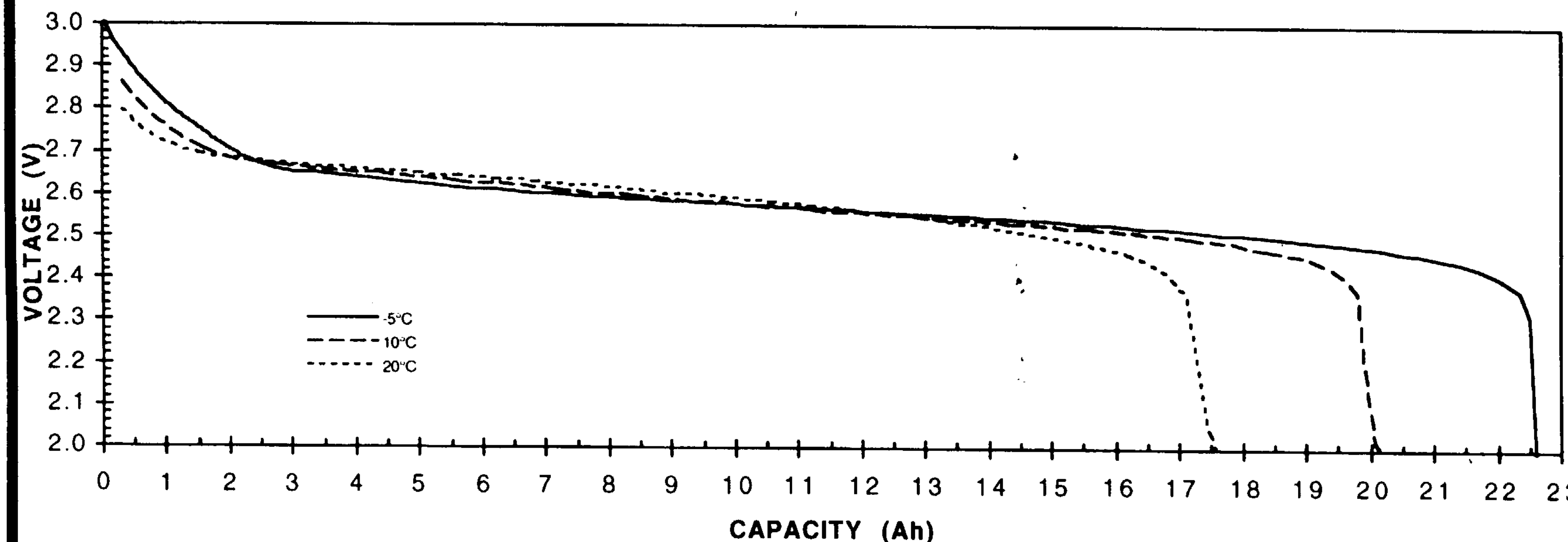

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FIGURE 7:VOLTAGE TRANSIENT OBTAINED AT 21% STATE OF CHARGE

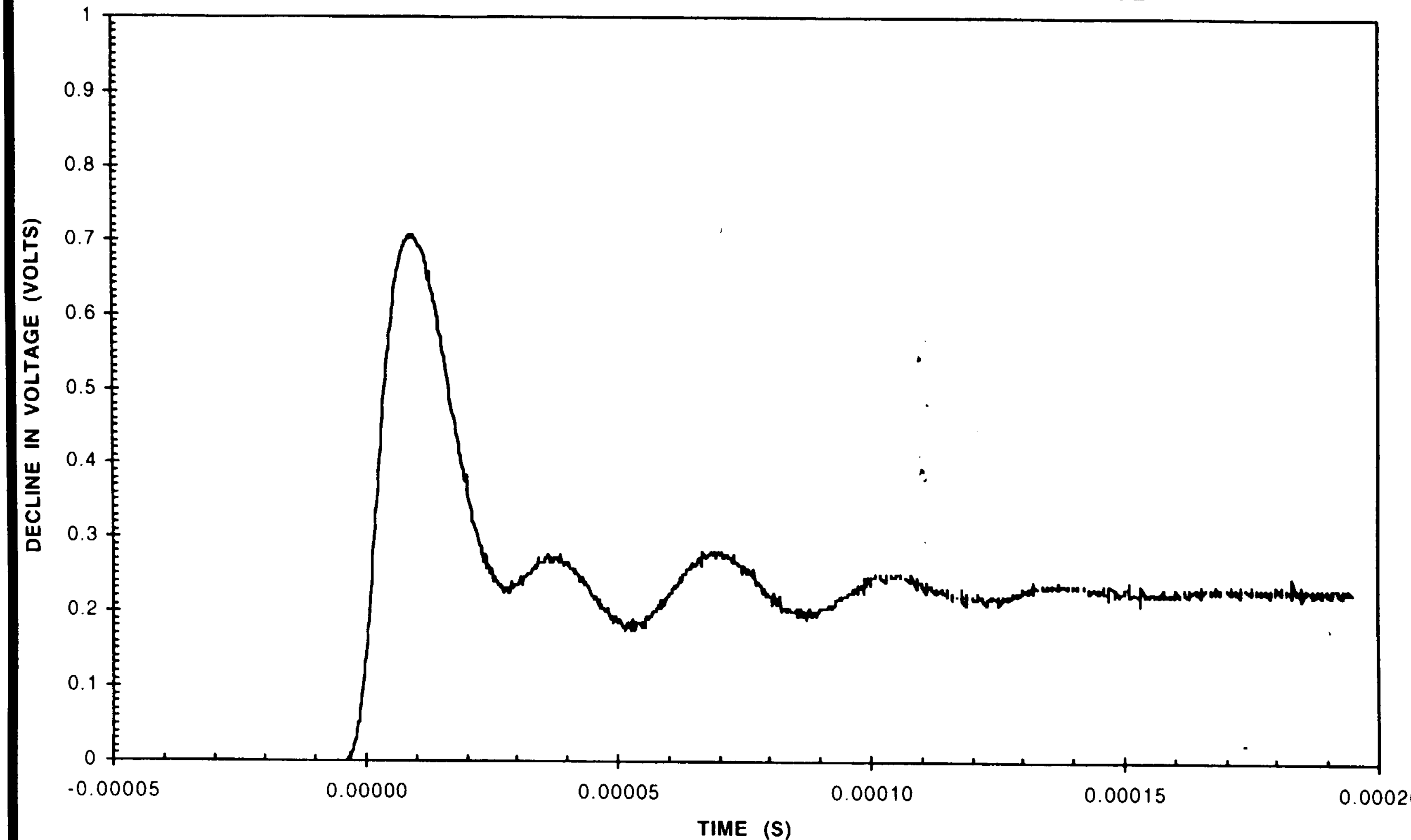

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FIGURE 8. VARIATION OF END-OF-PULSE VOLTAGE WITH THE STATE-OF-CHARGE

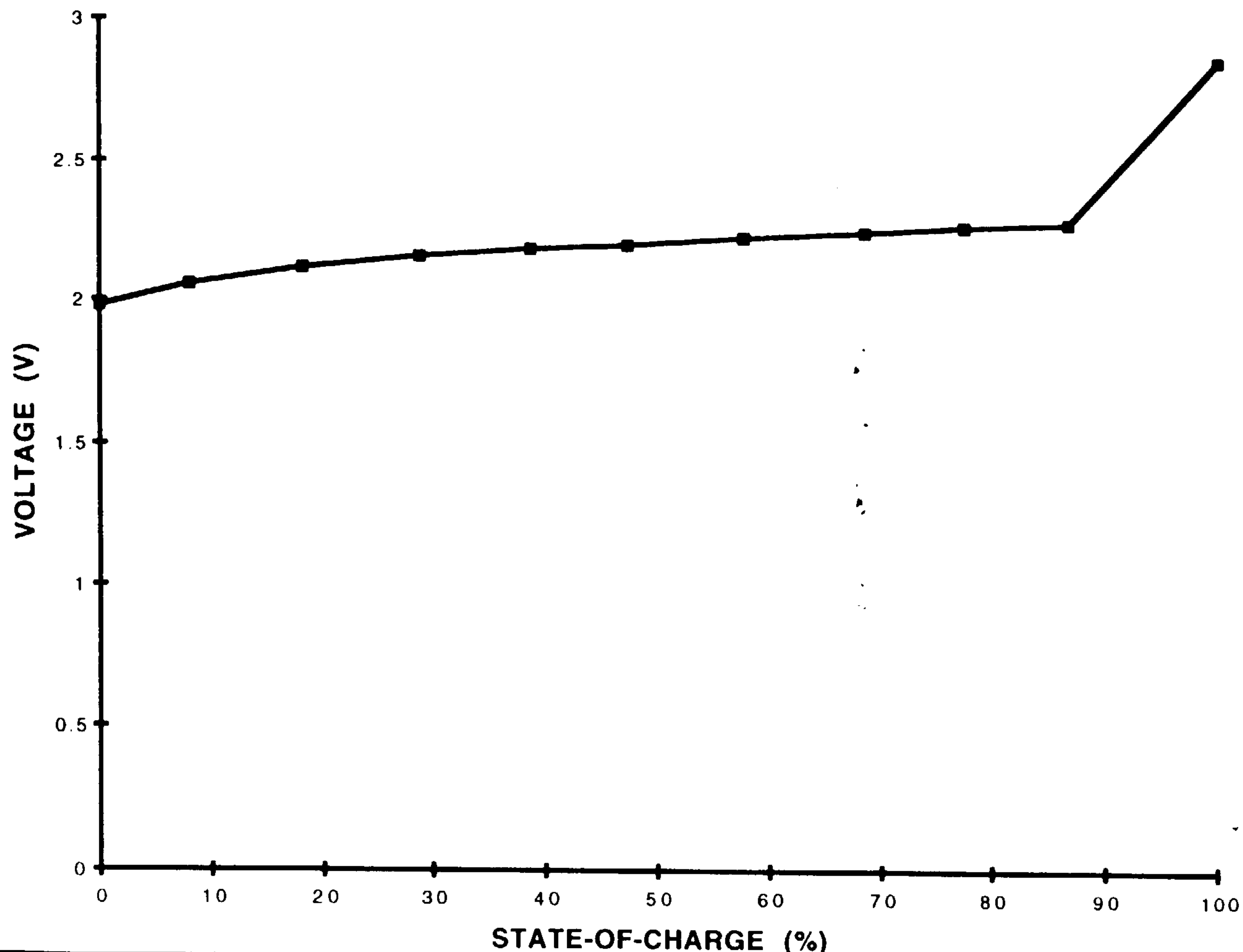

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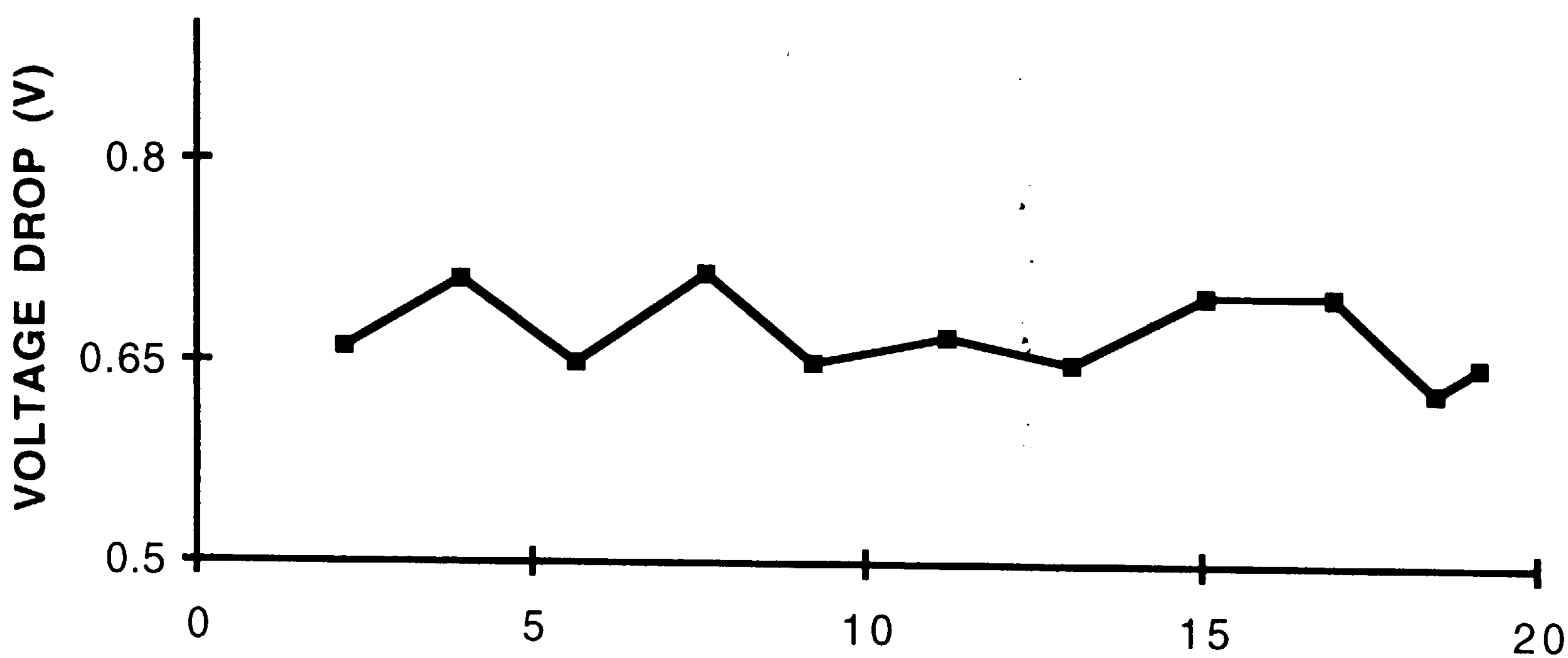
FIGURE 9. VARIATION OF INITIAL DROP IN VOLTAGE WITH THE STATE- OF-CHARGE



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Cycle	Temp (°C)	Current Charge (A)	Current Discharge (A)	L1-007 EOCV (V)	L1-007 Mid-Dch V (V)	L1-007 Capacity (Ah)	L1-013 EOCV (V)	L1-013 Mid-Dch V (V)	L1-013 Capacity (Ah)	L1-027 EOCV (V)	L1-027 Mid-Dch V (V)	L1-027 Capacity (Ah)	L1-028 EOCV (V)	L1-028 Mid-Dch V (V)	L1-028 Capacity (Ah)
1	10	0.8	8	2.976	2.495	19.57	2.970	2.498	19.42	2.976	2.498	19.57	2.998	2.495	19.77
2	0	1.6	8	3.082	2.491	20.27	3.076	2.498	20.17	3.080	2.498	20.23	3.093	2.499	19.45
3	10	1.6	8	2.992	2.513	18.64	2.990	2.516	18.57	2.993	2.510	18.68	3.005	2.519	17.80
4 *	10	1.6	8	3.010	2.482	16.36	3.008	2.488	16.32	3.010	2.480	16.36	3.022	2.492	14.90
5	20	1.6	8	2.941	2.548	16.45	2.941	2.552	16.34	2.943	2.545	16.58	2.944	2.558	15.67
6	-5	1.86	1.86	3.044	2.567	22.61	3.043	2.570	22.51	3.042	2.566	22.69	3.048	2.573	21.71
7	10	1.86	1.86	2.992	2.576	20.13	2.991	2.576	20.08	2.992	2.576	20.27	2.999	2.577	19.79
8	20	1.86	1.86	2.944	2.607	17.59	2.945	2.610	17.48	2.945	2.609	17.75	2.949	2.611	16.96
9	-5	9.26	9.26	3.258	2.470	21.16	3.252	2.478	21.10	3.265	2.471	21.21	3.233	2.482	20.43
10	10	9.26	9.26	3.135	2.483	20.53	3.129	2.487	20.53	3.144	2.482	20.61	3.115	2.492	19.74
11	20	9.26	9.26	3.019	2.489	18.96	3.020	2.491	19.03	3.032	2.487	19.17	3.004	2.494	18.54
12	10	14.81	14.86	3.220	2.429	20.21	3.213	2.434	20.21	3.235	2.426	20.28	3.193	2.437	19.52
13	15	14.81	14.86	3.190	2.428	19.98	3.184	2.433	19.89	3.204	2.425	20.05	3.160	2.436	19.20
14	20	14.81	14.86	3.143	2.429	19.55	3.135	2.431	19.48	3.158	2.425	19.66	3.114	2.433	18.91

* 72-hour open circuit stand