Naval Surface Warfare Center
Carderock Division
West Bethesda, MD 20817-5700

NSWCCD-TR-98/005 April 1997

Survivability, Structures, and Materials Directorate
Technical Report

Development of HWAM Li_xCoO_2 Reserve Battery

by

Charles J. Kelly (Alliant Techsystems, Inc.)

Edited by Charles W. Fleischmann (Advanced Technology & Research Corporation)

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The Alliant Techsystems' development program for a reserve, Hand-Emplaced Wide Area Munition (HWAM) Battery successfully demonstrated the capability of a lithium metal/lithium cobalt dioxide electrochemical system to meet the tactical needs of the HWAM. Extensive safety testing, as part of a developmental program, proved that internal and external short circuit abuses do nothing to change the benign behavior of the power source. Because of its reserve design, long term storage has no effect on the battery's readiness when called upon to supply power for HWAM Standby, Alert, and Launch modes. Fourteen ampere-hours of reserve capacity, demonstrated in fully-developed hermetic cell hardware, can be increased to above twenty ampere-hours with small adjustments in volume. This production-ready design demonstrated extensive safety, fresh power from reserve storage, and an affordable unit price in practical production quantities.

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Preface

Contract No. N60921-93-C-0060, Option 7, awarded to Alliant Techsystems, Inc. by the Naval Surface Warfare Center, and funded by Office of Naval Research, developed large (100 Ah) rechargeable lithium/lithium cobalt oxide cells for batteries to propel undersea vehicles. As built, these cells were in the discharged state because the available precursor cathode material was of the electrochemically-discharged chemical composition. Charged precursor cathode material was not only unavailable, but its chemical stability was unknown and suspect. Obtaining it required development of a preparatory process and an understanding of its handling requirements for cathode manufacture. Recognizing that there could be advantages to building cells in the charged state because the user could put them immediately into service, and that applications needing reserve cells require them, the Navy was pleased to include a development effort to prepare charged precursor cathode material when given the opportunity *via* Army funding. Under Option Item 7 to the contract, the Army (Project Manager for Mines, Countermine, and Demolitions) funded development of charged lithium/lithium cobalt oxide cells to power Hand-Emplaced Wide Area Munitions (HWAM). This effort intended to develop reserve cells, which were also capable of a limited number of charge/discharge cycles, as an alternate to the baseline system, lithium/thionyl chloride, a non-rechargeable battery.

Chapter 1

Introduction

The first goal of this program was to conduct a cell and battery design analysis such that the final battery design would comply with the specified weight and specific geometric volume identified in Customer Specification No. 29224A Figure 1-1, Reserve Battery Outline and Interface. This specification is for the Hand-Emplaced Wide Area Munitions (HWAM). To meet the second goal, the battery's unit cell would have its design detailed for eventual demonstration build and test. The battery design analysis was required by contract to include the following key elements:

- design for battery rechargeability,
- battery state-of-charge indication,
- design circuitry to control recharge,
- comparison of the advantages/disadvantages of an internal/external reservoir,
- battery production cost analysis,
- battery environmental issues of manufacture and disposal,
- safety of the battery design and analysis of probability of battery explosion on internal or external short circuit.

The battery design analysis, once completed, was the basis for a detailed cell design. The cell design was documented by a drawing package. Revision updates to the drawing package resulted from the contract-required execution of cell fabrication and testing. The final drawing package is given as Appendix A. The cell development process was one of verification by experiment of key concerns regarding form factor, reserve capability, rate, and environmental limits for an advanced electrochemistry, namely, lithium/lithium cobalt dioxide (Li/Li_xCoO_2). The steps were as follows:

- The cell design was evaluated in single-cell, bolt-together test fixtures of a configuration that represented the final cell internal design, except the number of plates per cell were not the same as that anticipated for the final design.
- In a parallel effort, the cell build procedures were optimized, particularly with regard to the synthesis process for manufacturing electrochemically-charged lithium cobalt dioxide for cell cathodes.
- Next, the cell design was demonstrated in single cell test fixtures containing multi-plate electrodes of anticipated full-cell design quantities. Voltage versus discharge rate data obtained from these tests were used to project battery performance for a three-cell, series design at full Hand-Emplaced Wide Area Munitions (HWAM) load requirements.
- Finally, cells were constructed of the final design in hermetically-welded cell cases and tested at the environmental extremes outlined in the contract specification.

SPECIFICATION NO. 29224A

NOTES:

1. TERMINAL STYLE SHALL BE SUITABLE FOR SOLDERING ON NO. 22 AWG WIRE. PIN NUMBERS TO IDENTIFY FUNCTION AND LOCATION ONLY.

② SURFACE TO BE FLAT WHEN INSTALLED IN A BASE ASSEMBLY FIXTURE WITHIN 0.005 IF MIDSECTION OF SURFACE A BOWS TO THE RIGHT. FLATNESS CONTROL NOT REQUIRED IF MIDSECTION OF SURFACE A BOWS TO THE LEFT AS LONG AS 2.870 DIMENSION IS NOT EXCEEDED.

③ LABEL TO BE LOCATED ON THIS SURFACE SHALL BE MARKED IN ACCORDANCE WITH MIL-STD-130 WITH THE FOLLOWING INFORMATION.

SUPPLIER NAME/CAGE
TDS NAME/CAGE
PART NO. 12908045 ITEM NAME
(WAM RESERVE BATTERY) AND
AND LOT DATE CODE.

TERMINAL PIN	FUNCTION
1	+12 VDC
2	BATTERY INITIATE
3	+12 VDC RETURN
4	BATTERY INITIATE RETURN

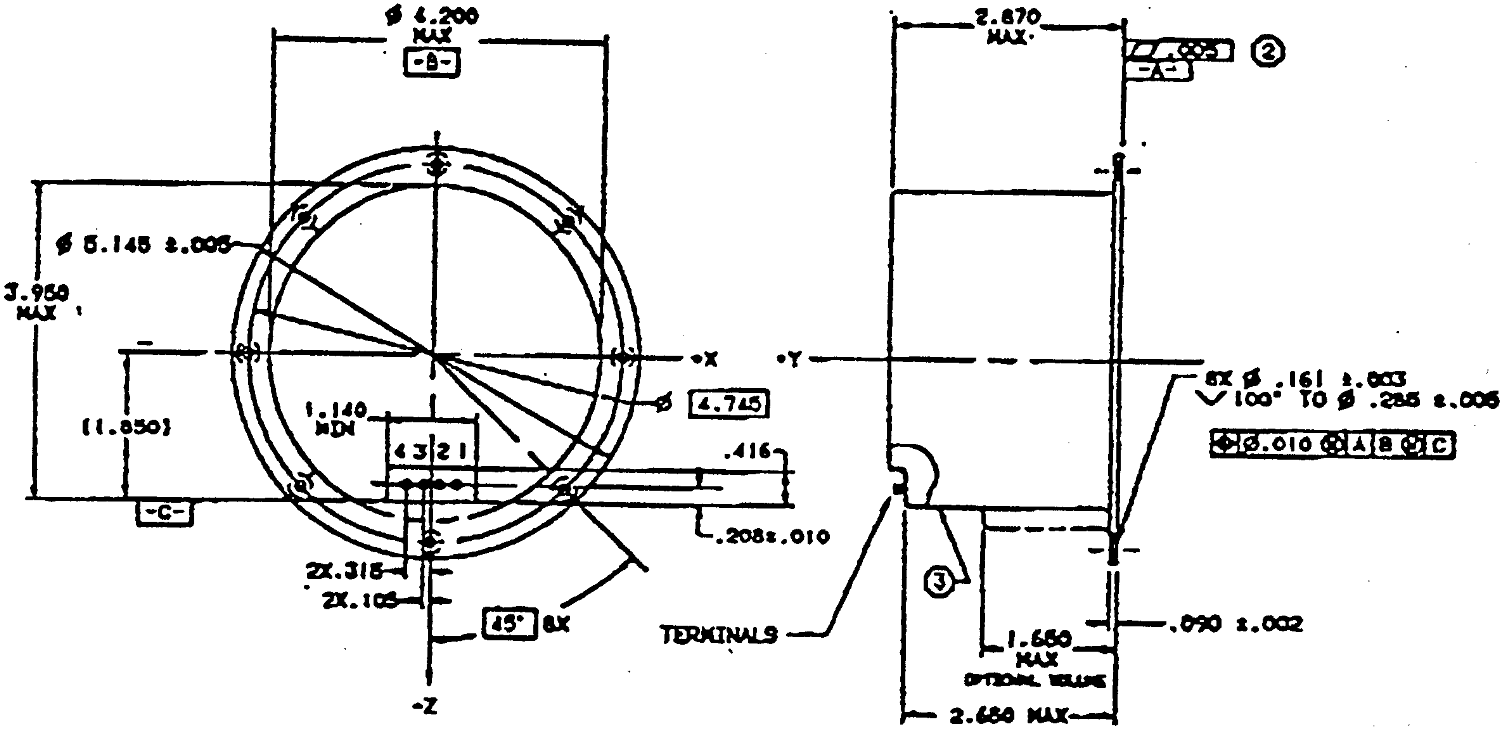


Figure 1-1. Reserve Battery Outline and Interface

Chapter 2

Requirements

The battery electrical specifications, physical requirements, and environmental conditions are outlined in Table 2-1. In a similar manner, Figure 1-1 is a reproduction of the HWAM Battery outline drawing from Specification No. 29224A, dated 17 August 1993. This drawing provides all of the interface information needed to mate the battery to the HWAM. Figure 2-1 is also a reproduction from Specification No. 29224A and schematically shows the desired battery activation time for both the hydraulic flow time, T_H (time for the electrolyte in the battery reservoir to reach the electrode stack), and the electrical rise time, T_r (time for the battery to come up in voltage from 0 volts to a minimum of 8 volts).

The power demands of the HWAM have a duration of a minimum of 180 days at "Standby" mode prior to device "Arming," followed by up to 30 days in the "Alert" mode, and finally ending on command in a terminal phase of engaging the threat and launch. Details of the power profile are shown in Figure 2-2. Because some use scenarios would benefit if the battery could be cycled a few times, the cycle life was determined.

Table 2-1. Form and Function Requirements
Reference: Spec. No. 29224A, 17 August 1993

Dimensions (Fig. 1-1): - Flange Diameter: - Case Diameter: - Height:	 5.145 in max. 4.200 in max. (3.95 in flat side diameter) 2.870 in max.
Weight:	3.0 pounds +0, -0.3 pounds
Leakage:	The battery shall be a hermetically sealed device.
Activation:	Activate in any orientation relative to the local horizontal. Voltage rise time: 0.5 seconds max. to 8.0V (2.67 V/cell) from first detectable voltage.
Voltage and Load: - Maximum Voltage (240 Ma): - Minimum Voltage (240 Ma): - Minimum Voltage for Ordnance Loads (3.75 A):	 15.0 volts (5.0 volts/cell) 10.0 volts (3.33 volts/cell) 8.0 volts (2.67 volts/cell)
Capacity: When discharged at a constant load of 400 ± 10 Ma, the battery shall maintain a minimum output voltage of 10 volts for the following number of hours:	32.5 hours at 145°F, 13.0 Ah 35.0 hours at 72°F, 14.0 Ah 26.5 hours at -25°F, 10.6 Ah
Temperature - Non Operating: **High Temperature - Operating:** **Low Temperature - Operating:**	The battery shall meet the requirements after exposure to temperatures from -50°F to +160°F. The battery shall meet the requirements during exposure to temperatures as high as +145°F. The battery shall meet the requirements during exposure to temperatures as low as -25°F.

SPECIFICATION NO. 29224A

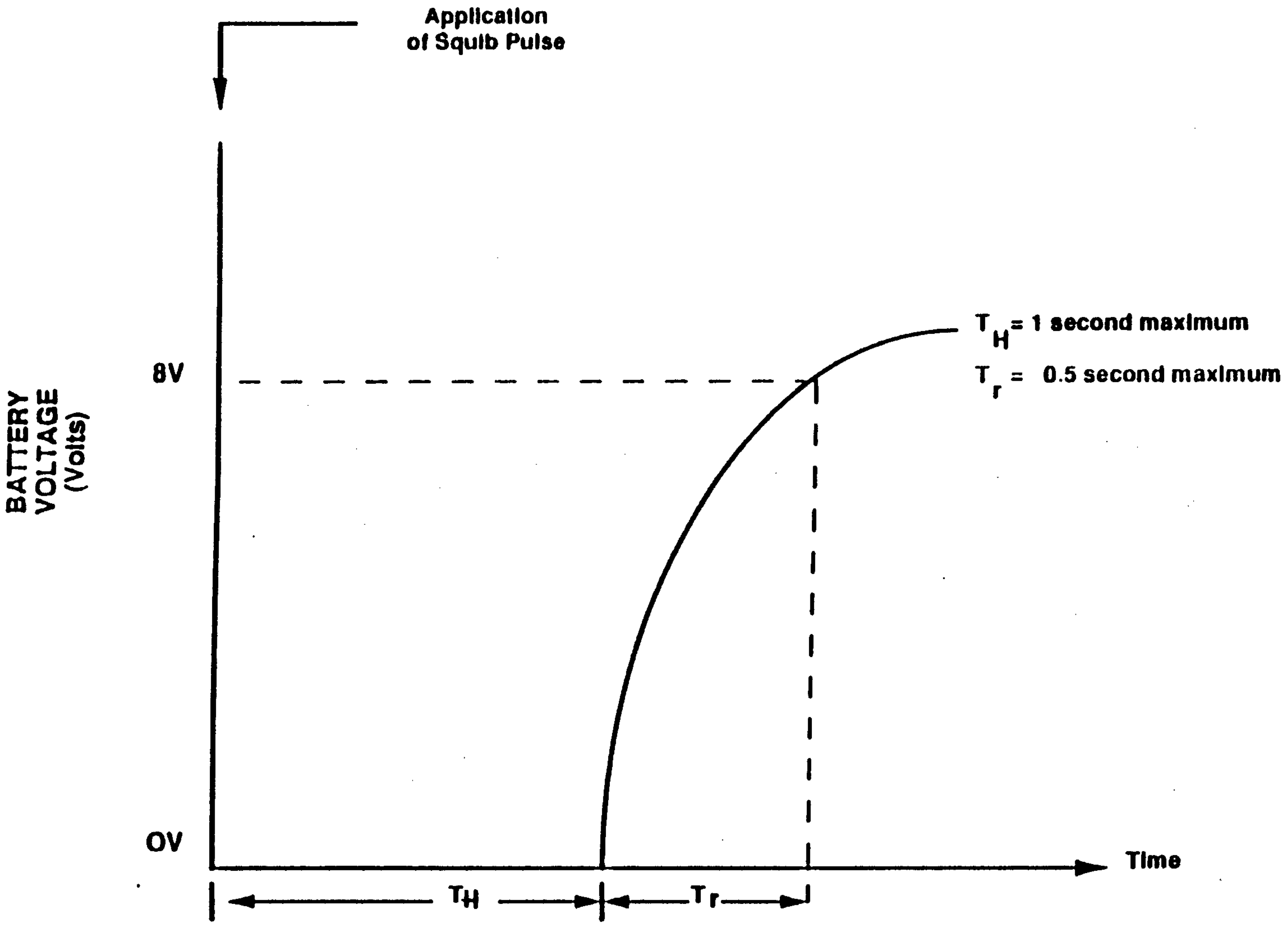
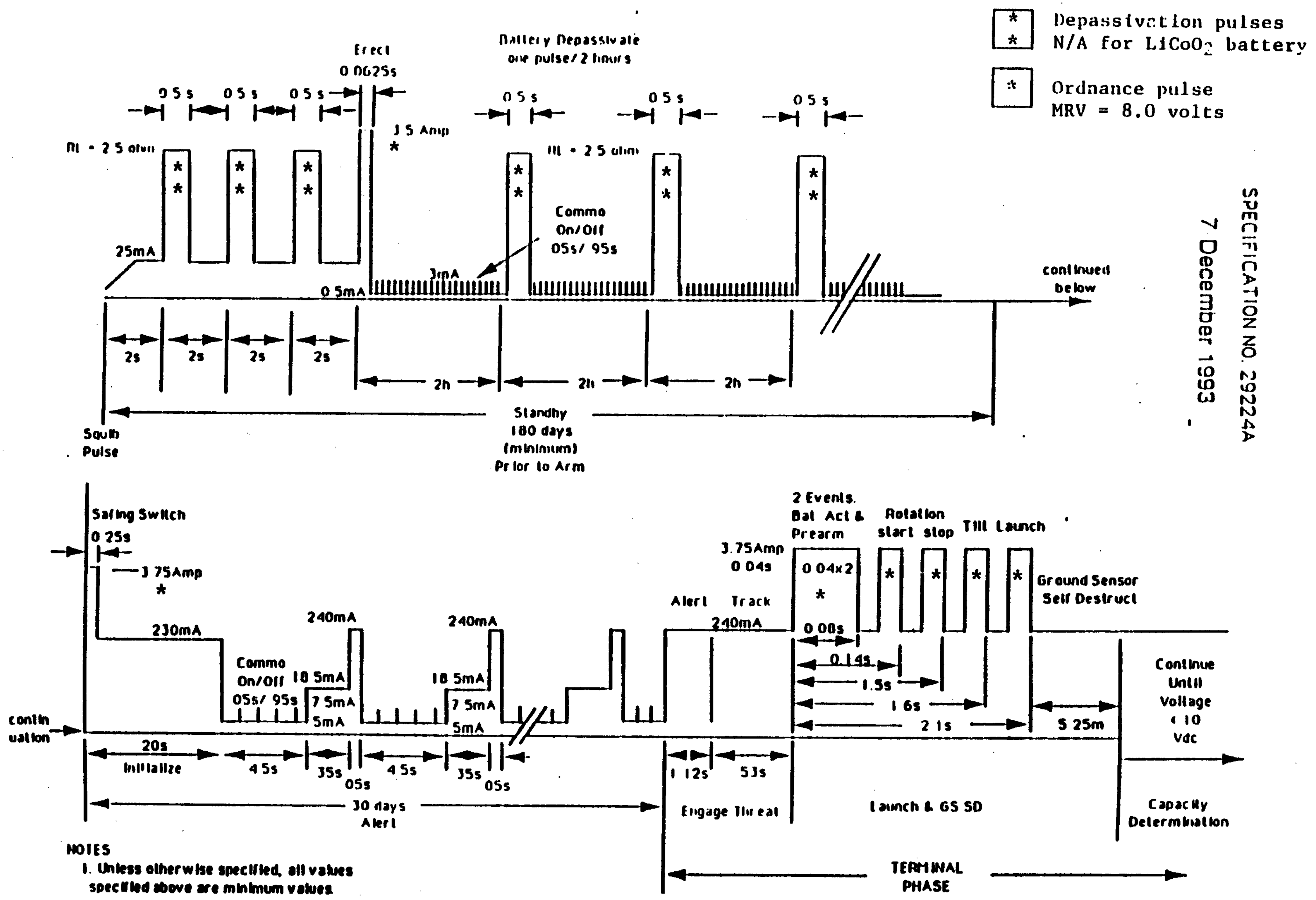


Figure 2-1. HWAM Activation Time Requirements



NOTES
1. Unless otherwise specified, all values specified above are minimum values

Figure 2-2. HWAM Power Profile

Chapter 3

Alliant Techsystems, Inc. Battery Design Development Philosophy

The strategy used by Alliant Techsystems, Inc., to develop a safe design for the HWAM power source contained the following key criteria:

- Separation of the three cells required for the voltage demand. Each cell is an hermetically sealed unit that remains electrically and electrochemically isolated over the 210 day minimum active life.
- Selection of an electrochemistry that is innately safer than the baseline system, lithium thionyl chloride; specifically, lithium/lithium cobalt oxide, which has the capability of high energy density and benign short circuit behavior.
- The electrochemistry must also be capable of reserve battery function. Lithium/lithium cobalt dioxide was further developed during this program to demonstrate reserve capability. A complete scale-up process for synthesizing electrochemically-precharged lithium cobalt dioxide was achieved.
- Maximize electrode surface area as a means of lowering the discharge rate to a conservative value, affording long battery Standby and Alert mode life.
- Design electrode shape to facilitate an overall battery structure that would conform to the envelope constraints of the HWAM Reserve Battery Outline and Interface as defined in Specification No. 29224A and shown in Figure 1-1 in this report.
- Design of a safety vent to release internal pressure should an abnormal pressure level occur. Note: During safety tests, an internal, built-in short circuit and externally applied short circuits did not result in sufficient internal pressure to open rupture-type diaphragm vents.

Chapter 4

Process Development

Rechargeable Li/Li$_x$CoO$_2$ cells are built[1,2] using LiCoO$_2$ as the active cathode material (*i.e.*, the x value in Li$_x$CoO$_2$ is unity). Cells are cycled by charging from the composition where x is unity to a value of x about 0.5. Therefore, when x = 1, the cell is in the discharged state. That state is employed for fabrication because it is commercially available, and it can be handled under ambient conditions.

When a reserve primary cell is required, as is the case for the HWAM application, the cell must be ready to discharge immediately upon activation. Therefore, the cell must be built in the charged state. For Li/Li$_x$CoO$_2$ cells, this means the cathode must be of the composition Li$_{\sim 0.5}$CoO$_2$. At the beginning of the development work on the HWAM battery, it was not known if the charged material could be synthesized chemically. Obviously, it could be synthesized electrochemically, within the cell as that occurs during each charge cycle. Nevertheless, it was not known if that material was stable outside the cell, or if it could be reprocessed into a cathode after electrochemical preparation and still maintain its state of charge.

Additionally, this positive electrode material had to be producible in quantities sufficient to meet production quantities of HWAM units. Experimentation proved that the only successful method of synthesizing charged Li$_x$CoO$_2$ was electrochemical. For this technique, a "Charging Cell" is fabricated without binder in the cathode. In this cell, the composition[*] of the cathode mix was 90 percent LiCoO$_2$ and 10 percent carbon. After charging, the "charged" Li$_{0.5}$CoO$_2$ mix is removed, rinsed, and dried for later fabrication into HWAM cathodes of particular shape and area. The fabrication was sufficiently novel to be patented.[3] The patent (Appendix B) provides additional details of the synthesis technique as well as amplifying its advantages. One notable advantage is the ability to employ stainless steel rather than aluminum as the current collector. A cell composed of these cathodes is then capable of storage in the dry state for an indefinite period of time (estimated at 20 years). A cell of such construction, with lithium metal anodes, is a reserve cell until electrolyte is supplied from a reservoir. The baseline electrolyte for these cells was 2-molar lithium hexafluoroarsenate with 0.4-molar lithium tetrafluoroborate ($2M$ LiAsF$_6$ + $0.4M$ LiBF$_4$) in methyl formate. Alliant uses the acronym DSMF for this electrolyte, for "Double Salt Methyl Formate." An alternate solvent, methyl acetate, was also evaluated as its cost is lower than the formate. This solvent, with the same salts, is called DSMA in the report. An alternate, using this solvent and only the hexafluoroarsenate salt is called SSMA to represent "Single Salt Methyl Acetate."

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[*] All percentages are by weight unless otherwise indicated.

A block diagram of the cathode fabrication process is shown in Figure 4-1. During process development, both the size of the Charging Cell, and the rate of charge were increased, adding significantly to the scaled-up yields. Figures 4-2 and 4-3 show that a progression of charge rate increase had no effect on the discharge capacity of quality control cells used to verify charged $Li_{0.5}CoO_2$ material performance. The number of Charging Cells built during this program and their respective data are shown in Table 4-1.

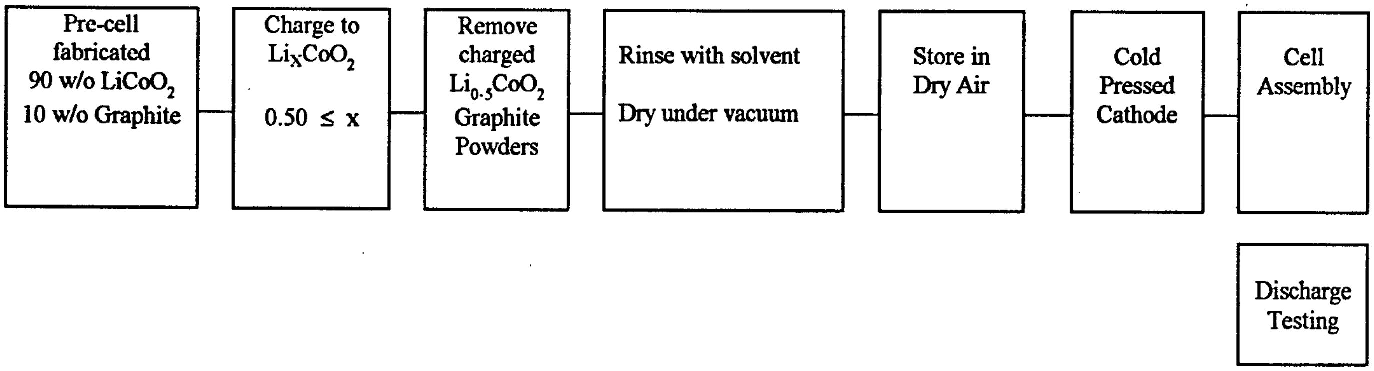


Figure 4-1. Block Diagram of Charging Process for $Li_{0.5}CoO_2$ and Subsequent Fabrication and Testing of A Cell.

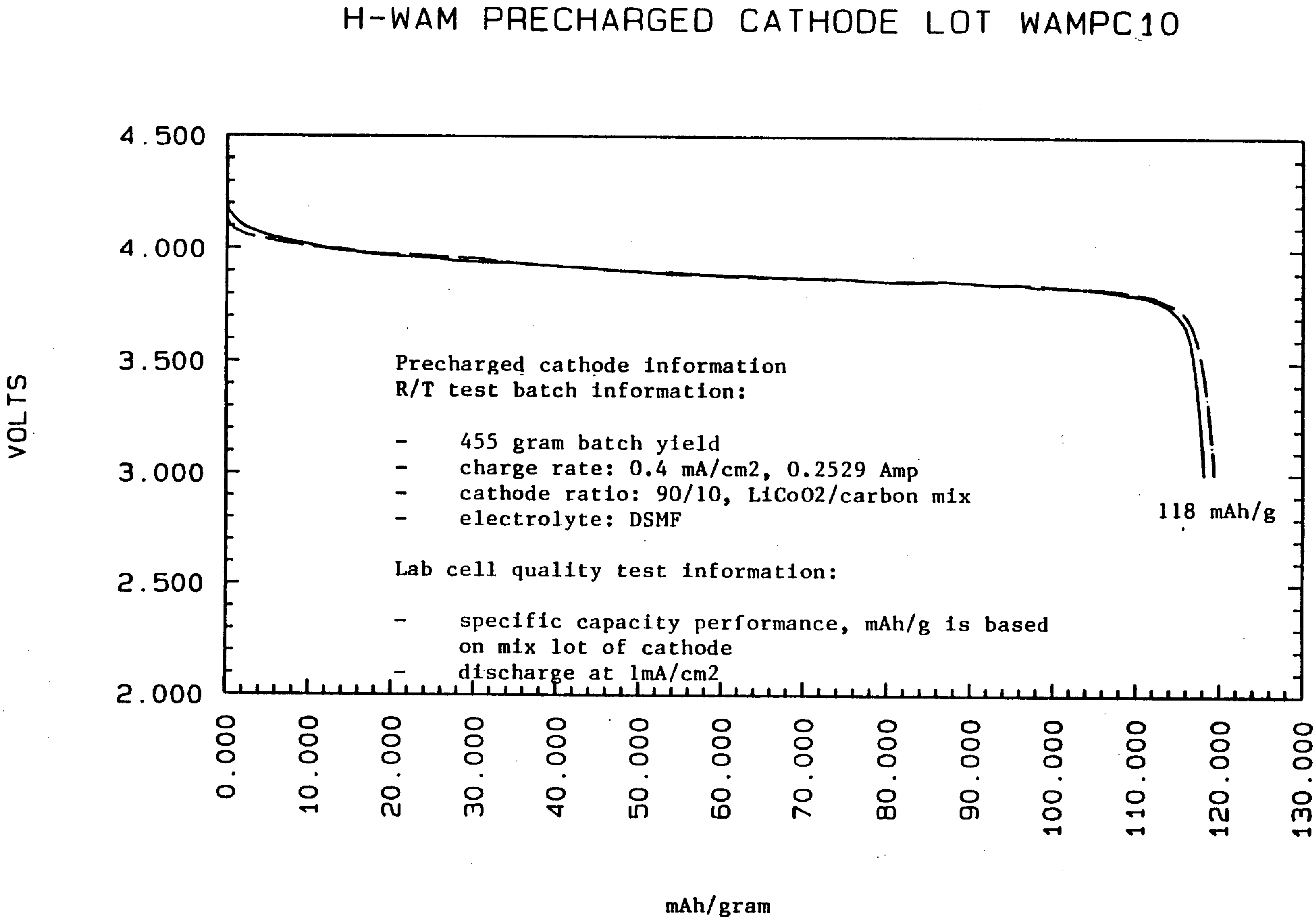


Figure 4-2. Discharge Tests of Low Rate Charged $Li_{0.6}CoO_2$

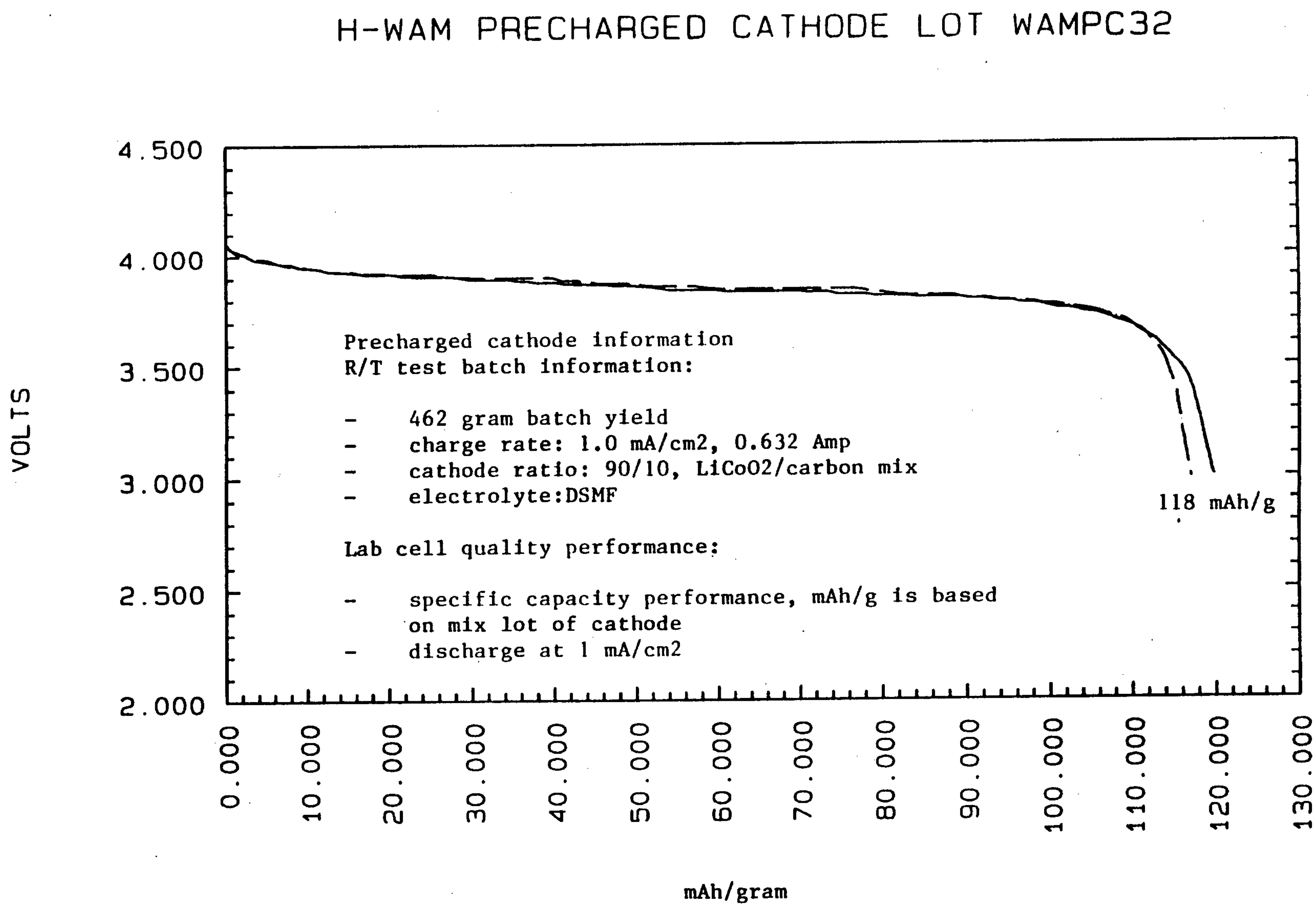


Figure 4-3. Discharge Test

Table 4.1. Fabrication Data for Charging Cells $Li_{0.5}CoO_2$ Material

H-WAM
Precharged Cathode Information

							BEFORE CHARGE		Test results After Charge				Lab Cell Evaluation 1 mA/cm_2	
CELL NUMBER	$LCoO_2$ Manufacturer	Manufacture's lot Number	$LiCoO_2$ Grade	Cathode Weight grams	Theoretical Capacity Ah 0.55 F/M*	Charge rate mA/cm_2	AC Imped. milli-ohms	OCV***	Capacity (AH)	End Voltage	AC Imp. milli-ohms	OCV After 24 hrs	OCV before Discharge	Average 2 cells mAh/gram**
WAMPC06	FMC	501-01-WBE4-003	Battery	449.20	60.881	0.4	186	3.437	60.881	4.257	140	4.237	4.288	121.49
WAMPC07	Johnson Matthey	F08C06	industrial	388.70	52.681	0.4	180	3.694	52.681	4.305	100	4.252	4.310	110.24
WAMPC08	FMC	501-01-WBE-003	Battery	474.90	71.515	0.4	200	3.593	71.520	4.095	50	4.025	4.085	90.70
WAMPC09	FMC	501-01-WBE-0003	Battery	465.40	70.085	0.8	160	3.582	70.090	4.217	32	4.136	4.156	111.51
WAMPC10	FMC	501-01-WBE-0003	Battery	455.25	61.700	0.4	120	3.64	61.700	4.245	30	4.226	4.283	118.78
WAMPC12	FMC	501-01-WBE-0003	Battery	426.87	57.854	0.4	110	3.644	57.854	4.266	50	4.234	4.267	120.72
WAMPC13	FMC	501-01-WBE-0003	Battery	390.87	52.972	0.4	115	3.560	52.972	4.212	48	4.163	4.200	114.14
WAMPC14	FMC	501-01-WBE-0003	Battery	450.70	61. 079	0.4	145	3.545	61.079	4.288	32	4.159	4.092	115.41
WAMPC15	FMC	501-01-WBE-0003	Battery	443.50	60.110	0.4	145	3.520	60.110	4.189	28	4.087	4.037	102.01
WAMPCI6	FMC	501-01-WBE-0003	Battery	464.61	62.969	0.4	100	3.590	62.969	4.285	48	4.169	4.230	111.44
WAMPC17	FMC	501-01-WBE-0003	Battery	445.65	60.399	0.4	50	3.590	60.399	4.290	46	4.245	4.330	114.97
WAMPCI8	FMC	501-01-WBE-0003	Battery	473.49	64.172	0.4	80	3.630	64.172	4.265	55	4.245	4.300	118.32
WAMPC25	FMC	501-01-WBE-0003	Battery	370.441	50.206	0.4	180	3.630	50.206	4.287	52	4.2331	4.233	114.88
WAMPC26	FMC	501-01-WBE-0003	Battery	448.30	60.758	1.0	180	3.629	60.758	4.270	55	4.233	4.300	117.07
WAMPC27	FMC	501-01-WBE-0003	Battery,	467.20	63.320	0.4 / 0.2	130	3.428	63.320	4.248	60	49229	4.275	115.24
WAMPC28	FMC	501-01-WBE-0003	Battery	466.70	63.252	1.0	170	3.430	63.252	4.306	55	4.300	4.275	114.39
WAPC29	FMC	501-01-WBE-0003	Battery	454.70	61.626	1.0	105.000	3.620	61.626	4.338	80	4.275	4.240	119.16
WAMPC30	FMC	501-01-WBE-0003	Battery	453.40	61.449	1.0	95	3.630	61.449	4.238	70	4.220	4.200	116.31
W AMPC32	FMC	501-01-WBE-0003	Battery	462.30	63.274	1.0	175	3.560	63.274	4.316	38	4.264	4.277	118.45

Note:
Cathode surface: 632.26 cm^2
WAMPCI I Shaded due to a burr in the grid edge
WAMPC13 used a solid aluminum current collector
WAMPCIS through WAMPC23 used 10 psi CO_2 head pressure to drive the electhalyte into the calls
WAMPC19 through WAMPC24 shortedd during the charge cycle
WAMPC24,25 used a solid aluminum current collector with holes in it in place of aluminum grid. plus 3 layers of 3M-E003 separator plus I layer of celgard 2300 par Interface to help preven prevent shorting. No CO_2
WAMPC25 (New test fixture)
WAMPC26 Aluminum grid, 1.0mA/cm^2 charge rate, 3 layers 3M-E003 + I layer celgard 2300 per interface
WAMPC27, Aluminum grid, 0.4mA/cm^2 for the first (3/4%) Ah, then 0.2 mA/cm^2 for the remaining (1/4%) Ah
WAMPC28 through WAMPC32 built like WAMPC26

*0.55 Faradays per mole, i.e., x in Li_xCoO_2 is 0.45.
**active material only (Li_xCoO_2) does not include inert components of the mix.
***OCV=open circuit voltage, in volts.

Chapter 5

Test Results

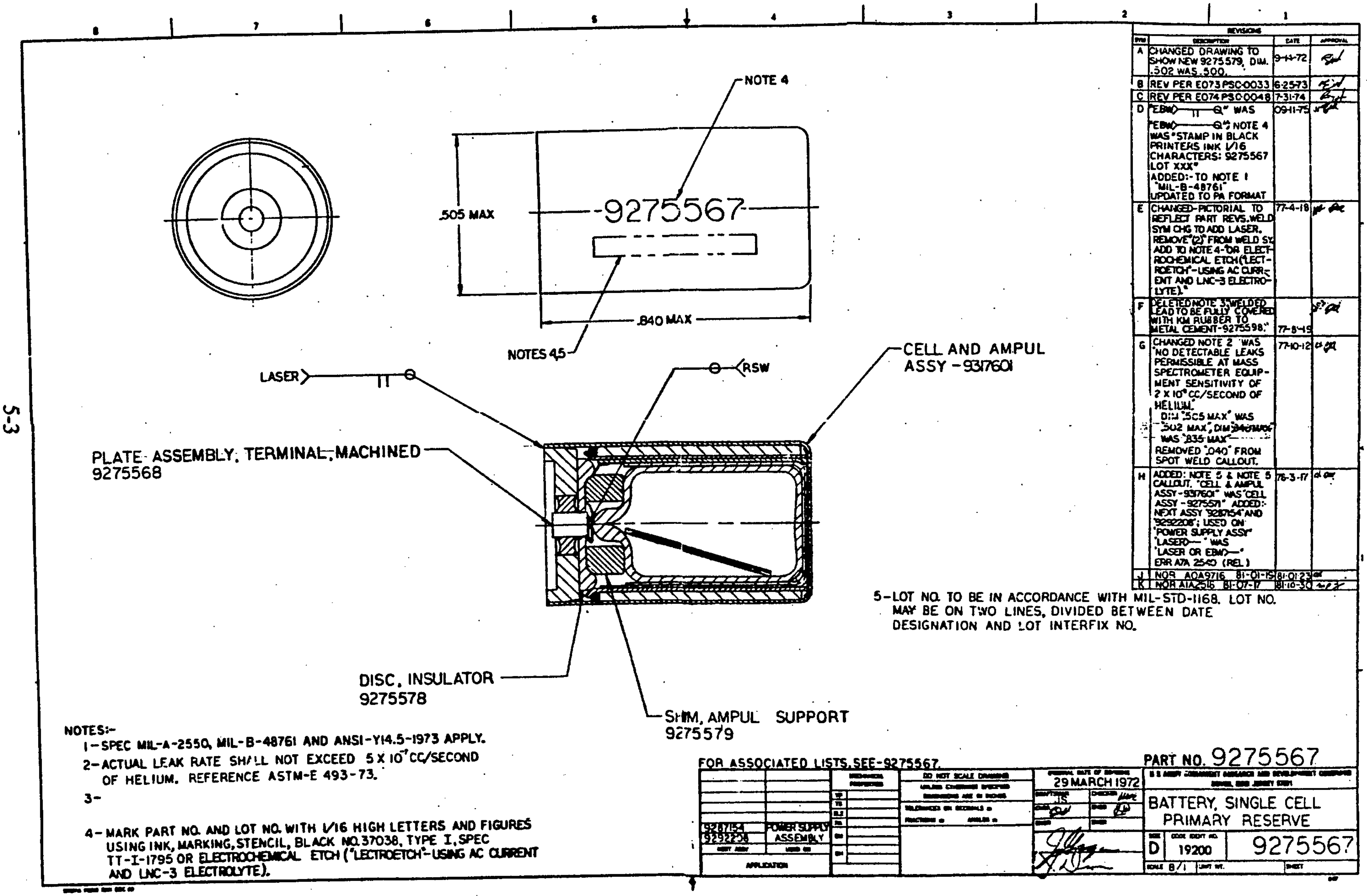
Following the scheme of Alliant Techsystems' Design/Development Philosophy, testing was broken down into a number of categories. Given below is an outline of the testing of precharged Li/Li$_{0.5}$CoO$_2$ cells. Following that are representative results of the cells tested in the various categories.

Section Title	TEST ENVIRONMENT
Preprogram Testing	• Modified Picatinny Cell 9275567 stored at room temperature and at 149°F discharged at room temperature. • Flat plate cell cycled at HWAM rates at room temperature tests.
Fixtured Cell Testing at Environmental States	• Room temperature multi-plate cell tests. • Cold temperature multi-plate cell tests.
Hermetic Cell Performance Testing at Environmental States	• Room temperature performance tests. (WAMH05) • Four-month storage at room temperature followed by -25°F discharge performance test. (WAMH07) • Three-month storage at 65°F followed by 145°F discharge performance test. (WAMH20) • Three cells in series; discharge performance at room temperature.
Hermetic Cell Safety Testing	• External short circuit safety test. (WAMH08 and WAMH22) • Internal short circuit safety test. (WAMH09) • External short-circuit and discharge reversal safety test. (WAMH18) • Short electrolyte fill discharge safety test. (WAMH06)

Preprogram Testing

Preprogram testing, done as part of Naval Surface Warfare Center Option 7 to the 100 Ah Program, Contract N60921-93-C-0060, evaluated precharged Li$_{0.5}$CoO$_2$ cathode material in an Army munitions cell which is a production item, Picatinny Arsenal Cell 9275567 (Alliant Techsystems' ATK G2666), Figure 5-1, modified for that purpose. The modification consisted of replacing the vanadium pentoxide cathode of the G2666 by a Li$_{0.5}$CoO$_2$ cathode, and, for some cells, using only the AsF_6-salt in lieu of the DSMF electrolyte of the G2666. The lithium metal anode and Veritek Type M separator were the same as for the G2666. The storage and test matrix of 26 of these cells is shown in Figure 5-2. Results of testing to this matrix is shown in Figure 5-3 for a typical fresh cell and in Table 5-1 for all stored cells summarized in hours of run time to 3.33 volts. That voltage corresponds to the cut off voltage per cell for HWAM applications. For three cells connected in series, ten volts is the minimum HWAM voltage.

Preprogram testing of a flat plate cell was done as an early attempt to fabricate flat plate cathodes from dry precharged $Li_{0.5}CoO_2$/graphite mix material. Characterization of these cells included cycle life testing. The flat plate cells were fabricated with microporous polypropylene (Celgard 2300) separators (See Section 6) and cycled through a test profile that included an initial pulse load of 5.0 mA/cm^2 to begin each discharge. The pulses were at the same pulse rate anticipated for the HWAM battery (3.75 amp equivalent). Following the pulse, each discharge continued at a rate designed to test the ability of the cathode. The rates were increased for successive cycles, first at 0.5 mA/cm^2, second at 1.0 mA/cm^2, and third at 2.0 mA/cm^2. Then the process was repeated. All of this testing was conducted at room temperature. Figure 5-4 is a plot of one of two cells tested to this regime. As expected, the cycle life was less than for cells built[1] to achieve about 50 cycles because the formulation of the electrolyte for those cells included dissolved carbon dioxide, a component known to improve the cycle life of lithium metal anodes. It may be seen from the results in Table 5-1, that the SSMA performed as well as the DSMA. That result is desirable as it reduces cost.



REVISIONS			
SYM	DESCRIPTION	DATE	APPROVAL
A	CHANGED DRAWING TO SHOW NEW 9275579, DIM. .502 WAS .500.	9-11-72	
B	REV PER E073 PSC-0033	6-25-73	
C	REV PER E074 PSC-0048	7-31-74	
D	"EBW⟩—‖—Q" WAS "EBW⟩——Q"; NOTE 4 WAS "STAMP IN BLACK PRINTERS INK 1/16 CHARACTERS: 9275567 LOT XXX" ADDED:- TO NOTE 1 "MIL-B-48761" UPDATED TO PA FORMAT	09-11-75	
E	CHANGED-PICTORIAL TO REFLECT PART REVS. WELD SYM CHG TO ADD LASER. REMOVE "(2)" FROM WELD SY. ADD TO NOTE 4- "OR ELECTROCHEMICAL ETCH ("LECTROETCH"-USING AC CURRENT AND LNC-3 ELECTROLYTE)."	77-4-18	
F	DELETED NOTE 3, "WELDED LEAD TO BE FULLY COVERED WITH KM RUBBER TO METAL CEMENT-9275598."	77-8-19	
G	CHANGED NOTE 2 "WAS "NO DETECTABLE LEAKS PERMISSIBLE AT MASS SPECTROMETER EQUIPMENT SENSITIVITY OF 2 X 10^{-8} CC/SECOND OF HELIUM." DIM ".505 MAX" WAS ".502 MAX", DIM ".840 MAX" WAS ".835 MAX" REMOVED ".040" FROM SPOT WELD CALLOUT.	77-10-12	
H	ADDED: NOTE 5 & NOTE 5 CALLOUT. "CELL & AMPUL ASSY-9317601" WAS "CELL ASSY - 9275571" ADDED: NEXT ASSY "9287154" AND "9292208"; USED ON "POWER SUPPLY ASSY" "LASER⟩—" WAS "LASER OR EBW⟩—" ERR A7A 2540 (REL)	78-3-17	
J	NOR AOA9716 81-01-15	81-01-23	
K	NOR A1A2516 81-07-17	81-10-30	

5-LOT NO. TO BE IN ACCORDANCE WITH MIL-STD-1168. LOT NO. MAY BE ON TWO LINES, DIVIDED BETWEEN DATE DESIGNATION AND LOT INTERFIX NO.

NOTES:-

1-SPEC MIL-A-2550, MIL-B-48761 AND ANSI-Y14.5-1973 APPLY.

2-ACTUAL LEAK RATE SHALL NOT EXCEED 5 X 10^{-7} CC/SECOND OF HELIUM. REFERENCE ASTM-E 493-73.

3-

4-MARK PART NO. AND LOT NO. WITH 1/16 HIGH LETTERS AND FIGURES USING INK, MARKING, STENCIL, BLACK NO. 37038, TYPE I, SPEC TT-I-1795 OR ELECTROCHEMICAL ETCH ("LECTROETCH"-USING AC CURRENT AND LNC-3 ELECTROLYTE).

Figure 5.1. Picatinny Cell Modified with a Precharged $Li_{0.5}$ Co_{O2} Cathode

G6382-FA-2000

NSWC/ARDEC Precharged $Li_{0.5}CoO_2$ Reserve Cells
Option 7 - Contract No. N60921-93-C-0060
Picatinny 9275567 Modified Cells, Performance Verification (ATK G2666)
Test Matrix

Notes:

Placed in Storage:	**Dec. 12, 1994**
Removed from Storage:	**June 16, 1995**

ATK No. G2666
Rated Capacity = .15 amp hour
3.3K ohms = 1 week rate

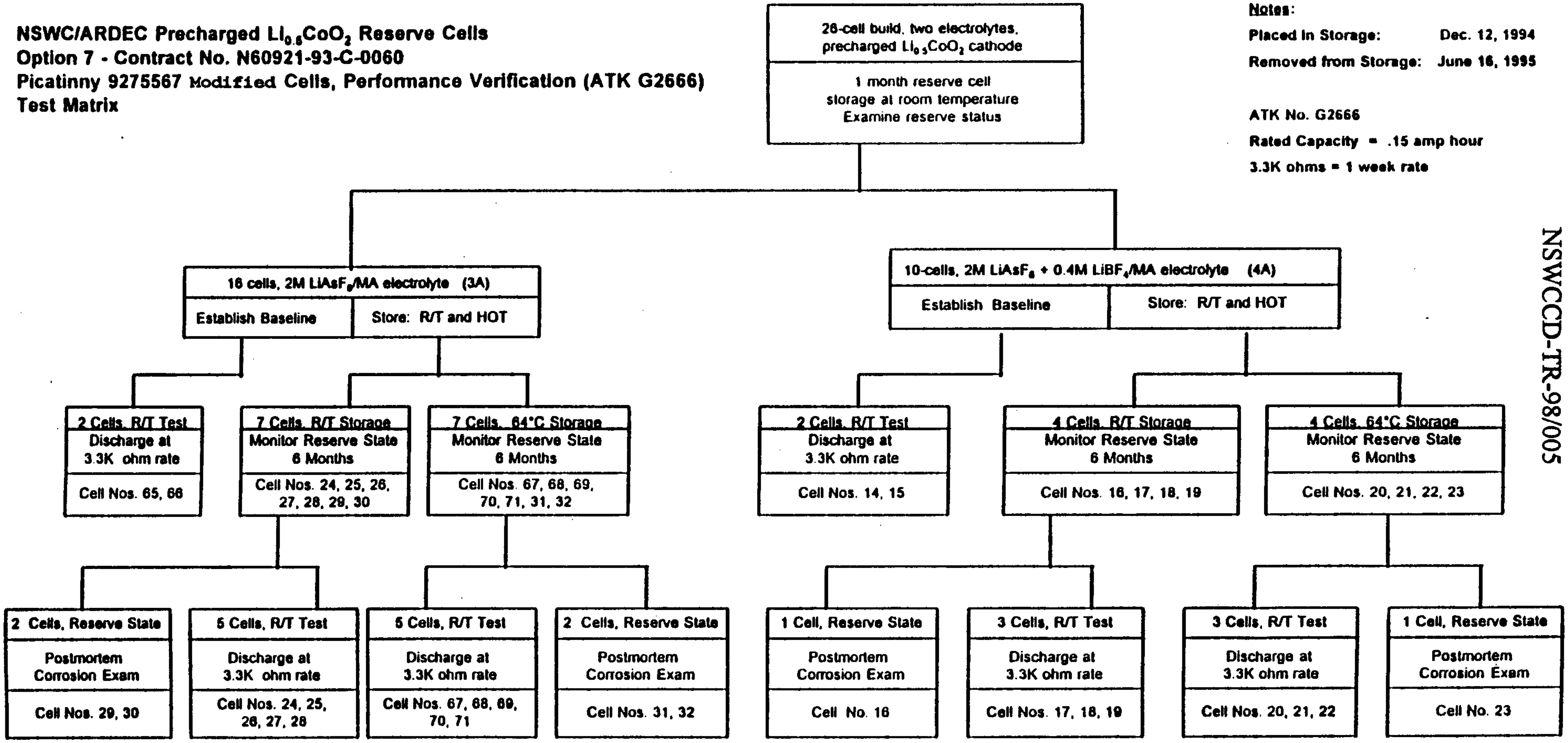
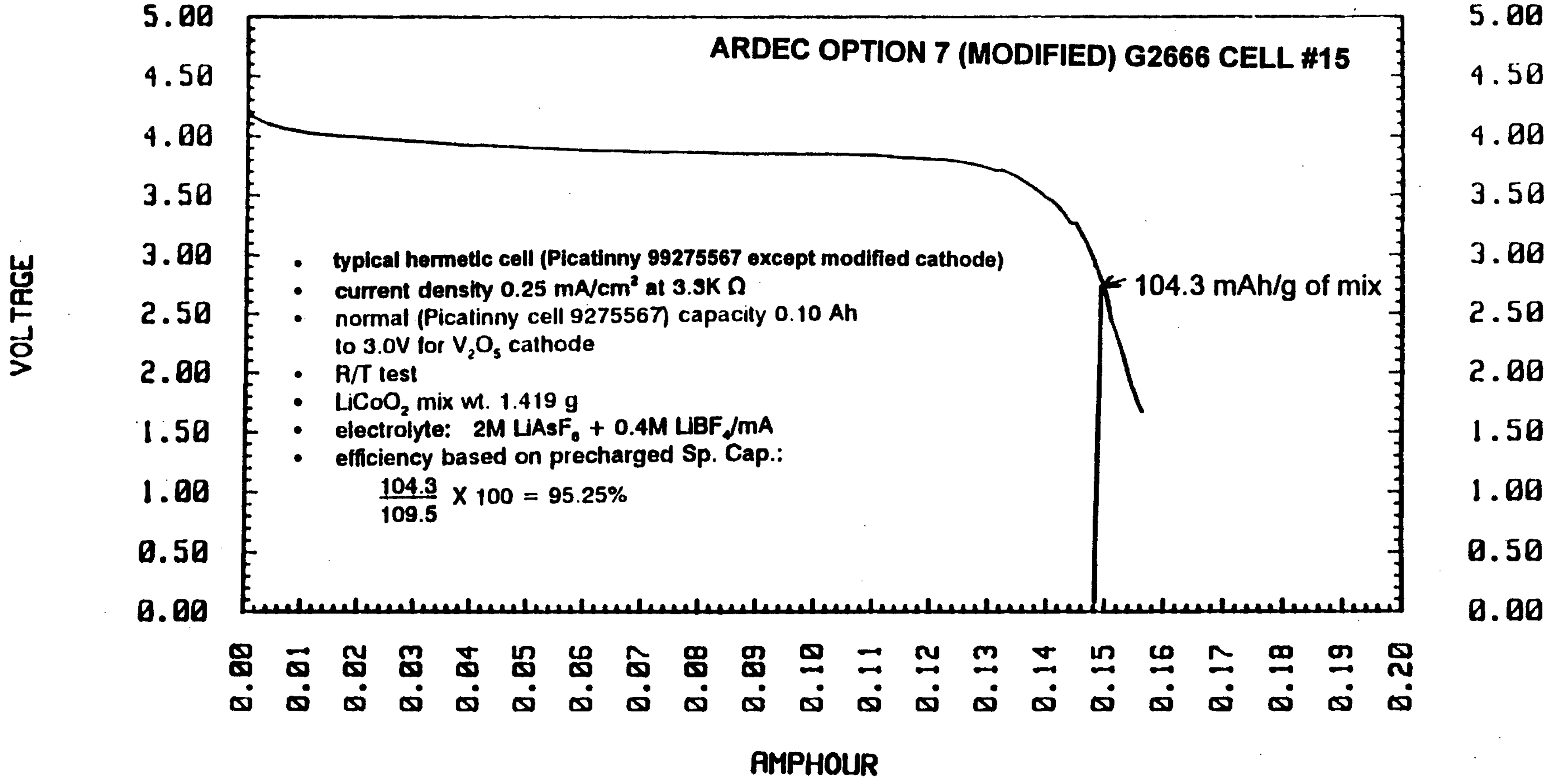


Figure 5-2. Storage and Test Matrix for Option 7, Picatinny Cell (Modified with $Li_{0.5}CoO_2$ Cathodes)



ARDEC OPTION 7 (MODIFIED) G2666 CELL #15

104.3 mAh/g of mix

- **typical hermetic cell (Picatinny 99275567 except modified cathode)**
- current density 0.25 mA/cm^2 at 3.3K Ω
- normal (Picatinny cell 9275567) capacity 0.10 Ah to 3.0V for V_2O_5 cathode
- R/T test
- $LiCoO_2$ mix wt. 1.419 g
- electrolyte: 2M $LiAsF_6$ + 0.4M $LiBF_4$/mA
- efficiency based on precharged Sp. Cap.:

$$\frac{104.3}{109.5} \times 100 = 95.25\%$$

Figure 5-3. Fresh Discharge Performance of Picatinny Reserve Cell in Small Hermetic Hardware (Modified Picatinny Cell 99275567)

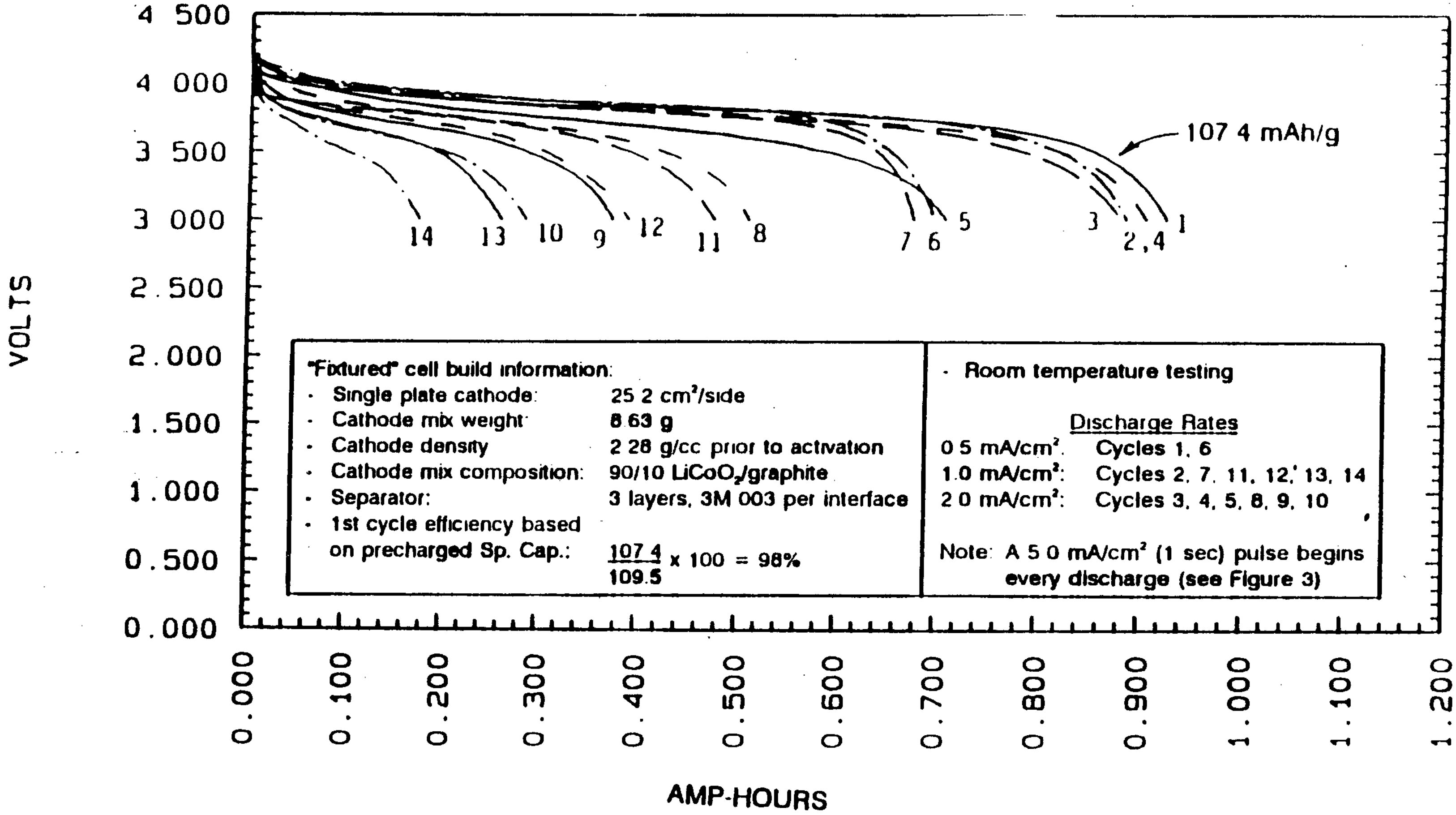


Figure 5-4. **Subcell No. 103 of HWAM Type, Reserve Battery Design, Using Precharged $LiCoO_2$ Cathode** and Cycled After First Discharge at the Indicated Rates

Table 5-1. Modified Picatinny 9275567 Cells with Precharged Cathodes $LiCoO_2$
Stored in Reserve State - 6 Months
Discharged with 3.3K Ohm Load

Cell No.	Channel No.	Stored Condition	Electrolyte	Hours to 3.33 Volts	
17	71	6 months R/T	DSMA	122	Average Run Time: 121.66 hours
18	72		DSMA	122	
19	73		DSMA	121	
24	61	6 months R/T	SSMA	121	Average Run Time: 120.60 hours
25	62		SSMA	120	
26	63		SSMA	119	
27	64		SSMA	121	
28	65		SSMA	122	
Equivalent to 10 Years Reserve Storage					
20	74	6 months, 60°C	DSMA	115	Average Run Time: 114.0 hours
21	75		DSMA	113	
22	76		DSMA	114	
67	66	6 months, 60°C	SSMA	114	Average Run Time: 115.40 hours
68	67		SSMA	115	
69	68		SSMA	116	
70	69		SSMA	117	
71	70		SSMA	115	
Notes:	SSMA: 2M $LiAsF_6$ / MA DSMA: 2M $LiAsF_6$ + 0.4M $LiBF_4$ / MA 3.33 Volt Cutoff				

Fixtured Cell Testing at Environmental States

Fixtured cell testing on this program had the purpose of simulating a full HWAM cell (one of three needed to meet the HWAM power requirements), without the long lead preparation needed to create a hermetic cell case. Photographs of a typical HWAM fixtured cell case and cell assembly are shown in Figures 5-5 through 5-8. Drawings of the fixture are included in Appendix A, HWAM Cell Drawing Package.

Fixtured cell testing done at room temperature is summarized in Table 5-2. These tests all had a background load of 400 milliamperes and pulse loads of 3.75 amperes every 5 hours. This regime was used to simplify the complex and lengthy power profile of the actual HWAM (Figure 2-2). It was particularly interesting to note that all of the pulse loads stayed above 2.67 volts. In a three-cell seriesed battery, 2.67 volts per cell provides the 8.0 volt battery voltage that all pulses must exceed. Also, run time, counted to 3.33 volts, exceeded 35 hours. Please refer to Figure 5-9 as a typical example. Voltage history during pulse loads is detailed in Figure 5-10. Each pulse load consisted of four, 3.5 ampere, 0.5 second pulses, with a 2.0 second open circuit between pulses. During this test phase we also checked voltage rise time during activation from a remote reservoir. Since design and build of an actual HWAM reservoir is not a part of this program, only T_R, or time to raise voltage against cell internal resistance, was measured. This was done without external load applied and is shown in Figure 5-11. Based on the results in the Modified Picatinny Cell 9275567, all cells were built with SSMA electrolyte.

Fixtured cell cold temperature testing proved to be the first performance challenge of the program. Testing at -25°F presented difficulties for the design selections made up until that time. In particular, the 400 milliampere background load caused cells to reach the 3.3 volt cutoff well ahead of required run time. Two design items were varied during this study in an effort to achieve the -25°F load sustaining goal. Cell stack compression and separator type were the variables. Additionally, re-examination of the HWAM power profile showed a 240 milliampere background load to be more realistic to the standby needs than 400 milliampere, which had been primarily specified for the purpose of faster discharge, to hasten test time. Thus a new test profile was programmed, and it is shown in Figure 5-12.

At the conclusion of the fixtured cell testing effort, the combination of elements that held the most promise were an 11-plate cathode cell stack, either Whatman DBSB30A or Veretek TYPE M Separator, and no stack compression. Figure 5-13 showing performance of cell WAMF11 (Whatman separator) and Figure 5-14 for cell WAMF12 (Veretek Separator) shows the ability of the cell design to maintain a 240 milliampere background load and pulse support above 2.67 volts all at the -25°F temperature extreme.

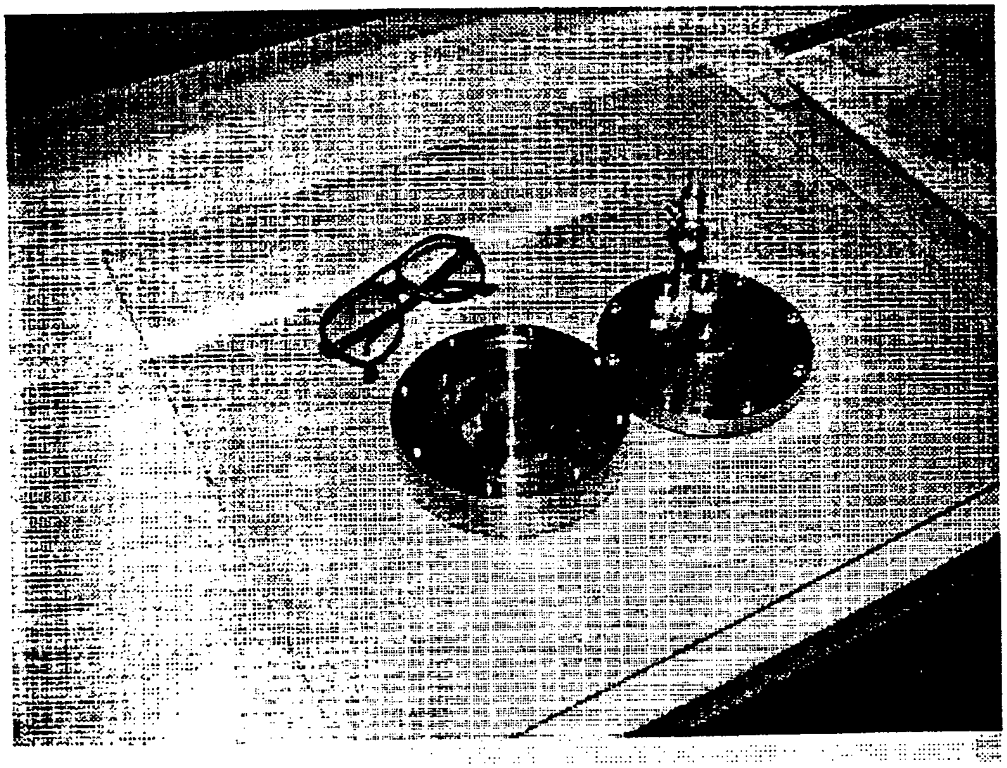


Figure 5-5. HWAM Single Cell Hardware Test Fixture

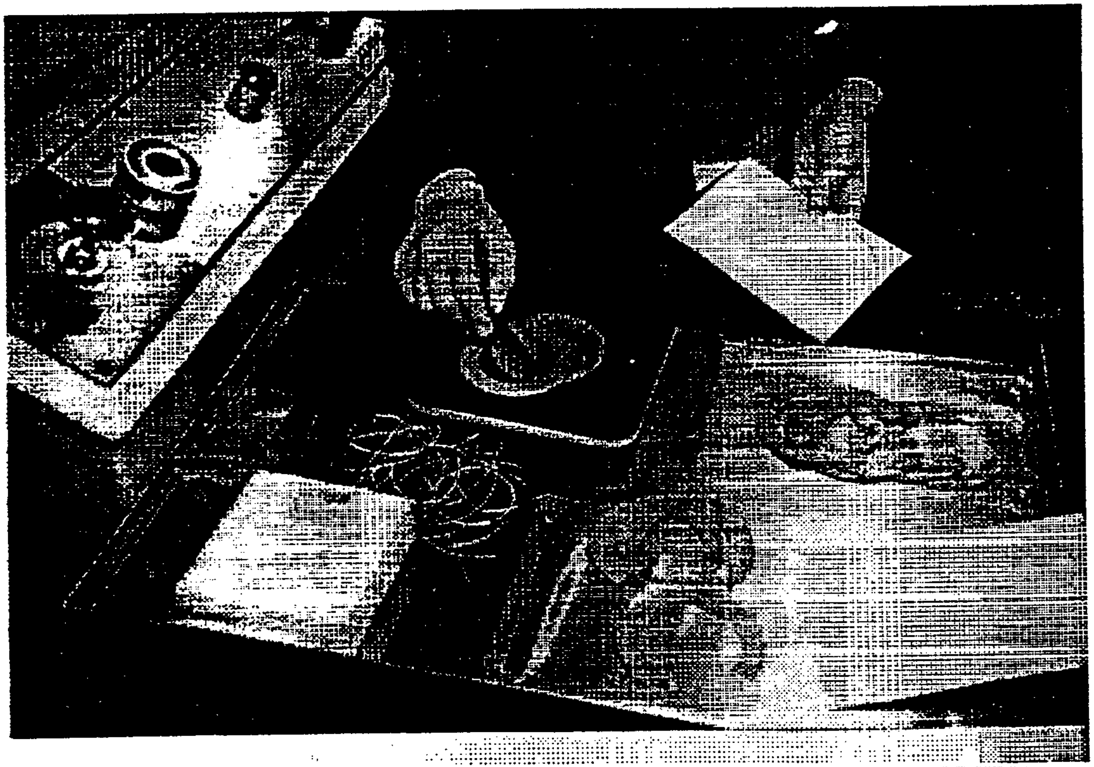


Figure 5-6. HWAM Anode Assembly - Lithium Foil Press and Trim

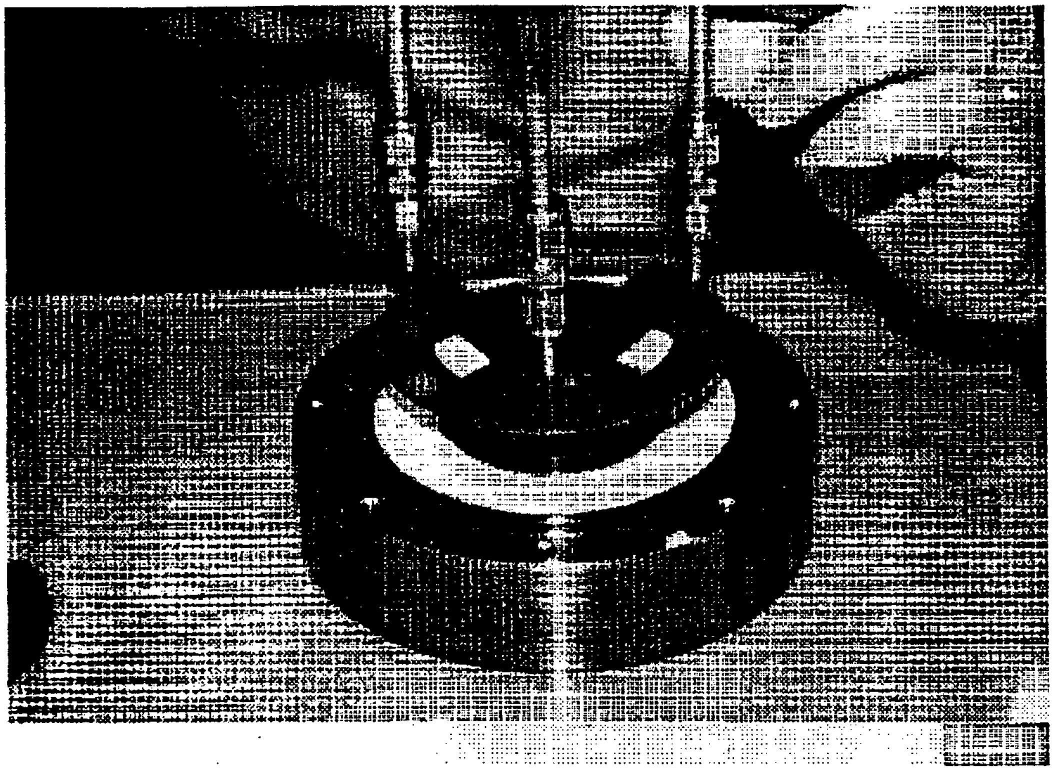


Figure 5-7. HWAM Cathode Assembly Installation

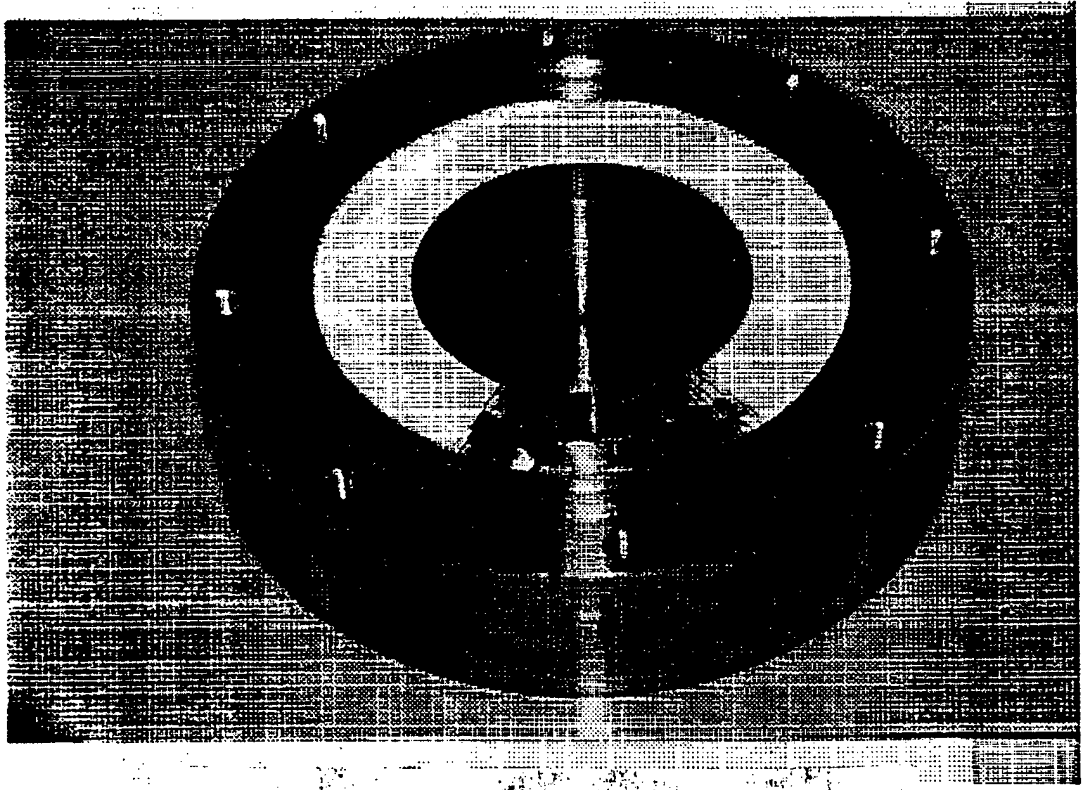


Figure 5-8. HWAM Assembled Cell Stack

Table 5-2. HWAM Fixtured Cell* Test Data at Room Temperature

Cell Number			WAMF01	WAMFO2	WAMFO3	WAM05	WAM06	WAMF07
Test Date			10/3/95	10/6/95	10/11/95	10/20/95	11/7/95	11/14/95
Test Temperature			R/T	R/T	R/T	R/T	R/T	R/T
Open Circuit voltage (volts), before test			4.160	4.062	4.160	4.190	4.140	4.110
Activation time (milliseconds)			345		595			280
First sequence of pulses								
3.50A		Initial	3.070	2.588	3.228	3.291	2.800	2.882
3.50A		End	2.966	2.350	3.144	3.291	2.840	2.901
3.50A		Initial	3.144	2.766	3.270	3.313	3.010	3.049
3.50A		End	2.990	2.322	3.156	3.234	2.880	2.936
3.50A		Initial	3.196	2.842	3.293	3.327	3.055	3.113
3.50A		End	3.006	2.316	3.162	3.245	2.905	2.965
3.50A		Initial	3.230	2.916	3.293	3.342	3.111	3.154
3.50A		End	3.020	2308	3.169	3.252	2.919	2.986
Second Pulse (5 hour)								
400mA	Voltage before pulse		3.822	-	3.790	3.886	3.819	3.844
3.75A		Initial	3.294	-	3.225	3.371	3.208	3.321
3.75A		End	3.190	-	3.120	3.33	3.120	3.248
ThirdPulse (10 hour)								
400mA	Voltage before pulse		3.758	-	3.736	3.839	3.790	3.792
3.75A		Initial	3.226	-	3.222	3.341	3.203	3.288
375A		End	3.116	-	3.118	3.289	3.118	3.200
Fourth Pulse (15 hour)								
400mA	Voltage before pulse		3.704	-	3.666	3.816	3.760	3.782
3.75A		Initial	3.174	-	3.120	3.345	3.181	3.278
3.75A		End	3.044	-	3.008	3.283	3.100	3.212
Fifth Pulse (20 hour)								
400mA	Voltage before pulse		3.668	-	3.607	3.802	3.726	3.753
3.75A		Initial	3.100	-	3.100	3.330	3.131	3.254
3.75A		End	2.916	-	2.916	3.267	3.061	3.183
Sixth Pulse (25 hour)								
400mA	Voltage before pulse		3.626	-	3.515	3.780	3.683	3.695
3.75A		Initial	3.086	-	2.911	3.304	3.091	3.194
3.75A		End	2.998	-	2.772	3.2431	3.000	3.114
Seventh Pulse (30 hour)								
400mA	Voltage before pulse		3.594	-	3.421	3.741	3.365	3.570
3.75A		Initial	3.064	-	2.795	3.266	3.000	3.063
3.75A		End	2.976	-	2.648	3.212	2.950	2.988
Cell Capacity (Ah)			18.81	15.93	15.19	15.43	14.96	15.67
Delivered Capacity (Ah) to 3.33 volts			13.32	-	13.6	***	14.24	13.39
Total run time (hours) to 3.33 volts			33.30	-	34.00	***	35.59	33.33
Cell capacitance (nf)			12.83	13.16	14.15	15.7	16.2	24.5
Precharged $LiCoO_2$ capacity (mAh/gram)			121.49	118.78	111.51	117.43	114.14	115.41

Note:

WAMF01: Zero % Compression Vacuum dried cathodes (no heat), 10 cathodes @60 mil. thick, uncoated cell fixture

WAMF02. Zero % Compression, Baked cathodes at 170 deg. C under vacuum, 10 cathodes @ 60 mil. thick, uncoated call fixture

WAMF03. 4 % Compression, Vacuum dried cathodes (no heat), 10 cathodes @ 60 mil. thick

WAMF04. 10 % Compression, shorted when applying compression, cell was not tested, 10 cathodes @ 60 mil. thick

WAMF05. 4.6 % compression, vacuum dried cathodes (no heat), 11 cathodes @ 54 mil. Thick, 2m LiAsF6/MA

*** the cell was removed from test at 32.53 hours @ 3.72 volts to evaluate the lithium reserve

WAMFO6 4.6% compression, Vacuum dried cathodes (no heatt). 11 cathodes @ 54 mil.thick. 2m LiAsF6/MA

WAMF07: 3.0% compression, Vacuum dried cathodes (no hest). 13 cathodes @ 46 mil. thick, 2 layers of separator per interface

* Electrolyte for all cells was 2M $LiAsF_6$ in methyl acetate

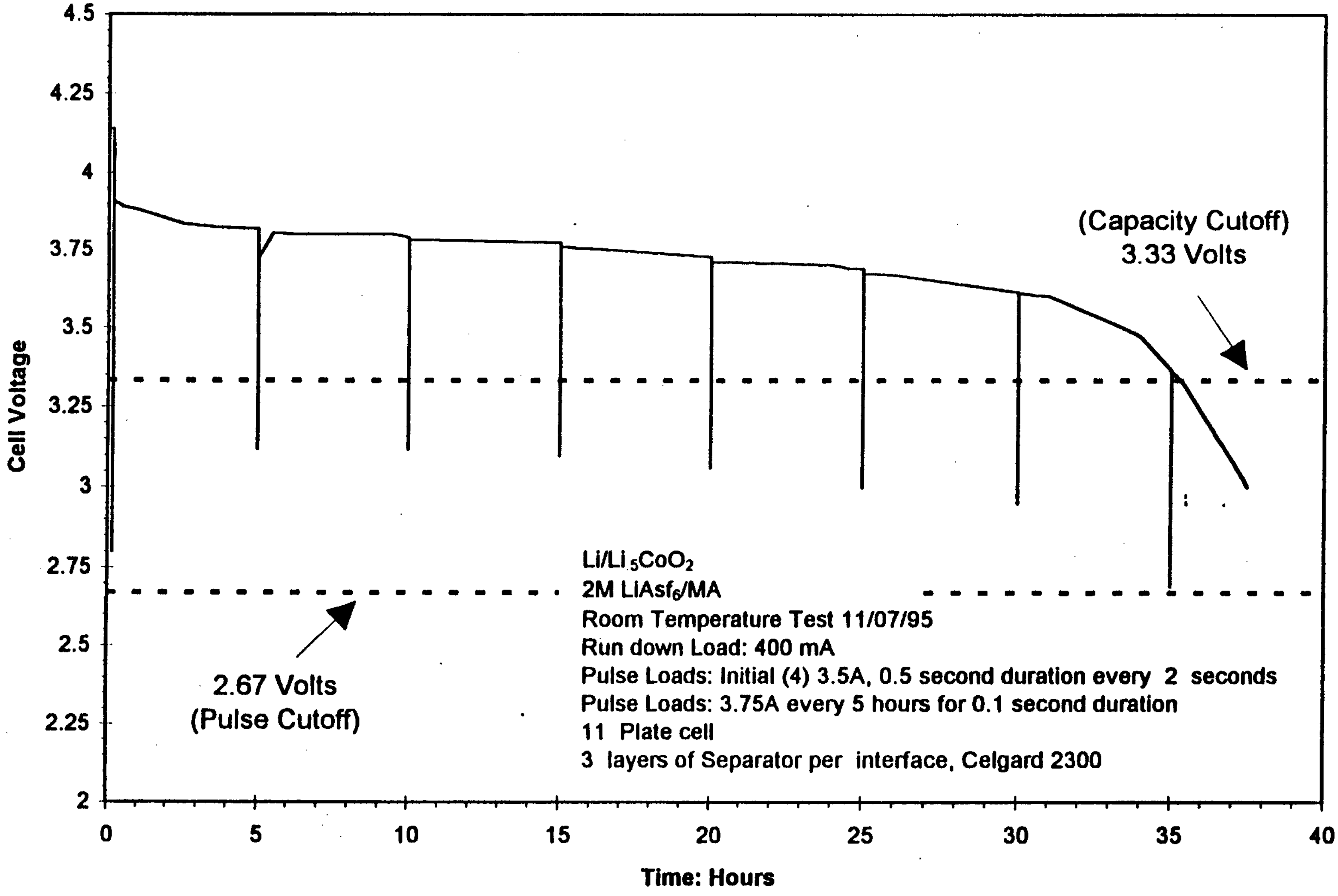


Figure 5-9. Pulse and Capacity Run Down Profile, Cell WAMF06

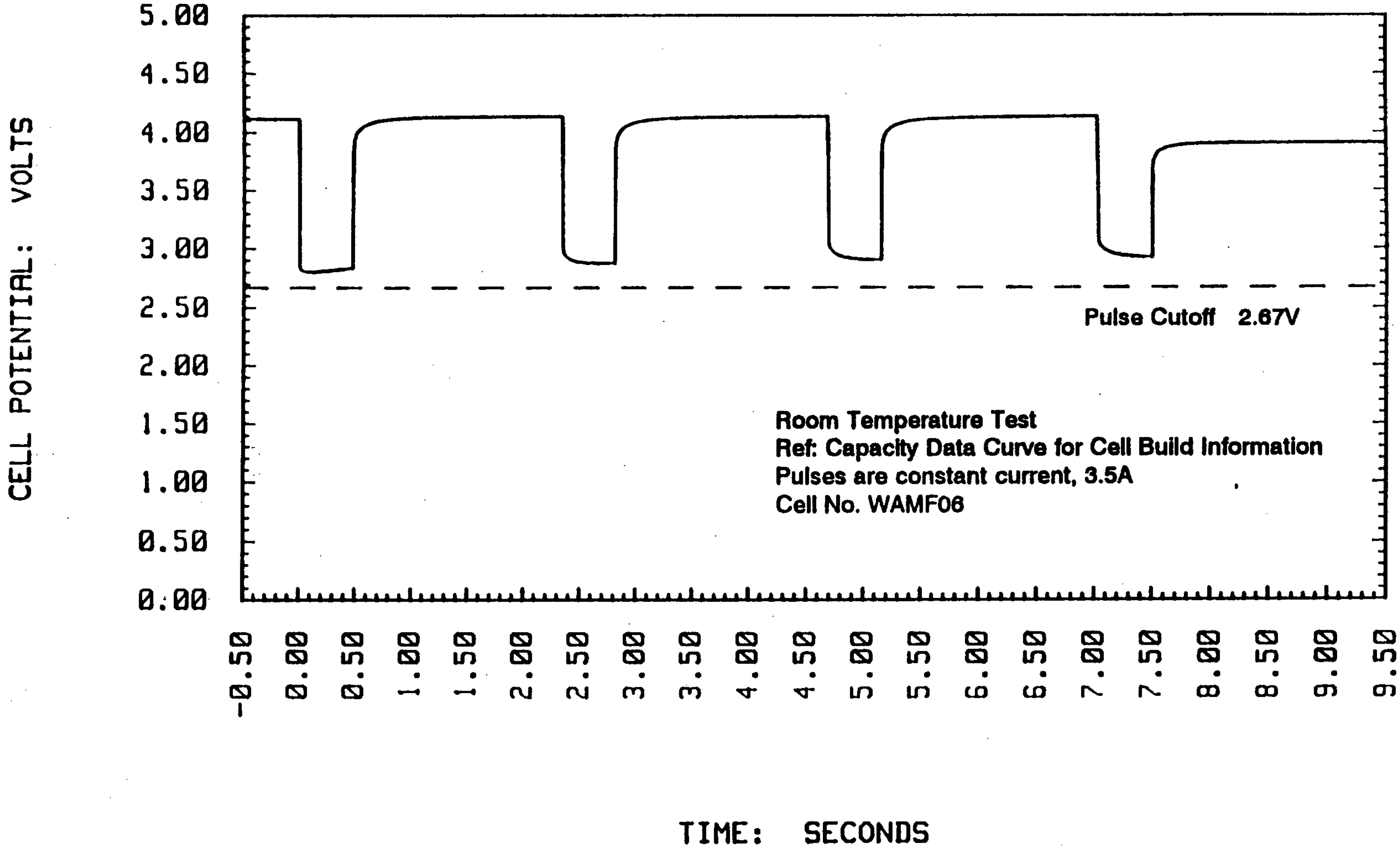


Figure 5-10. Pulse Profile of (4) 3.5 Amp, 0.5 Second Duration at Beginning of Life

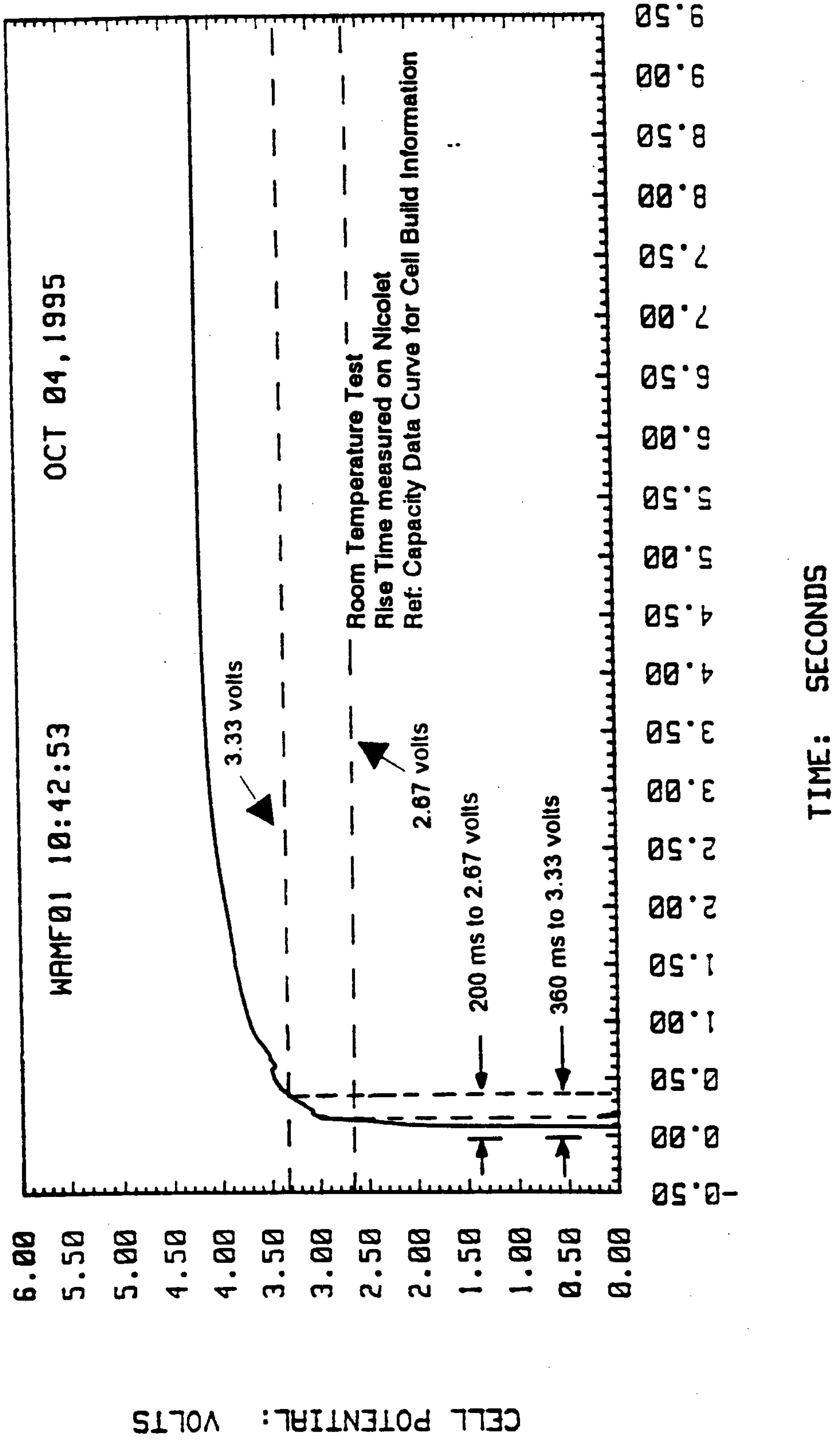


Figure 5-11. No Load Voltage Rise Time (T_R)

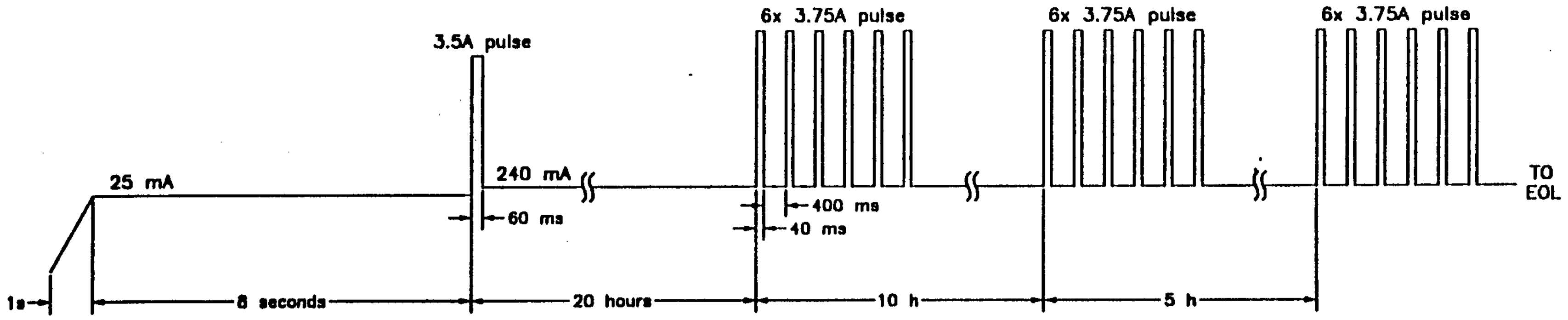


Figure 5-12. Fixtured Cell Test Profile

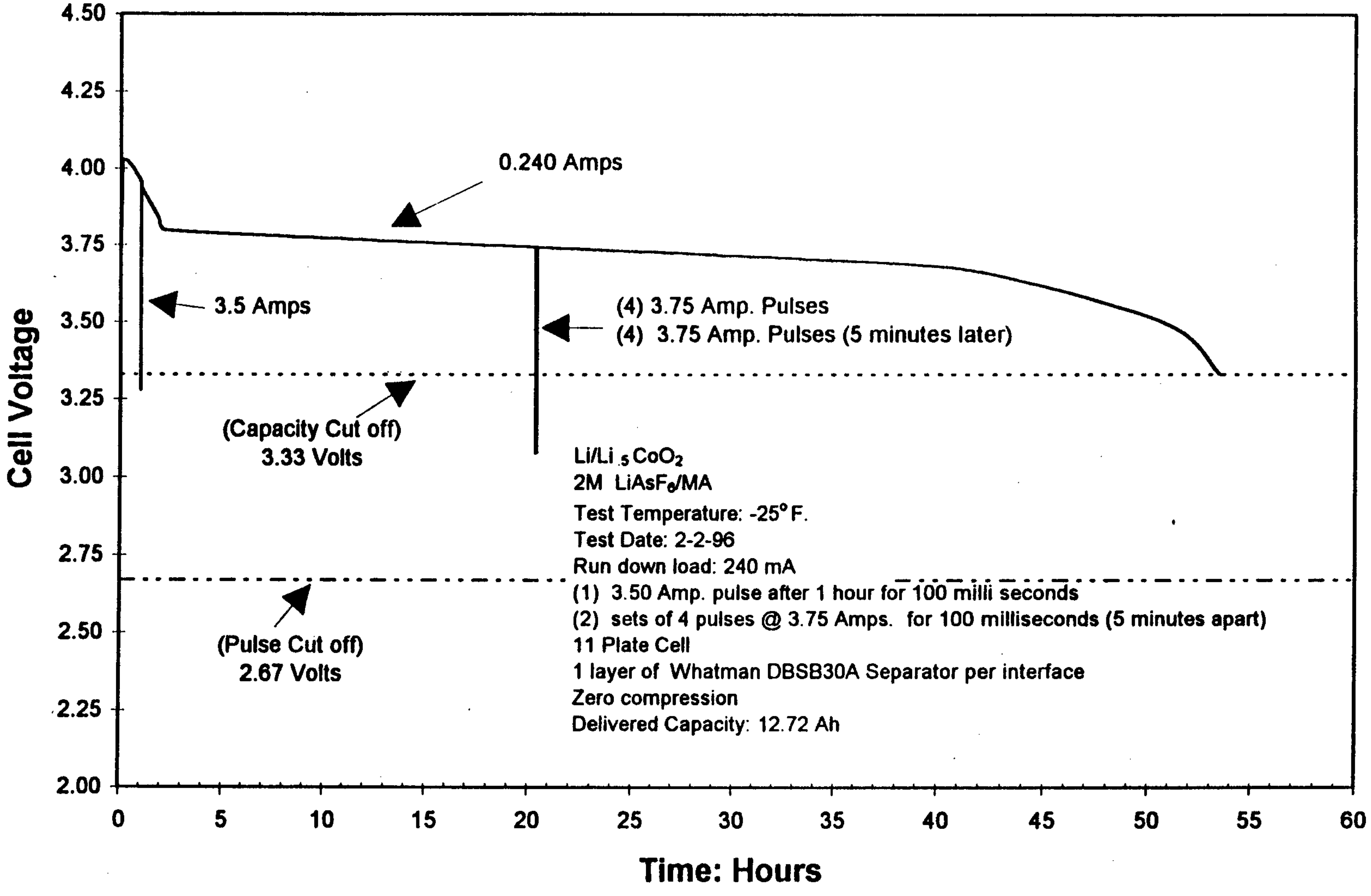


Figure 5-13. Pulse and Capacity Discharge Profile, Cell WAMF11

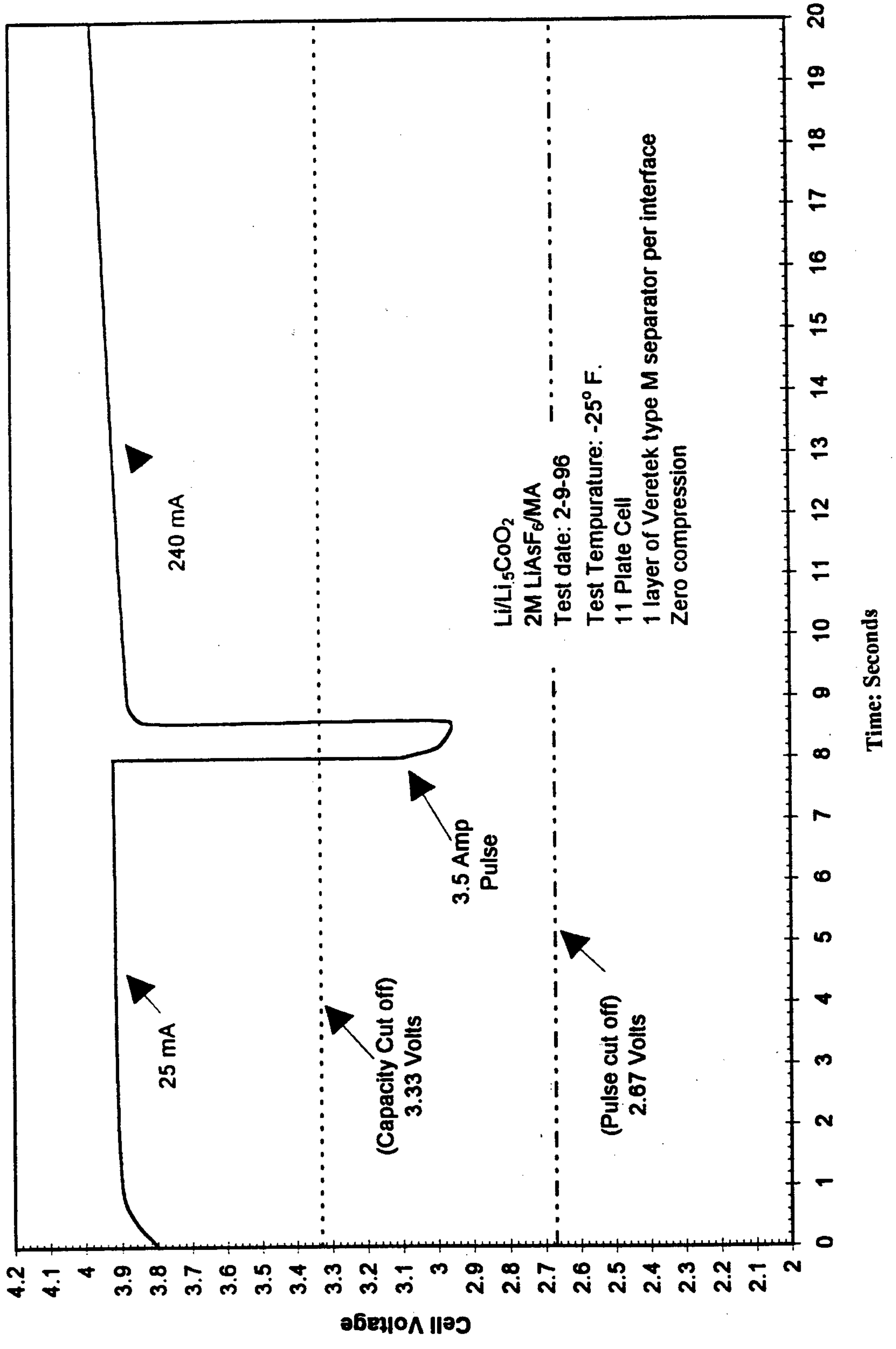


Figure 5-14. Erect Pulse, 8 Seconds After Activation (WAMF12)

Hermetic Cell Performance Testing at Environmental States

Hermetic cell testing essentially moved the same electrode stack designed during the fixtured cell work into a fully-configured metal cell case. The hermetic cell case and cover were designed to facilitate electrode stack assembly. Sealing the cover onto the cell case required a laser welder to follow a computer-defined path conforming to the cells "C"-shaped geometry. Once sealed, the cells were able to be flooded with electrolyte by means of the fill tube in the terminal end of the cell. Reference to Figure 5-15 for a graphic illustration of the "C"-shaped cell. It was necessary during testing to place the hermetic cells into a test fixture that simulated the battery housing and its external support. The housing is shown in Figure 5-16, in cutaway, as part of the complete HWAM concept battery. Since development of the battery reservoir was not a part of this program, a remote steel sample cylinder was used to hold the cell's electrolyte prior to pressure activation.

Performance testing first concentrated on run time evaluation and capacity achieved at a given temperature. Room temperature performance was verified and was found to equal that obtained in the fixture cell testing. More than 57 hours of run time (13.865 Ah) were obtained from cell WAMH05. Please refer to Figure 5-17 for pertinent data on this test. None of the 3.75-ampere pulses went below the minimum limit of 2.67 volts. Performance was ended when the continued background current of 240 amperes caused the voltage to descend to 3.3 volts. In a 3-cell HWAM battery concept 3.3 volts is equivalent to the 10-volt minimum operating voltage.

A pivotal point was reached in performance testing when cold temperature test results proved to be poorer than expected. These are presented in Appendix B. Design changes made during the fixture cell testing were not enough and an additional change had to be made. Much of the testing had already been conducted with the two molar single salt, methyl acetate electrolyte (SSMA). The more expensive, but better at cold temperatures, double salt methyl formate electrolyte (DSMF) had to be substituted. This was demonstrated in a cell stored for three months at 160°F and in a cell stored for three months at room temperature (See data for WAMH 23 and 24 in Appendix B).

Note that Alliant Techsystems' recommendation is that the DSMF electrolyte is necessary for cold temperature operation and is thus the preferred electrolyte for the HWAM battery. In reviewing the test data of this report, remember that many earlier tests are for cells with the SSMA electrolyte. It is Alliant Techsystems' position that the methyl formate electrolyte does not represent a significant change when conducting safety tests and, as such, the safety test results reported for the methyl acetate electrolyte could be accepted as comparable to those expected for the methyl formate electrolyte.

High temperature performance at 145°F was checked on a cell that had been stored for three months at the specification minimum temperature of -65°F. The test temperature and maximum operating temperature is 145°F. Cell number WAMH20, (Figure 5-18), produced a better than expected 60 hours of run time, 14.365 Ah capacity. Pulse handling capability was, as before, not the life limiting issue. Cutoff at the minimum required voltage, 3.33 volts, was due to background load; but only after required the run time was exceeded. Similar results were obtained for cell WAMH 21, similarly stored, but discharged at room temperature. (See Appendix B)

Capacity testing on three hermetic cells connected in series used cells numbered WAMH01, WAMH03, and WAMH04. These three cells functioned as a single HWAM battery and provided voltage above 10 volts for more than 56 hours. The capacity of the battery was 13.65-ampere hours. Figure 5-19 shows the discharge. The reason for the pulsed voltage delay for the first pulse of 3.5 amperes is not known. Electrolyte delivery was via a single reservoir and should have been completed over the one hour of open circuit duration prior to loading the battery with the 3.5-ampere pulse.

Cold temperature testing at -25°F was conducted on cell number WAMH07 after the change was made to the double salt, methyl formate electrolyte. This cell delivered the best overall capacity of any cell, 14.8-ampere hours. Figure 5-20 shows that it also performed well on pulse handling except for the initial pulse of 3.5 amperes. Some exposure of the lithium anode during the fabrication phase of the cell, when dry room conditions were less than ideal due to a power failure, is suspected to have produced a passive layer on its surface. However, that assumption has not been substantiated.

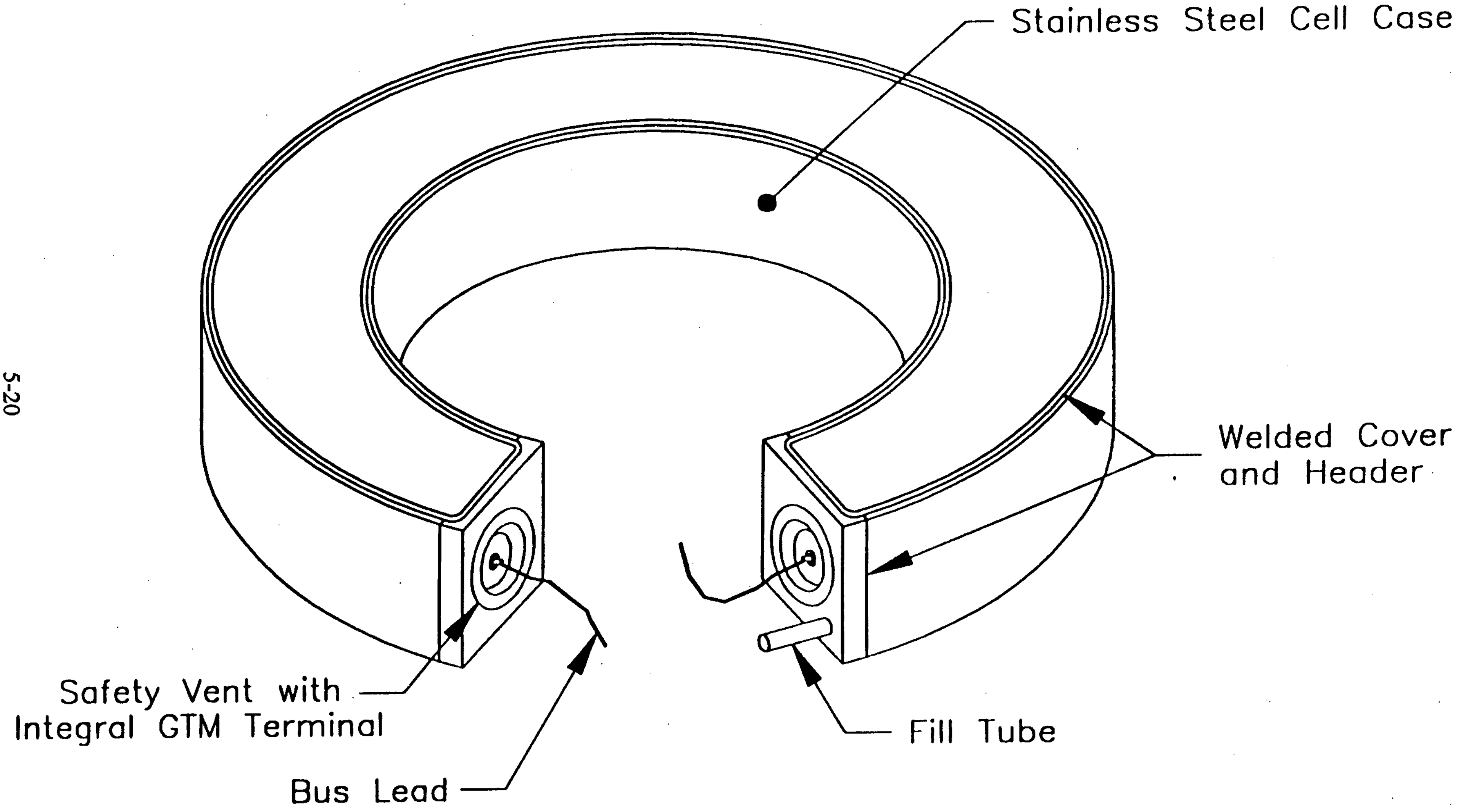


Figure 5-15. Individual Cell Case

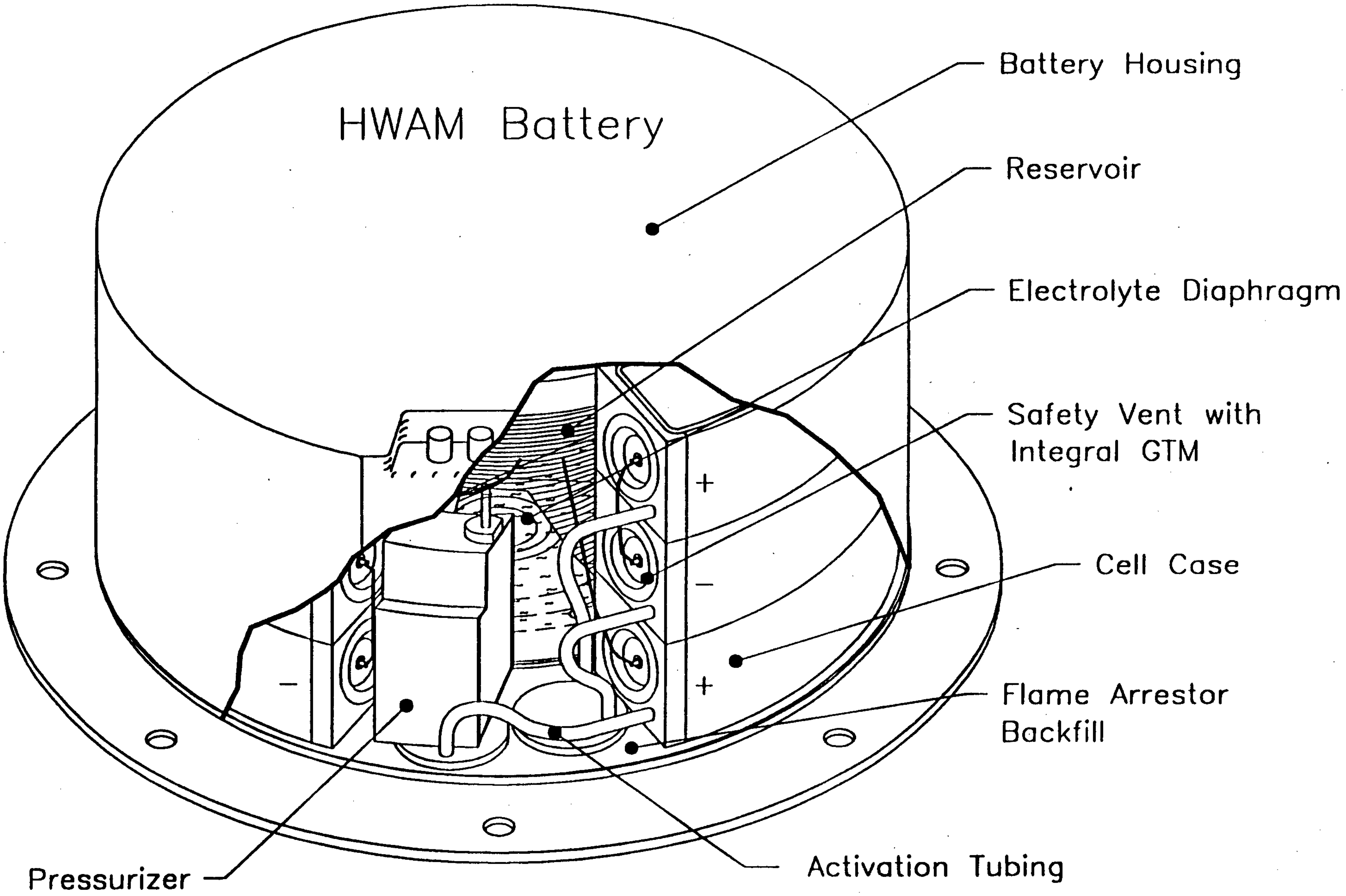


Figure 5-16. HWAM Battery

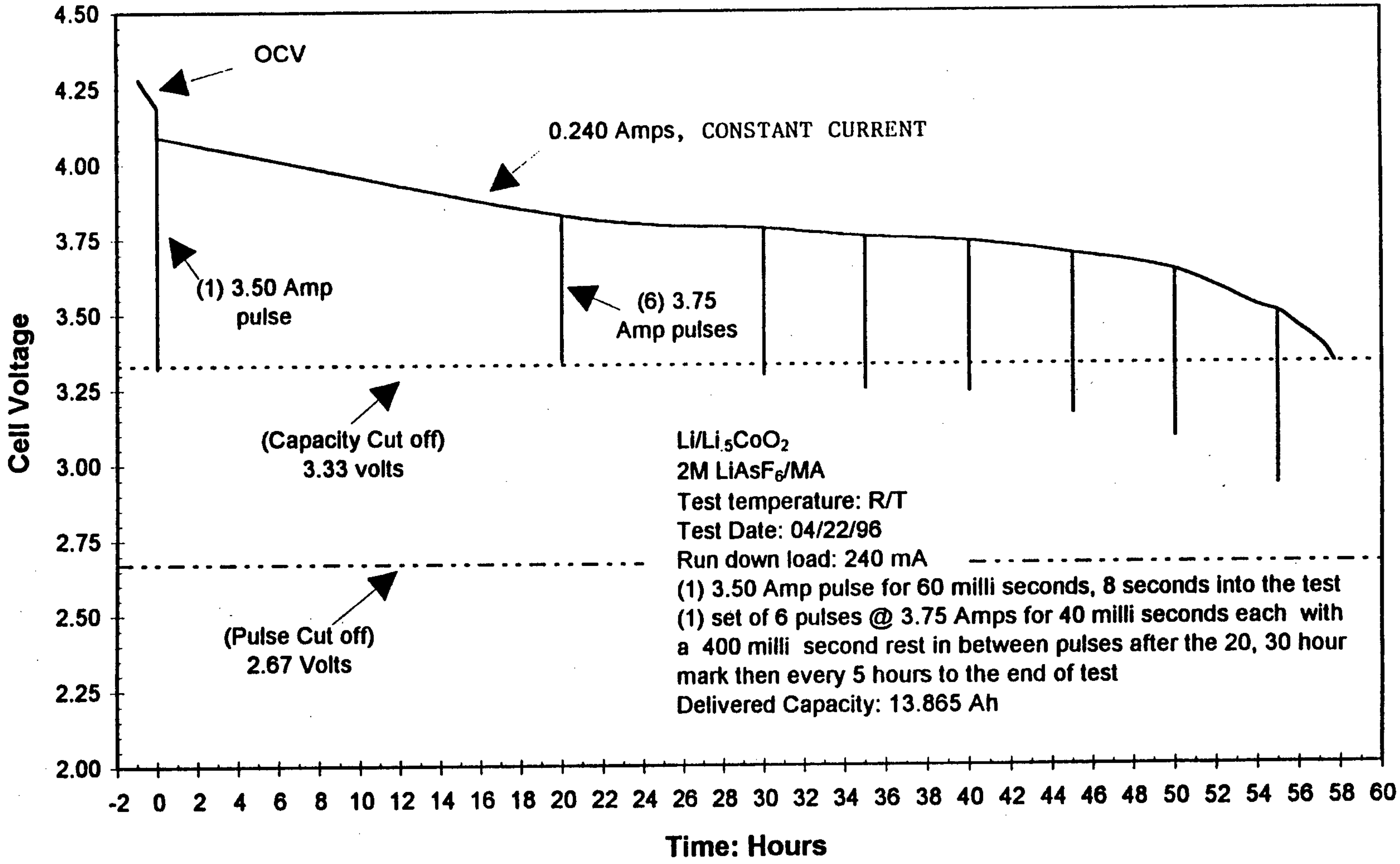
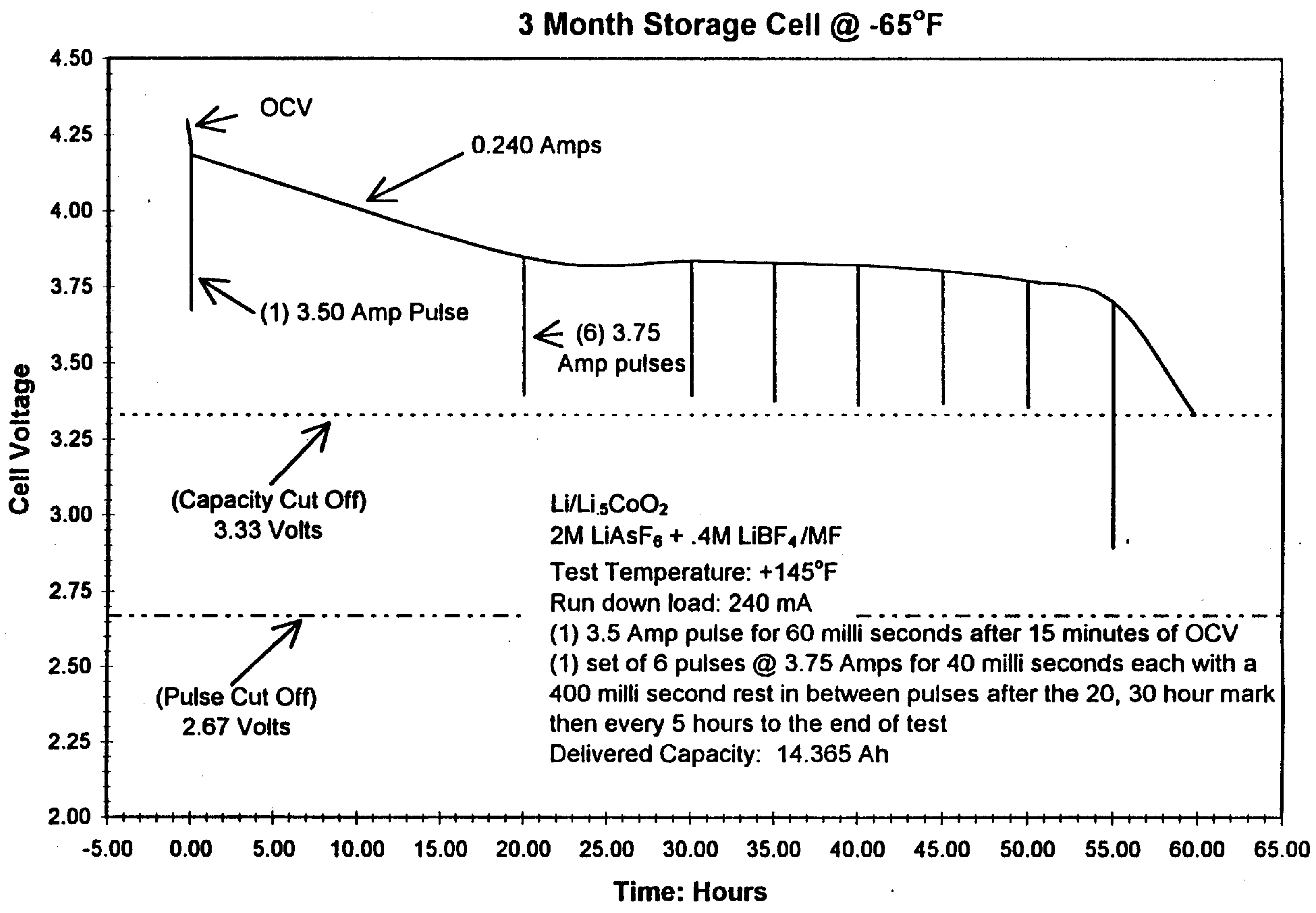
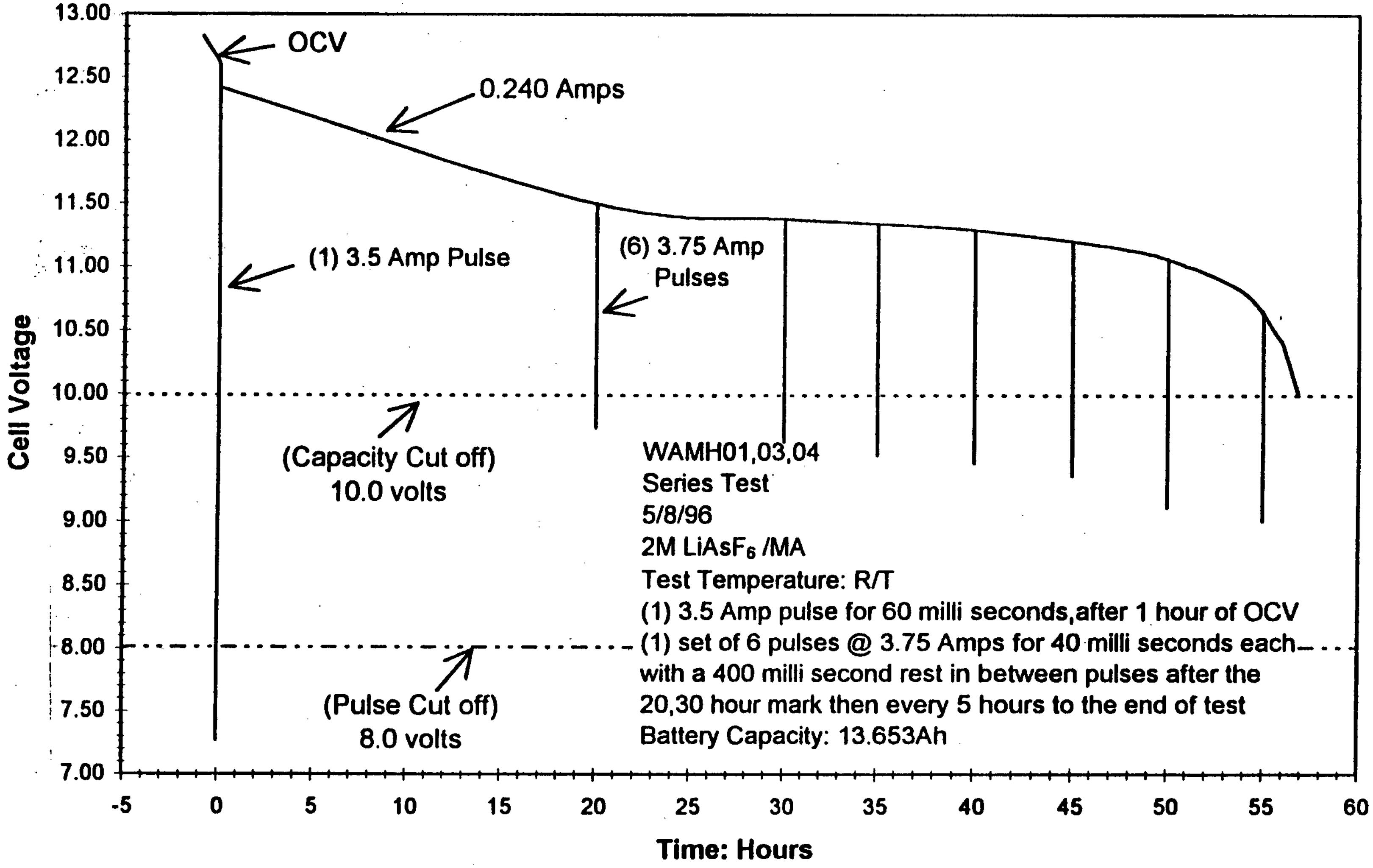


Figure 5-17. Pulse and Capacity Discharge Profile, Cell WAMH05



Li/Li_5CoO_2
$2M\ LiAsF_6 + .4M\ LiBF_4/MF$
Test Temperature: +145°F
Run down load: 240 mA
(1) 3.5 Amp pulse for 60 milli seconds after 15 minutes of OCV
(1) set of 6 pulses @ 3.75 Amps for 40 milli seconds each with a 400 milli second rest in between pulses after the 20, 30 hour mark then every 5 hours to the end of test
Delivered Capacity: 14.365 Ah

Figure 5-18. Pulse and Capacity Discharge Profile, Cell WAMH20



WAMH01,03,04
Series Test
5/8/96
2M $LiAsF_6$ /MA
Test Temperature: R/T
(1) 3.5 Amp pulse for 60 milli seconds,after 1 hour of OCV
(1) set of 6 pulses @ 3.75 Amps for 40 milli seconds each
with a 400 milli second rest in between pulses after the
20,30 hour mark then every 5 hours to the end of test
Battery Capacity: 13.653Ah

Figure 5-19. Pulse and Capacity Discharge Profile, Series Test

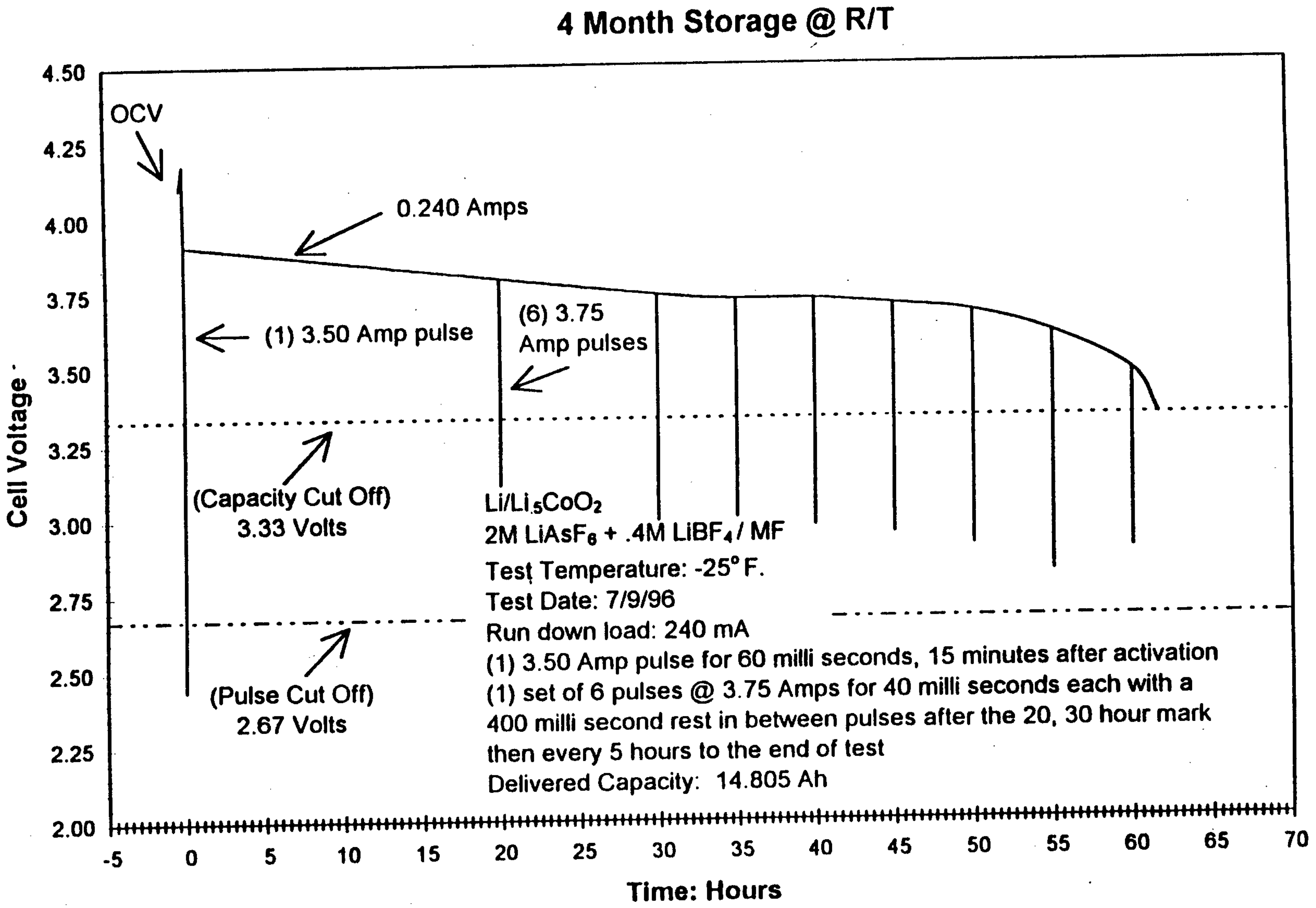


Figure 5-20. Pulse and Capacity Discharge profile, Cell WAMH07

Hermetic Cell Safety Testing

First in the series of safety tests was an external short circuit test of cell number WAMH08. This cell was activated and allowed to develop full open circuit voltage before the external short was applied by way of a relay. The short was conducted at room temperature (approximately 72°F). The maximum short circuit current developed was 41-amperes. The short circuit was maintained for 30 minutes during which time the temperature increased to 92°F then gradually declined. Figures 5-21(a) and 5-21(b) show the short circuit record and the discharge capacity that followed while under a load of 12 ohms. At no time did the cell rupture or vent. The safety vent diaphragms in the cell terminal header remained intact throughout the entire test. A total of 7.2 ampere-hours were removed during the 12 ohm discharge. The test was repeated with similar results using cell WAMH19 (See Appendix C).

The next short circuit test was also applied externally, but to a cell that had been stored for three months in the reserve-state. This cell, number WAMH22, was activated with the substituted electrolyte; the double salt methyl formate. During the course of the applied short circuit, a maximum current of 30 amperes and a maximum temperature of 116°F were developed. The run time of useful cell capacity, removed after the short circuit provided 30 hours across a 12 ohm load. This load was equivalent to about 0.3 amperes, slightly more than the normal HWAM background load of .24 amperes. (See Figure 5-22(a) and 5-22(b)) The cell did not vent. It remained hermetic throughout the test and subsequent discharge.

To further investigate the effects of cell short circuit behavior, a short circuit test was arranged in which the short was internal to the cell. This was done by fabricating a cell stack (cell number WAMH09) without key separators between electrodes. Specifically, two separators were left out of the middle of the stack and two separators were left out of the top of the stack. In these locations, anode and cathode plates were in direct contact. This fabrication represented the case of misassembly or assembler error. Cell activation occurred at room temperature and the maximum temperature developed during 30 minutes of short circuit was 85°F. After removing the short circuit, a 12 ohm resistive load was applied to rundown the cell. A total of 4.9 ampere-hours were removed during that load application. No venting or rupture occurred during the short circuit. Figure 5-23 provides a profile of the test. Following the internal short circuit test, another external short circuit test was conducted, followed by discharge into reversal with the 12 ohm resistive load. Cell number WAMH18 was the subject cell. No venting or case rupture occurred. The maximum temperature developed during the short circuit was 147°F with a maximum short circuit current of 22 amperes (Figures 5-24(a-c)).

Finally, an abuse test was conducted to simulate the scenario of an underfilled cell stack. This would happen if the reservoir collapsing force misfired or partially closed the reservoir. In an unlikely case where only 10% of the electrolyte in the reservoir is delivered to the cell stack a severe electrolyte starved condition would exist. Cell WAMH06 was tested under these conditions while being loaded with the full background load of 240 mA. Initially, after 2 hours of open circuit, a 3.5-ampere pulse was applied prior to the background load. No venting or case rupture occurred and 1.38 ampere-hours of capacity were removed (Figure 5-25).

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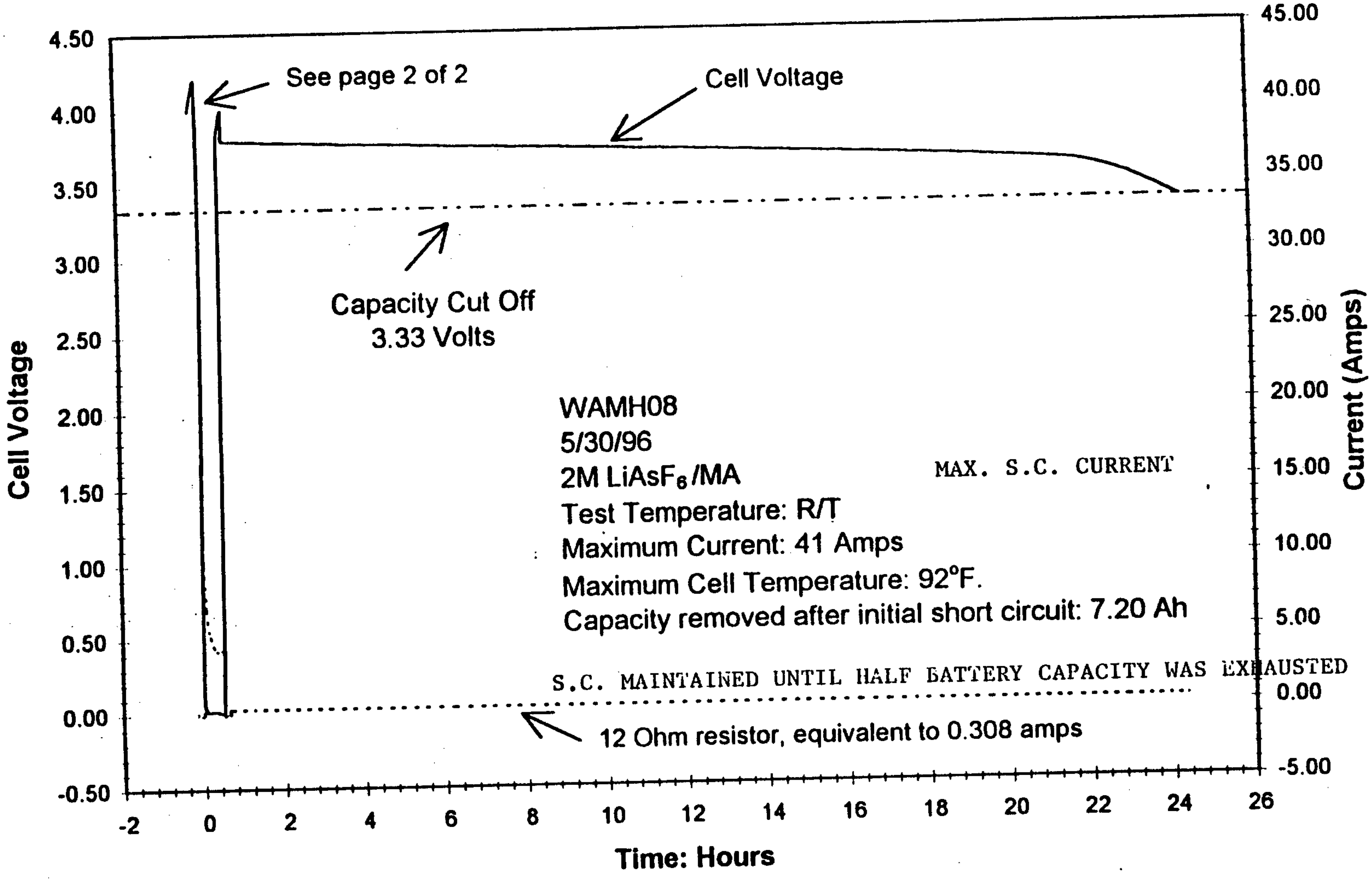

Figure 5-21(a). External Short Circuit Test, WAMH08

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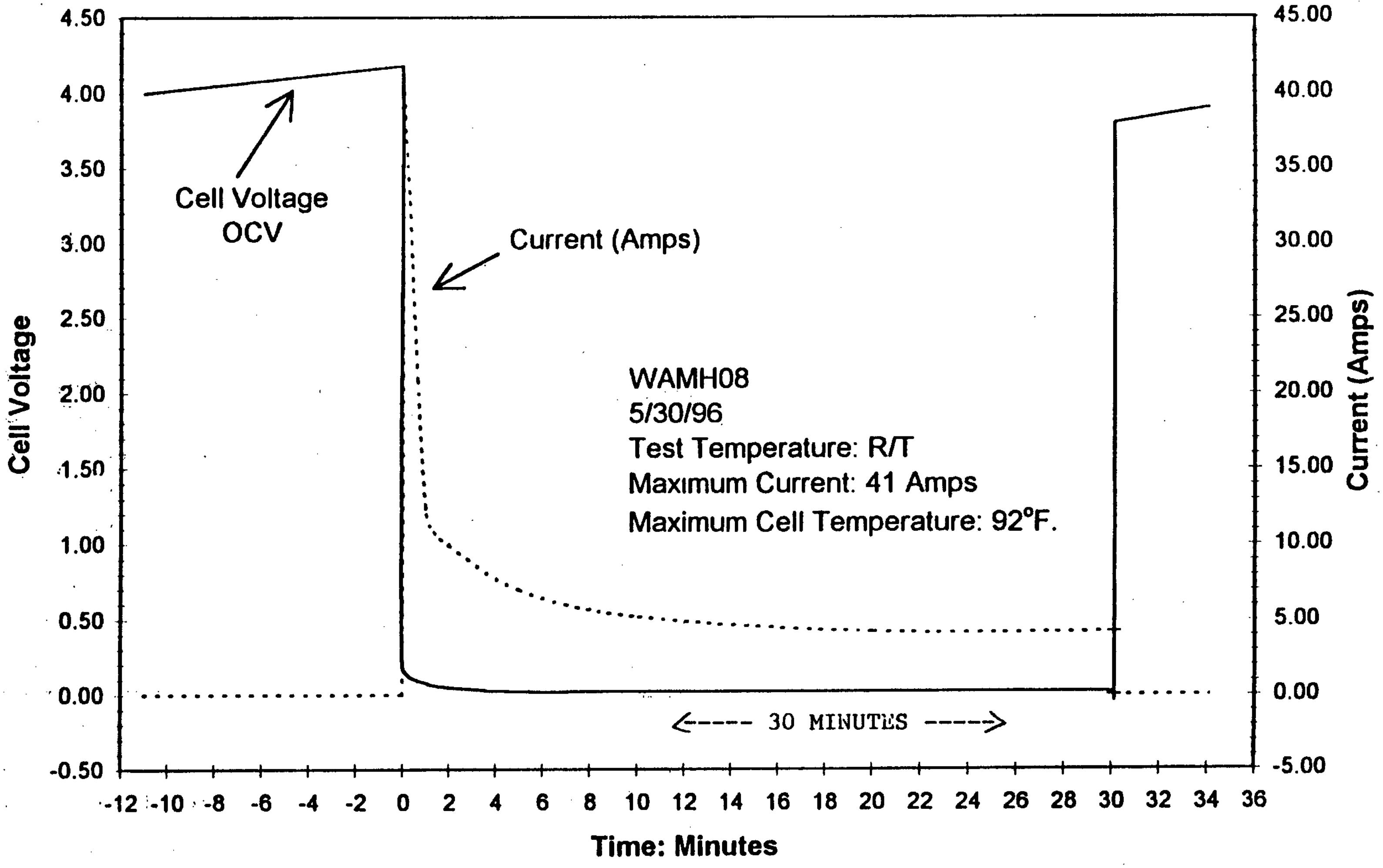

Figure 5-21(b). External Short Circuit Test, WAMH08

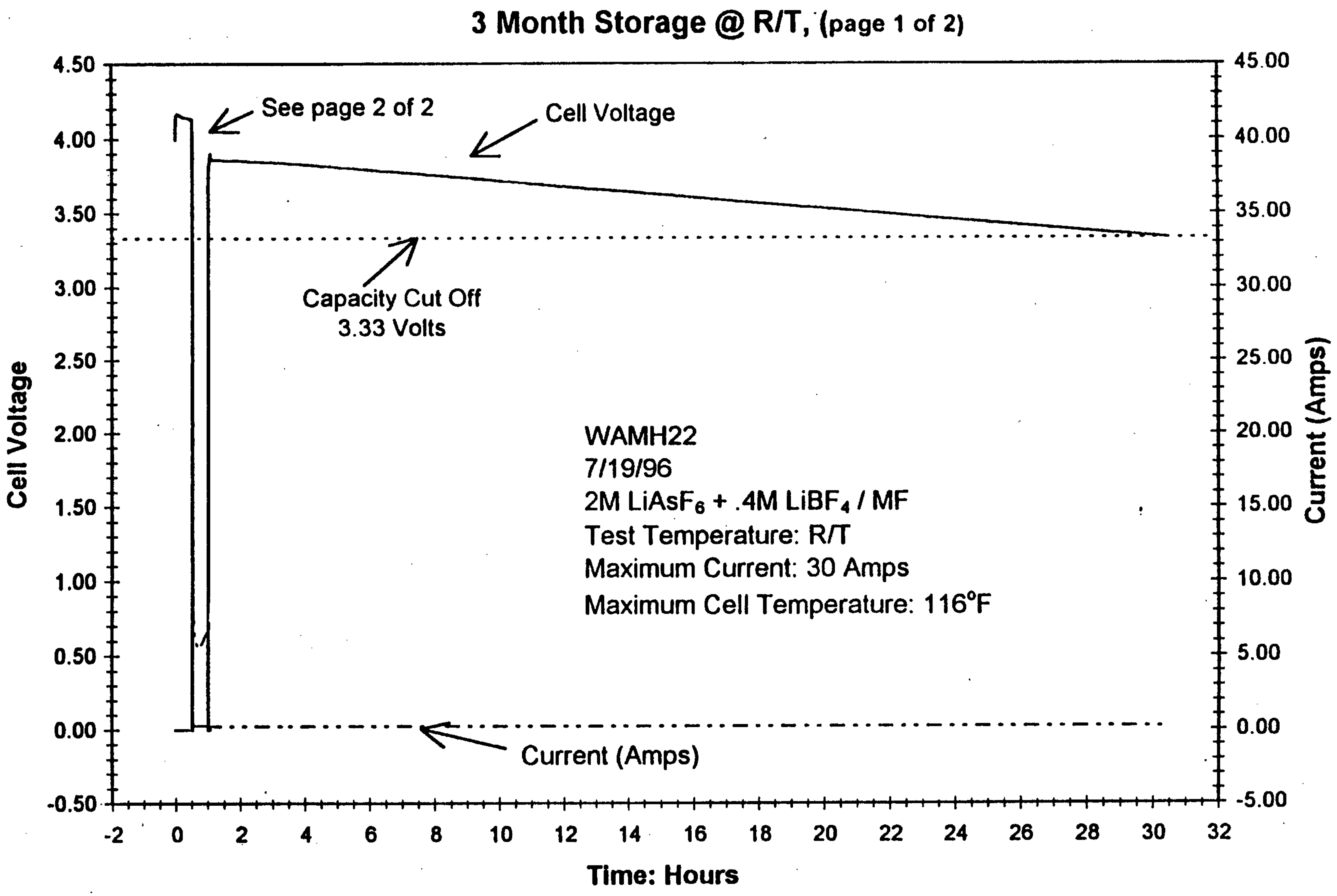

Figure 5-22(a). External Short Circuit Test, WAMH22

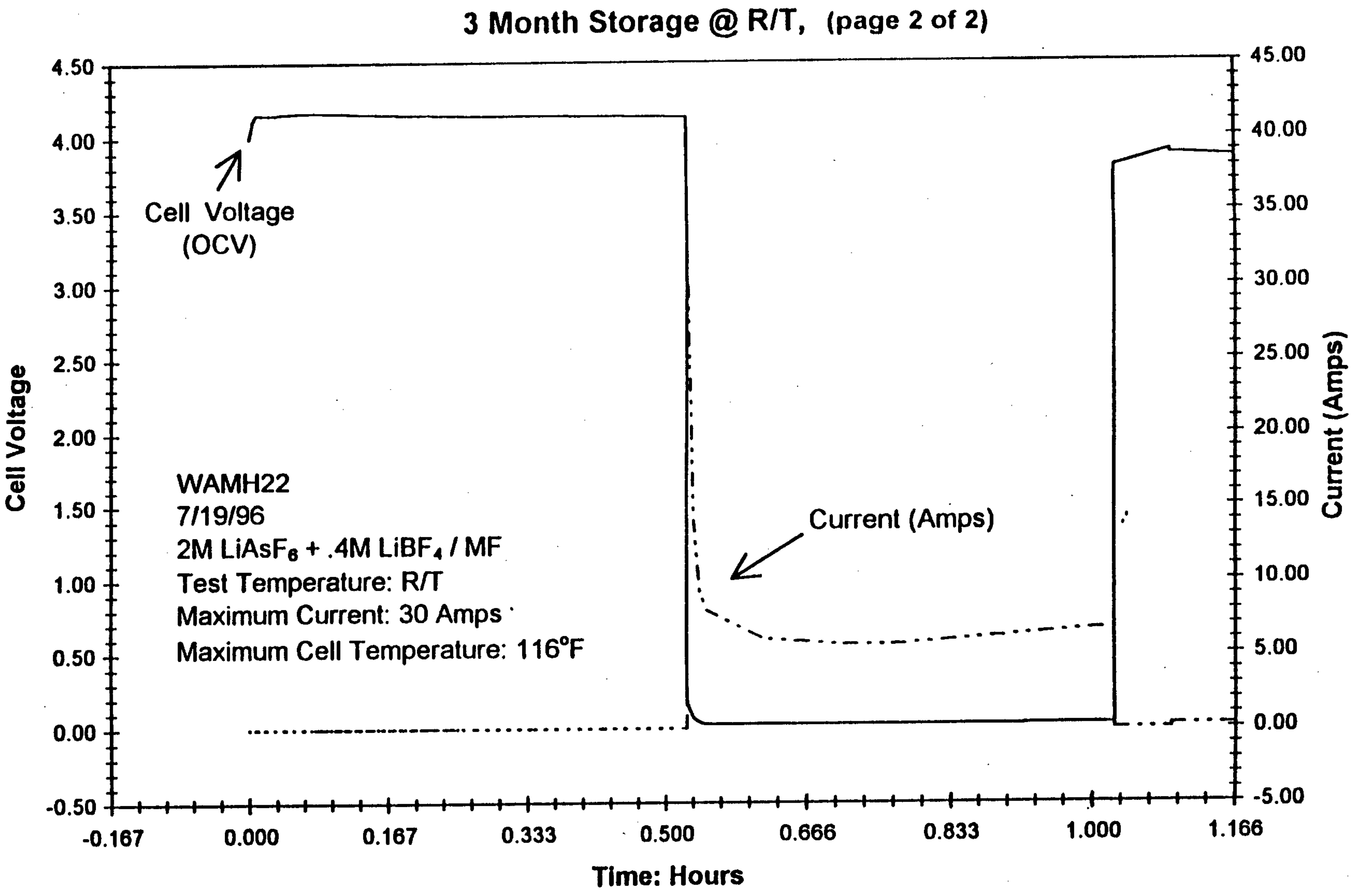

Figure 5-22(b). External Short Circuit Test, WAMH22

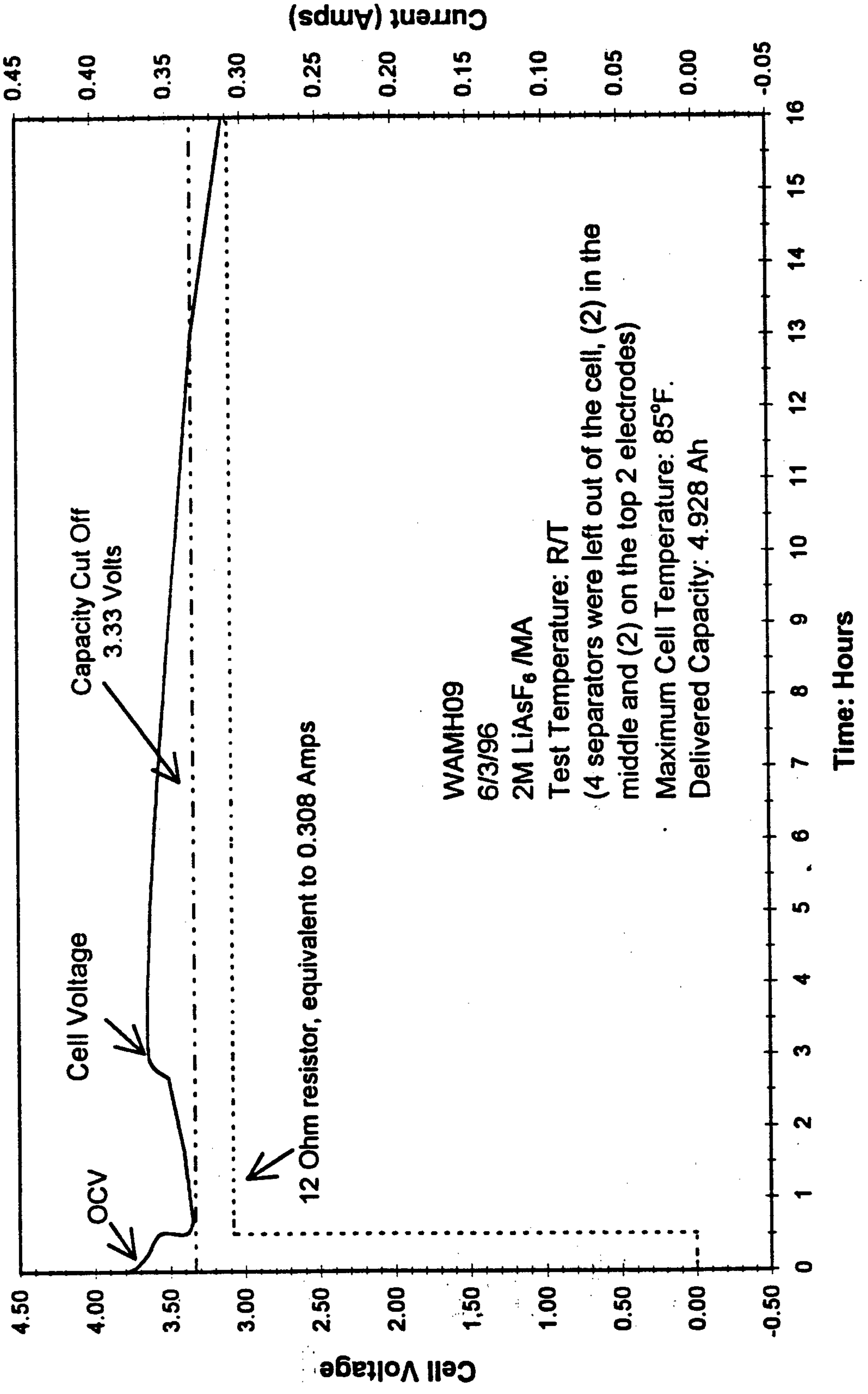

Figure 5-23. Internal Short Circuit Test and Capacity Discharge Profile, Cell WAMH09

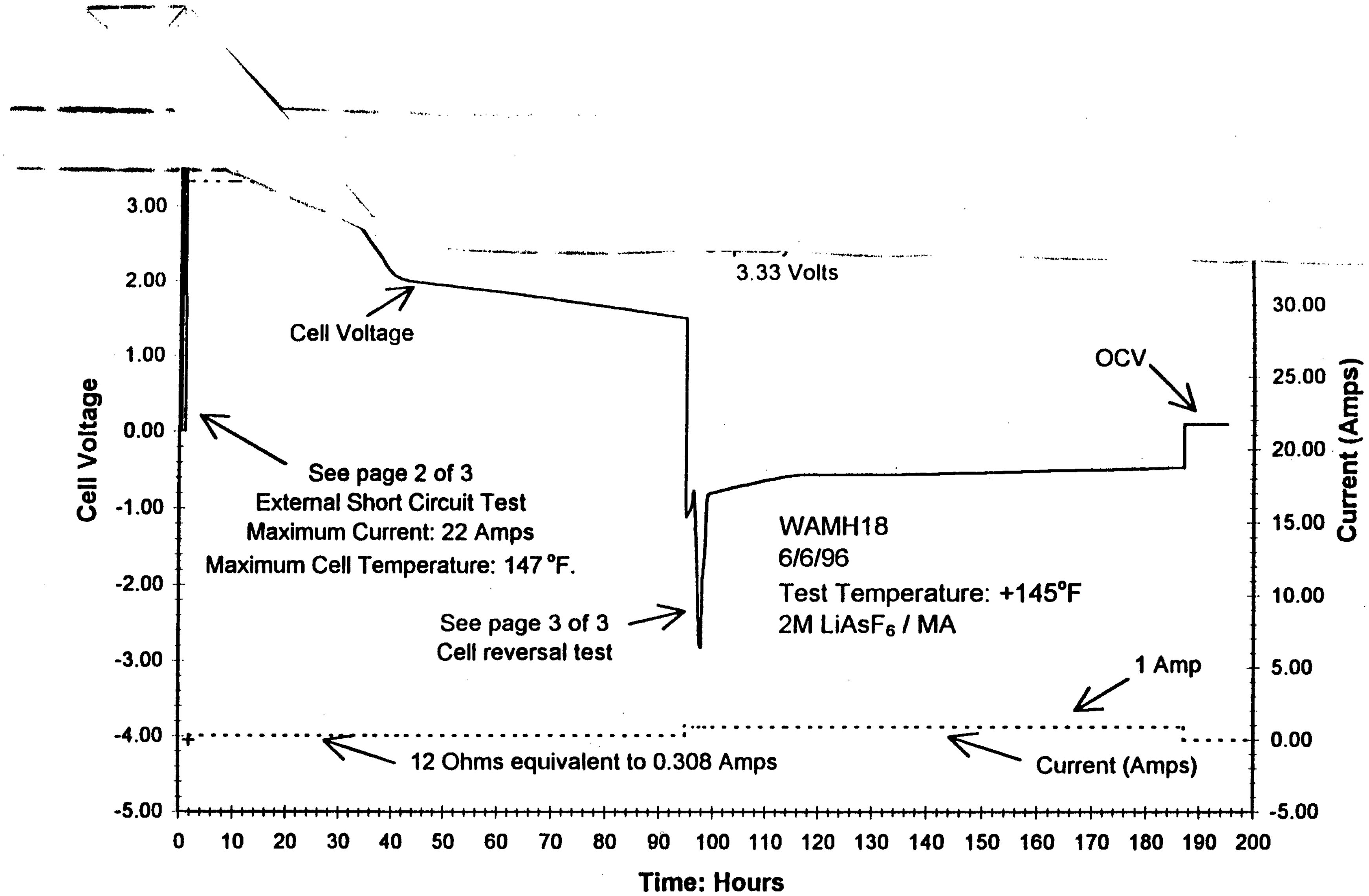

Figure 5-24(a). Short Circuit and Cell Reversal Test, WAMH18

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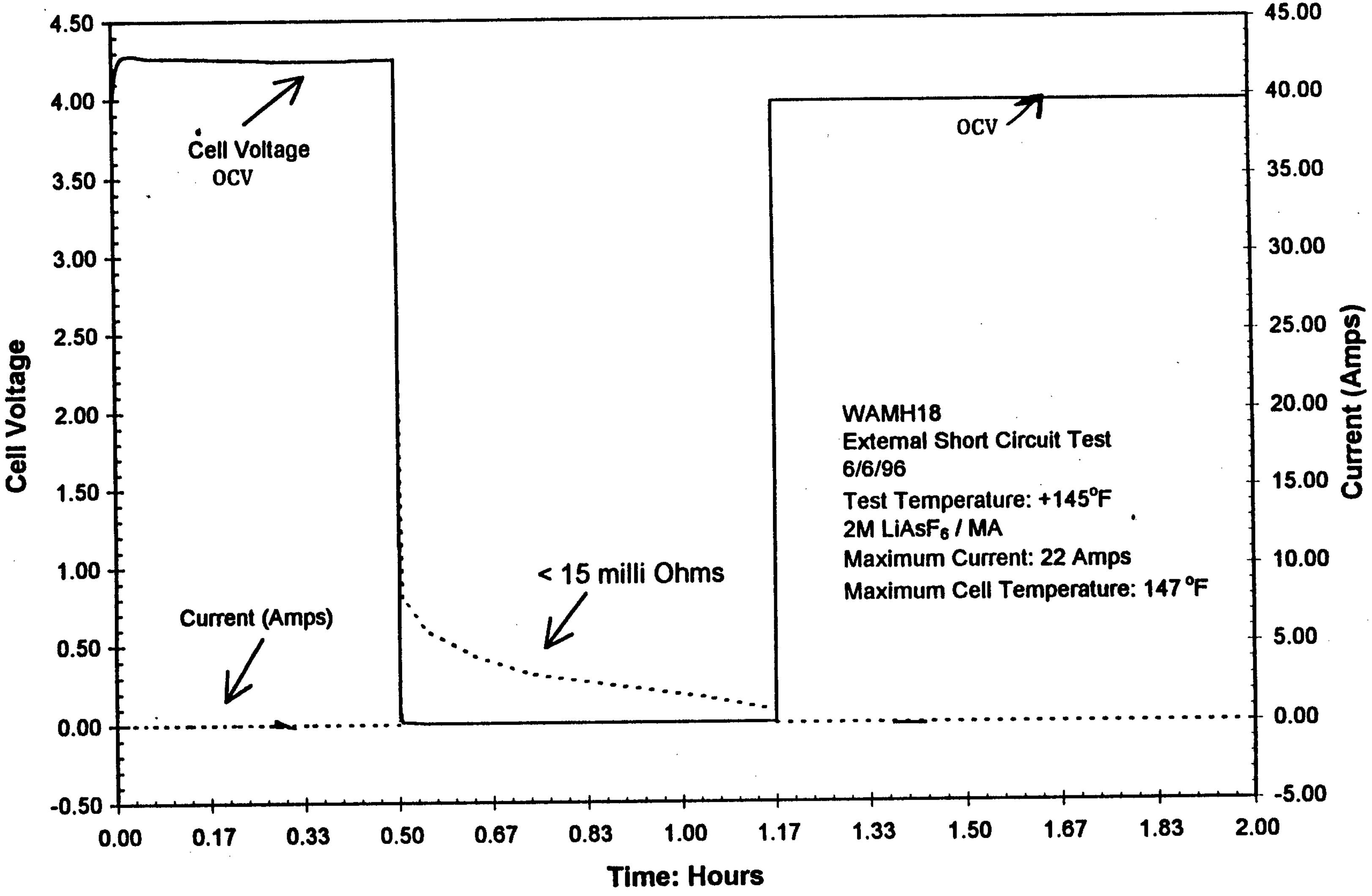


Figure 5-24(b). Short Circuit and Cell Reversal Test, WAMH18

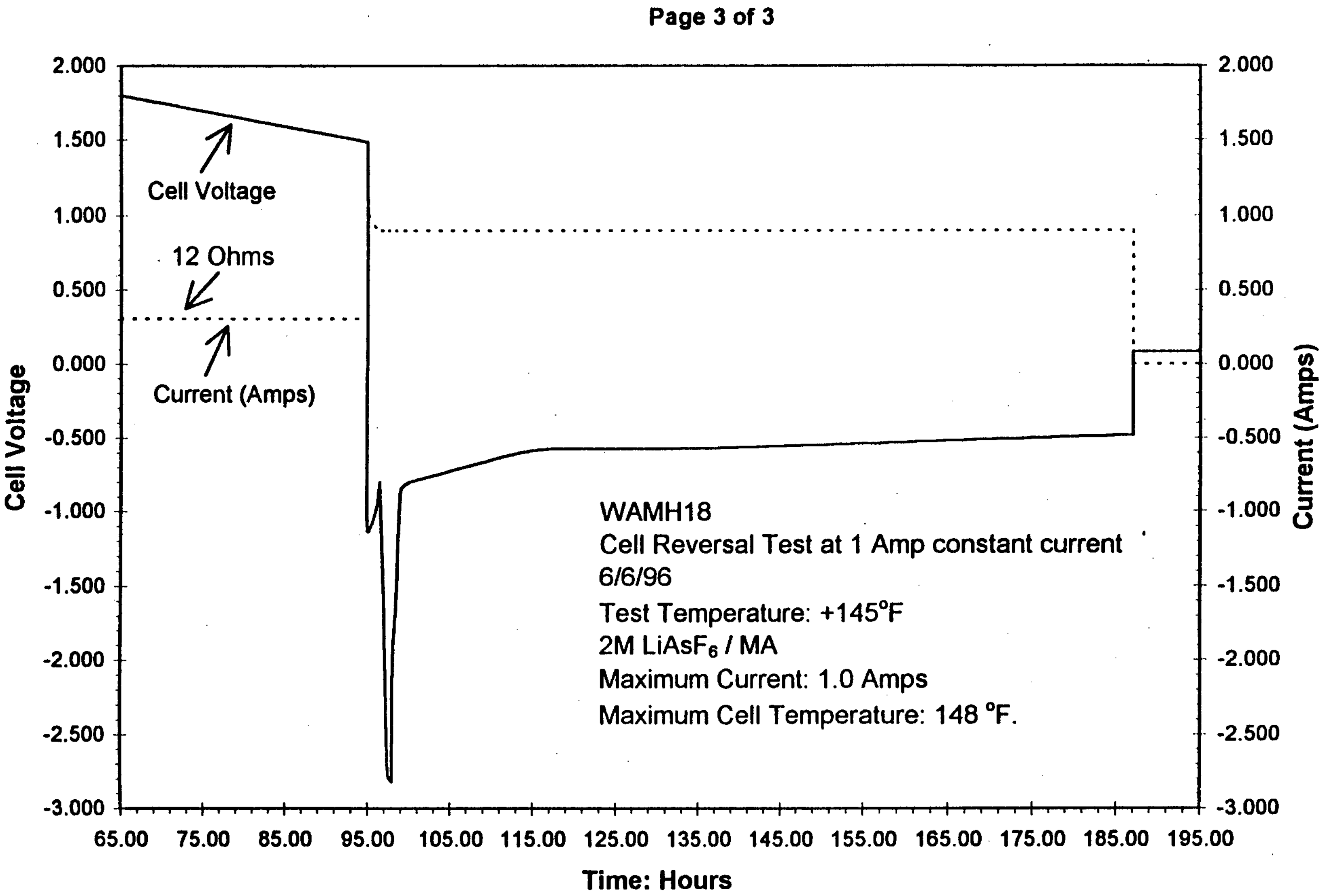


Figure 5-24(c). Short Circuit and Cell Reversal Test, WAMH18

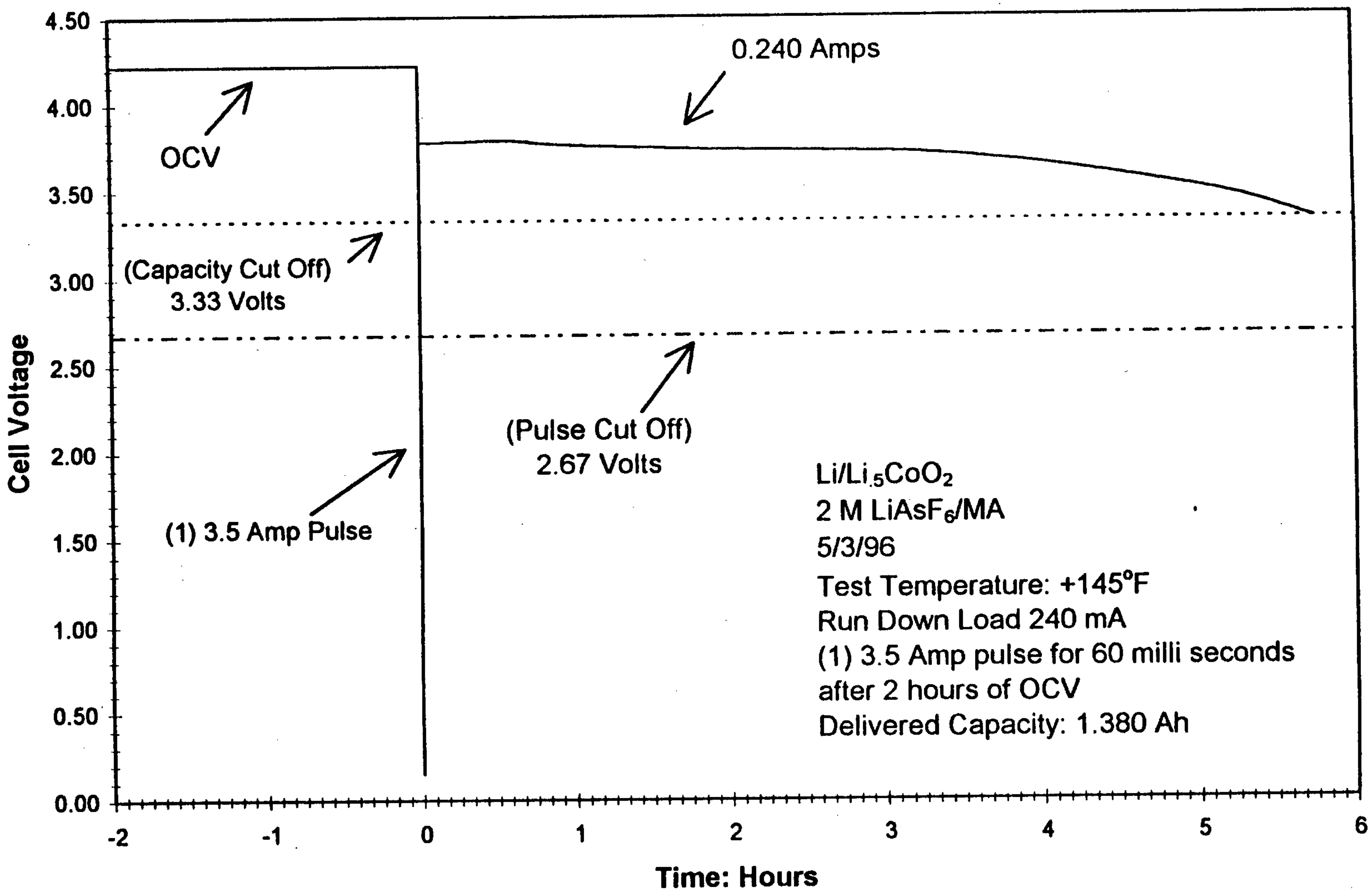


Figure 5-25. Abuse Test, Activated with 10% Electrolyte, WAMH06

Chapter 6

Studies

Alliant Techsystems Inc. committed several engineering studies to further the information base on the HWAM battery. Some of the studies were directed toward maximizing power of a reserve battery design beyond the current values while restricting the battery to the space allotment of Specification No. 29224A (Figure 1-1). The studies are listed below and described further in this chapter.

- Cell Improvement Studies
- Comparison of $Li_{0.5}CoO_2$ with Thionyl Chloride ($SOCl_2$) performance and safety
- Battery Life-Expectancy, reserve and active
- Battery Disposal and Pollution Prevention
- Battery Projected Unit Price Cost
- Battery Design Analysis
- Capacity Calculations for an Active Battery Design
- Capacity Required by $SOCl_2$ Battery for Depassivation Pulses
- Reserve Battery Concept with External Reservoir

Cell Improvement Studies

Building an hermetically sealed, HWAM configured cell in the laboratory is time consuming because of the lack of production tooling and automation. At the same time, many choices are available to the designer for materials selection. Design choices need to be made rapidly because of schedule constraints. The selection process during cell design is based on experience; then, the most likely materials are tried in prototype cells. A fast approach is to experiment with a smaller cell configuration to eliminate the cost of trying every variable in full-size cell hardware. This was the path chosen on this program. Fortunately, a very good small cell, a modified Alliant Techsystem's production cell, Picatinny Arsenal Cell 9275567 (Figure 5-1), was an excellent choice for this work. It has hermetic construction and lends itself to modification by using alternate materials. The cathode, for instance, a mixture of vanadium oxide and graphite is constructed by pressing. Processing of the HWAM cathode, a mixture of cobalt oxide and carbon, is nearly identical. As a whole, the validity of choosing the Picatinny cell as the test vehicle is a good one. Only two attributes are not accurately matched with this test cell. They are:

<u>The activation methods</u> - *via* a glass ampul *in situ*, for the modified ATK G2666. The electrodes are wetted once the ampul is broken. In the case of the HWAM

cell, a remote reservoir feeds the electrodes once a gas pressure driver ruptures a metal diaphragm. The pressure-driven electrolyte conceivably wets the electrodes rapidly, as opposed to the capillary action electrolyte feed of a broken ampul.

Electrode compression - The modified ATK G2666 is constructed bobbin style, without positive pressure on the electrode sandwich. The HWAM cell is a stacked arrangement of flat plates that receive a positive compression when the case cover is welded in place. However, compression was kept to a minimum.

Physical comparison between the two cells is made in Table 6-1. The table shows that the current density is identical for the two cells as well as being close in gravimetric parameters such as the cathode specific capacity. The variables evaluated were: temperature, separator type, cathode mix ratio and electrolyte type.

Table 6-1. Physical Comparisons

Attribute	HWAM	G2666 (Modified)
Cathode Area / Cell (cm^2)	729.2	5.24
Cathode Mix Wt./Cell (grams)	150	1.45
Cathode (Li_xCoO_2) Wt./Cell (grams)	132.3	1.28
Cathode Volume/Cell (cm^3)	49.9	0.428
Cathode Thickness (inches)	.027 (per side)	.030
Cathode Density (grams mix/cc)	3.0	3.39
Cathode Loading (grams mix/cm^2)	0.206	0.277
Cathode Capacity (mAh/cm^2)	24.5	33.0
Lithium Area/Cell (cm^2)	800.6	3.94
Lithium Weight/Cell (grams)	6.5	.054
Lithium Thickness (inches)	.006 (per side)	.010
Lithium Capacity (mAh/cm^2)	31.4	52.9
Defining Area/Cell (cm^2)	729 (cathode)	3.94 (anode)
Defining Capacity (mAh/cm^2)	28.5 (cathode)	33.0 (cathode)
Cell Capacity (Ah)	17.9	0.121
Current (c.d.) @ 400 mA (HWAM)	400 mA (.55 mA/cm^2)	2.16 mA (.55 mA/cm^2)
Current (c.d.) @ 3.75 Amps (HWAM)	3,750 mA (5.14 mA/cm^2)	20.27 mA (5.14 mA/cm^2)

The first test series evaluated three types of separators which were: Celgard 2300, Veretek 141-583, and Whatman BSB-3DA. Two different mix ratios of Li_xCoO_2 and carbon graphite were employed. The ratios compounded were one of 90%-10% and 81%-19% of Li_xCoO_2/Graphite. Graphite is added for conductivity, but it displaces Li_xCoO_2. Two different current density levels were evaluated. They were 0.5 mA/cm^2 corresponding to HWAM background load rates and 5.0 mA/cm^2 which corresponds to HWAM pulse load rates (3.75 amperes). Four test temperatures were also a part of this test series, 28°F, 75°F, 0°F, and -25°F

(See Figures 6-1 through 6-9). Mix ratios of Li_xCoO_2 and graphite made no significant difference in performance. High percentages of graphite reduce the cost of the battery since Li_xCoO_2 is an expensive product. Using a non-microporous separator such as Veretek or Whatman does limit the battery to being primary and not capable of recharges. Other microporous separators would need to be identified for a rechargeable HWAM battery.

The test results showed clearly that non-woven separators, i.e., Veretek or Whatman, were superior to Celgard for electrical activation from the reserve state and overall discharge performance.

$Li_{0.5}CoO_2$ COMPARISON WITH $SOC1_2$

Prior to developing the Li/Li_xCoO_2 system to power the HWAM, the Army developed Li/$LiSOC1_2$ for this application. A specific advantage of Li/$Li_{0.5}CoO_2$ electrochemistry over Li/$SOCl_2$ is due to the higher load voltage, 3.85 volts versus 3.4 volts. The open circuit voltage in both cases is about 0.2 volts higher. Lithium anodes passivate with time when exposed to $SOC1_2$ at open circuit or low rate discharge, unless extremely low. A voltage dip occurs at the beginning of discharge unless the passivation has been removed. That can be done by applying a high rate discharge pulse. Such pulses are shown in Figure 2-3. The Li/$LiCoO_2$ system does not require depassivation pulses. Furthermore, lithium/lithium cobalt dioxide is safer than lithium/thionyl chloride for all the reasons outlined in the Safety Study attached as Appendix D.

The thionyl chloride system is not rechargeable. While Li/Li_xCoO_2 can be recharged. This was demonstrated in this work (See Section 5-1 and Figure 5-4). Furthermore, under the base contract, of which this work was an option item, Li/Li_xCoO_2 was developed as a rechargeable system.[1] It is being developed for the Navy for rechargeable propulsion power, specifically as prismatic 100 Ah cells. Those cells use a microporous separator. The rapid rise time required by HWAM negated a microporous separator because it is slow to wet. Microporous separators would be needed for rechargeability . Therefore, further development work would be required to develop a separation system that would permit rapid rise time and rechargeability.

Lithium/thionyl chloride, on the other hand, has better rate capability than does lithium/lithium cobalt oxide. The difference is at least an order of magnitude in current density, i.e., 3-4 mA/cm^2 for Li/$LiCoO^2$ and 30-40 mA/cm^2 for Li/SOC1.[2] Energy density is another advantage of Li/$SOC1_2$. Practical values of 80 Wh/lb for Li/$LiCoO_2$ versus 200 Wh/lb for Li/$SOC1_2$ in 100 to 200 ampere-hour cell sizes. Nevertheless, the Li/$LiCoO_2$ system is sufficiently energetic for HWAM.

Both Li/$LiCoO_2$ and Li/$SOC1_2$ have excellent power capability, and both have good low temperature performance, which make them the primary electrochemistry choices for HWAM. Figures 6-10 and 6-11, and Table 6-2 give comparison data between $LiCoO_2$ and $SOC1_2$. The $SOCl_2$ comparisons are for two very different embodiments of the electrochemistry. They are both reserve cells, but the HED battery (Alliant Techsystem's G2666B1), a version of the Alliant's G26666 (Figure 5-1) based on the oxyhalide cathode instead of vanadium oxide, has a 1 Watt-hour capacity while the SPM unit (Alliant Techsystem's G3070A2)is a 4000 Watt battery for powering sonobuoys. These batteries have been produced on production lots. Further information on these power sources may be found in Appendix E, taken from an Alliant Techsysems marketing brochure.[4]

Battery Life Expectancy

Life expectancy for $Li/Li_{0.5}CoO_2$ batteries is excellent as shown by real time test data of hermetic cells. The Picatinny cell 9275567, modified with the HWAM cathode of precharged lithium cobalt dioxide, was activated and placed on a slow rundown load (150K-ohms) equivalent to the HWAM 7 months background rate. The cell ran for 7.13 months (5,136 hours). This was then compared with a fresh cell of the same type that was activated and discharged at a fast rate, 31 hours (900 ohms). The fresh cell yielded 132 milliampere-hours of capacity, whereas the slowly discharged cell yielded 134 milliampere-hours of capacity. Essentially, no loss in life expectancy for slow, long time use. These tests were conducted at room temperature and are plotted together in Figure 6-12. No tests were conducted on cells that were first activated, and then left on open circuit for 7 months, followed by a fast discharge. However, in many ways the test presented is a better representation of HWAM requirements. Life tests at temperature extremes also need to be conducted in a future program.

HWAM Active $Li/Li_{0.5}CoO_2$ Battery

One of the tasks requested during the development of the HWAM $Li/Li_{0.5}CoO_2$ battery was an evaluation of the capacity of an active battery using the same volume constraints as the HWAM Reserve Battery. Nominal capacity for the reserve battery was 14 ampere-hours. Using the volume displaced by the reservoir for additional electrode space, an active battery was designed with a cross-section as shown in Figure 6-13. The component electrode design summary is shown in Table 6-3. The nominal capacity expected from this design is 35-ampere-hours. The weight budget for the active battery design is shown in Table 6-4. Total battery weight is 4.5 pounds. If a weight maximum of 3.0 pounds (present specification, see Table 2-1) were to be imposed on the battery design, then the maximum expected capacity would be 22.4 ampere-hours.

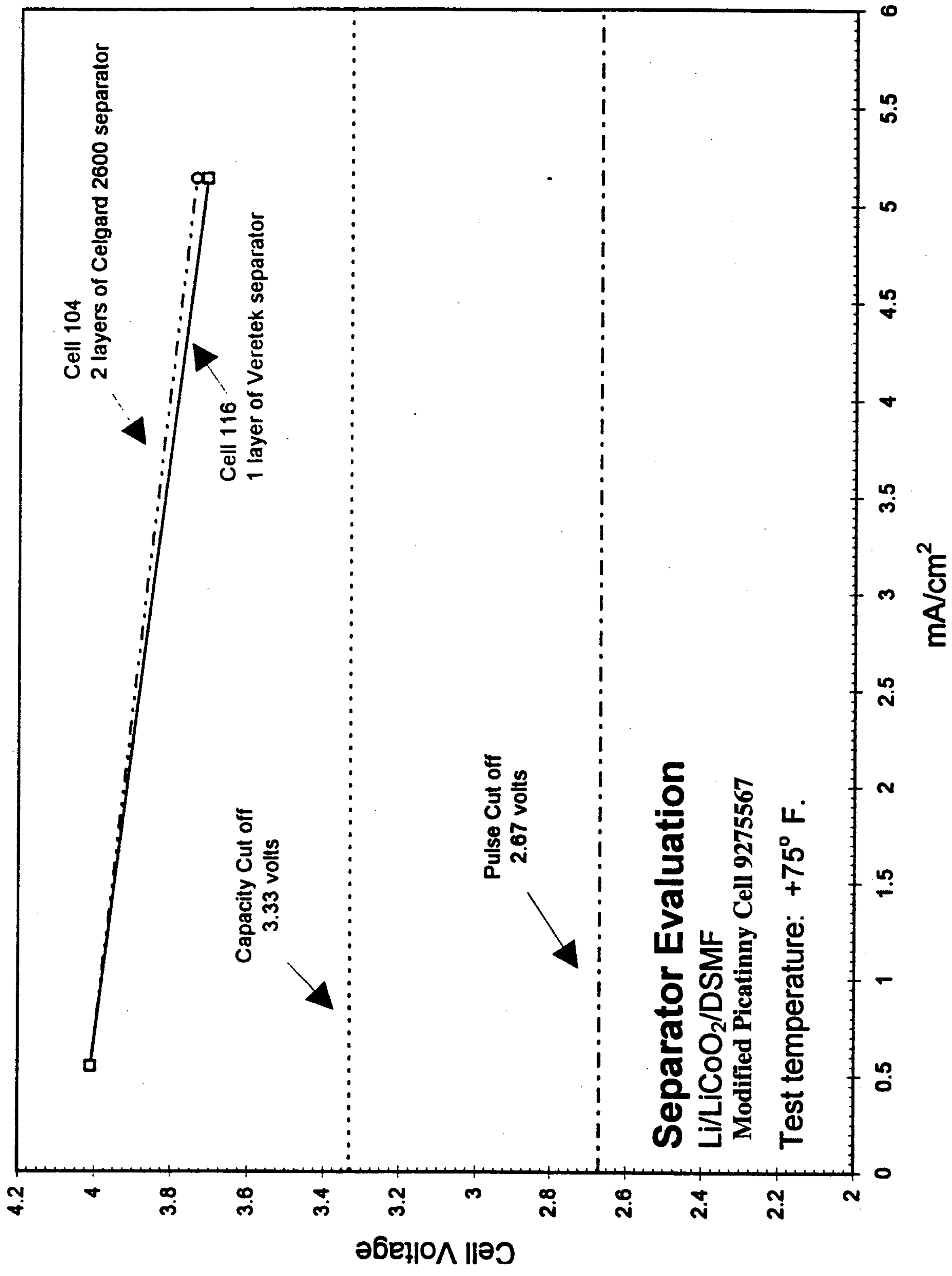


Figure 6-1. Separator Evaluation, +75°F

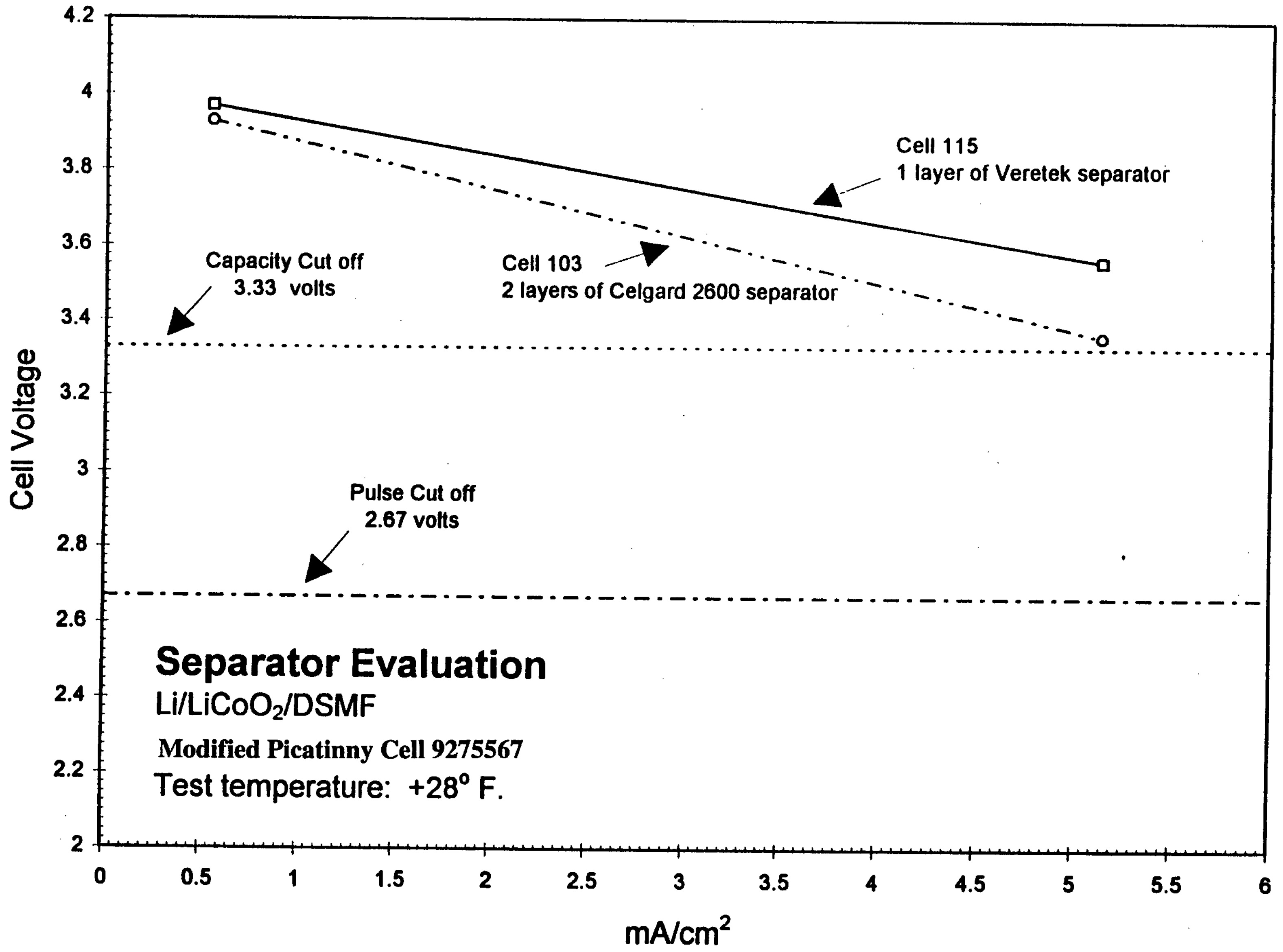


Figure 6-2. Separator Evaluation, +28°F

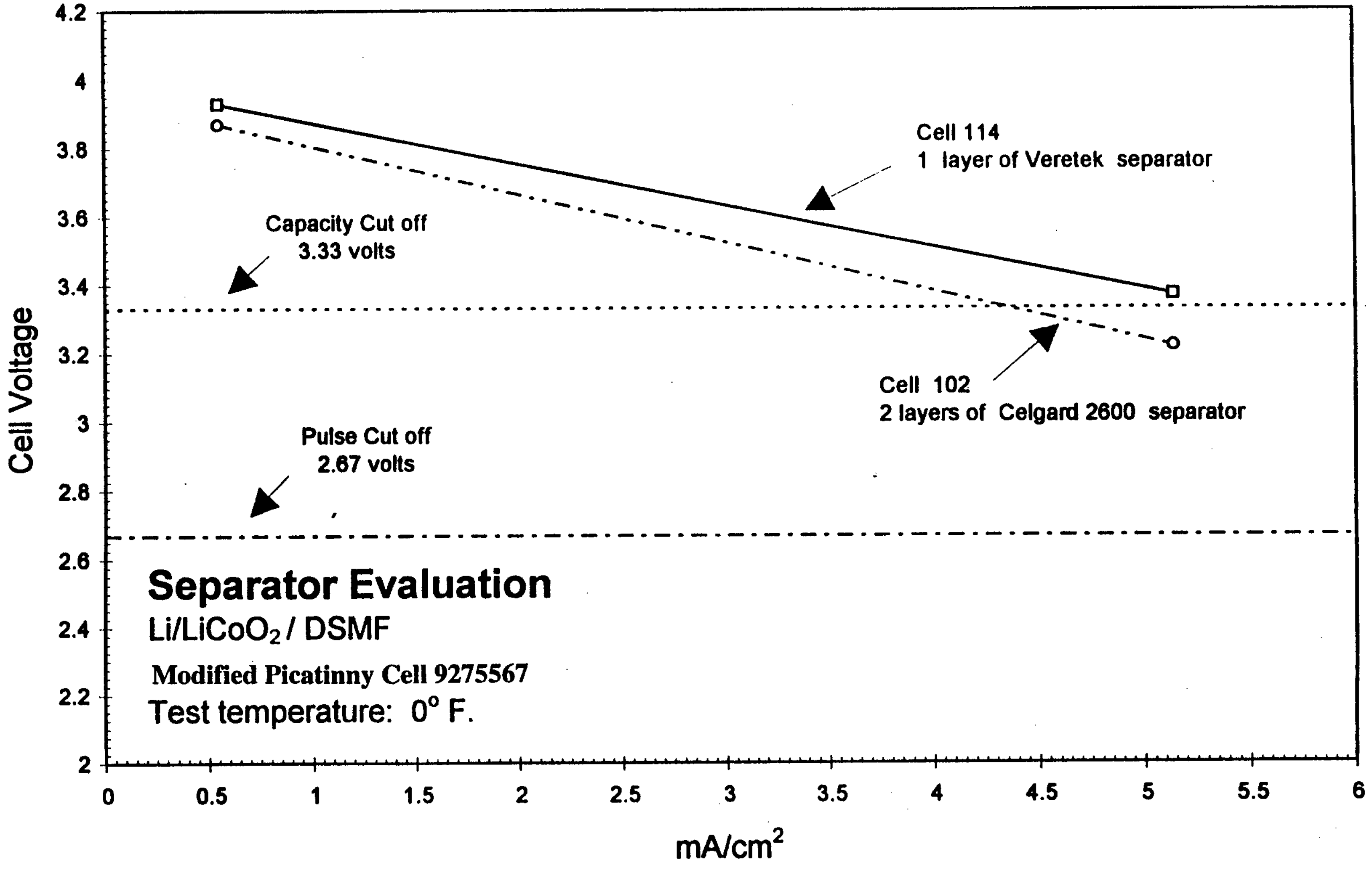


Figure 6-3. Separator Evaluation, 0°F

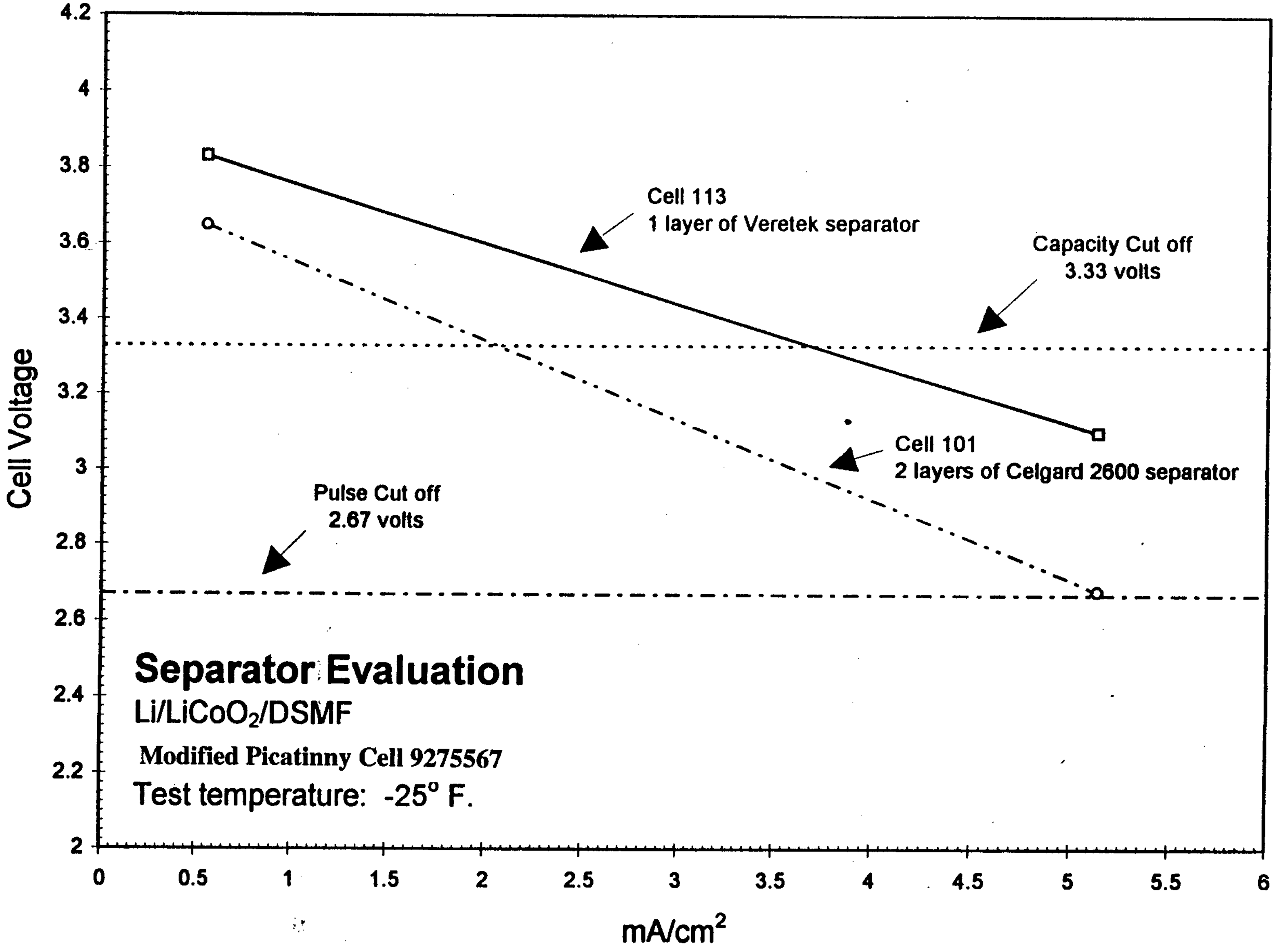


Figure 6-4. Separator Evaluation, -25°F

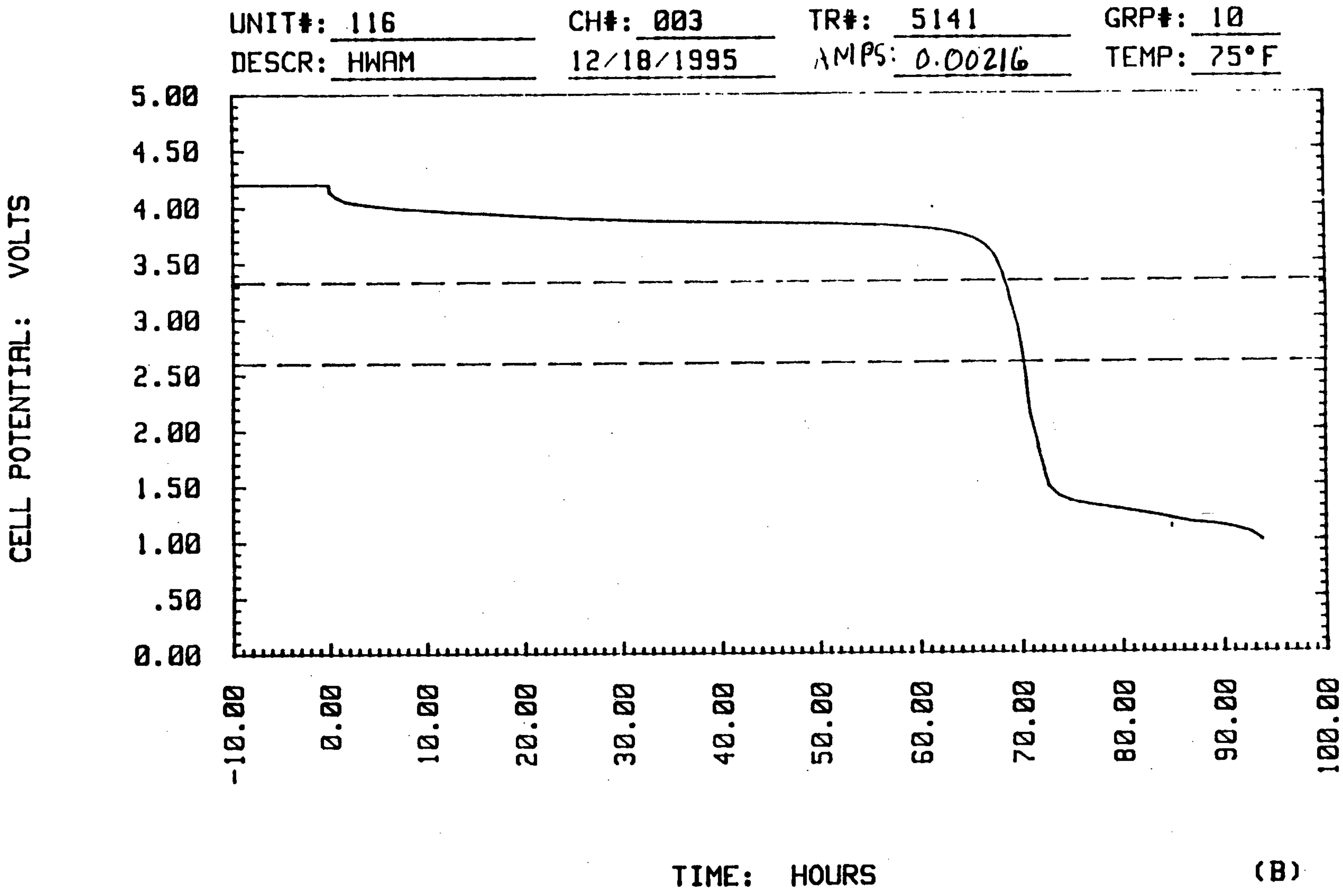


Figure 6-5. Modified Picatinny Cell 9275567, Li/Li$_x$CoO$_2$/DSMF, 1 Layer Veretek

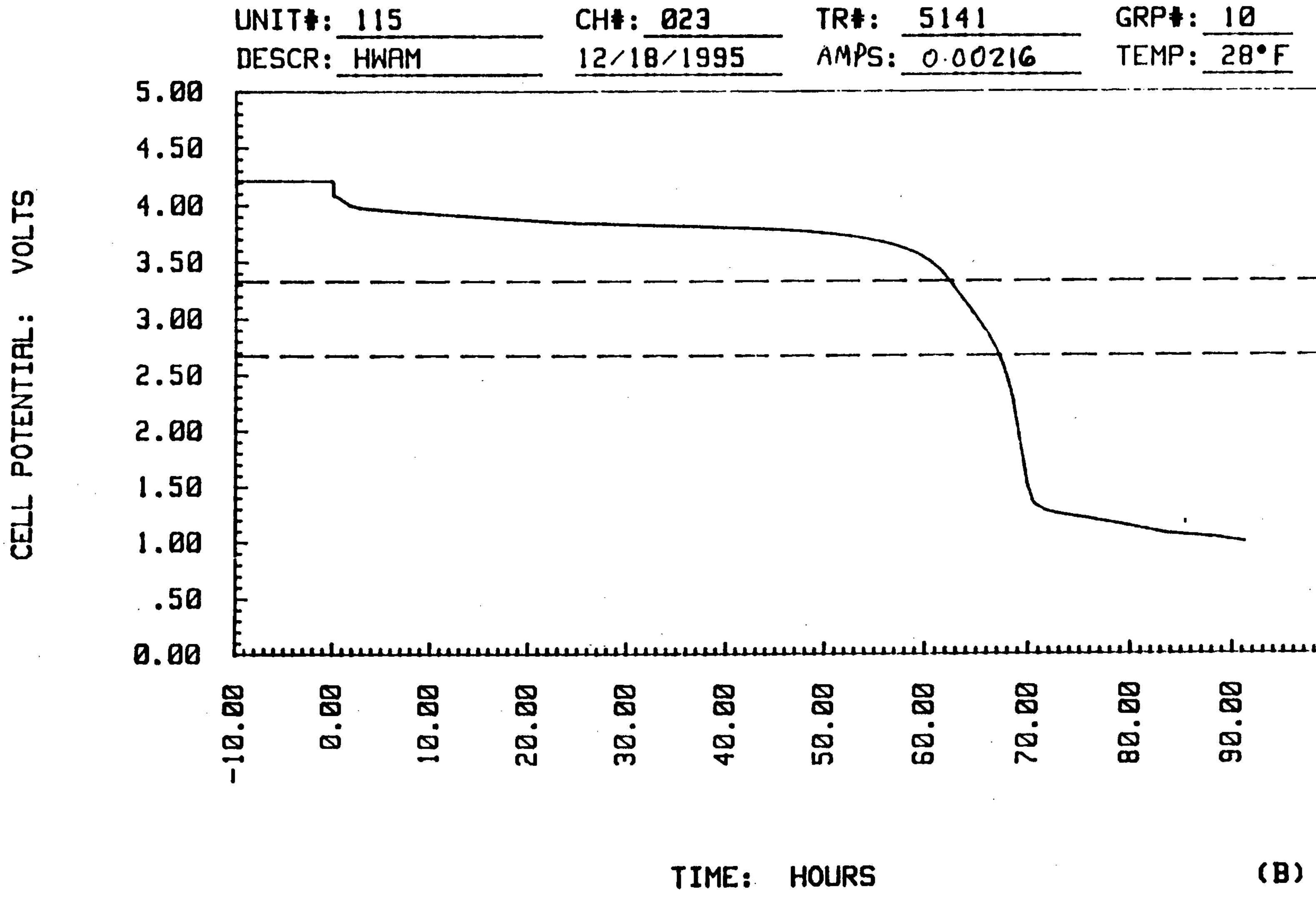


Figure 6-6. Modified Picatinny Cell 9275567, Li/Li$_x$CoO$_2$/DSMF, 1 Layer Veretek

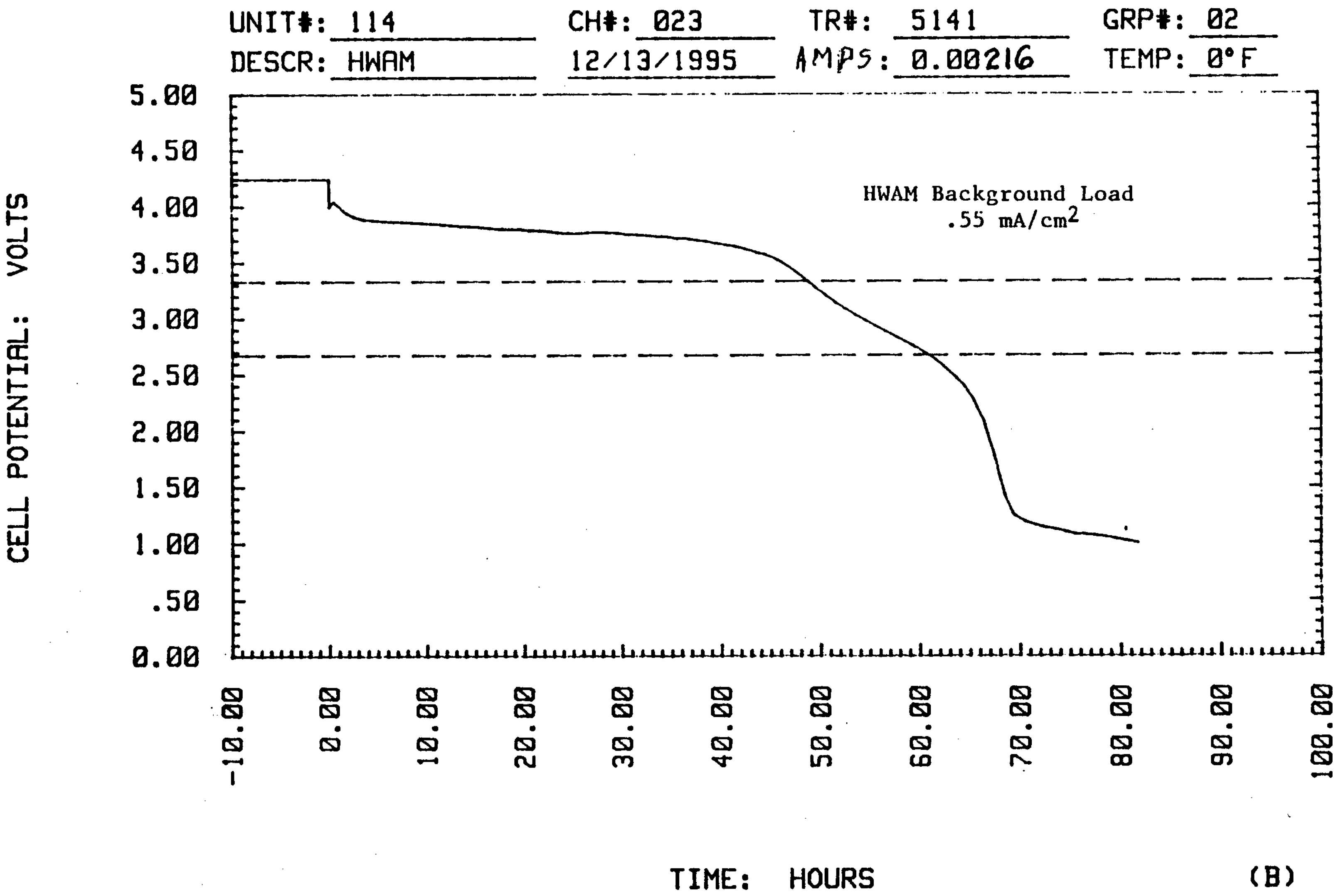


Figure 6-7. Modified Picatinny Cell 9275567, Li/Li$_x$CoO$_2$/DSMF, 1 Layer Veretek

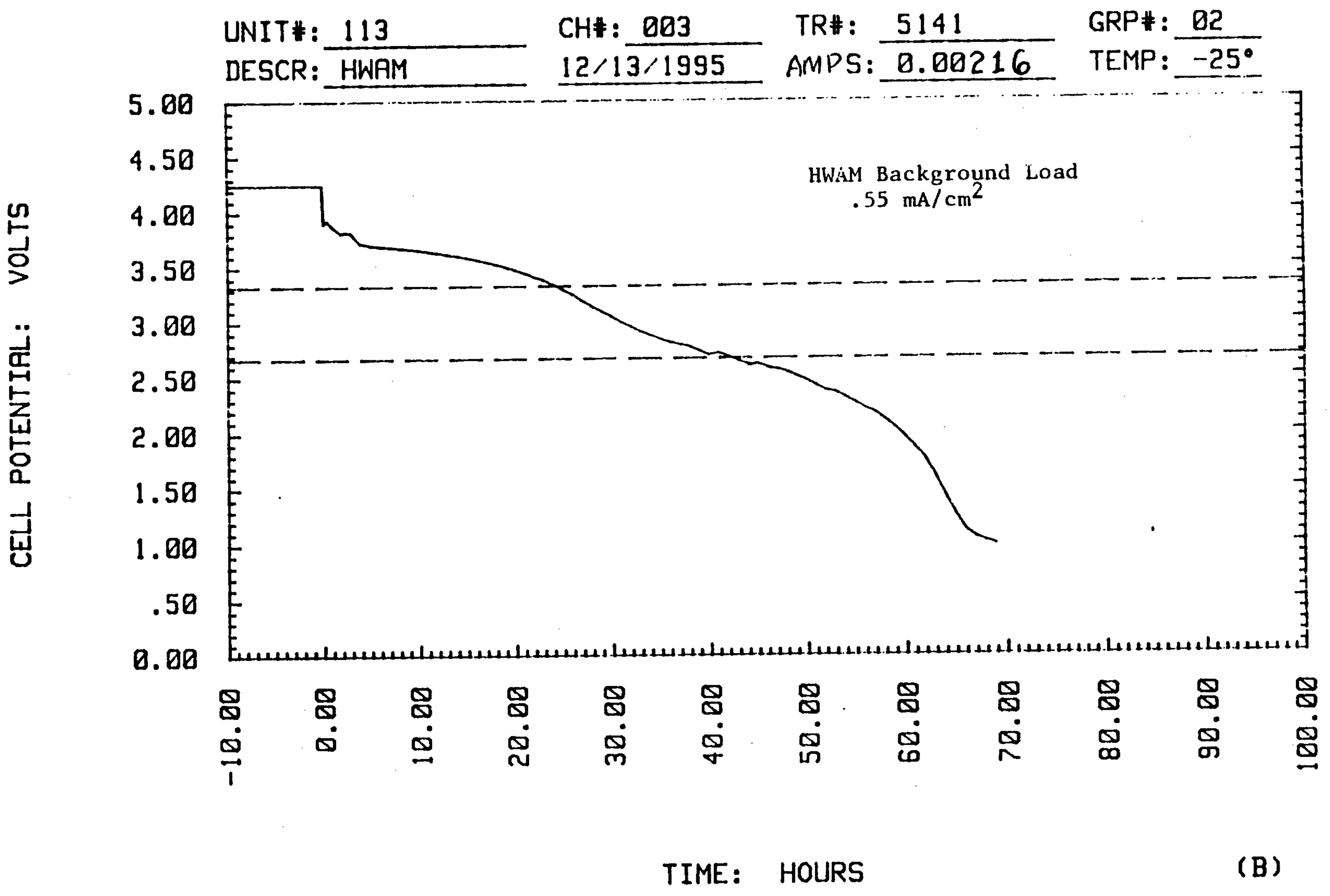


Figure 6-8. Modified Picatinny Cell 9275567, Li/Li$_x$CoO$_2$/DSMF, 1 Layer Veretek

Modified Picatinny Cell 9275567

Li_xCoO_2 Cathode
Veretek Separator
DSMF Electrolyte
Discharged @ .55 mA/cm^2 (equivalent to 400mA on HWAM cell)

Temperature Cutoff Voltage	-25°F	0°F	+28°F	+75°F
3.33 volts (10 volts)	27.8 11.1	48.2 19.3	60.1 24.0	68.6 27.4
3.0 volts (9 volts)	33.3 13.3	53.9 21.65	64.2 25.7	69.6 27.8
2.67 volts (8 volts)	42.3 16.9	61.2 24.5	67.3 26.9	70.4 28.2

Running Hours (Test Cell) Amp Hours (equivalent) for HWAM

Figure 6-9. Cell Capacity Versus Cutoff Voltage

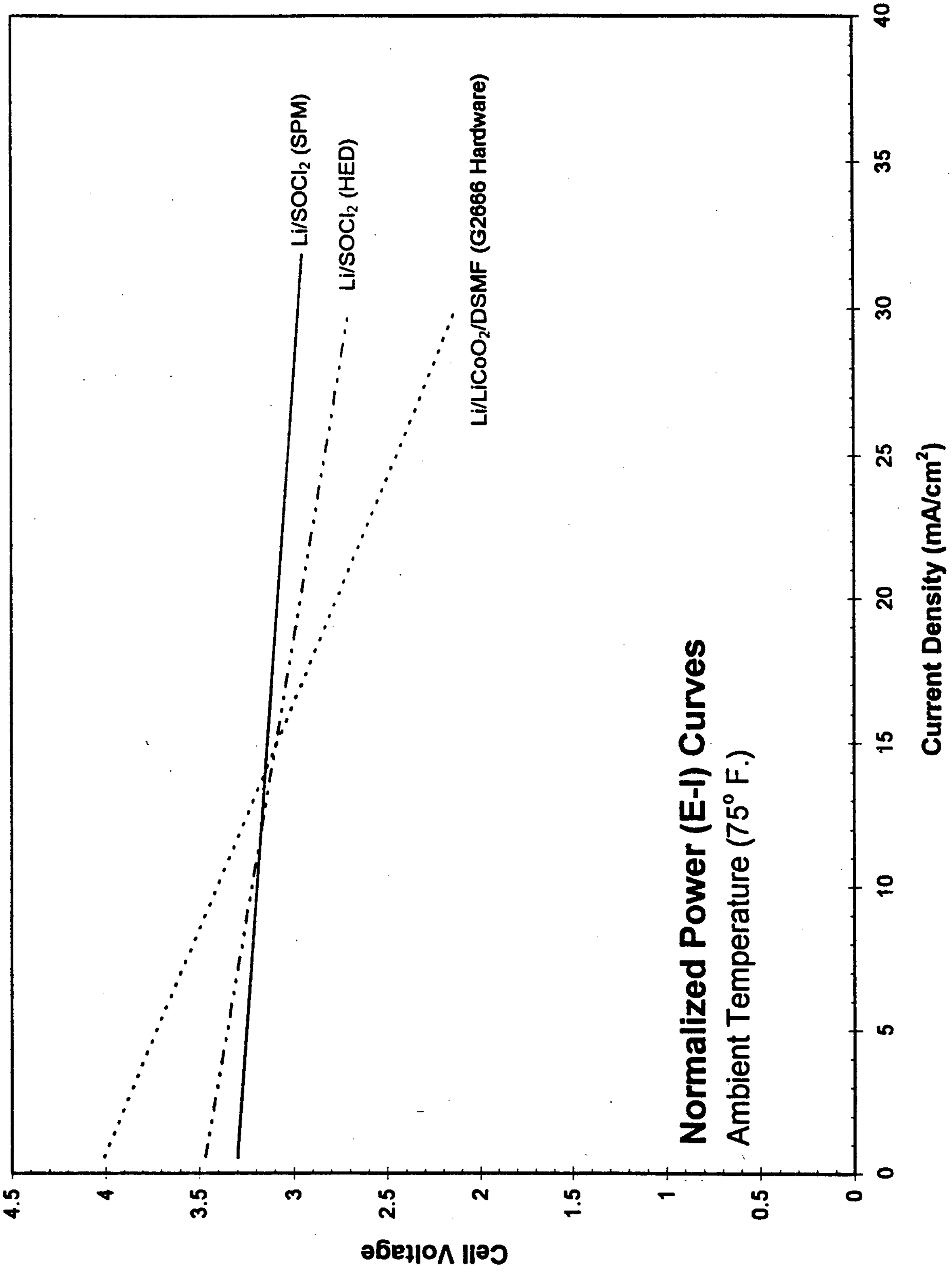


Figure 6-10. Normalized Power Curves for Li/Li$_{0.5}$CoO$_2$ and Li/SOCl$_2$

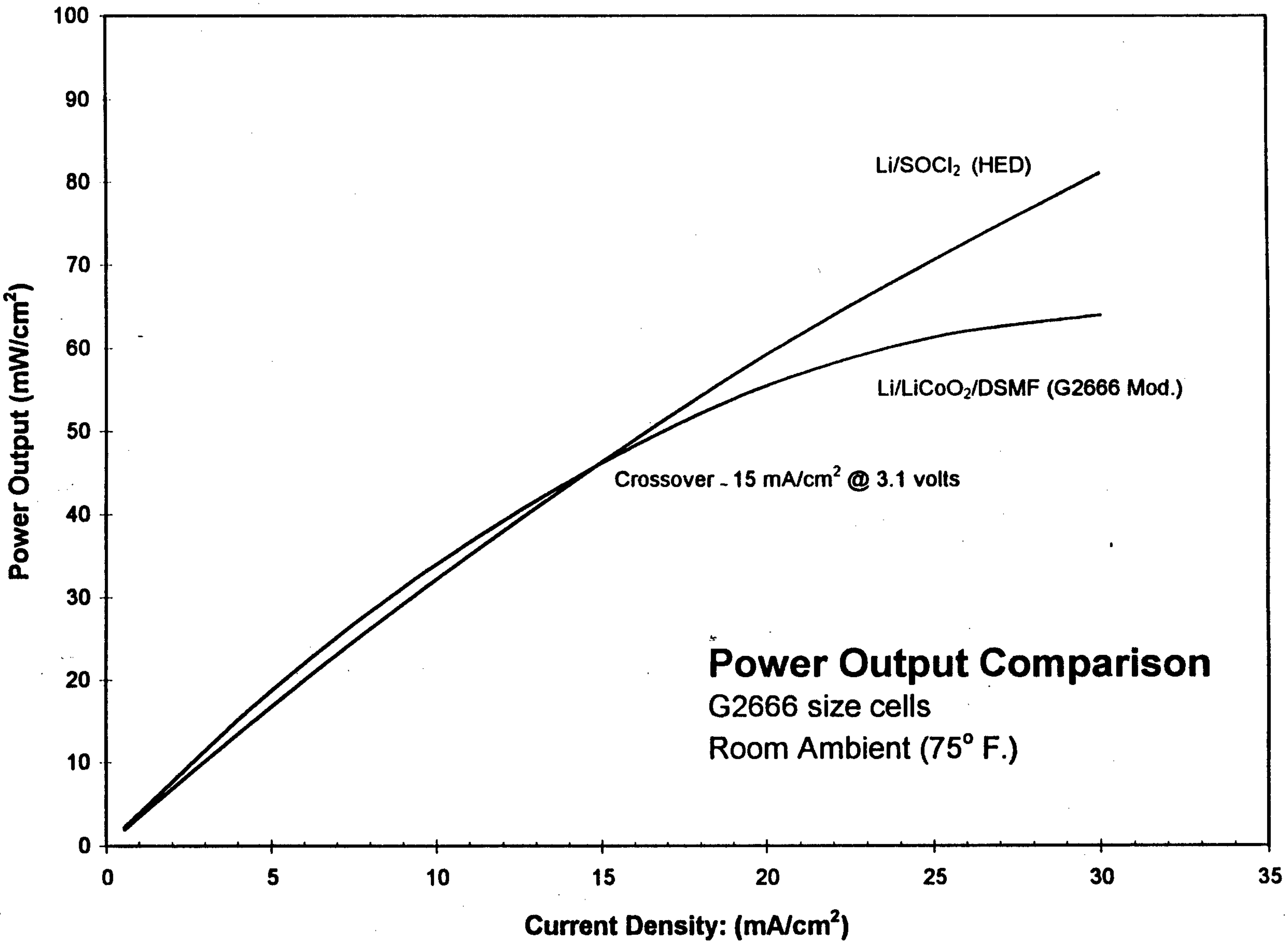


Figure 6-11. Power Output Comparison Between $Li/Li_{0.6}CoO_2$ and $Li/SOCl_2$

Table 6-2. Capacity Comparison Between Li/$Li_{0.5}CoO_2$ and Li/$SOC1_2$ in Same Size Hermetic Cells*

Energy Comparison

Modified Picatinny Cell
9275567 (Li_xCoO_2)
DSMF Electrolyte
1 Veretek Separator
Weight: 6.33 grams
Volume: 2.66 cc (.163 in^3)

HED ($SOC1_2$)
$SOC1_2$ Electrolyte
1 Glass Separator
Weight: 5.27 grams
Volume: 2.66 cc (.163 in^3)

Discharged at 2.16 mA
Milliamp hours to cut-off voltage

Temperature Cutoff Voltage	-25°F	0°F	+28°F	+75°F
3.33 volts	60.0 0.9	104.1 0.9	129.8 1.3	148.2 260.5
3.0 volts	71.9 77.3	116.4 158.5	138.7 205.2	150.3 284.3
2.67 volts	91.4 114.5	132.2 182.3	145.4 211.68	152.6 288.6

	Li_xCoO_2 , mAh
HED, mAh	

* Both cells have the same external dimensions and have similar construction features including the ampul reservoir.

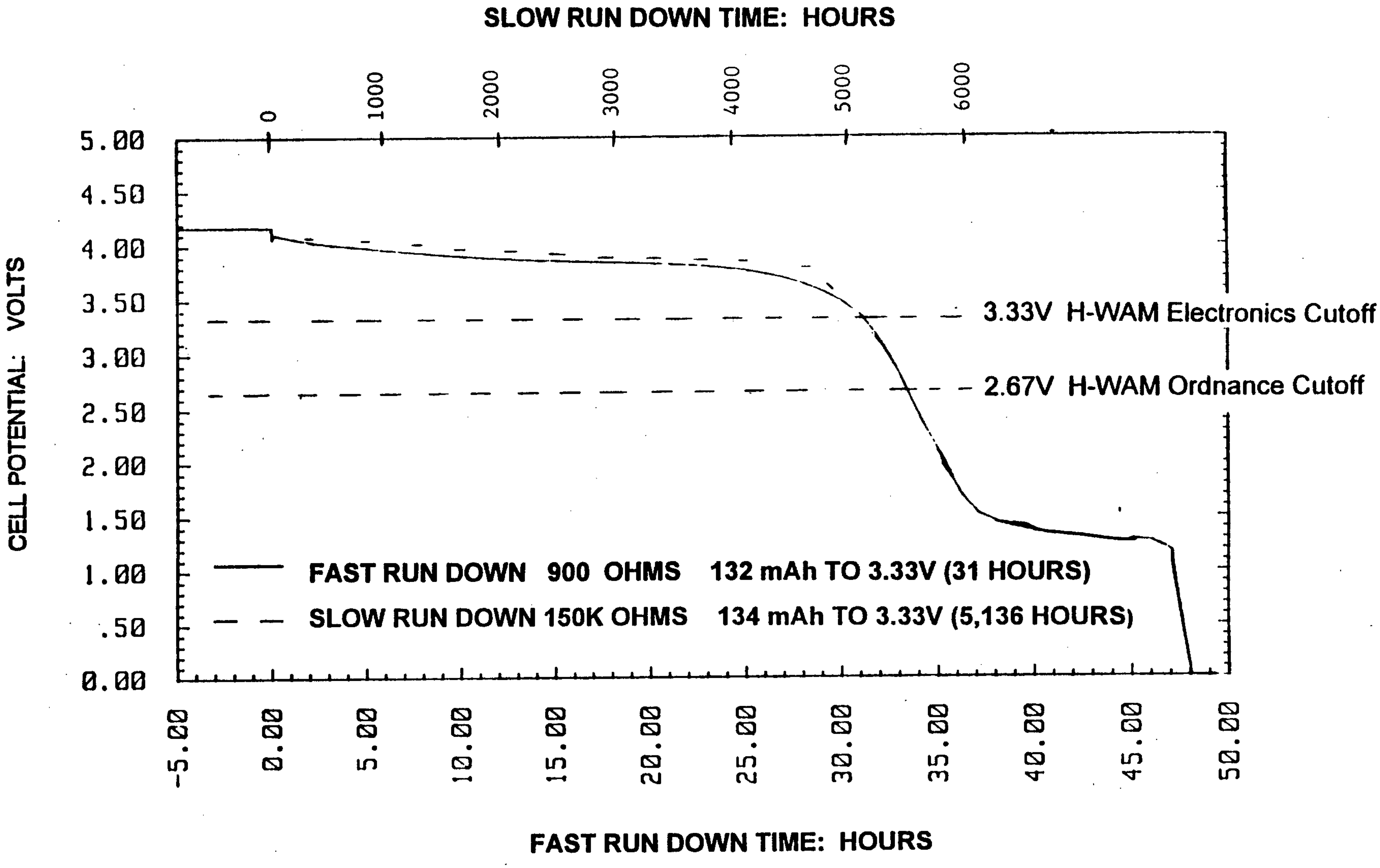


Figure 6-12. Fast Run Down Versus Slow Run Down of Picatinny Hermetic Cells, Picatinny #9275567 (Modified), Room Temperature

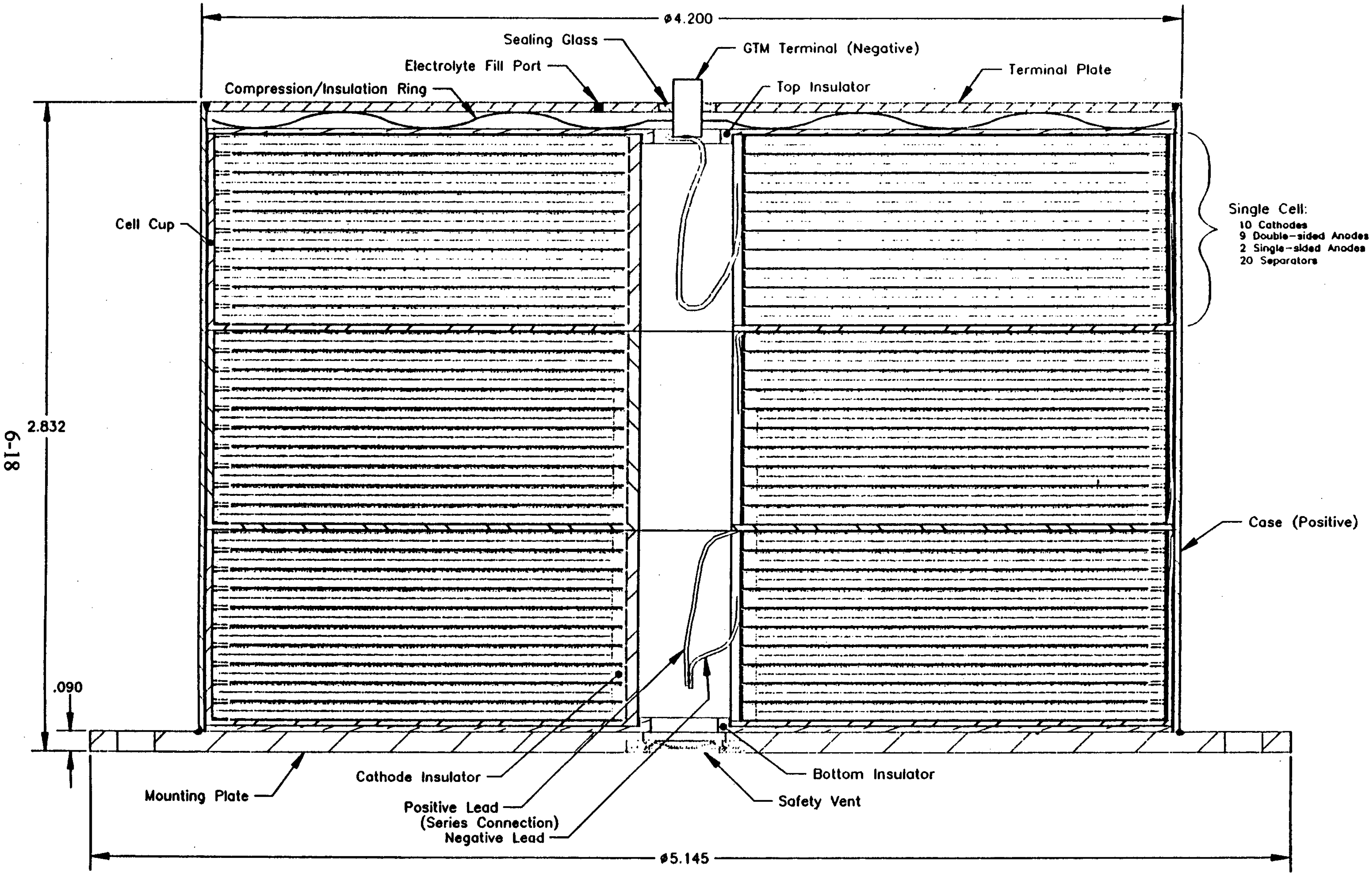


Figure 6-13. HWAM Active Battery Design

Table 6-3. HWAM Active Battery Electrode Design

Component	OD (in)	ID (in)	Thickness (in)	Surface Area (in^2)	Volume (in^3)	Volume (cm^3)	# /Cell	Vol /Cell (cm^3)	Total #
Cathode:	4.04	0.62	0.06	12.52	0.75	12.31	10	123.07	30
Anode:									
Single Sided	3.94	0.52	0.007	11.98	0.08	1.37	2	2.75	6
Double Sided	3.94	0.52	0.013	11.98	0.16	2.55	9	22.97	27
Separator:	4.08	0.50	0.005	12.88	0.06	1.06	20	21.10	60
Cathode Insulator:	0.62	0.50	0.06	0.11	0.01	0.10	10	1.04	30

Battery Capacity: **37.45 Ah**

Table 6-4. HWAM Active Battery Weight Summary

Component	Weight (g)	No./Battery	Weight/Battery (g)
Cell Cup	23.45	3	70.34
Anodes, Complete Assembly:			
Single Sided	1.26	6	7.55
Double Sided	1.82	27	49.06
Separators	0.43	60	25.64
Cathodes, Complete Assembly	36.92	30	1107.64
Electrolyte	280.22	1	280.22
Leads, Positive/Negative	3.28	6	19.66
Compression/Insulation Ring	16.22	1	16.22
Insulator, Top/Bottom	9.21	2	18.42
GTM Terminal	0.55	1	0.55
Insulator, Intra-Cell	1.76	2	3.52
Terminal Plate	70.67	1	70.67
Battery Case	117.87	1	117.87
Mounting Plate	241.42	1	241.42
Battery Vent	1.56	1	1.56
		Total:	2030.34 (g) 4.47 (lbs)
This active battery was designed to the same volume as the current reserve HWAM battery without regard to weight. If the battery is designed to conform to the weight restriction of 3 lbs. - 0.3 lbs., the capacity would be:			
	22.47 Ah		

$Li/Li_{0.5}CoO_2$ Capacity Not Lost To Depassivation Requirements

Since $Li/Li_{0.5}CoO_2$ cells do not passivate with storage, the need for depassivation pulses to clean-up electrode surfaces does not exist. Thionyl chloride systems do passivate and clean-up capacity contingency must be factored into battery design. For one of the study tasks, Alliant Techsystems was asked to calculate the capacity saved by not needing depassivation pulses in the $Li/Li_{0.5}CoO_2$ HWAM battery. Calculations, given below, show that a nominal 2 ampere-hours of additional capacity are needed to compensate for passivation clean-up.

Energy Removed - Depassivation Pulses
Estimated Battery Voltage - 3.2 vpc x 4 = 12.8 volts
Load Resistance (Fig. 3 spec 29224A) = 2.5 ohms
Pulse Duration* (Fig. 3 spec 29224A) = 0.5 sec.
Pulse Interval (Fig. 3 spec 29224A) = 1 every 2 hours
Days Under Load (Fig. 3 spec 29224A) = 180 days minimum

$$\text{Pulse Current} = \frac{12.8 \text{ volts}}{2.5 \text{ ohms}} = 5.12 \text{ amps}$$

$$\text{Amp Hours/Pulse} = 5.12 \text{ amps} \times .5 \text{ sec} \times \frac{1 \text{ hour}}{3600 \text{ seconds}} = .000711 \text{ amp hours}$$

Number of Pulses:

$$\frac{1 \text{ pulse}}{2 \text{ hrs.}} \times \frac{24 \text{ hours}}{\text{day}} \times 180 \text{ days minimum} = 2160 \text{ minimum}$$

Capacity Removed At Any Assumed Low-Rate Efficiency:

2160 pulses minimum x .000711 amp hours/pulse = 1.53 amp hours minimum

<u>However</u>: As the rate of discharge is increased, the system deliverable capacity is lowered as a result of increasing losses due to irreversible processes occurring within the cell. The capacity reduction due to the high current (5 amp) pulses would be considerably greater than the same capacity removed at the nominal .625 milliamp standby current. Based on published data,[4] (5 amp) capacity would be 25-35% less than at the low standby nominal rate. Therefore, using a capacity 30% less, the resultant effect on capacity (compared with a steady low rate discharge without the depassivation pulses) would be:

$$1.53 \text{ amp hrs. minimum} \times \frac{100\%}{(100\% - 30\%)} = 2.19 \text{ amp hours}$$

---

[*] An unofficial change proposal from the HWAM device manufacturer dated 4/18/95 indicates a doubling of the depassivation pulse duration from 0.5 sec. to 1 sec. with no change in frequency or load. Under this regime the capacity removed would also double to 3.0 amp hours (180 days minimum) and the expected reduction would be on the order of 4 - 4 1/2 amp hours.

Unit Price Cost Estimate For HWAM Reserve Battery

The estimate was based on ground rules and assumptions which are highlighted below:

- Bidding rates are Alliant Techsystems' Fiscal Year 1997.
- The HWAM Battery Design has considered ease of manufacturability. As of this writing, it has not been optimized or tooled.
- Based on input at the Milestone Meeting 2/22/96, the need for "smart control" electronics for the HWAM battery is not a priority at this time and therefore is not included in the design or costed.
- Material costs were based on actual purchase orders placed in 1995 and have not been upgraded to present day.
- Labor estimates use an 85% learning curve for projected builds prior to reaching the lowest estimated UPC. The start of the learning curve assumes having completed at least 200 pre-production units.
- Non-recurring tooling is separately funded and not included in the UPC.
- The battery lot builds are consecutive and are scheduled closely, such that workstations and tool setups dedicated to HWAM battery production do not need to be torn down. The build of 5,000 batteries follows the 3,000 battery build which follows the 1,000 HWAM Reserve Battery build.

  The Unit Price Cost goals are shown below for the quantities listed:

first 1,000 units	$3,000 each
following 3,000 units	$2,000 each
following 5,000 units	$1,500 each

Design changes necessary to accomplish the UPC goals are:

- A common Tefzel$^{\text{TM}}$ molded reservoir of the type shown in Figure 6-14 but not limited to the oversized reservoir shown.
- A revised activation system of the type shown in Figure 6-14 but not limited to that configuration.
- Work with vendors to improve parts designs for producibility, which may require some vendor non-recurring cost to reduce part unit costs.
- A cathode fabrication method that is more cost effective than pressed cathodes.

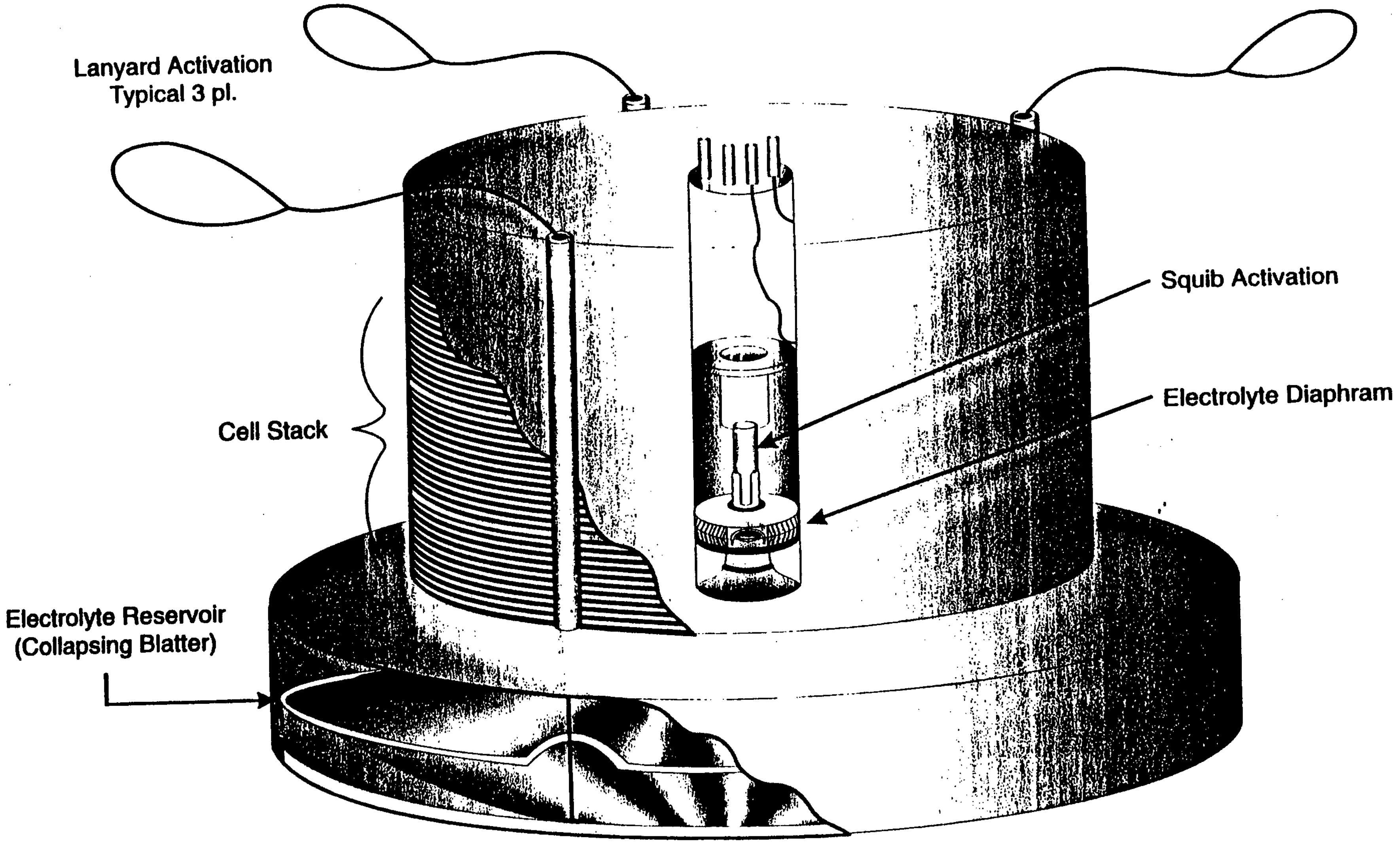


Figure 6-14. HWAM Reserve Battery, 30 Ampere-Hour Capacity

REFERENCES

1. Lin, H. P. W.; Kelly, C. J.; Chua, D. L.; Smith, P. H.; James, S. D.; and Fleischmann, C. W., "Development of a 30-Ampere-Hour Lithium/Lithium Cobalt Oxide Rechargeable Battery," **NAVSWC TR 91-184,** 30 Sept 1994.

2. Lin, H. P. W.; Kelly, C. J.; Chua, D. L.; Smith, P. H.; James, S. D.; Murphy, T. C.; Fleischmann, C. W.; and Zoski, G. D., "Rechargeable Lithium Cells with High Energy Density Transition Metal Compound Cathodes – Characterization in AA-Size Cells," **CARDIVNSWC-TR-95/034,** Apr 1996.

3. Lin H.P. W. and Burgess, K., "Synthesis of Charged Li_xCoO_2 $(0 < x < 1)$ for Primary and Secondary Batteries," U. S. Patent No. 5,667,660, Sept 16, 1997.

4. Linden, D., Chapter 14, "Lithium Cells," in **Handbook of Batteries,** Second Edition, Linden, D., Ed., McGraw-Hill, New York, 1995, p. 14-1, especially Figure 14.27, pp. 14.36, 14.37.

5. **Designer's Casebook**, Honeywell Power Sources Center, 1985.

Appendix A

HWAM Drawing Package

LITHIUM

H-WAM Battery
Device No. G3169A1
Drawing Package

22 February 1996

[E60222-2.ppt]*paw

ALLIANT TECHSYSTEMS

H-WAM DRAWING LIST

Drawing Package Requirements:

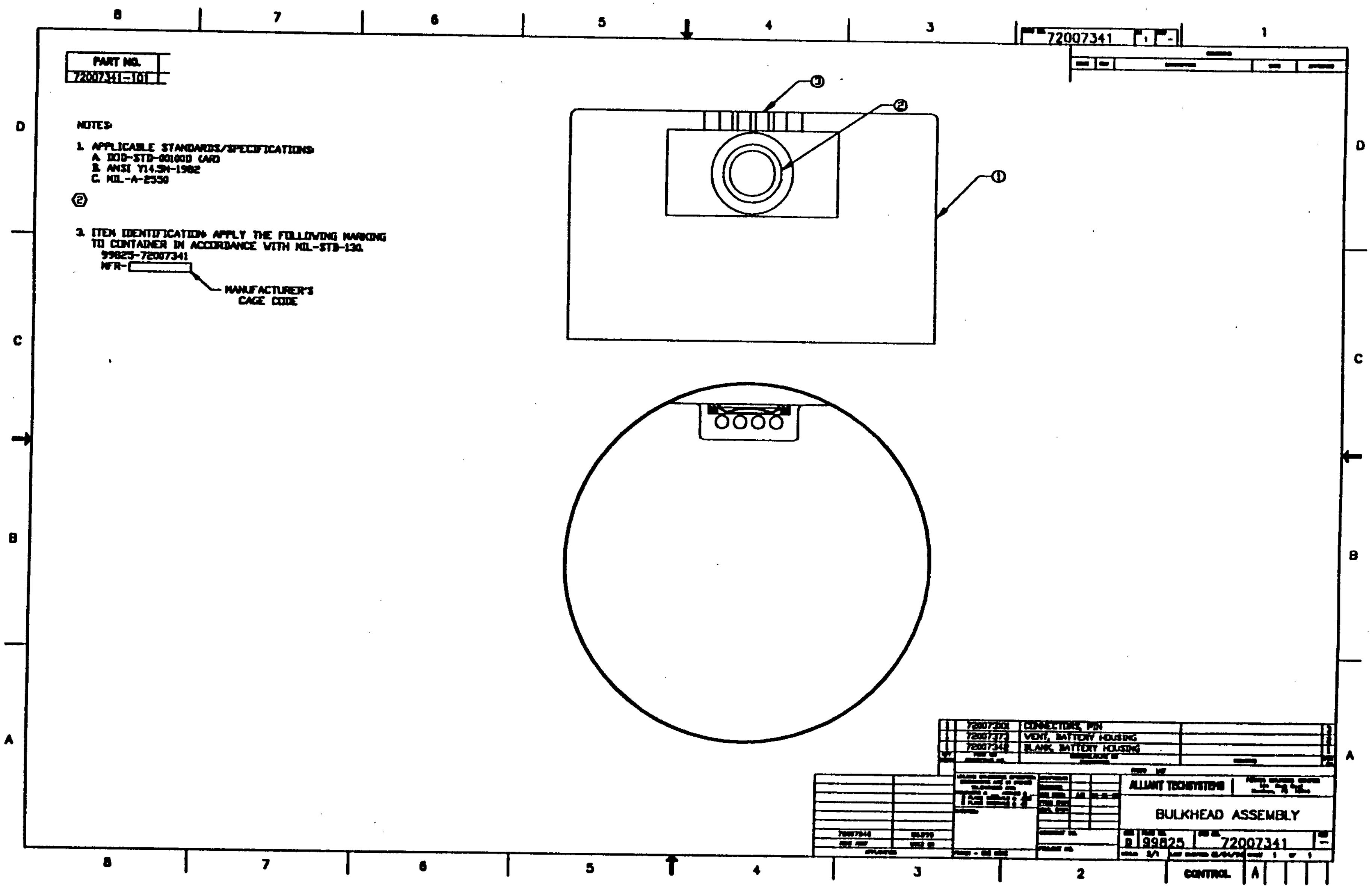
Drawing	Drawing Number	Used On/Next Assy
Battery Assembly	72007340	-
Battery Housing Assembly	72007341	72007340
Battery Housing Blank	72007342	72007341
Pressurizer	72007346	72007340
Bulkhead Assembly	72007347	72007340
Reservoir Housing	72007348	72007347
Insulator, Intra-Cell	72007349	72007340
Cell Case Assembly	72007350	72007340
Cell Case/Headers Assembly	72007351	72007350
Cell Case	72007352	72007351
Cell Case Cover	72007353	72007350
Cathode Separator Assembly	72007354	72007350
Anode Separator Assembly, Single-Sided	72007355	72007350
Anode Separator Assembly, Double-Sided	72007356	72007350
Anode Assembly, Single-Sided	72007357	72007355
Anode Assembly, Double-Sided	72007358	72007356
Cathode Assembly	72007359	72007354
Anode, Lithium Foil	72007360	72007357,58
Cathode Current Collector	72007361	72007359
Anode Current Collector	72007362	72007357,58
Header Assembly, Positive	72007363	72007351
Header, Positive	72007364	72007363
Tube, Fill	72007365	72007363
Eyelet, GTM	72007366	72007375
Spring, Compression	72007367	72007340
Header Assembly, Negative	72007368	72007351
Header, Negative	72007369	72007368
Electrolyte Diaphragm, Inlet	72007370	72007347
Electrolyte Diaphragm, Outlet	72007371	72007347
Vent, Cell Case	72007372	72007375
Battery Housing Vent	72007373	72007341
Tubing, Activation	72007374	72007340
Cell Case Vent/GTM Eyelet Assembly	72007375	72007363,68
Bulkhead	72007376	72007347
Cathode Lead Assembly	72007378	7200xxxx
Anode Lead Assembly	72007379	7200xxxx
Ball	72007975	72007347
Lead Routing Assembly	720073xx	7200xxxx
Pin Connectors (Outside Housing)	720073xx	72007341

Spec Control Drawings:

Drawing	Drawing Number	Used On/Next Assy
Separator Material	72007377	72007354,55,56
Glass, Sealing	7200xxxx	7200xxxx
Electrolyte - 2M LiAsF6/MA	7200xxxx	7200xxxx
Flame Arrestor Material	7200xxxx	7200xxxx
Cathode Process Spec.	7200xxxx	7200xxxx
Tefzel (ETFE)	7200xxxx	72007351

HWDWGLST

2/15/96



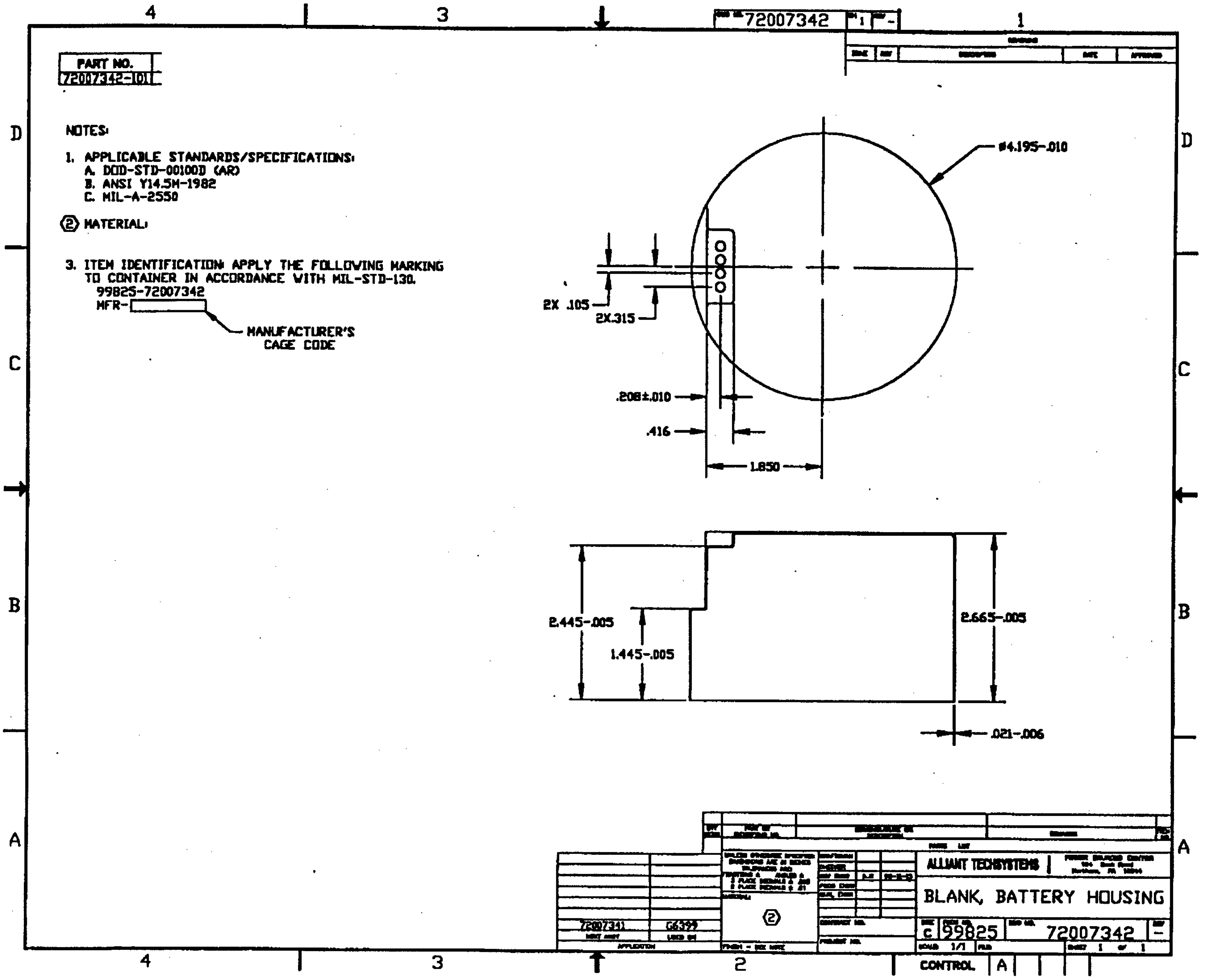
PART NO.
72007341-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

②

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007341
   MFR-☐ MANUFACTURER'S CAGE CODE



NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL:

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007342
   MFR-☐ — MANUFACTURER'S CAGE CODE

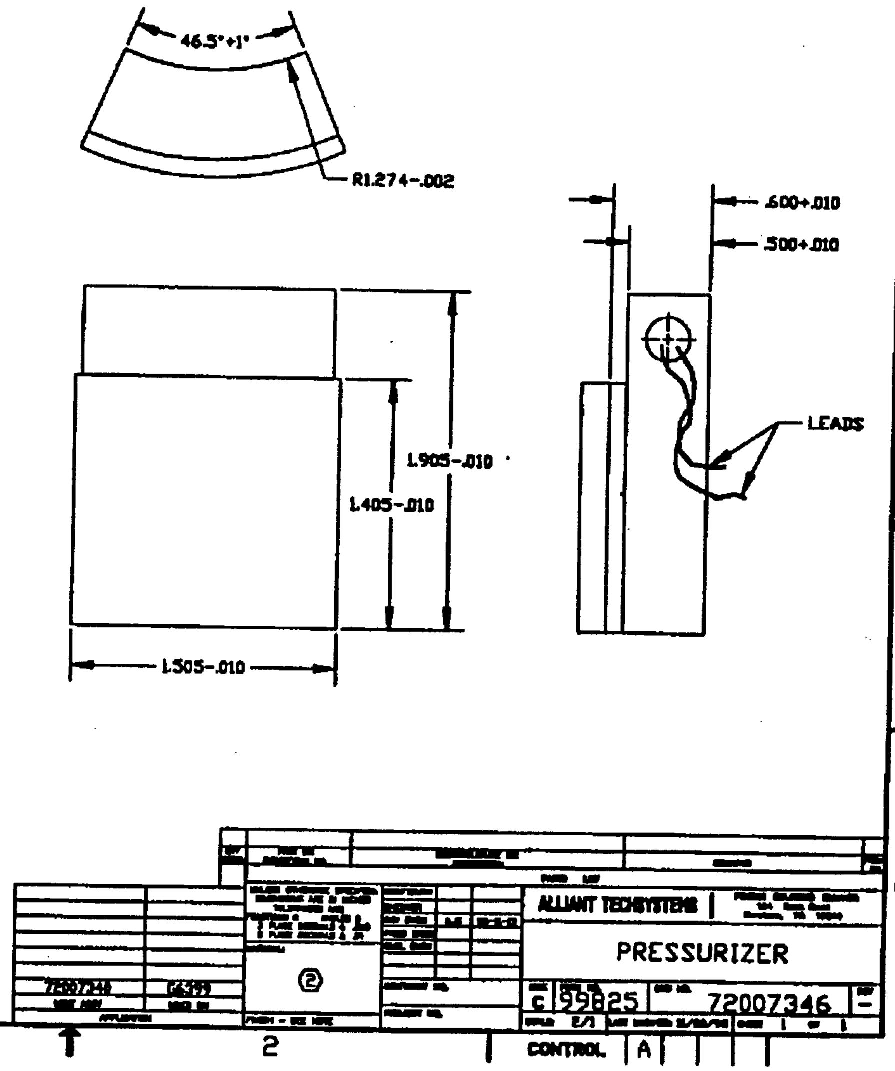
PART NO.
72007346-101

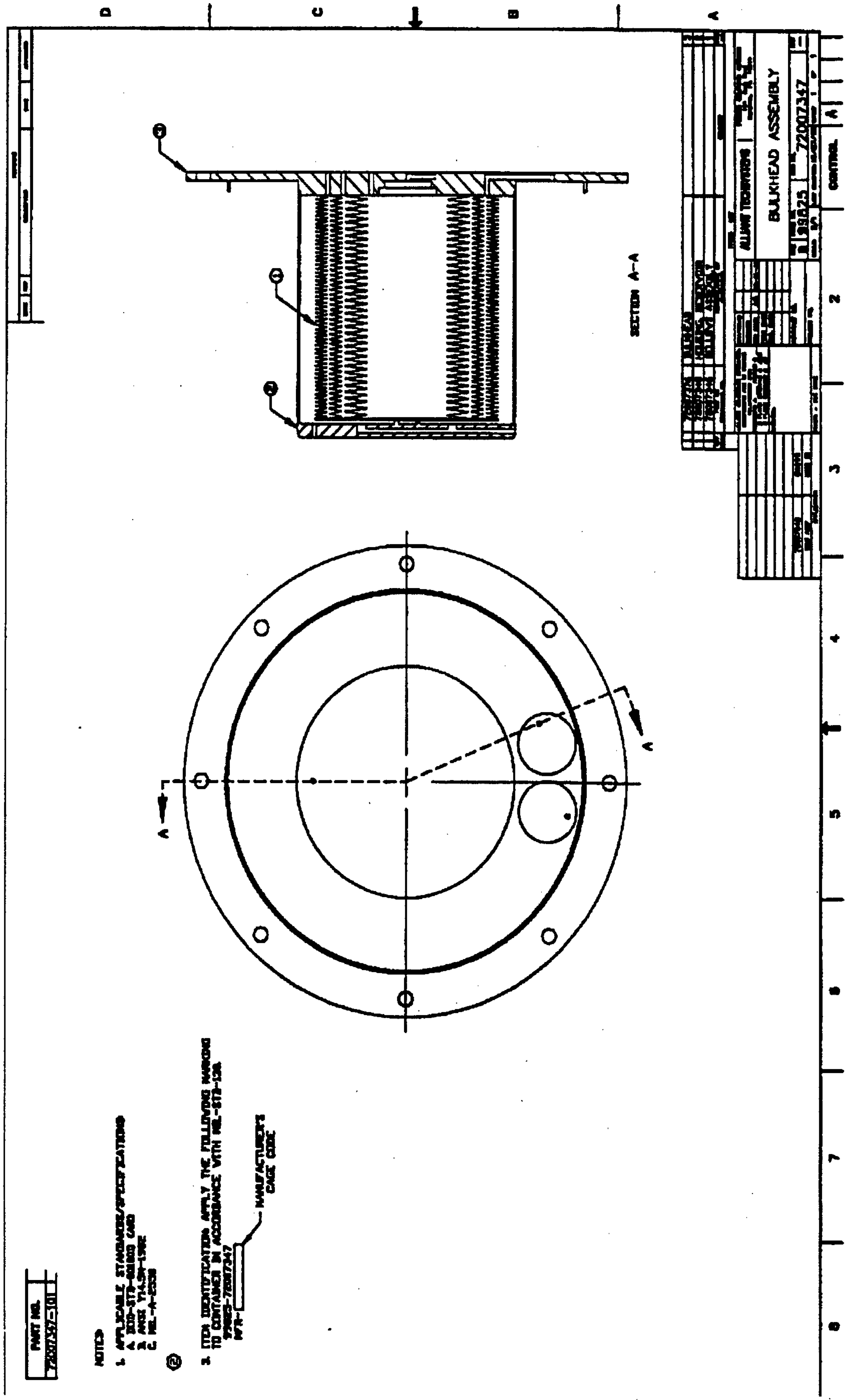
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

②

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007346
   MFR-☐ MANUFACTURER'S CAGE CODE

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A
BULKHEAD ASSEMBLY
ALLIANT TECHSYSTEMS
99625
72007347
A
CONTROL
PART NO.
72007347-01
NOTES
1. APPLICABLE STANDARDS/SPECIFICATIONS
3. ITEM IDENTIFICATION APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130
MANUFACTURER'S CAGE CODE
D
C
B
A
1
2
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4
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7
8

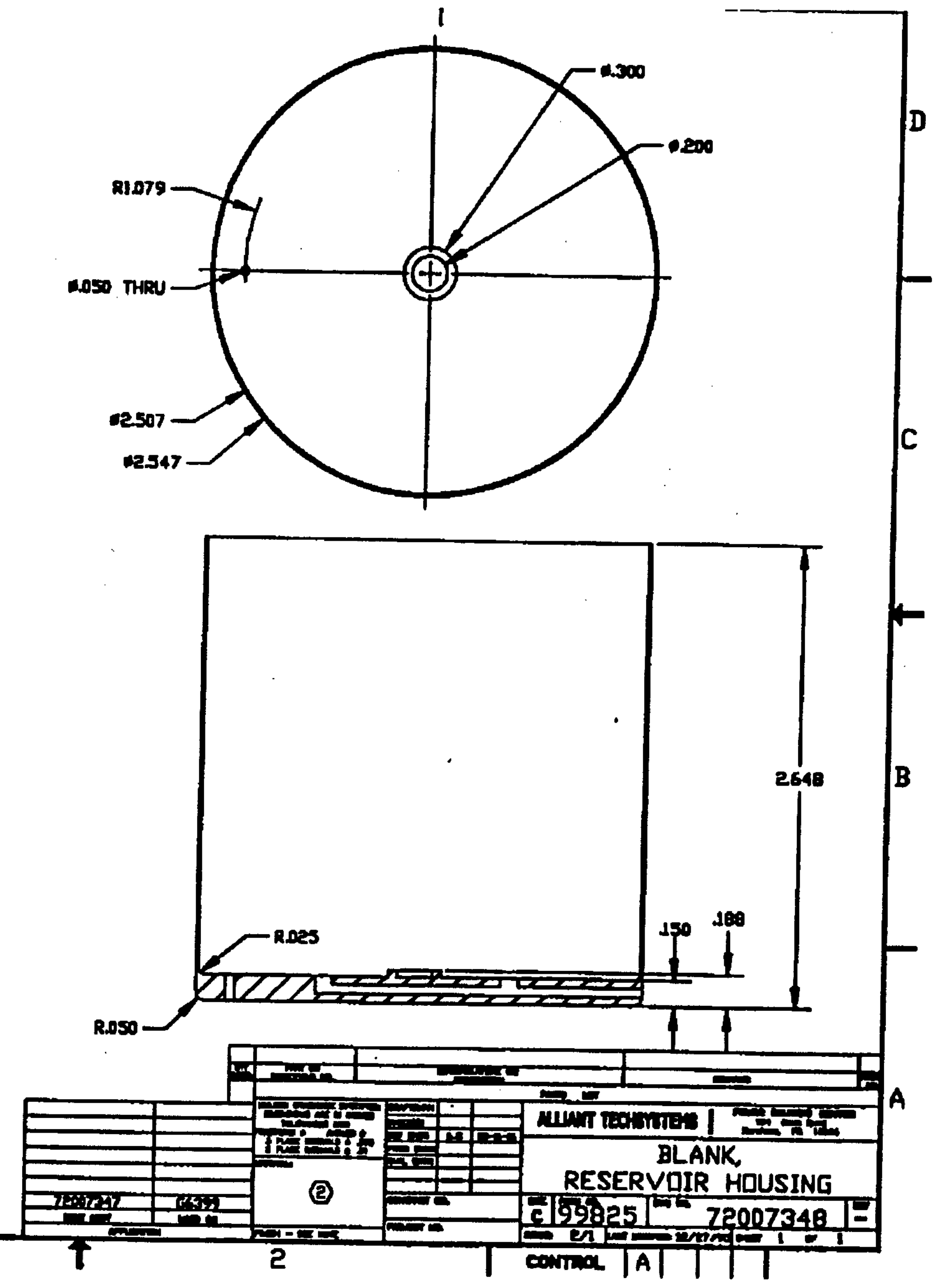
72007348-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: SHEET, PLATE AND STRIP, TYPE 316L, ANNEALED.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007348
   MFR-☐ — MANUFACTURER'S CAGE CODE



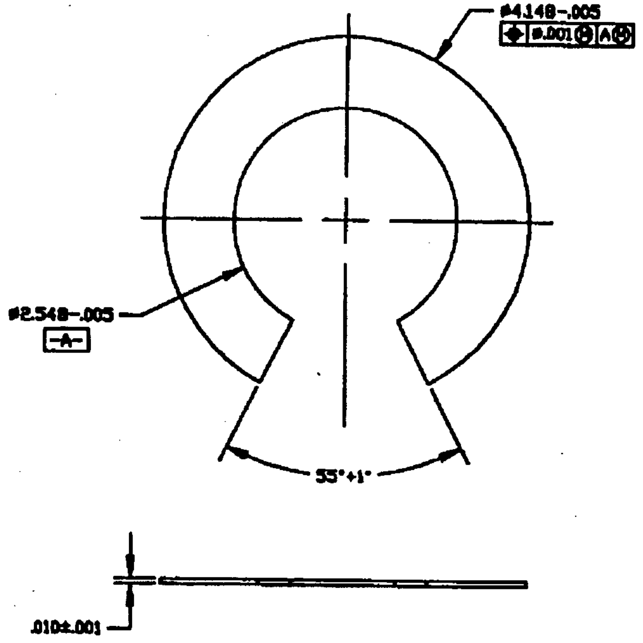
PART NO.
72007349-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: ETHYLENE TETRAFLUOROETHYLENE, ASTM D3159, TYPE II, SHEET MOLDED, STRESS RELIEVED.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007349
   MFR-☐ — MANUFACTURER'S CAGE CODE



ALLIANT TECHSYSTEMS

INSULATOR, INTRA-CELL

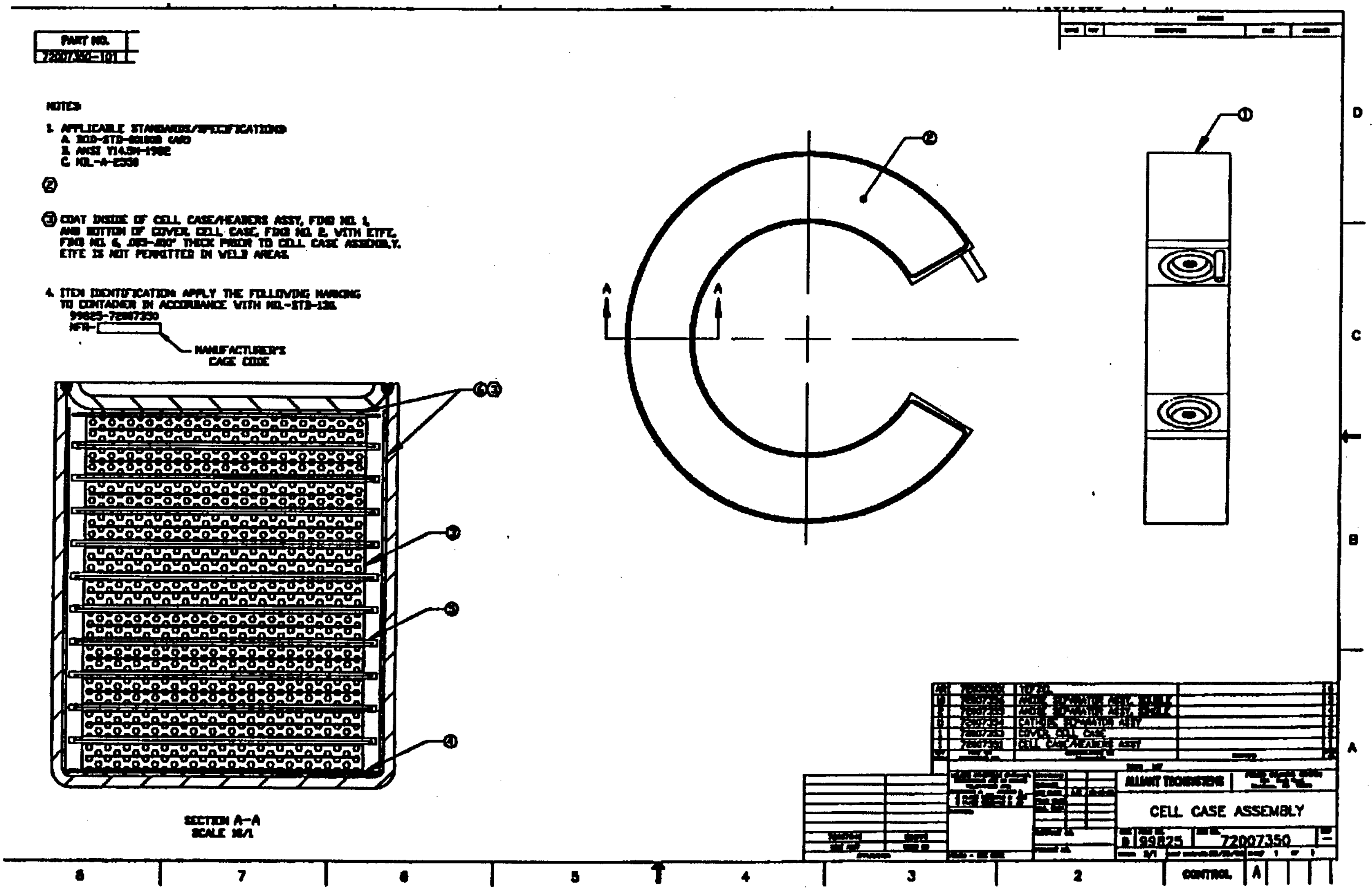
C 99825 72007349 —

SCALE 1/1 SHEET 1 OF 1

7200734[illegible] G6399

②

CONTROL A



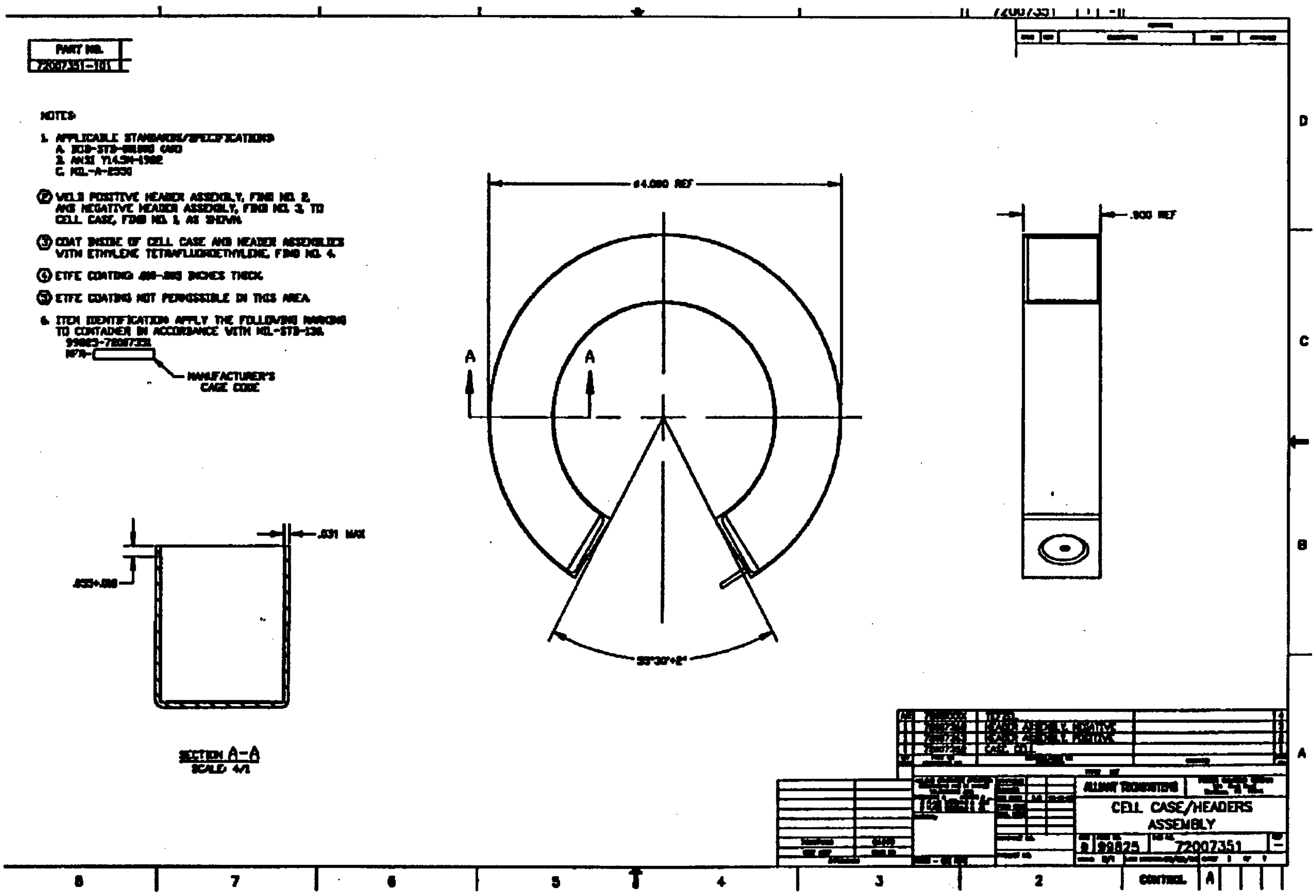
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100B (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

②

③ COAT INSIDE OF CELL CASE/HEADERS ASSY, FIND NO. 1, AND BOTTOM OF COVER, CELL CASE, FIND NO. 2, WITH ETFE, FIND NO. 6, .005-.010" THICK PRIOR TO CELL CASE ASSEMBLY. ETFE IS NOT PERMITTED IN WELD AREAS.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130
   99825-72007350
   MFR-
   MANUFACTURER'S CAGE CODE



NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-[illegible] CARD
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

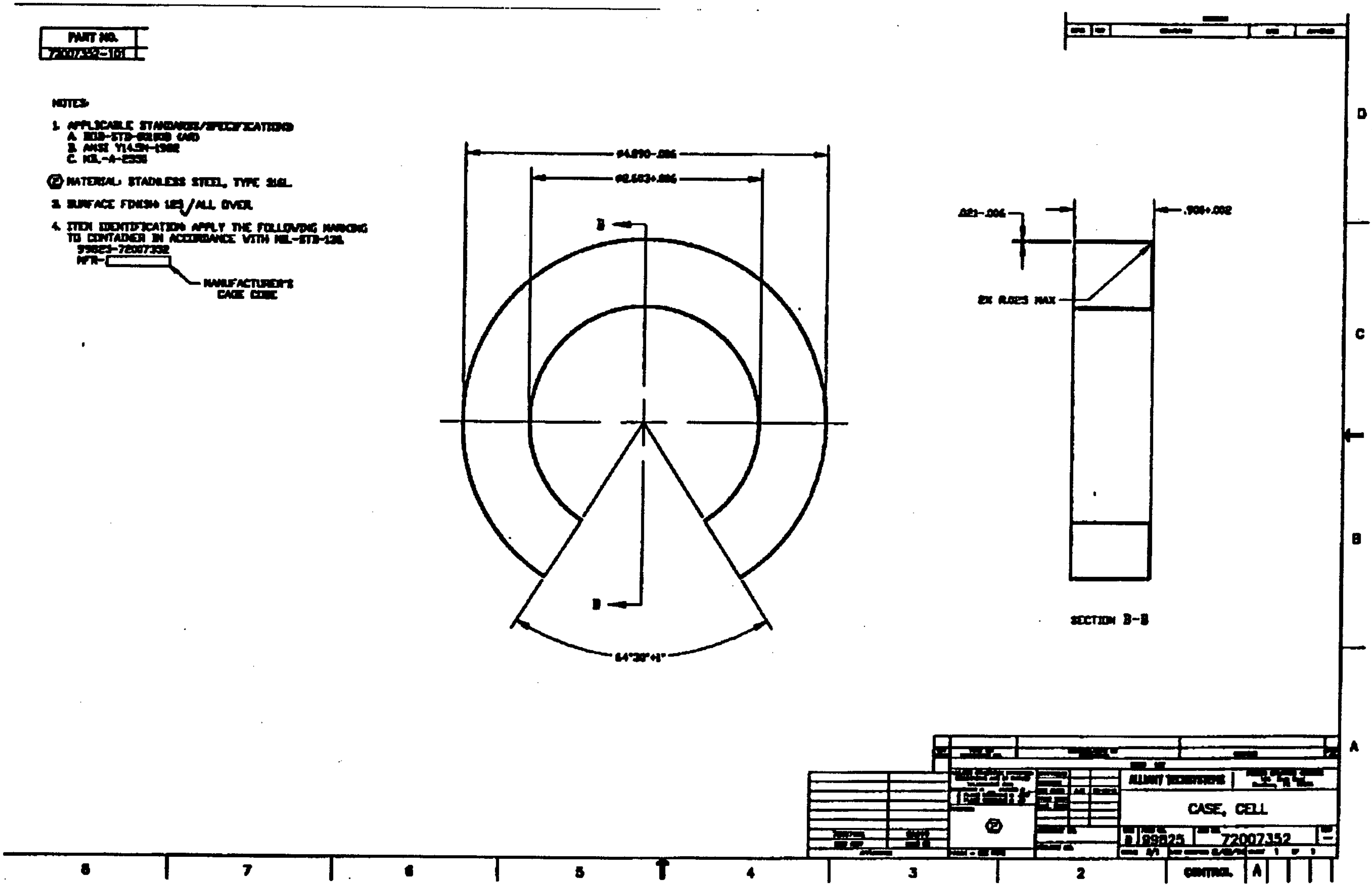
② WELD POSITIVE HEADER ASSEMBLY, FIND NO. 2, AND NEGATIVE HEADER ASSEMBLY, FIND NO. 3, TO CELL CASE, FIND NO. 1, AS SHOWN.

③ COAT INSIDE OF CELL CASE AND HEADER ASSEMBLIES WITH ETHYLENE TETRAFLUOROETHYLENE, FIND NO. 4.

④ ETFE COATING [illegible] INCHES THICK.

⑤ ETFE COATING NOT PERMISSIBLE IN THIS AREA.

6. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007351
   MFR- ☐ MANUFACTURER'S CAGE CODE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B. ANSI Y14.5M-1982
C. MIL-A-2550
② MATERIAL: STAINLESS STEEL, TYPE 316L
3. SURFACE FINISH 125/ALL OVER
4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130
99825-72007352
MFR-
MANUFACTURER'S CAGE CODE
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⌀2.683+.006
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.021-.006
.908+.002
2X R.025 MAX
SECTION B-B
D
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ALLIANT TECHSYSTEMS
CASE, CELL
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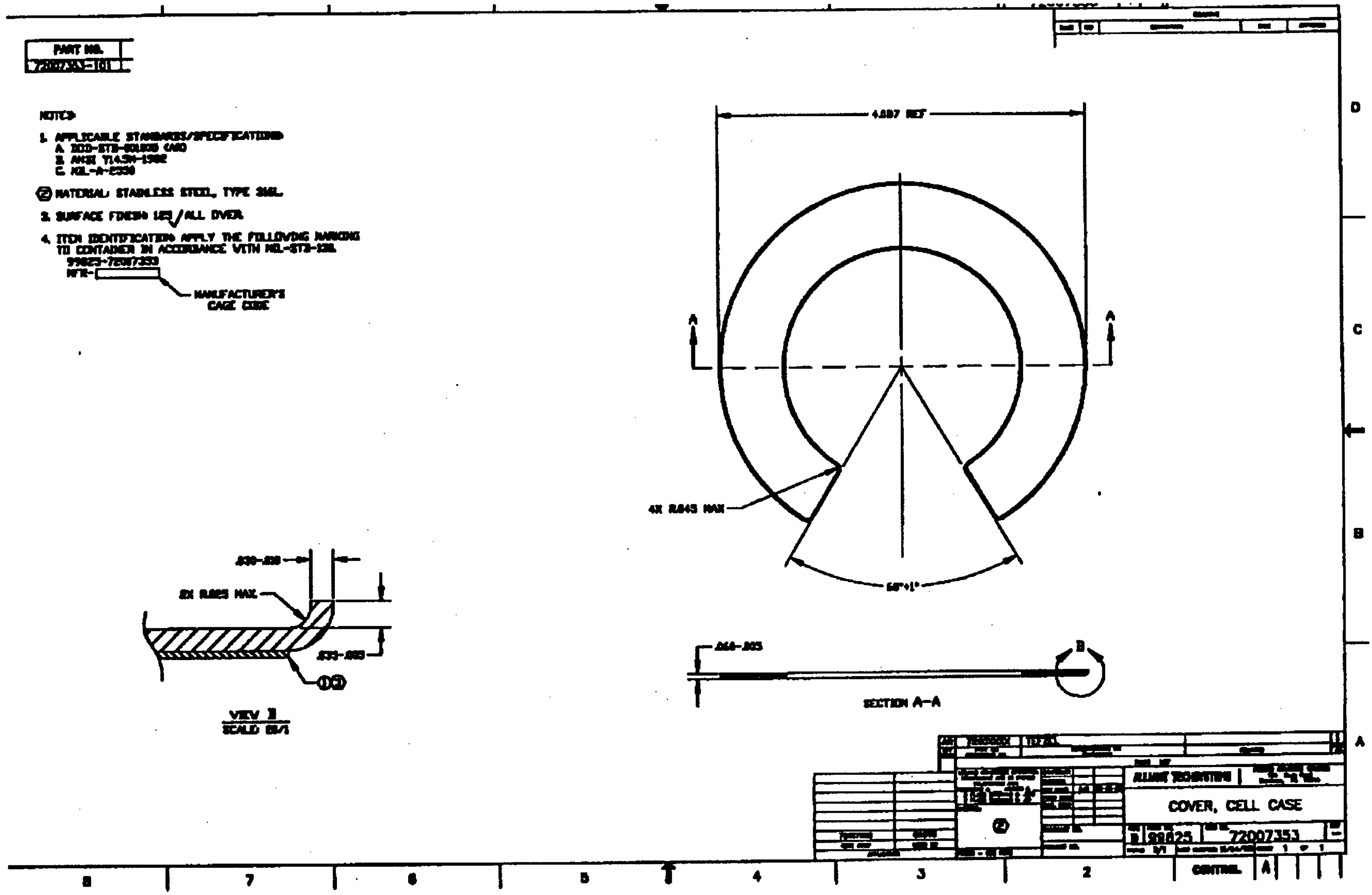
99825
72007352
CONTROL
A



NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS
   A. DOD-STD-[illegible] (AO)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL, TYPE 316L.

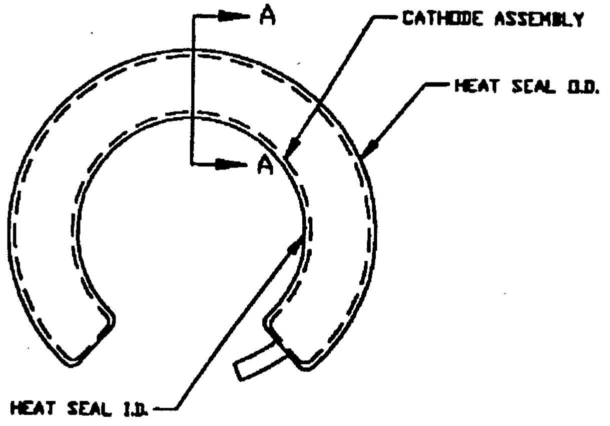
3. SURFACE FINISH: 125/ALL OVER

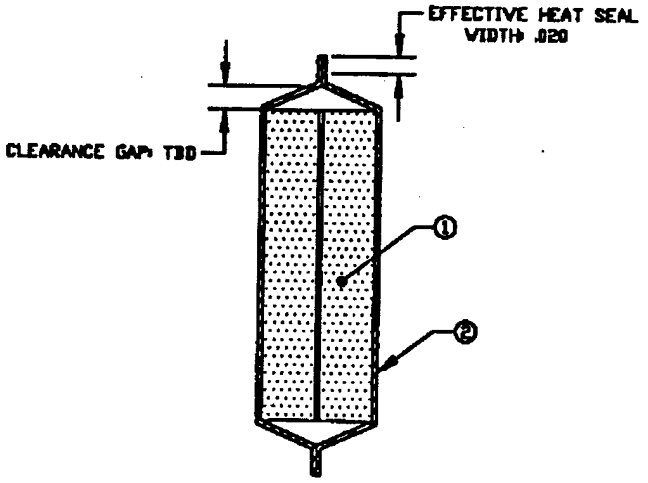
4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007353
   MFR-☐ MANUFACTURER'S CAGE CODE

PART NO.
72007354-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550
2. ASSEMBLY OPERATIONS AND STORAGE OF FINISHED ASSEMBLIES SHALL BE CONDUCTED IN A DRY ENVIRONMENT WITH LESS THAN 5 PERCENT RELATIVE HUMIDITY.
3. DO NOT STORE FINISHED ANODE SEPARATOR ASSEMBLY ABOVE ROOM TEMPERATURE.
4. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.
5. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007354
   MFR-☐ — MANUFACTURER'S CAGE CODE





SECTION A-A
SCALE: 5/1

AR	72007377	SEPARATOR MATERIAL		2
1	72007359	CATHODE ASSEMBLY		1

72007354	G4299

ALLIANT TECHSYSTEMS

CATHODE SEPARATOR ASSEMBLY

C 99825 72007354 —

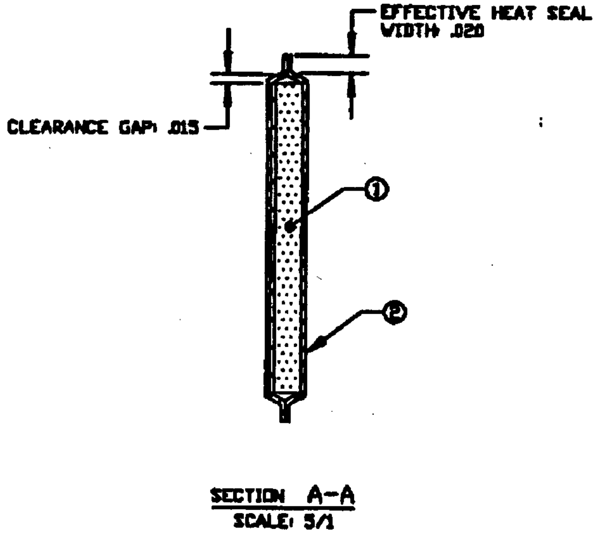
SCALE 1/1 SHEET 1 OF 1

CONTROL A

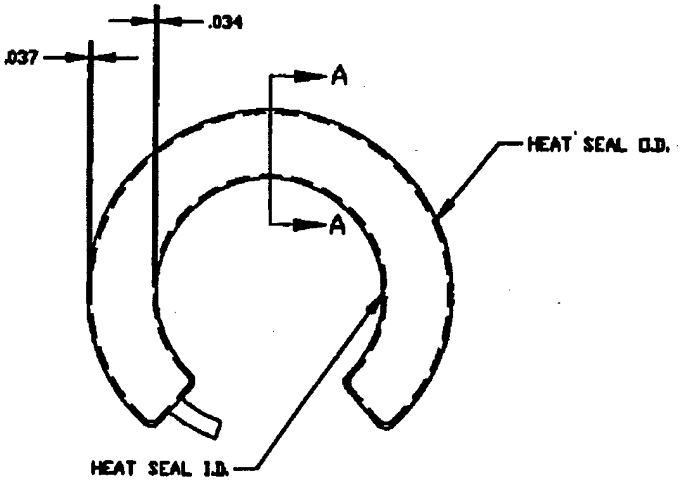
PART NO.
72007355-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550
2. ASSEMBLY OPERATIONS AND STORAGE OF FINISHED ASSEMBLIES SHALL BE CONDUCTED IN A DRY ENVIRONMENT WITH LESS THAN 5 PERCENT RELATIVE HUMIDITY.
3. DO NOT STORE FINISHED ANODE SEPARATOR ASSEMBLY ABOVE ROOM TEMPERATURE.
4. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.
5. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007355
   MFR-☐ — MANUFACTURER'S CAGE CODE



SECTION A-A
SCALE: 5/1



AR	72007377	SEPARATOR MATERIAL	2
1	72007357	ANODE ASSEMBLY, SINGLE-SIDED	1

72007350	G6399

ALLIANT TECHSYSTEMS

ANODE SEPARATOR
ASSEMBLY, SINGLE-SIDED

C 99825 72007355 —

1/1 SHEET 1 OF 1

CONTROL A

PART NO.
72007356-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550
2. ASSEMBLY OPERATIONS AND STORAGE OF FINISHED ASSEMBLIES SHALL BE CONDUCTED IN A DRY ENVIRONMENT WITH LESS THAN 5 PERCENT RELATIVE HUMIDITY.
3. DO NOT STORE FINISHED ANODE SEPARATOR ASSEMBLY ABOVE ROOM TEMPERATURE.
4. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.
5. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
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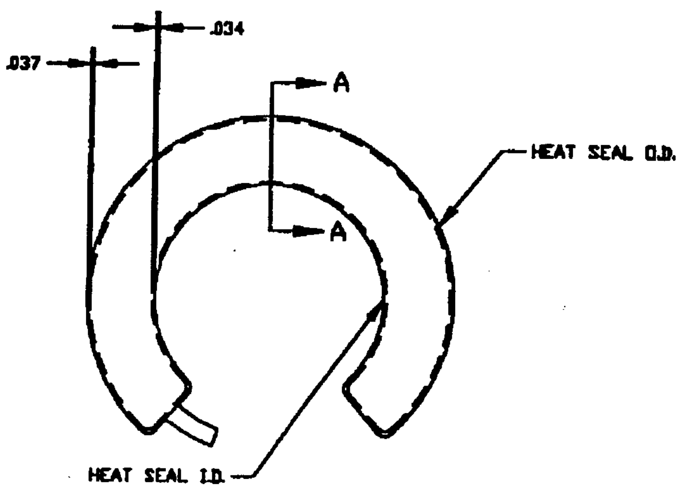
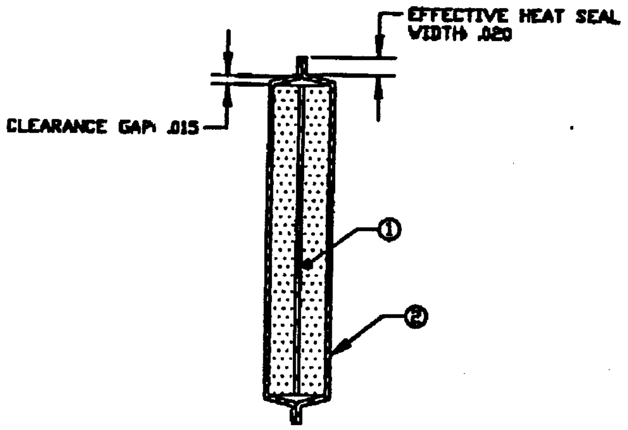
   MFR-☐ — MANUFACTURER'S CAGE CODE





SECTION A-A
SCALE: 5/1

AR	72007377	SEPARATOR MATERIAL		2
1	72007358	ANODE ASSEMBLY, DOUBLE-SIDED		1

ALLIANT TECHSYSTEMS

ANODE SEPARATOR
ASSEMBLY, DOUBLE-SIDED

C 99825 72007356

1/1 SHEET 1 OF 1

72007350

CONTROL A

PART NO.
72007357-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   - A. DOD-STD-00100D (AR)
   - B. ANSI Y14.5M-1982
   - C. MIL-A-2550

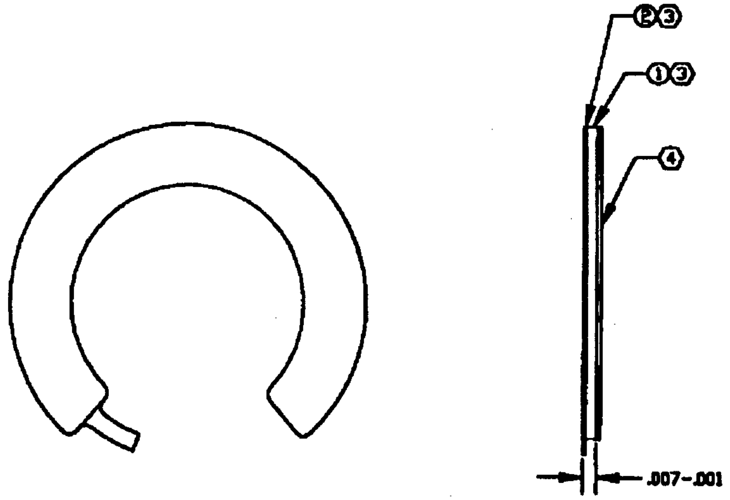
2. ASSEMBLY OPERATIONS AND STORAGE OF FINISHED ASSEMBLIES SHALL BE CONDUCTED IN A DRY ENVIRONMENT WITH LESS THAN 5 PERCENT RELATIVE HUMIDITY.

③ LAMINATE ANODE, FIND NO. 1, TO ANODE COLLECTOR, FIND NO. 2, AS SHOWN.

④ SURFACE INDICATED SHALL BE COATED WITH POLYETHYLENE FILM, .002±.001 THICK, APPROXIMATE COLOR-TRANSPARENT YELLOW.

5. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.

6. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007357
   MFR-☐ — MANUFACTURER'S CAGE CODE



1	72007362	CURRENT COLLECTOR, ANODE		2
1	72007368	ANODE, LITHIUM FOIL		1

72007355

ALLIANT TECHSYSTEMS

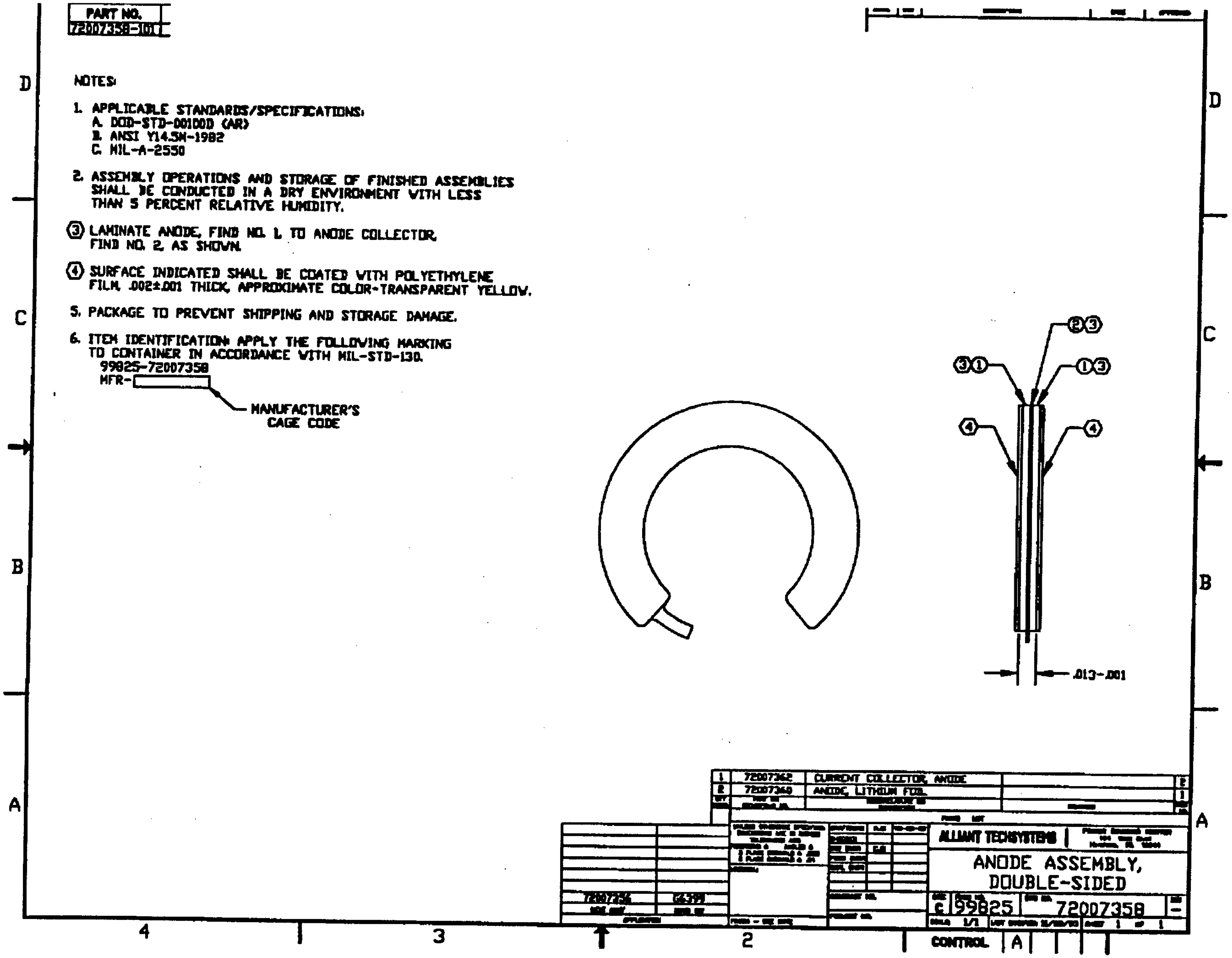
ANODE ASSEMBLY, SINGLE-SIDED

C 99825 72007357

1/1

SHEET 1 OF 1

CONTROL A



PART NO.
72007358-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550
2. ASSEMBLY OPERATIONS AND STORAGE OF FINISHED ASSEMBLIES SHALL BE CONDUCTED IN A DRY ENVIRONMENT WITH LESS THAN 5 PERCENT RELATIVE HUMIDITY.

③ LAMINATE ANODE, FIND NO. 1 TO ANODE COLLECTOR, FIND NO. 2, AS SHOWN.

④ SURFACE INDICATED SHALL BE COATED WITH POLYETHYLENE FILM, .002±.001 THICK, APPROXIMATE COLOR-TRANSPARENT YELLOW.

5. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.
6. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007358
   MFR-☐

1	72007362	CURRENT COLLECTOR, ANODE		2
2	72007360	ANODE, LITHIUM FOIL		1

ALLIANT TECHSYSTEMS

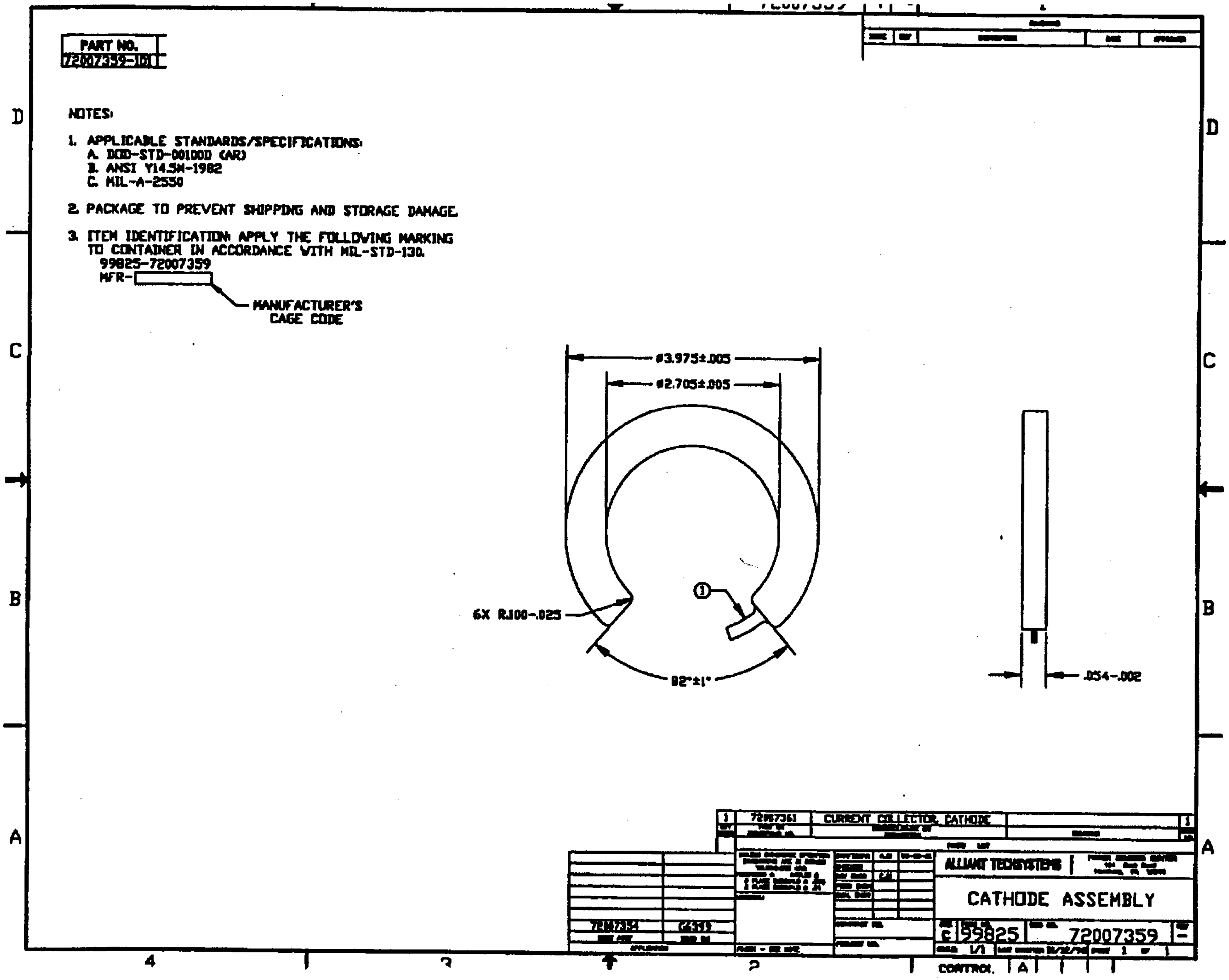
ANODE ASSEMBLY, DOUBLE-SIDED

C 99825 72007358

SCALE 1/1 SHEET 1 OF 1

72007356 G6399

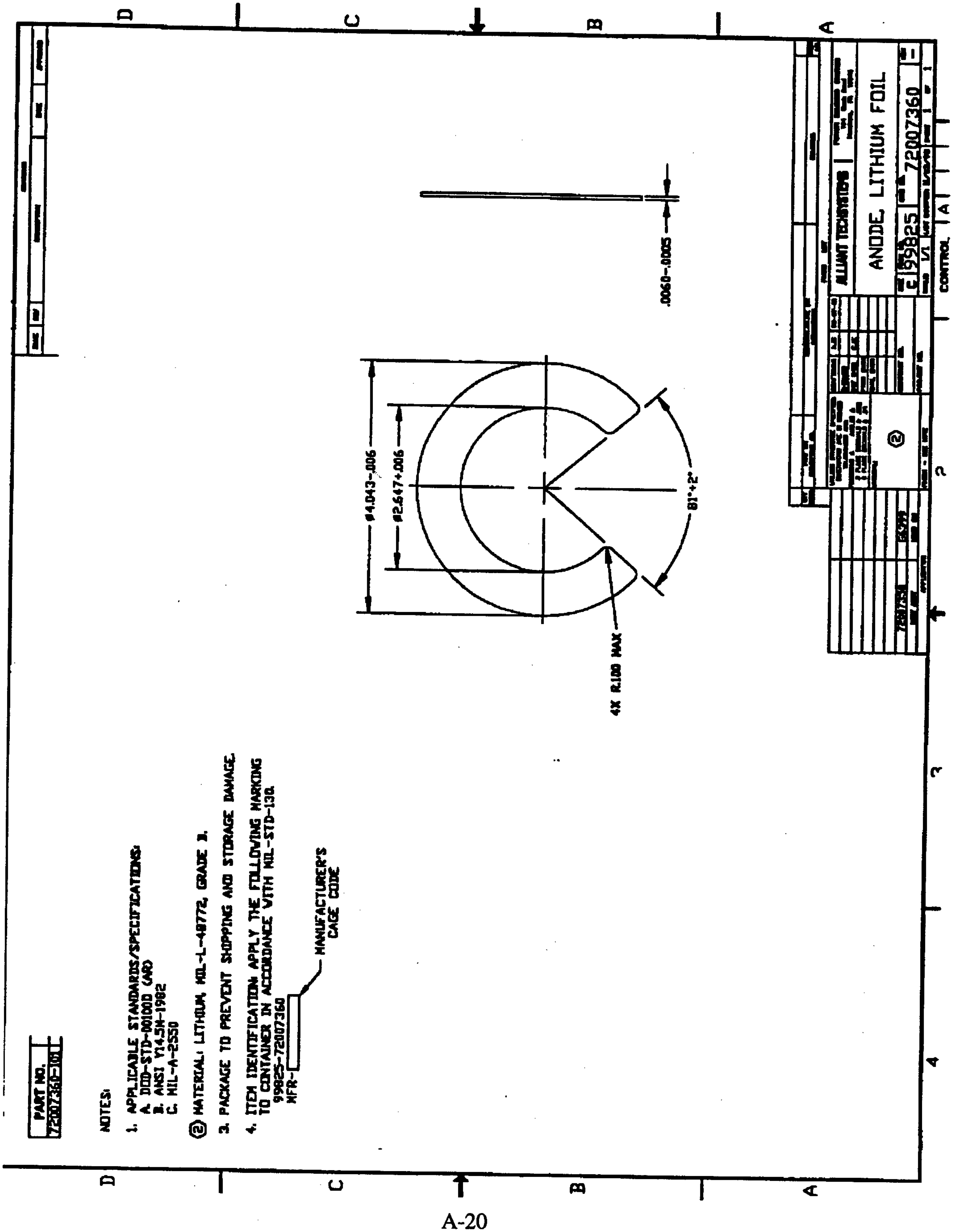
CONTROL A



PART NO.
72007359-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550
2. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.
3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007359
   MFR-☐ — MANUFACTURER'S CAGE CODE



PART NO.
72007360-101

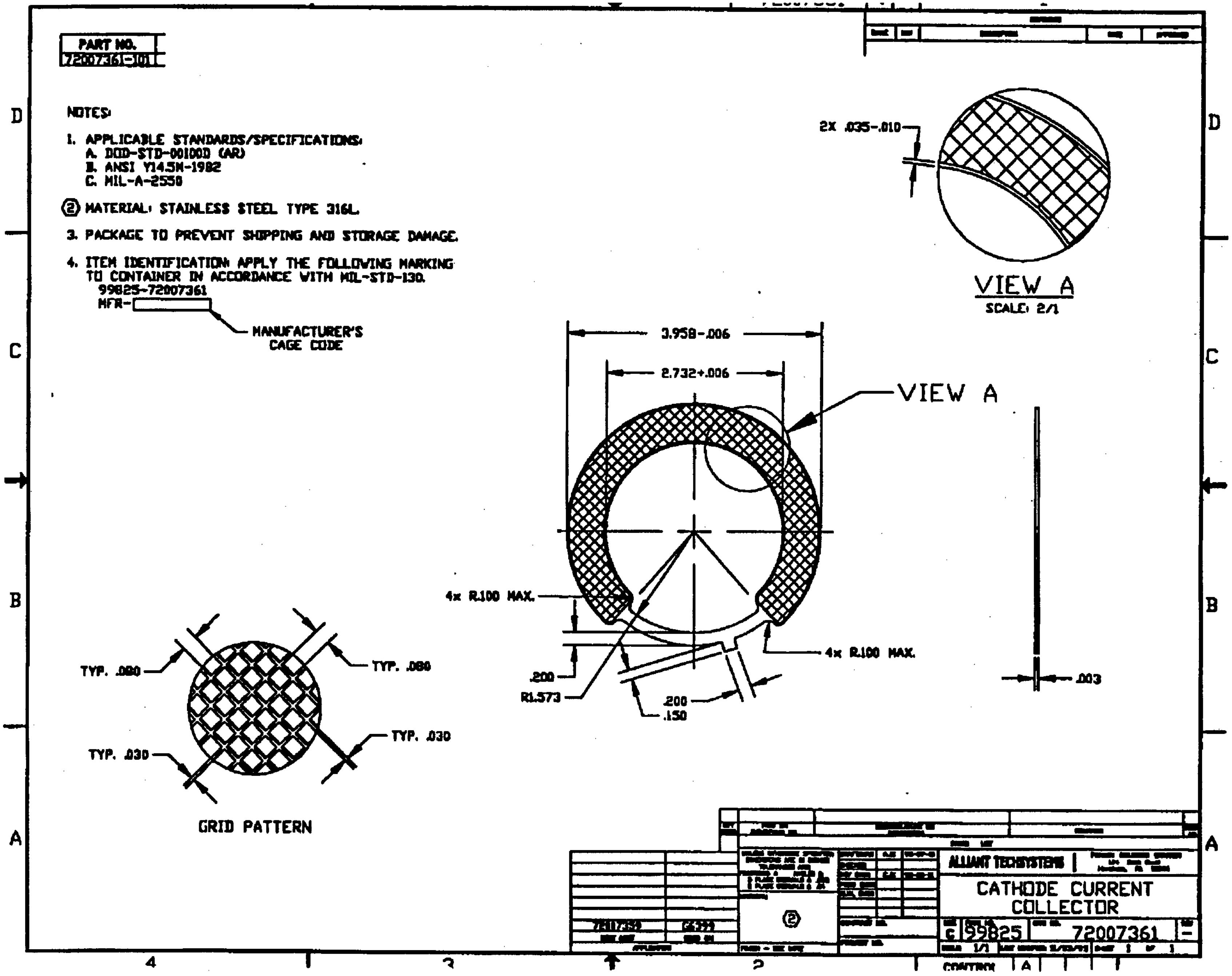
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: LITHIUM, MIL-L-49772, GRADE B.

3. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007360
   MFR-☐ MANUFACTURER'S CAGE CODE



PART NO.
72007361-101

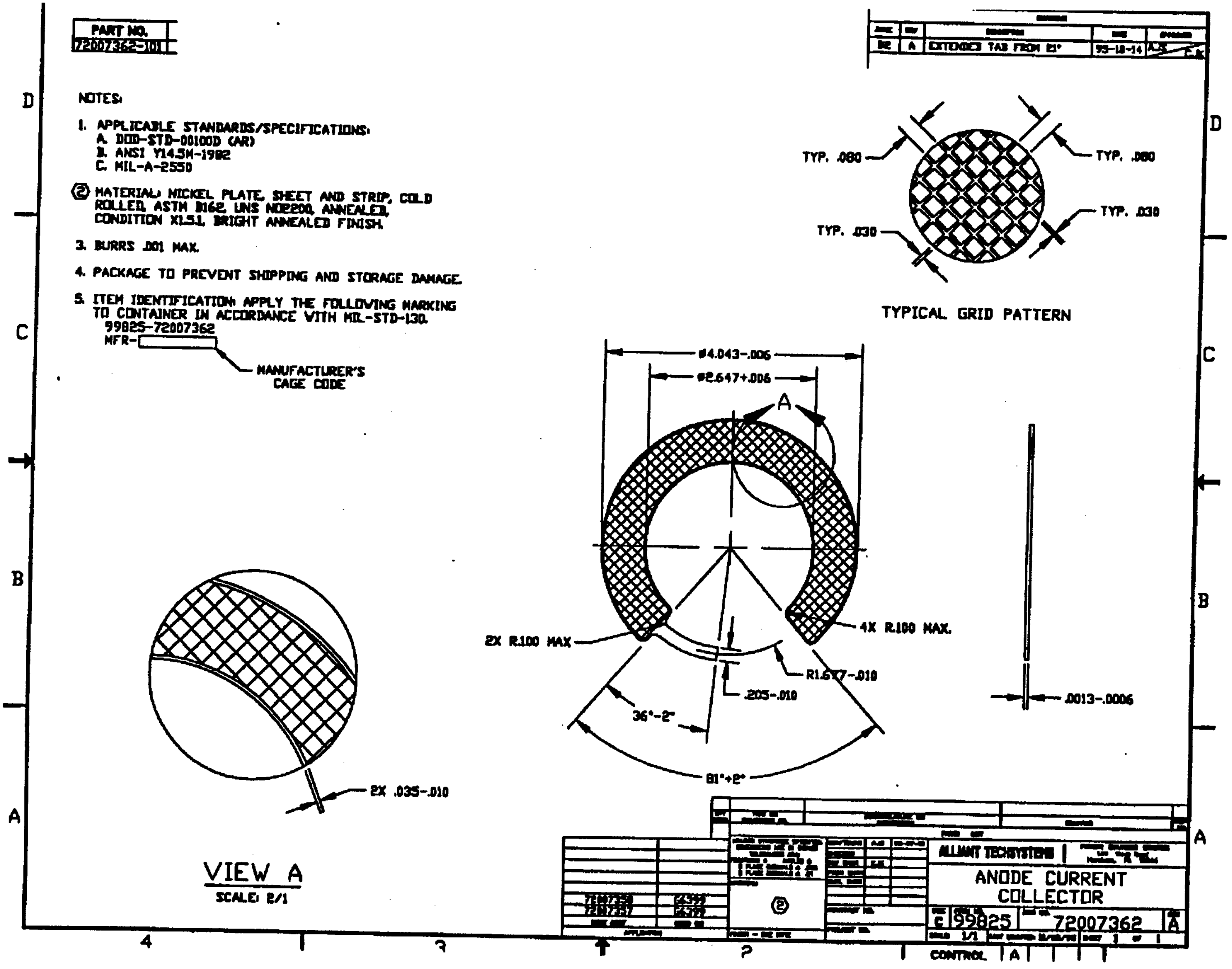
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL TYPE 316L.

3. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007361
   MFR-



PART NO.
72007362-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   - A. DOD-STD-00100D (AR)
   - B. ANSI Y14.5M-1982
   - C. MIL-A-2550

② MATERIAL: NICKEL PLATE, SHEET AND STRIP, COLD ROLLED, ASTM B162, UNS N02200, ANNEALED, CONDITION X1.5.1, BRIGHT ANNEALED FINISH.

3. BURRS .001 MAX.

4. PACKAGE TO PREVENT SHIPPING AND STORAGE DAMAGE.

5. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007362
   MFR-☐ MANUFACTURER'S CAGE CODE

TYPICAL GRID PATTERN

VIEW A
SCALE: 2/1

ANODE CURRENT COLLECTOR

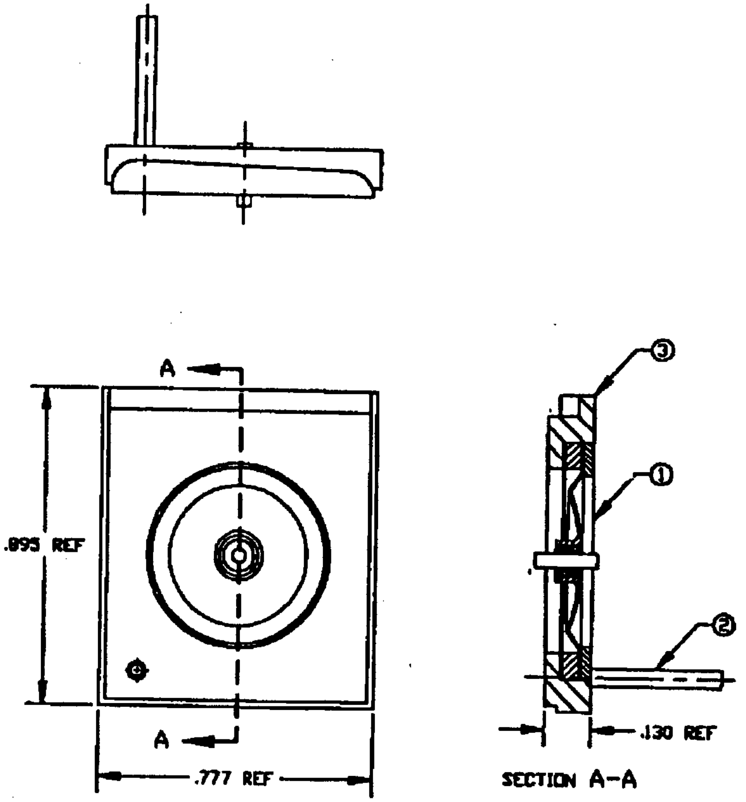
PART NO.
72007363-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

②

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007363
   MFR-☐ — MANUFACTURER'S CAGE CODE



1	72007364	HEADER, POSITIVE		3
1	72007365	FILL TUBE		2
1	72007373	CELL VENT/GTN EYELET ASSY		1

ALLIANT TECHSYSTEMS

HEADER ASSEMBLY, POSITIVE

C 99825 72007363 —

4/1 1 1

CONTROL A

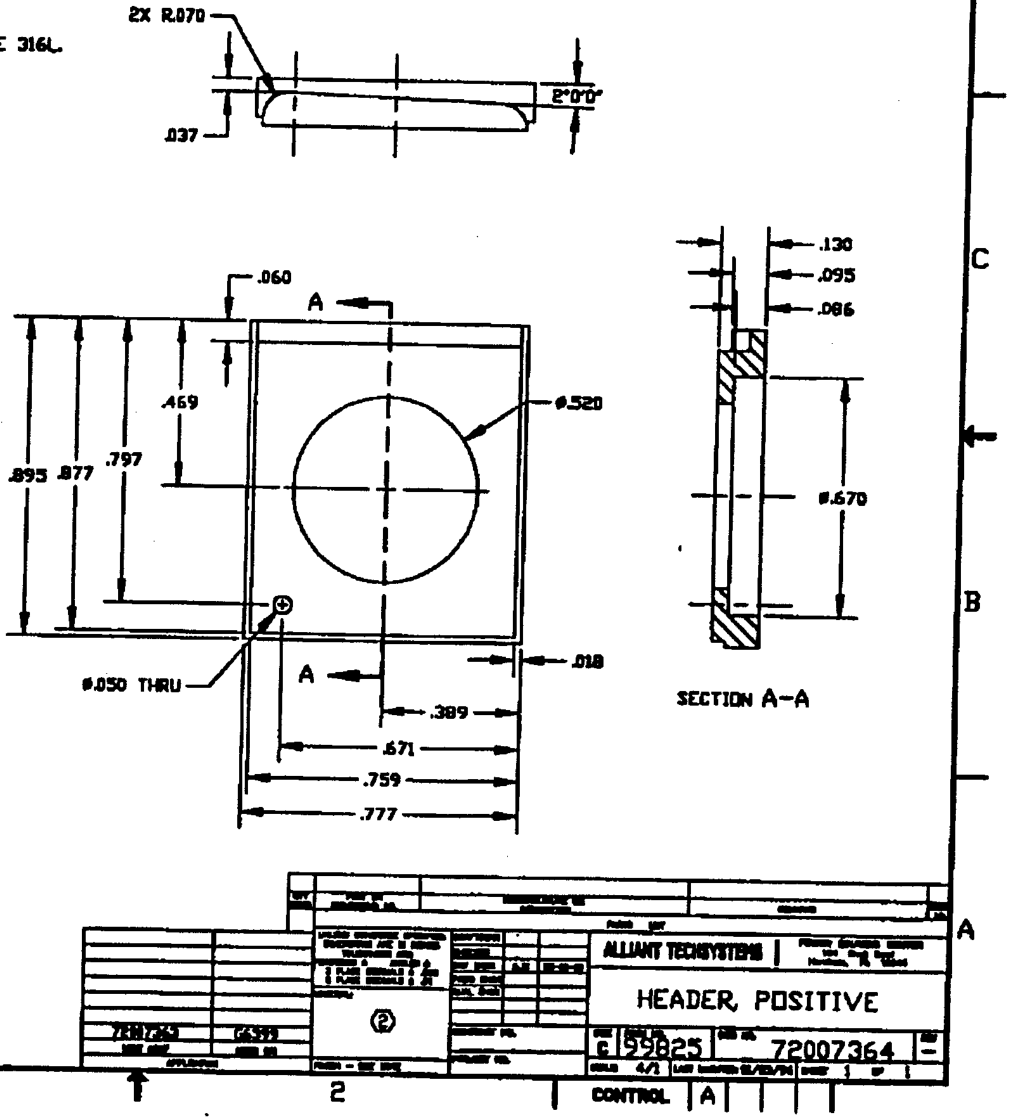
72007364-101

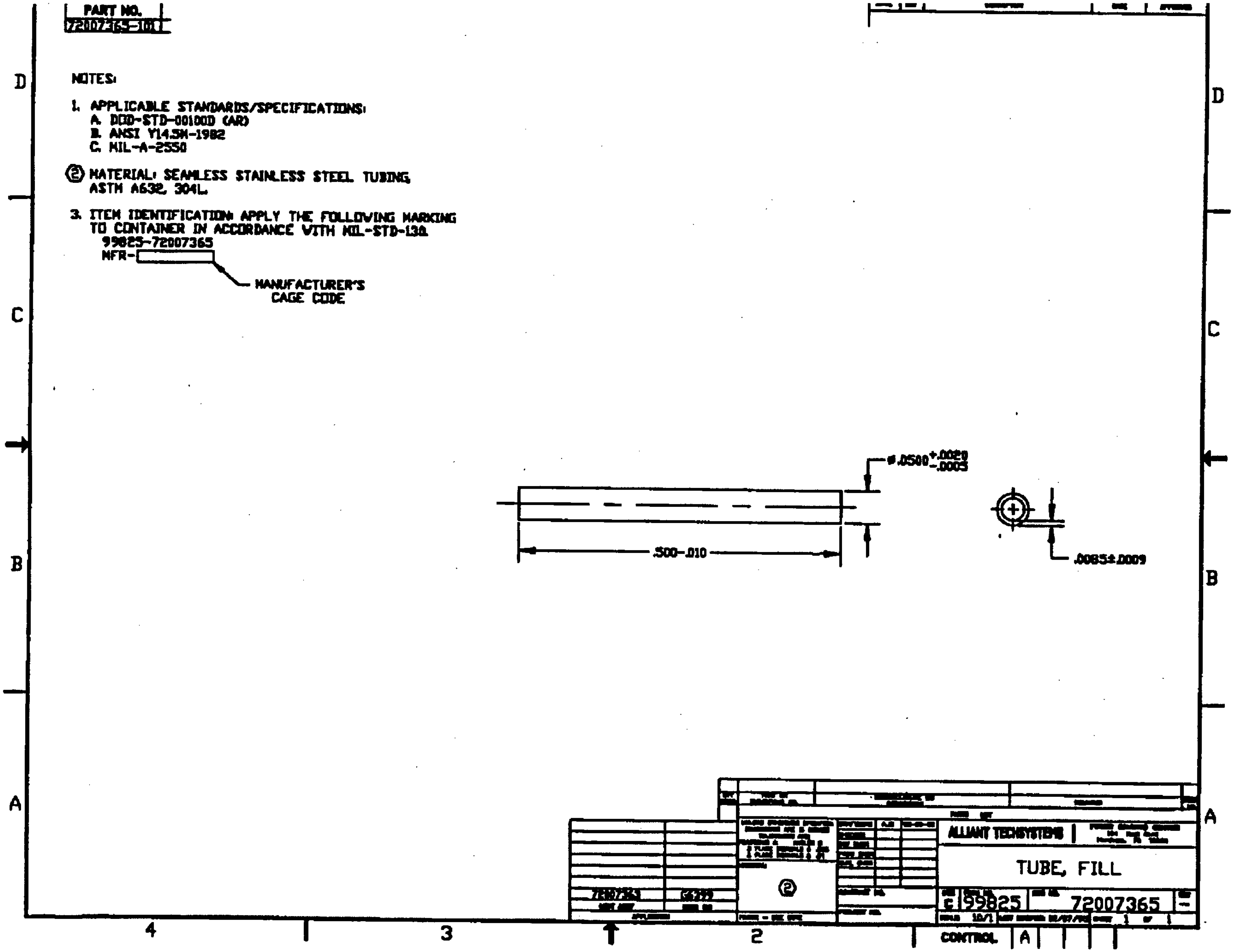
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316L.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007364
   MFR-☐ MANUFACTURER'S CAGE CODE





PART NO.
72007365-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: SEAMLESS STAINLESS STEEL TUBING ASTM A632, 304L.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007365
   MFR-

72007366-101

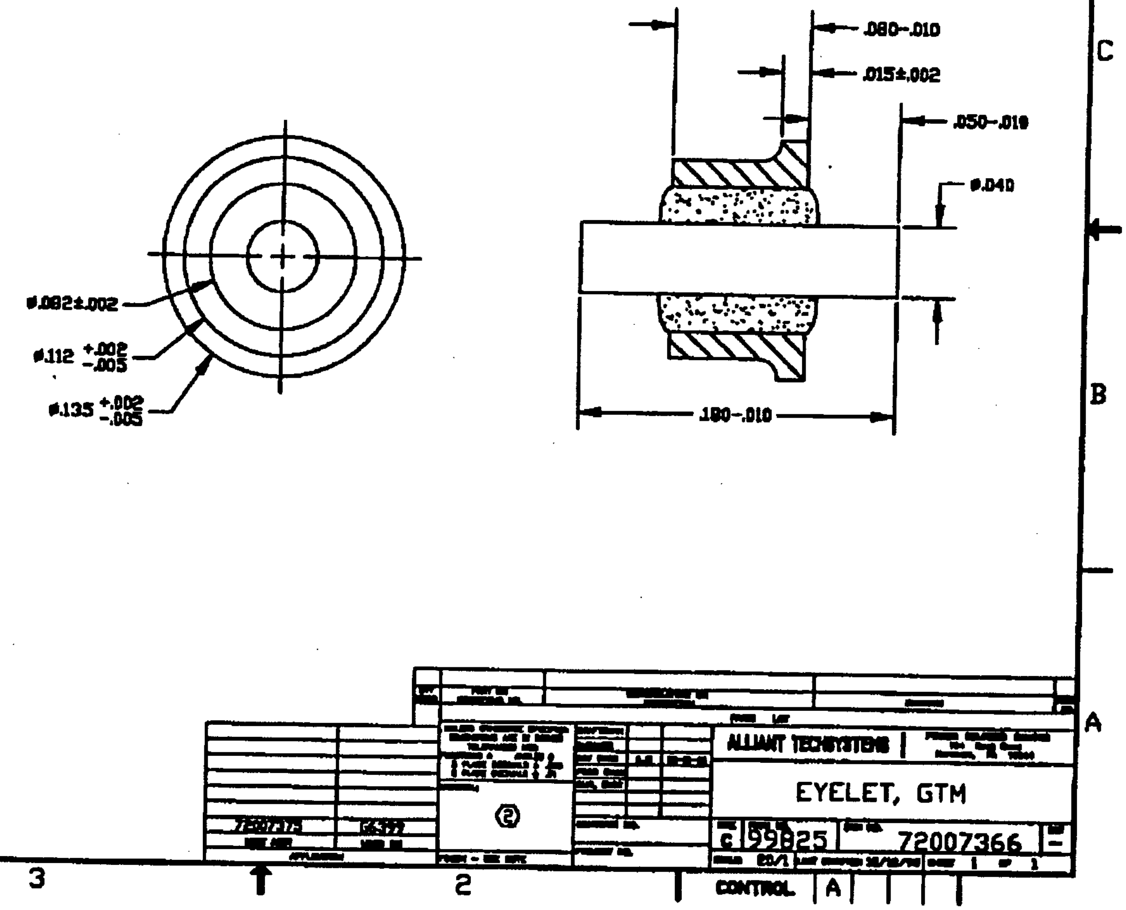
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   - A. DOD-STD-00100D (AR)
   - B. ANSI Y14.5M-1982
   - C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316L.
   - A. PIN - MOLYBDENUM
   - B. GLASS - TA-23
   - C. BODY - KOVAR, NICKEL-PLATED

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.

99825-72007366
MFR-☐ — MANUFACTURER'S CAGE CODE



APPLICATION		REVISIONS			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED
72007340	G6399	-	H-WAM	9/22/95	AJS

SUGGESTED SOURCE(S) OF SUPPLY

PART NO.	VENDOR ADDRESS	VENDOR CAGE CODE	VENDOR PART NUMBER	ITEM IDENTIFICATION
72007367	LEE SPRING COMPANY 1462 62nd STREET BROOKLYN, NY 11219 FSCM NO. 84630	TBD	TBD	99825-72007367 MFR-LC-021AB-3MW

SPECIFICATION CONTROL DRAWING

REV STATUS OF SHEETS	REV	-	-	-											
	SHEET	1	2	3											

PART NO. 72007367-101

CONTRACT NUMBER	
COMPUTER GENERATED	DRAWN BY AJS
	DATE 95-09-22
SYSTEM PPT WINDOWS	CHECKER
SOFTWARE REVISION 4.0	ENGINEER AJS
	MATL ENGR
DISK NO. -	QUAL ENGR
	PRODUCTION APPR
FILENAME	PROGRAM APPROVAL

ALLIANT TECHSYSTEMS INC., POWER SOURCES CENTER
104 Rock Road, Horsham, Pennsylvania 19044

SPRING, COMPRESSION

SIZE	CAGE CODE	DWG NO.
A	99825	72007367
SCALE: NONE	UNIT WT	SHEET 1 OF 3

PROJ END ITEM CONTROL -

1.0 REQUIREMENTS:

1.1 MATERIAL: STEEL WIRE, MUSIC SPRING QUALITY, ASTM A228.

1.2 SPECIFICATIONS:

	REQUIREMENTS
1.2.1 MUSIC WIRE DIAMETER	.021 +/- .001
1.2.2 OUTSIDE DIAMETER	.148 +/- .003
1.2.3 APPROX. LOAD AT SOLID HEIGHT	4.0 LBS
1.2.4 FREE LENGTH	.374 NOM.
1.2.5 SPRING RATE LB/IN	20.0 +/- .2
1.2.6 SOLID HEIGHT	.185 NOM.
1.2.7 ZINC PLATE, ASTM B633	.0002 THK.
1.2.8 TYPE OF ENDS	SQUARE NOT GROUND
1.2.9 DIRECTION OF WIND	OPTIONAL

2.0 QUALITY ASSURANCE PROVISIONS:

2.1 RESPONSIBILITY FOR INSPECTION: UNLESS OTHERWISE SPECIFIED IN THE CONTRACT OR PURCHASE ORDER, THE CONTRACTOR IS RESPONSIBLE FOR THE PERFORMANCE OF THE INSPECTION REQUIREMENTS. THE CONTRACTOR MAY USE HIS OWN OR ANY OTHER FACILITIES APPROVED BY THE GOVERNMENT FOR THE PERFORMANCE OF INSPECTION REQUIREMENTS SPECIFIED HEREIN. THE GOVERNMENT RESERVES THE RIGHT TO PERFORM ANY OF THE INSPECTIONS SET FORTH IN THE DRAWING WHERE SUCH INSPECTIONS ARE DEEMED NECESSARY TO ASSURE THAT SUPPLIES CONFORM TO PRESCRIBED REQUIREMENTS.

2.2 INSPECTION CONDITIONS: UNLESS OTHERWISE SPECIFIED, THE INSPECTION SHALL BE CONDUCTED AT ROOM AMBIENT TEMPERATURE.

2.3 QUALITY CONFORMANCE: UNLESS OTHERWISE SPECIFIED AND WHEN APPLICABLE, THE QUALITY CONFORMANCE TEST USED IN DETERMINING THE ACCEPTABILITY OF PRODUCTS SHALL BE IN ACCORDANCE WITH THE CONTRACTOR'S INSPECTION PLAN. INSPECTION OF EACH LOT OF MATERIAL SUBMITTED FOR ACCEPTANCE SHALL BE PERFORMED BY THE CONTRACTOR. CERTIFIED TEST DATA WITH ACCOMPANYING TEST RESULTS ARE ACCEPTABLE.

SIZE	CAGE CODE	DWG. NO.	
A	99825	72007367	
SCALE:	NONE	UNIT WT	SHEET 2 OF 3

PROJ

END ITEM

CONTROL -

SH3

DWG NO. 72007367

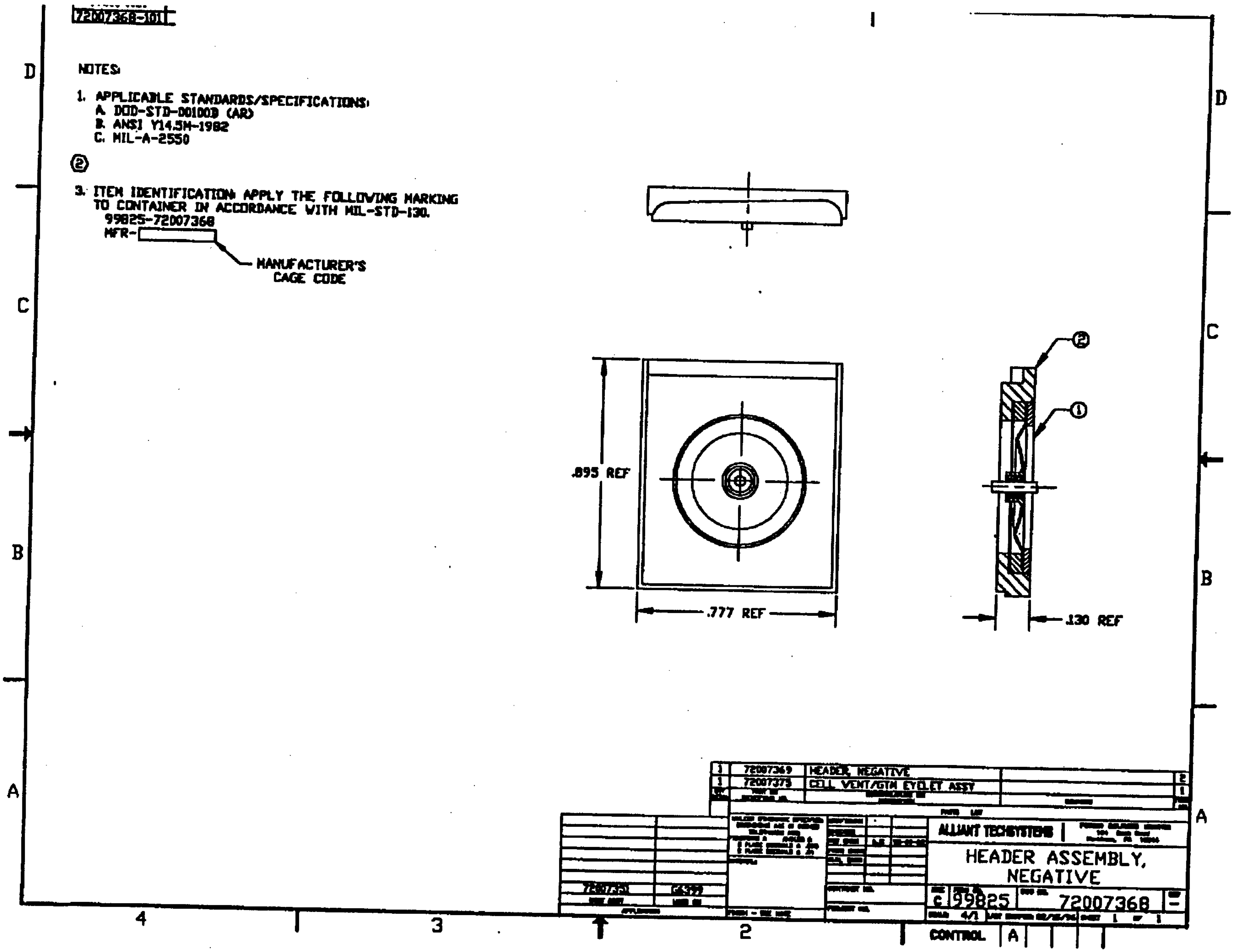
3.0 MARKING:

3.1 RUBBER STAMP OF STENCIL "99825-72007373" IN ACCORDANCE WITH MIL-STD-130, IN .125" HIGH CHARACTERS ON ITEM CONTAINER, USING BLACK STENCIL INK, TT-I-1795, TYPE II.

4.0 IDENTIFICATION OF THE SUGGESTED SOURCE(S) OF SUPPLY HEREON IS NOT TO BE CONSTRUED AS A GUARANTEE OF PRESENT OR CONTINUED AVAILABILITY AS A SOURCE OF SUPPLY FOR THE ITEM(S).

SIZE A	CAGE CODE 99825	DWG. NO. 72007367	
SCALE: NONE		UNIT WT	SHEET 3 OF 3

PROJ END ITEM CONTROL -



72007368-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

②

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007368
   MFR-☐ — MANUFACTURER'S CAGE CODE

1	72007369	HEADER, NEGATIVE	2
1	72007375	CELL VENT/GTM EYELET ASSY	1

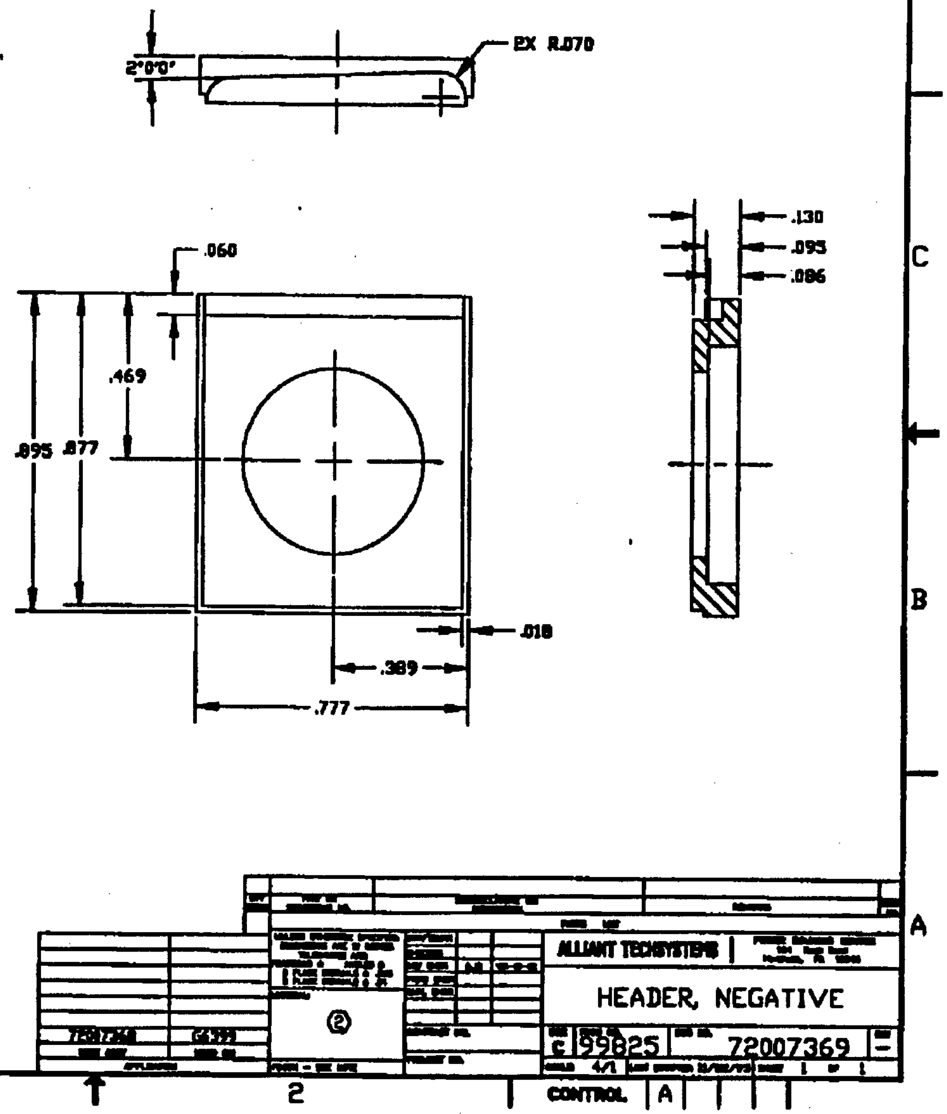
PART NO.
72007369-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316L.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007369
   MFR-☐ MANUFACTURER'S CAGE CODE



PART NO.
72007370-101

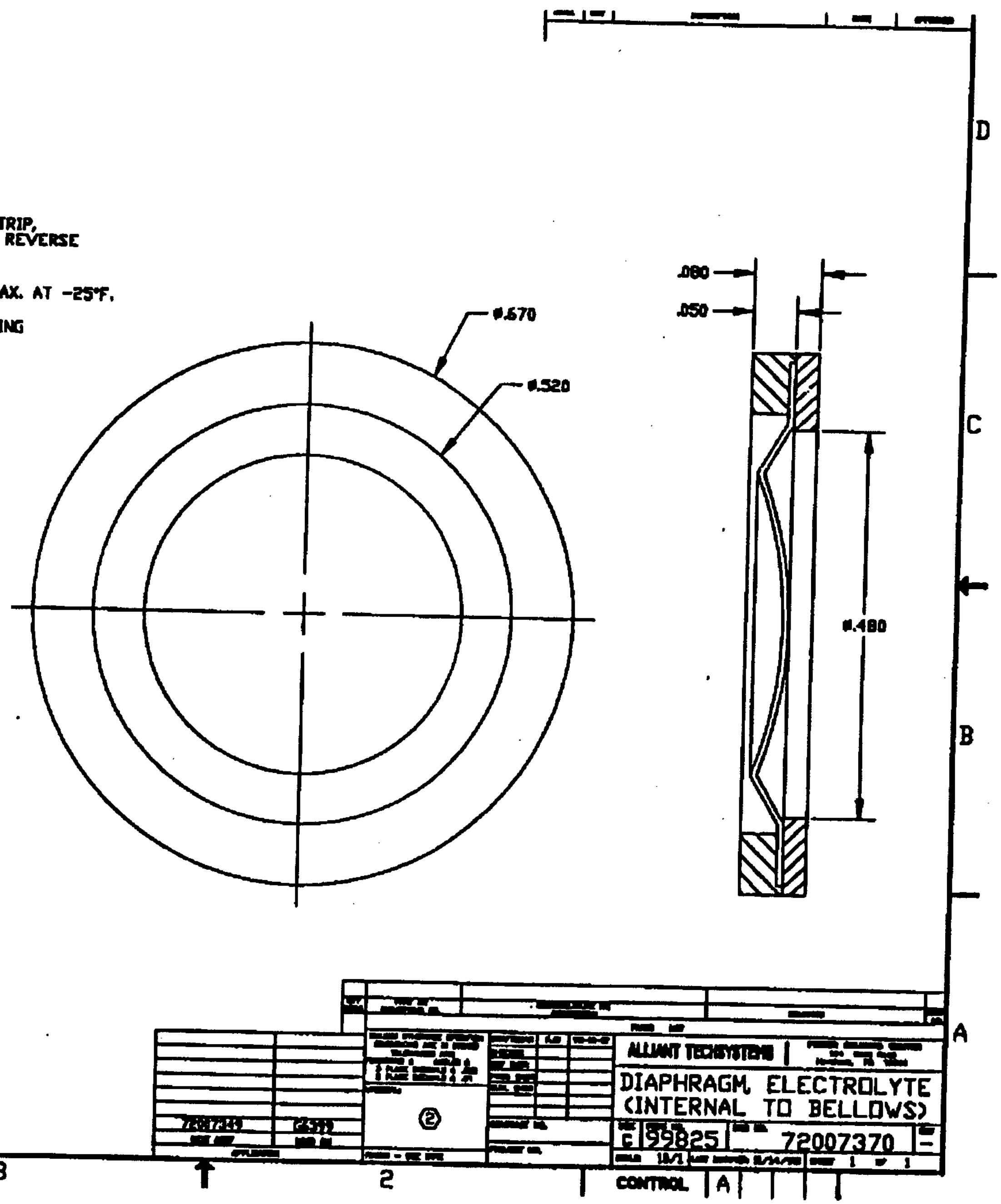
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316, USED ON RINGS. NICKEL 200 FRUSTRUM REVERSE BUCKLING RUPTURE DISK.

3. BURST PRESSURE: 100 PSI MIN AT 145°F, 150 PSI MAX. AT -25°F.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007370
   MFR-☐ — MANUFACTURER'S CAGE CODE



PART NO.
72007371-301

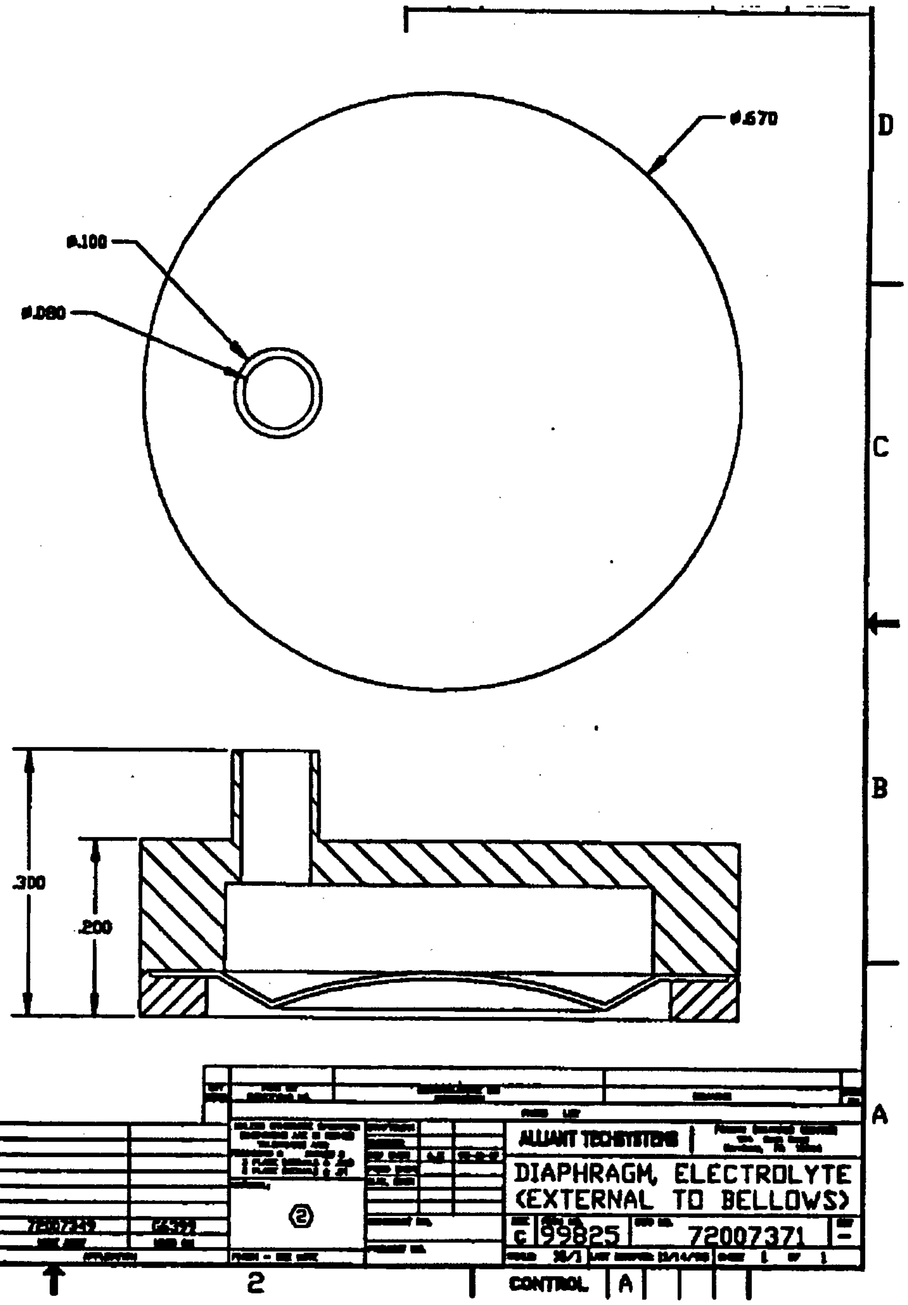
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316, USED ON RINGS. NICKEL 200 FRUSTRUM REVERSE BUCKLING RUPTURE DISK .

3. BURST PRESSURE: 100 PSI MIN AT 145°F, 150 PSI MAX. AT -25°F.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007371
   MFR-☐ MANUFACTURER'S CAGE CODE



PART NO.
72007372-101

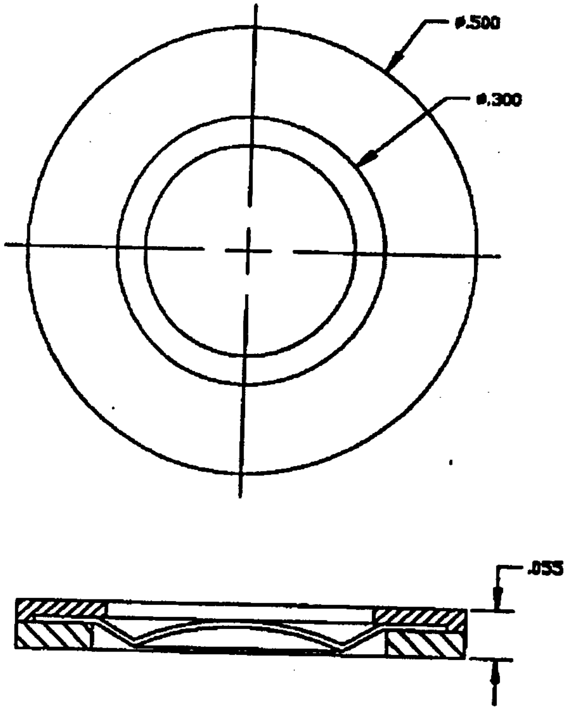
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316, USED ON RINGS. NICKEL 200 FRUSTRUM REVERSE BUCKLING RUPTURE DISK.

3. BURST PRESSURE: 215 PSI MIN AT 145°F, 300 PSI MAX. AT -25°F.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007372
   MFR-☐ MANUFACTURER'S CAGE CODE



ALLIANT TECHSYSTEMS

VENT, CELL CASE

C 99825 72007372

SCALE 10/1 SHEET 1 OF 1

②

CONTROL A

PART NO.
72007373-101

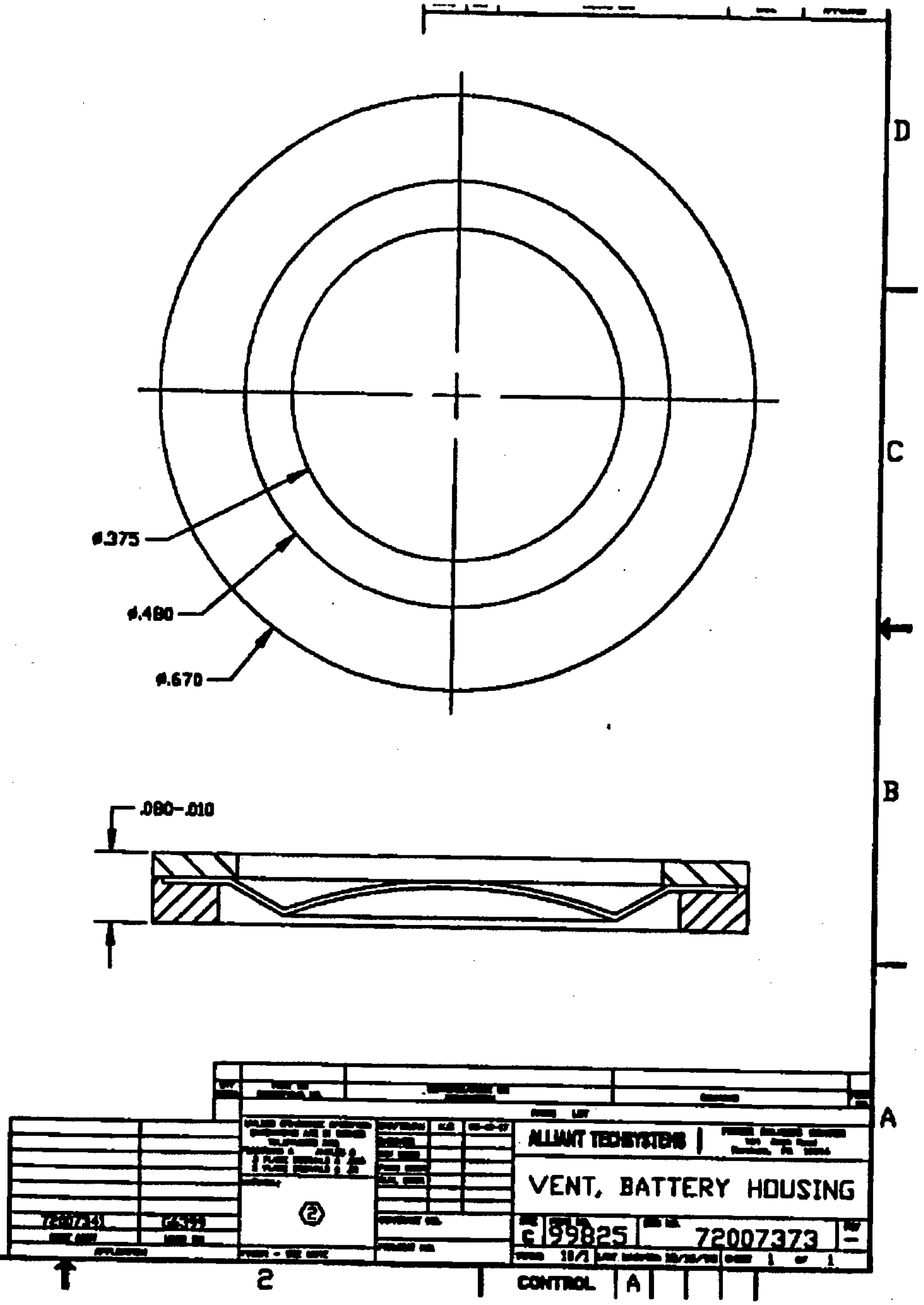
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   - A. DOD-STD-00100D (AR)
   - B. ANSI Y14.5M-1982
   - C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316, USED ON RINGS. NICKEL 200 FRUSTRUM REVERSE BUCKLING RUPTURE DISK.

3. BURST PRESSURE: 100 PSI MIN AT 145°F, 150 PSI MAX. AT -25°F.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007373
   MFR-☐ — MANUFACTURER'S CAGE CODE



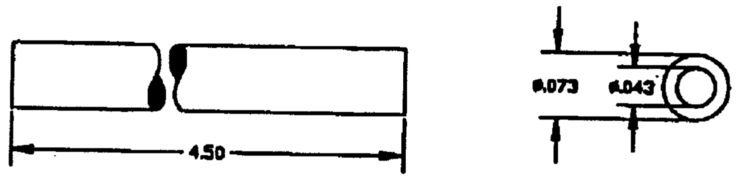
PART NO.
72007374-101

NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   - A. DOD-STD-00100D (AR)
   - B. ANSI Y14.5M-1982
   - C. MIL-A-2550

② MATERIAL: ETHYLENE TETRAFLUOROETHYLENE EXTRUSION (TUBING) IN ACCORDANCE WITH AMS 3533. PRIOR TO MAKING PIECE PARTS, HELIUM LEAK CHECK REEL STOCK MATERIAL IN ACCORDANCE WITH MIL-STD-202, METHOD 112, TEST CONDITION C, PROCEDURE I. LEAK RATE NOT TO EXCEED 1 X 10 ATM CC/SEC OF HELIUM.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007374
   MFR-☐ — MANUFACTURER'S CAGE CODE



72007340 | [illegible]
APPLICATION

②

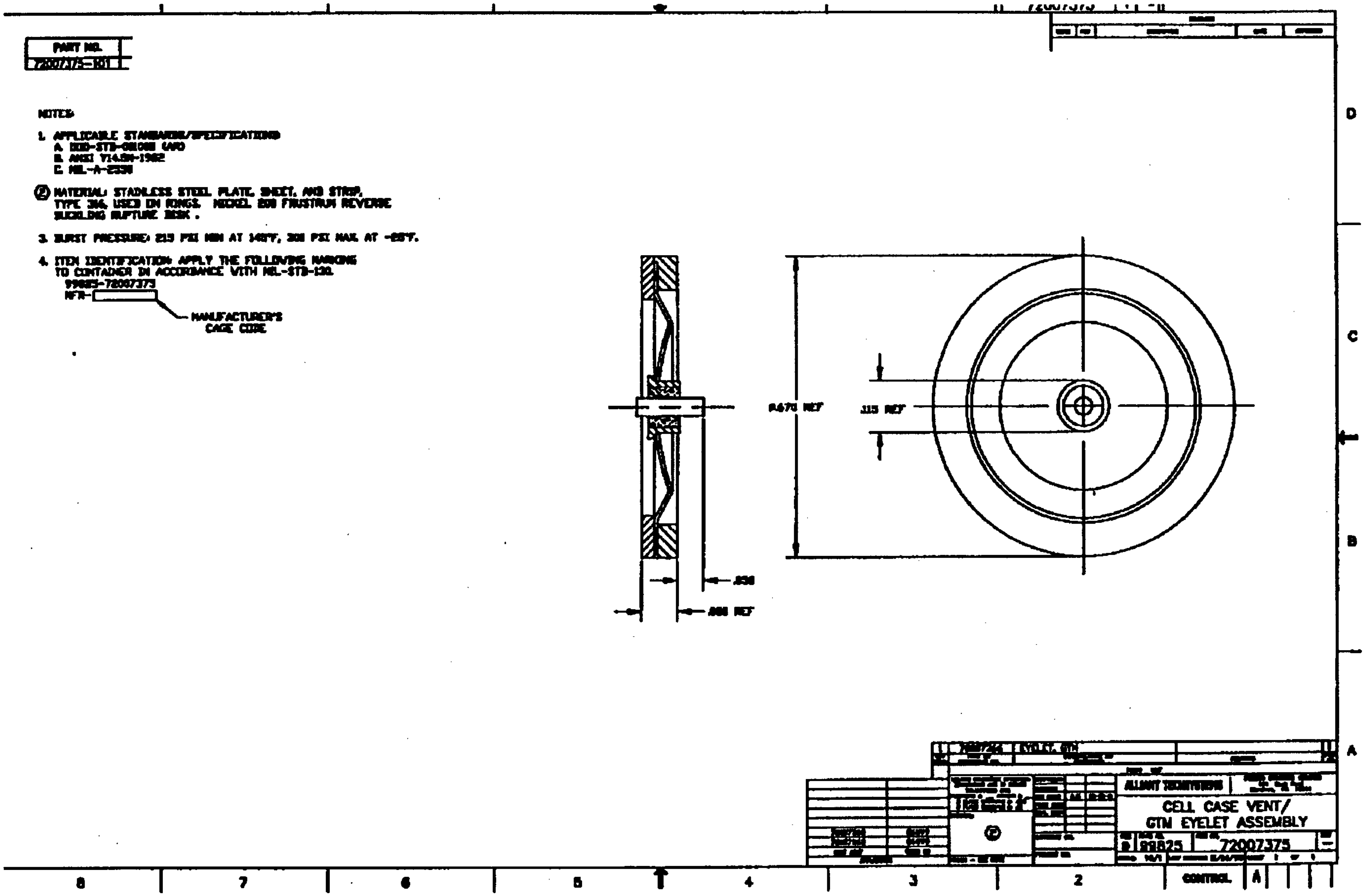
ALLIANT TECHSYSTEMS

TUBING, ACTIVATION

C 99825 72007374

SCALE 10/1 SHEET 1 OF 1

CONTROL A



PART NO.
72007375-101

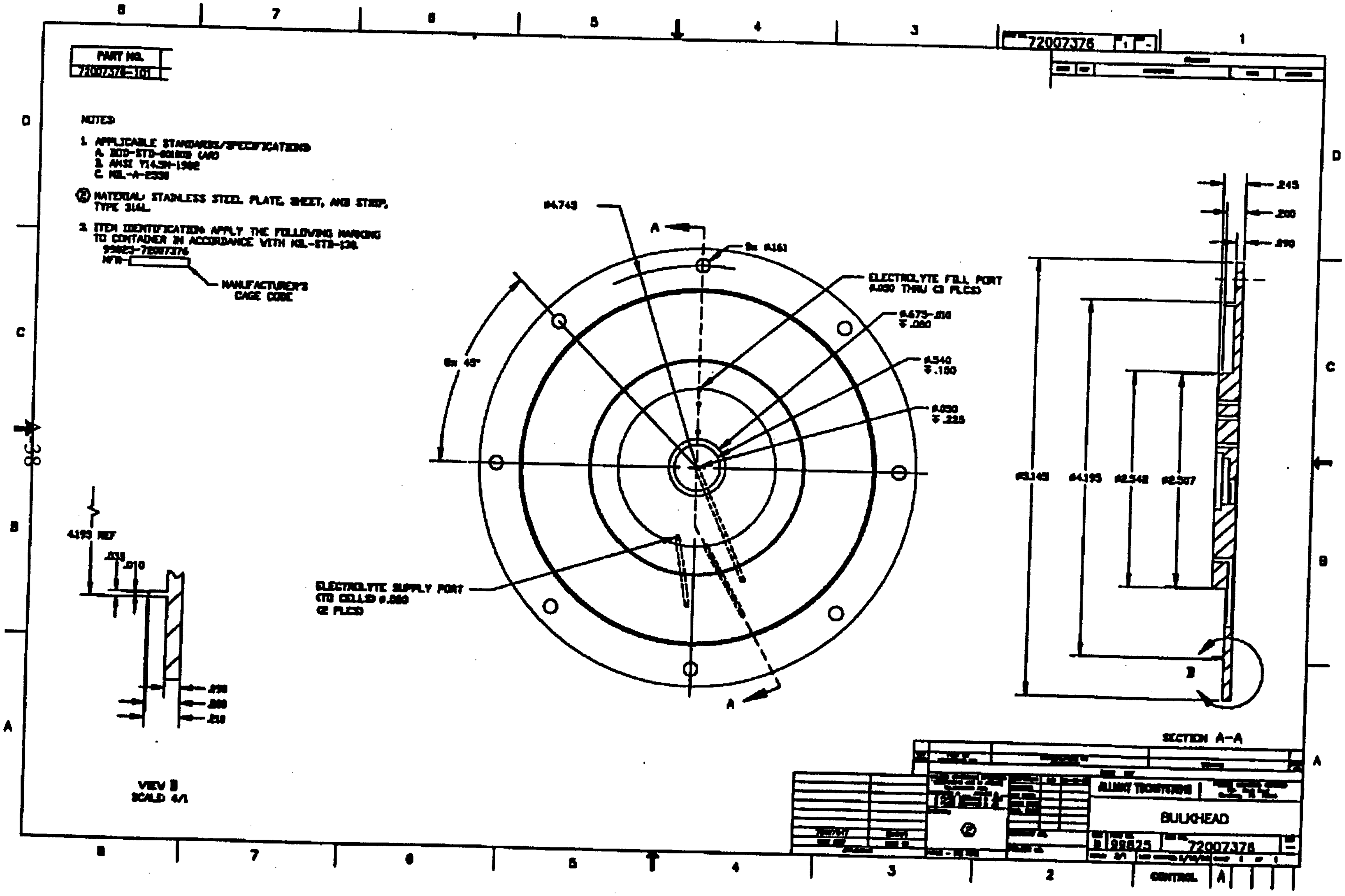
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100 (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316, USED ON RINGS. NICKEL 200 FRUSTRUM REVERSE BUCKLING RUPTURE DISK.

3. BURST PRESSURE: 215 PSI MIN AT 140°F, 300 PSI MAX AT -25°F.

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007375
   MFR-☐ — MANUFACTURER'S CAGE CODE



NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS
   A. DOD-STD-00100 (AO)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② MATERIAL: STAINLESS STEEL PLATE, SHEET, AND STRIP, TYPE 316L.

3. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007376
   MFR-☐ — MANUFACTURER'S CAGE CODE

72007975-101

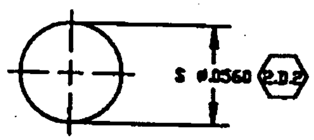
NOTES:

1. APPLICABLE STANDARDS/SPECIFICATIONS:
   A. DOD-STD-00100D (AR)
   B. ANSI Y14.5M-1982
   C. MIL-A-2550

② REQUIREMENTS:
   A. MATERIAL: STAINLESS AND HEAT-RESISTING STEEL BARS AND SHAPES, ASTM A276, CONFORMING TO THE CHEMICAL COMPOSITION OF UNS S44003 OR UNS S4404.
   B. HARDNESS: 58-65 HRC OR EQUIVALENT.
   C. TOLERANCE FOR INDIVIDUAL BALLS:
      1. ALLOWABLE BALL DIAMETER VARIATION: $10X10^{-6}$.
      2. ALLOWABLE DEVIATION FROM SPHERICAL FORM: $10X10^{-6}$.
      3. ALLOWABLE SURFACE ROUGHNESS (ARITHMETICAL AVERAGE): $1.0X10^{-6}$.
   D. TOLERANCE FOR LOTS OF BALLS:
      1. ALLOWABLE LOT DIAMETER VARIATION: $20X10^{-6}$.
      2. BASIC DIAMETER TOLERANCE: $\pm 100X10^{-6}$.
      3. ALLOWABLE BALL GAGE DEVIATION:
         A. HIGH: $+50X10^{-6}$.
         B. LOW: $-40X10^{-6}$.
      4. CONTAINER MARKING INCREMENT: $10X10^{-6}$.
   E. MATERIAL DENSITY: .277 LBS/CUBIC INCH.

3. IDENTIFICATION OF THE "SUGGESTED SOURCE(S) OF SUPPLY" HEREON IS NOT TO BE CONSTRUED AS A GUARANTEE OF PRESENT OR CONTINUED AVAILABILITY AS A SOURCE OF SUPPLY FOR THE ITEM(S).

4. ITEM IDENTIFICATION: APPLY THE FOLLOWING MARKING TO CONTAINER IN ACCORDANCE WITH MIL-STD-130.
   99825-72007975
   MFR-☐-☐
   MANUFACTURER'S CAGE CODE PART NO.



SUGGESTED SOURCE(S) OF SUPPLY

PART NO.	VENDOR		VENDOR PART NO.	ITEM IDENTIFICATION
	ADDRESS	CAGE CODE		
72007975	WINSTED PRECISION BALL CORP. 12 ROCKWELL ST. PO BOX 679 WINSTED, CT 06098-0679	27872		99825-72007975 MFR-

SPECIFICATION CONTROL DRAWING

ALLIANT TECHSYSTEMS

BALL

C 99825 72007975

CONTROL A

Appendix B

U.S. Patent NO.: 5,667,660 Synthesis of Charged Li_xCoO_2 ($0<x<1$) for Primary and Secondary Batteries

US005667660A

United States Patent [19]

Lin et al.

[11] **Patent Number:** **5,667,660**

[45] **Date of Patent:** **Sep. 16. 1997**

[54] **SYNTHESIS OF CHARGED LI_xCOO_2 (0<x<1) FOR PRIMARY AND SECONDARY BATTERIES**

[75] Inventors: **Hsiu-Ping W. Lin.** Princeton. N.J.; **Kevin Burgess.** Horsham. Pa.

[73] Assignee: **Alliant Techsystems Inc..** Hopkins. Minn.

[21] Appl. No.: **527.208**

[22] Filed: **Sep. 12. 1995**

[51] **Int. Cl.^{6}** **H01M 4/04**

[52] **U.S. Cl.** **205/59**: 429/218

[58] **Field of Search** 205/59; 429/218; 427/201. 126.6

[56] **References Cited**

U.S. PATENT DOCUMENTS

4.497.726	2/1985	Brule et al.	252/182.1
4.804.596	2/1989	Ebner et al.	429/194
4.818.647	4/1989	Plichta et al.	429/218
5.110.696	5/1992	Shokoohi et al.	429/218
5.296.319	3/1994	Bito et al.	429/218 X
5.427.875	6/1995	Yamamoto et al.	429/218 X

OTHER PUBLICATIONS

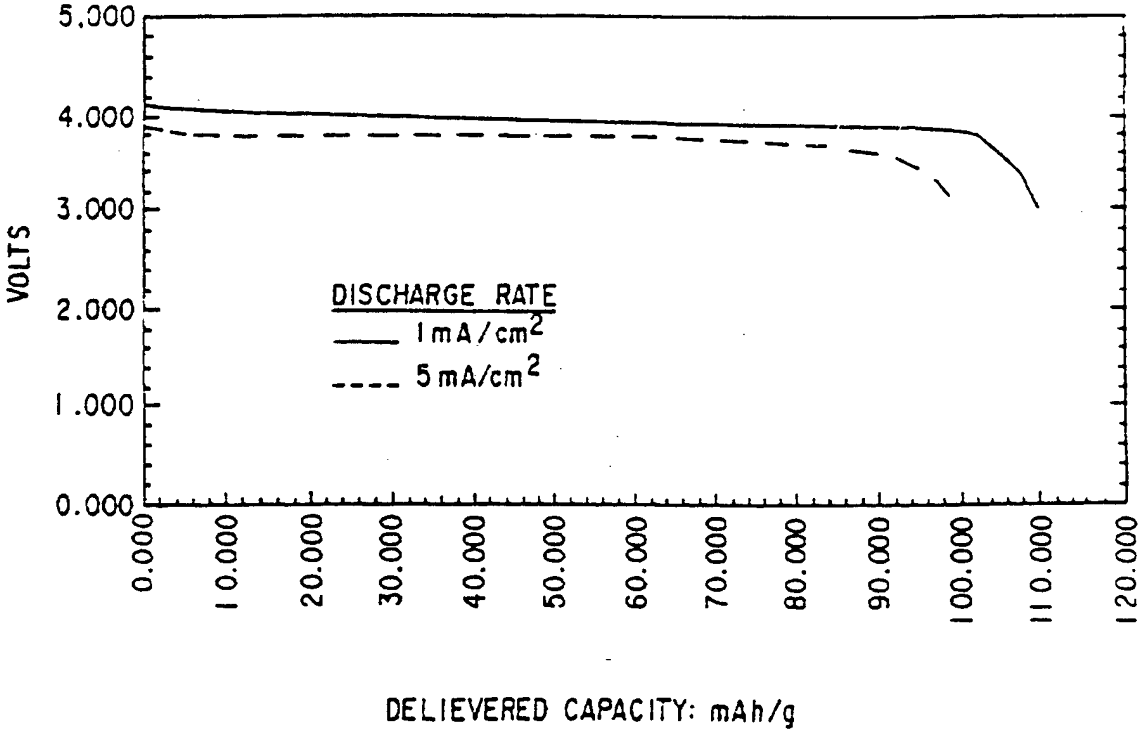
Gummow et al.. "Characterization of LT-$Li_xCo_{1-y}Ni_yO_2$ Electrodes for Rechargeable Lithium Cells". J. Electrochem. Soc.. vol. 140. No. 12. Dec. 1993. pp. 3365–3368.

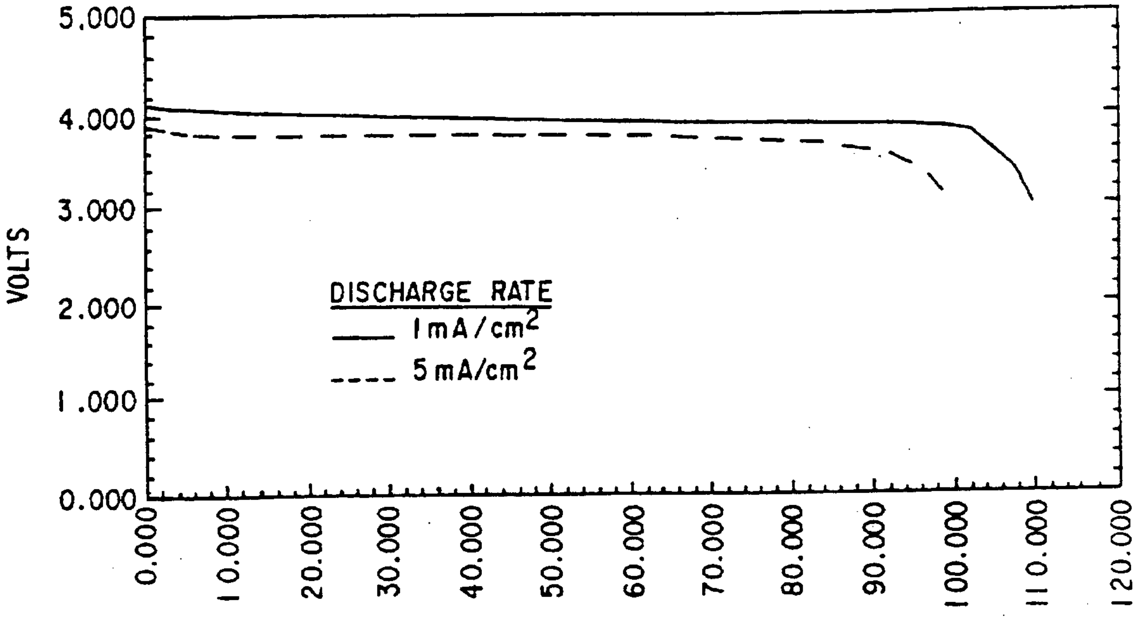
Primary Examiner—Stephen Kalafut
Attorney, Agent, or Firm—Haugen and Nikolai. P.A.

[57] **ABSTRACT**

A method for producing stable pre-charged Li_xCoO_2 as the cathode active metal in primary or secondary active metal non-aqueous cells and cells using such material are disclosed.

13 Claims, 5 Drawing Sheets





DELIEVERED CAPACITY: mAh/g

FIG. 1

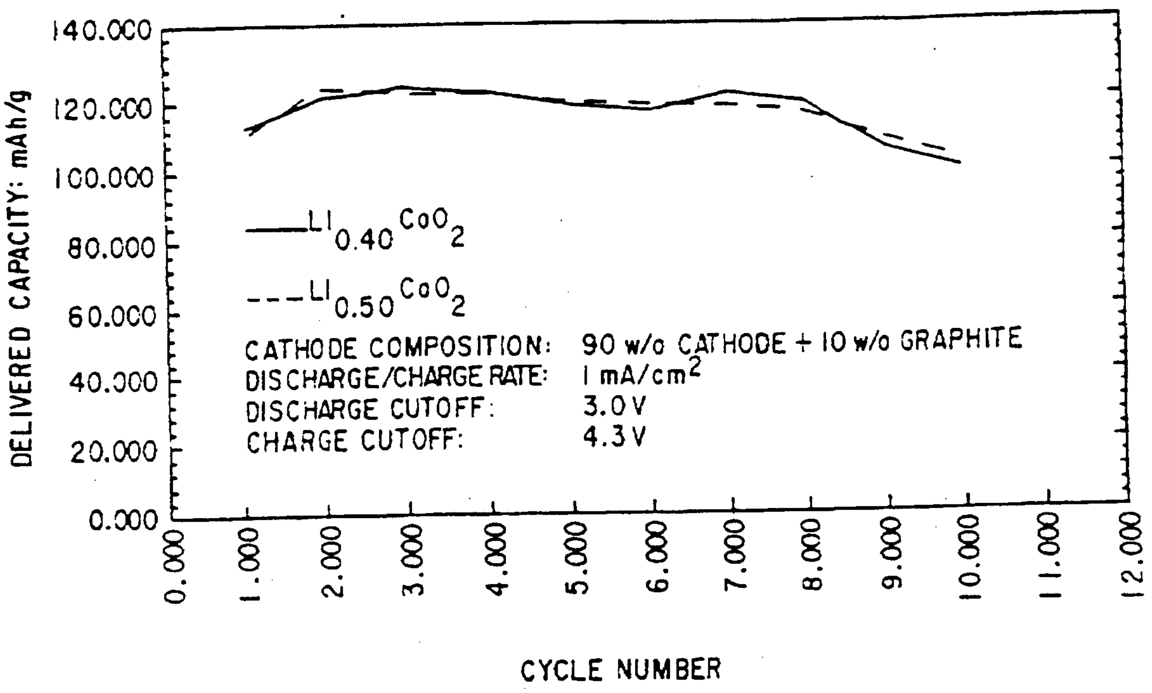

140.000
120.000
100.000
80.000
60.000
40.000
20.000
0.000
DELIVERED CAPACITY: mAh/g
0.000
1.000
2.000
3.000
4.000
5.000
6.000
7.000
8.000
9.000
10.000
11.000
12.000
CYCLE NUMBER
—— $LI_{0.40}CoO_2$
- - - $LI_{0.50}CoO_2$
CATHODE COMPOSITION: 90 w/o CATHODE + 10 w/o GRAPHITE
DISCHARGE/CHARGE RATE: 1 mA/cm^2
DISCHARGE CUTOFF: 3.0 V
CHARGE CUTOFF: 4.3 V

FIG. 2

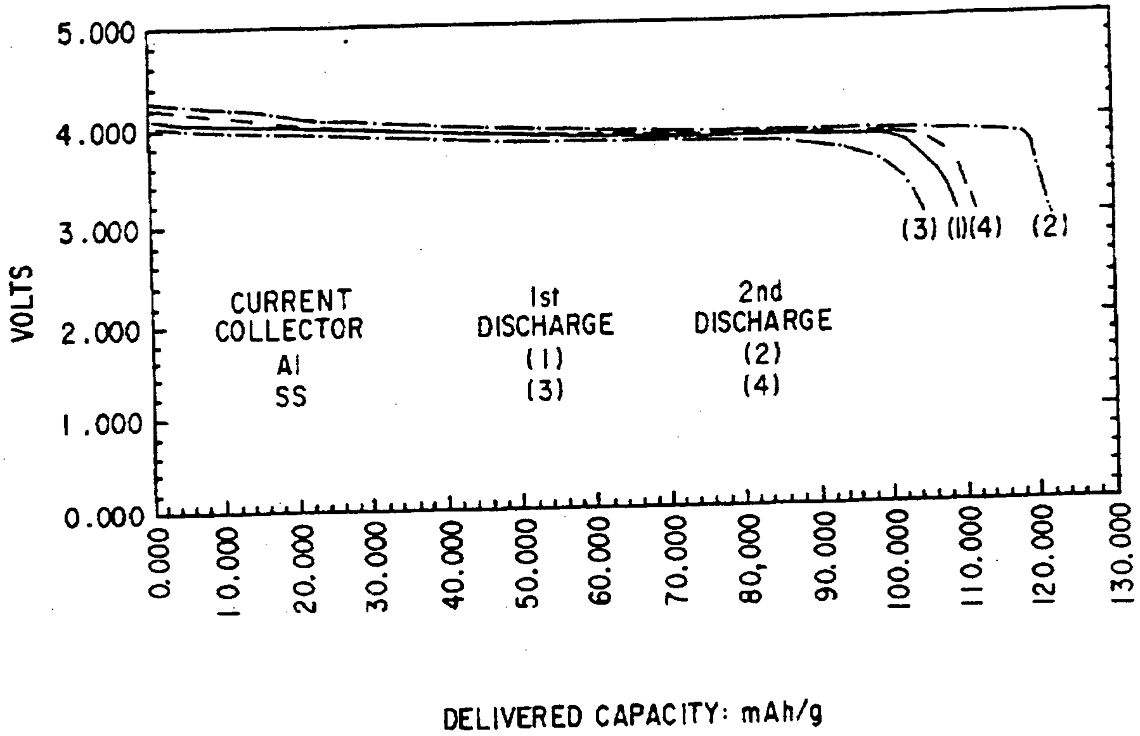

5.000
4.000
3.000
2.000
1.000
0.000
VOLTS
(3) (1) (4) (2)
CURRENT COLLECTOR
Al
SS
1st DISCHARGE
(1)
(3)
2nd DISCHARGE
(2)
(4)
0.000
10.000
20.000
30.000
40.000
50.000
60.000
70.000
80.000
90.000
100.000
110.000
120.000
130.000
DELIVERED CAPACITY: mAh/g

FIG. 3

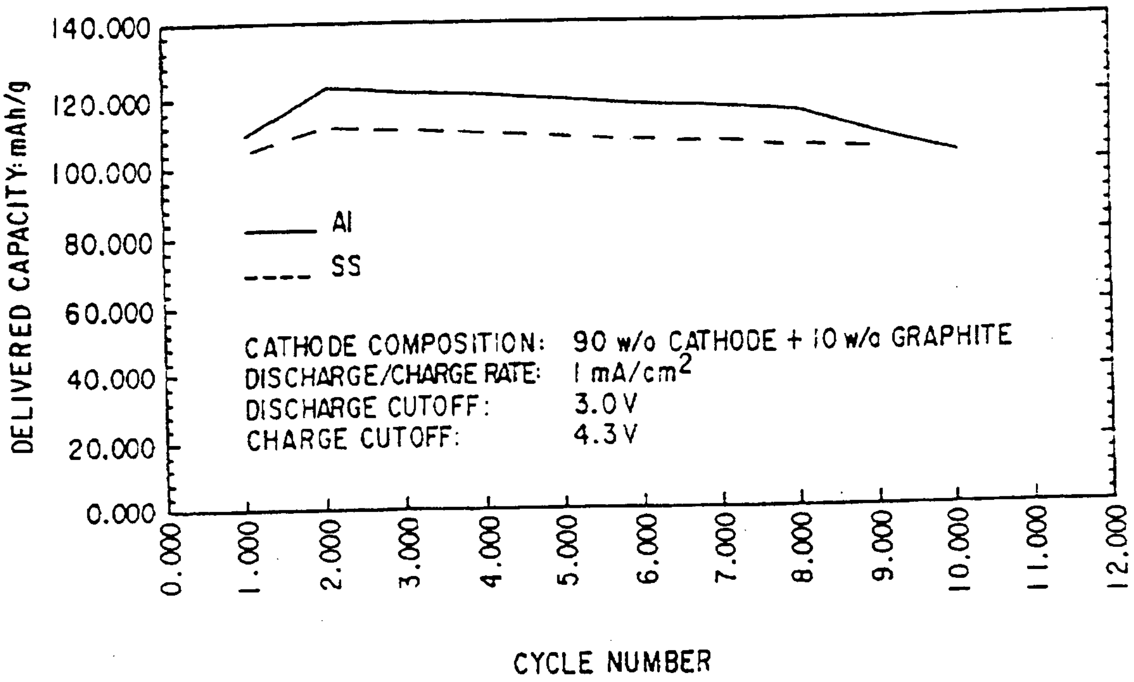

DELIVERED CAPACITY: mAh/g
140.000
120.000
100.000
80.000
60.000
40.000
20.000
0.000
Al
SS
CATHODE COMPOSITION: 90 w/o CATHODE + 10 w/o GRAPHITE
DISCHARGE/CHARGE RATE: 1 mA/cm2
DISCHARGE CUTOFF: 3.0 V
CHARGE CUTOFF: 4.3 V
0.000
1.000
2.000
3.000
4.000
5.000
6.000
7.000
8.000
9.000
10.000
11.000
12.000
CYCLE NUMBER

FIG. 4

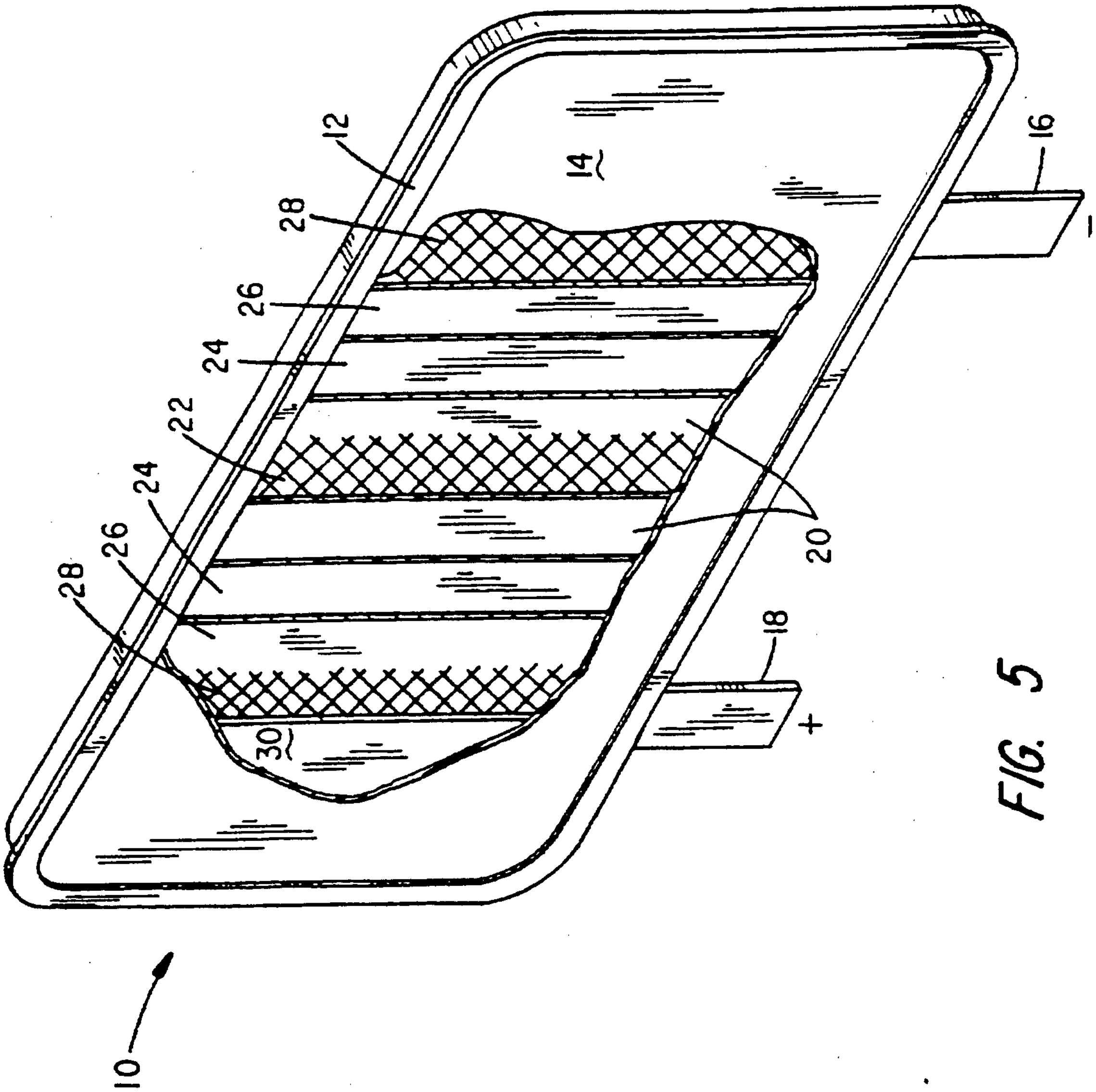


FIG. 5

SYNTHESIS OF CHARGED LI_xCOO_2 (0<x<1) FOR PRIMARY AND SECONDARY BATTERIES

BACKGROUND OF THE INVENTION

The Government has certain rights in this application pursuant to Contract N60921-93-C-0060 with the Department of the Navy.

1. Field of the Invention

The present invention is directed generally to the field of high energy, non-aqueous electrochemical cells and, more particularly, to improvements in such cells employing Li_xCoO_2 cathode material which enable the cathode material to be synthesized in a pre-charged state prior to incorporation in the cell.

2. Related Art

Non-aqueous, active metal cells have become well known for achieving very high energy densities or energy to weight ratios, i.e., higher than was previously known with other types of electrochemical cells. Active metal cells typically consist of a light, strongly reducing anode, normally of an alkali metal such as lithium (an aprotic, non-aqueous solvent into which an appropriate quantity of the salt of the anode metal has been dissolved to form a conductive solution, and an oxidizing agent as the cathode material. Such cells can be in the form of primary or secondary (rechargeable) cells.

It is further known to employ the material Li_xCoO_2 (0<x<1) as the active cathode material of such cells. For example, its use is disclosed in U.S. Pat. No. 4,497,726 and further discussed in Mizushima, K. et al. "Li_xCoO_2 (0<x<1): A New Cathode Material for Batteries of High Energy Density." Mat. Res. Bull., Vol. 15, 783 (1980). A lithium non-aqueous secondary electrochemical cell having an ester-based organic electrolyte solution and a cathode active material comprising Li_xCoO_2 (0<X<1) is illustrated and described in U.S. Pat. No. 4,804,596 to Walter B. Ebner and Hsiu-Ping W. Lin (an inventor in the present application) which is also assigned to the same assignee as the present application. That reference describes the use of Li_xCoO_2 as the active cathode material in a cell in combination with an ester-based electrolyte solution that can withstand the high operating and charging potentials characteristic of that system. The Li_xCoO_2 cathode material in that system, however, must be incorporated in the discharged state and thereafter charged. Furthermore, because of corrosion problems in stainless steel, an aluminum grid is required to withstand the initial charging voltage.

Lithium-cobalt oxide ($LiCoO_2$) and lithium-cobalt-nickel oxides ($LiCo_{1-y}Ni_yO_2$) ($0 \leqq y \leqq 1$) are described for use as electrodes for rechargeable lithium cells by R. J. Gummow and M. M. Thackeray in "Characterization of LT-$Li_xCo_{1-y}Ni_yO_2$ Electrodes for Rechargeable Lithium Cells", J. Electrochem. Soc., Vol. 140, No. 12, December (1993). They describe the use of acid leaching to improve the recycling properties of certain materials. Data supplied in the reference for the charge/discharge profiles of acid leached LT (Low Temperature) $LiCoO_2$, however, shows achievement of only about 63 mAh/g for the first discharge and this degrades quickly to <20 mAh/g in only four cycles. Certain Ni doped Li/LT-$LiCoNiO_2$ cells assembled in a charged state were found to be significantly more cycle tolerant. However, success was limited to Ni doped materials.

Thus, Li_xCoO_2 heretofore has been available for incorporation as a successful cathode material only in a fully discharged state because Li_xCoO_2 as it is known to exist in the charged state is not stable with respect to elevated temperatures normally required in the manufacturing environment. The batteries have, therefore, been assembled in the discharged state and charged prior to first use. The charging process has certain drawbacks. It results in the plating of an amount of lithium from the cathode onto the anode, and batteries have had to be designed to accommodate the extra lithium plated out of the cathodes during the initial charging after assembly; otherwise, internal shorting of the battery could be a problem. Also, the high voltage required to the initial charging of the battery has required the cathode collector to be made from aluminum rather than the preferred material, stainless steel. Other approaches have been tried to improve the cycle efficiency of Li_xCoO_2. Electrochemical titration has been used on pre-fabricated cathodes to obtain charged Li_xCoO_2 material. However, this process has been used with limited success as it produces only limited quantities of charged material and the final products have to be determined by the pre-fabricated shapes and compositions.

Accordingly, it is a primary object of the present invention to provide a synthesis for charged Li_xCoO_2 (0<X<1) suitable for use as the cathode active material in primary and secondary battery applications.

It is a further object of the present invention to provide a synthesis for charged Li_xCoO_2 (0<X<1) for primary and secondary cell applications in which the charged material is in a stable powdered form which can than be shaped and incorporated in any composition of cathode desired.

Other objects and advantages with respect to the present invention will occur to those skilled in the art through familiarity with the specification and claims herein.

SUMMARY OF THE INVENTION

The present invention provides a new cathode process in which charged Li_xCoO_2 cathodes can be manufactured in an efficient and cost-effective manner. The product is superior to acid-treated embodiments, delivering twice the capacity of those materials with improved cycling efficiency. The positive current collector for the cathode is not limited to aluminum. It may be stainless steel. The present invention provides a process to manufacture charged Li_xCoO_2, preferably where $0 \leqq x \leqq 0.5$, in a powdered form for use as a raw material in the subsequent manufacture of cathodes. The powdered form can be combined in any desired cathode composition and worked into any configuration or shape.

In the preferred process, pure $LiCoO_2$ commercially obtainable from FMC Corporation, for example, is used as the starting material. A small amount of solvent, for example, methyl formate (MF) is added to the $LiCoO_2$ powder to wet the powder and to form a wet slurry or paste. The material is then formed as a layer on a pre-cut metal grid, preferably of aluminum, and suitably provided with an electrical lead, and the surface thereafter smoothed. The pasted material is then sealed inside microporous separators which may be a polyethylene envelope which is itself thereafter sandwiched between two sections of lithium anode of approximately the same dimensions also provided with electrical connections. The three-plate stack which itself forms a large lithium cell is then confined in an alluminated trilaminated envelope with anode and cathode leads protruding out from the envelope. Next, electrolyte is injected into the bag and the large cell charged. After charging the desired amount, the cell is opened in a dry room and the cathode envelope opened and the material rinsed with solvent and vacuum dried.

The charged Li_xCoO_2 powder is now ready to be removed from the original aluminum charging grid and utilized in a cathode mixture in any manner desired. The value of x can be controlled by the amount of coulombic titration. and is preferably less than about 0.5.

The charged material is still in powdered form and can be used as raw cathode material for any batteries. The material is normally mixed with a conductive diluent such as carbon or graphite in a binder such as polytetrafluoroethylene (PTFE) and the cells can be used for primary or secondary applications without initial charging.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 represents the discharge performance of cells using the pre-charged $Li_{0.5}CoO_2$ cathodes in accordance with the invention at two discharge rates. 1 and 5 mA/cm^2;

FIG. 2 is a graphical representation of cycle performance of pre-charged $Li_{0.5}CoO_2$ cells over ten cycles;

FIG. 3 is a discharge plot of pre-charged $Li_{0.5}CoO_2$ cells at 1 mA/cm^2 rate comparing aluminum and stainless steel current collectors;

FIG. 4 shows cycle performance of pre-charged $Li_{0.5}CoO_2$ cathode cells over ten cycles comparing aluminum and stainless steel current collectors; and

FIG. 5 is a perspective schematic view with parts broken away of a charging system for producing pre-charged Li_xCoO_2 in accordance with the invention.

DETAILED DESCRIPTION

The present invention enables the advantages associated with the unusually high energy density of Li_xCoO_2 cathode material to be incorporated in a pre-charged state by subjecting it to a pre-charging process prior to incorporation in the cathode mixture. The process makes use of Li_xCoO_2 in the uncharged state and transforms it into a pre-charged Li_xCoO_2 ($0<x<1$) powdered raw cathode material for incorporation in a cathode mix suitable for any battery. primary. secondary. etc. in which such cathode material is desired. As a powder. the material can be worked into any shape or mixture combination required.

A system for pre-charging the $LiCoO_2$ powder for use as the cathode active material according to the invention is depicted in FIG. 5. The charging system generally takes the form of a rather large lithium cell shown generally at **10** and includes a metallic retaining shell having a retaining rim as shown at **12** which may be stainless steel and which further supports a metallized plastic bag **14**. preferably a trilaminated envelope having an aluminized inner surface (not shown). Protruding anode and cathode leads shown respectively at **16** and **18** are designed for external connection to a source of charging voltage. The $LiCoO_2$ **20** is pressed onto both sides of the metallic grid. preferably aluminum. **22**. Grid **22** which with a pair of semipermeable microporous polymer separators **24** is sandwiched between a pair of lithium anodes **26** with metallic. preferably nickel. current collectors **28**. This forms what is known as a three-plate stack cell with the cathode material sandwiched between a pair of large area anodes. This may be covered by a layer of material such as Tefzel 30 within the trilaminated metallized envelope **14**.

In the preferred embodiment of the process. finely divided $LiCoO_2$ powder. approximately −325 mesh. obtained in a substantially pure form from FMC Corporation. is combined with a small amount of solvent. such as methyl formate (MF). to form a heavy slurry or paste. The paste is then spread onto both sides of the pre-cut metallic grid **22** which is of a metal which can withstand the required charging voltage without corroding. such as aluminum. The thickness of the paste is typically 0.25" and that of the grid is 0.01". The surface of the paste may be made generally smooth using a stainless steel plate. or the like. The pasted material is then sealed inside separators **24** which may each be a layer of microporous polymer material. normally a polyethylene envelope. represented by separators which itself is thereafter sandwiched between the pair of lithium anodes **26** with nickel grids **28**. This sandwich or three-plate stack is thereafter confined inside the metallized (aluminized) trilaminated envelope (which may be polyethylene terephthalate). An electrolyte material is then injected into the bag to activate the cell. The electrolyte is preferably a 2 molar double salt methyl formate ($LiAsF_6+LiBF_y$) system but any suitable material including methyl acetate may be employed. The cell is typically charged at a potential of 4.3 volts. After charging. one trilaminated envelope was opened in a dry room and the internal cathode envelope cut open and the material rinsed with solvent and vacuum dried. The result was a charged Li_xCoO_2 powder in ready-to-use form in which the value of x can be controlled by the amount of coulombic titration and is preferably less than 0.5.

The typical grid size used experimentally has been about 9 cm by 19 cm which can process about 100 grams of $LiCoO_2$. This is enough material for about 25 size "AA" rechargeable $Li_{0.5}CoO_2$ cells. The system works well for fairly high production rates. The normal charging voltage is about 4.3V and about 5 mA of current. The metallized trilaminate envelope may be any compatible gas-tight system which is easy to apply and remove in the process.

As can be seen from the above. the construction of the cell charging system is simple and inexpensive and the charged material requires no special handling. Desired quantities of conductive diluent. such as carbon or graphite. and binder. such as polytetrafluoroethylene (PTFE). can be added and the material .processed into the finished cathode. Such cathodes. of course. can be used for primary or secondary applications without the initial charging $LiCoO_2$ requires.

The discharge performance of pre-charged $Li_{0.5}CoO_2$ cathodes is depicted in FIG. 1 for the discharge rates of 1 and 5 mA/cm^2. In addition. the delivered capacity. which was 113 mAh/g based on total cathode weight. is quite comparable to the typical delivered capacity of approximately 120 mAh/g $LiCoO_2$ after charging a cell manufactured in the discharge state. FIG. 2 confirms that the material is cyclable and so suitable for use in secondary cells.

The materials as processed in accordance with the present invention represent a drastic improvement over the acid leached materials previously known and are comparable to materials utilized in the cells previously assembled in the uncharged state. In addition. the positive current collector material for the cathode need not be limited to aluminum in the case of the pre-charged material and can be made from stainless steel or other materials. It had previously been found that stainless steel corroded because of the high required charging voltages in cells built with the discharged $LiCoO_2$ cathodes. FIGS. 3 and 4 compare cells utilizing aluminum and stainless steel positive current collectors. FIG. 3 depicts discharge performance of pre-charged $Li_{0.5}CoO_2$ at 1 mA/cm^2 during four discharge cycles. The Figure shows that results are comparable using either material as the positive current collector. FIG. 4 makes a similar comparison for secondary cell cycling and indicates that either material would also be satisfactory in this respect.

This invention has been described herein in considerable detail in order to comply with the Patent Statutes and to provide those skilled in the art with the information needed to apply the novel principles and to construct and use embodiments of the example as required. However. it is to be understood that the invention can be carried out by specifically different devices and that various modifications can be accomplished without departing from the scope of the invention itself.

We claim:

1. A method of preparing a cathode incorporating heat stabilized charged Li$_x$CoO$_2$ as the cathode active material comprising the steps of:

(a) preparing the cathode active material by:
  (1) providing a layer of particulate Li$_x$CoO$_2$ on a metallic current collector.
  (2) subjecting the Li$_x$CoO$_2$ on said current collector to a charging current voltage to plate out Li and produce charged Li$_x$CoO$_2$ ($0<x<1$). and
  (3) separating the charged particulate material from said current collector: and

(b) incorporating said particulate cathode active material in the cathode.

2. The method of claim 1 wherein ($0<x \leqq 0.5$) after charging.

3. The method of claim 1 wherein the charging voltage is from about 4.2 to about 4.3 volts.

4. The method of claim 1 wherein said current collector is aluminum.

5. The method of claim 1 wherein said charged particulate material is combined with quantities of a conductive diluent material.

6. The method of claim 5 wherein said diluent material is a form of carbon.

7. The method of claim 5 further comprising the step of combining said charged particulate material with a binder.

8. The method of claim 6 wherein said charged particulate material is further applied to a stainless steel current collector material.

9. The method of claim 7 wherein said charged particulate material is further applied to a stainless steel current collector material.

10. A method of preparing a cathode containing heat stabilized. charged Li$_x$CoO$_2$ ($0<x<1$) as the active material comprising the steps of:

(a) preparing the active material by:
  (1) creating a layer of powdered Li$_x$CoO$_2$ from a solvent slurry thereof on a metallic collector grid.
  (2) sandwiching the collector grid between a pair of lithium members separated by semipermeable separator membranes to form a three-plate stack.
  (3) confining the three-plate stack cell in a gas-tight environment.
  (4) providing electrolyte to the three-plate stack:
  (5) charging the cell using externally supplied power until an amount of charge corresponding to a value of x. where $0<x<1$ is achieved. and
  (6) separating the charged particulate material from said collector grid: and

(b) combining said separated charged particulate Li$_x$CoO$_2$ material into a cathode mix for application to a current collector for use in a non-aqueous electrochemical cell.

11. The method of claim 10 wherein the gas-tight environment is a metallized coated polymer envelope.

12. The method of claim 10 wherein the metallic collector grid is aluminum.

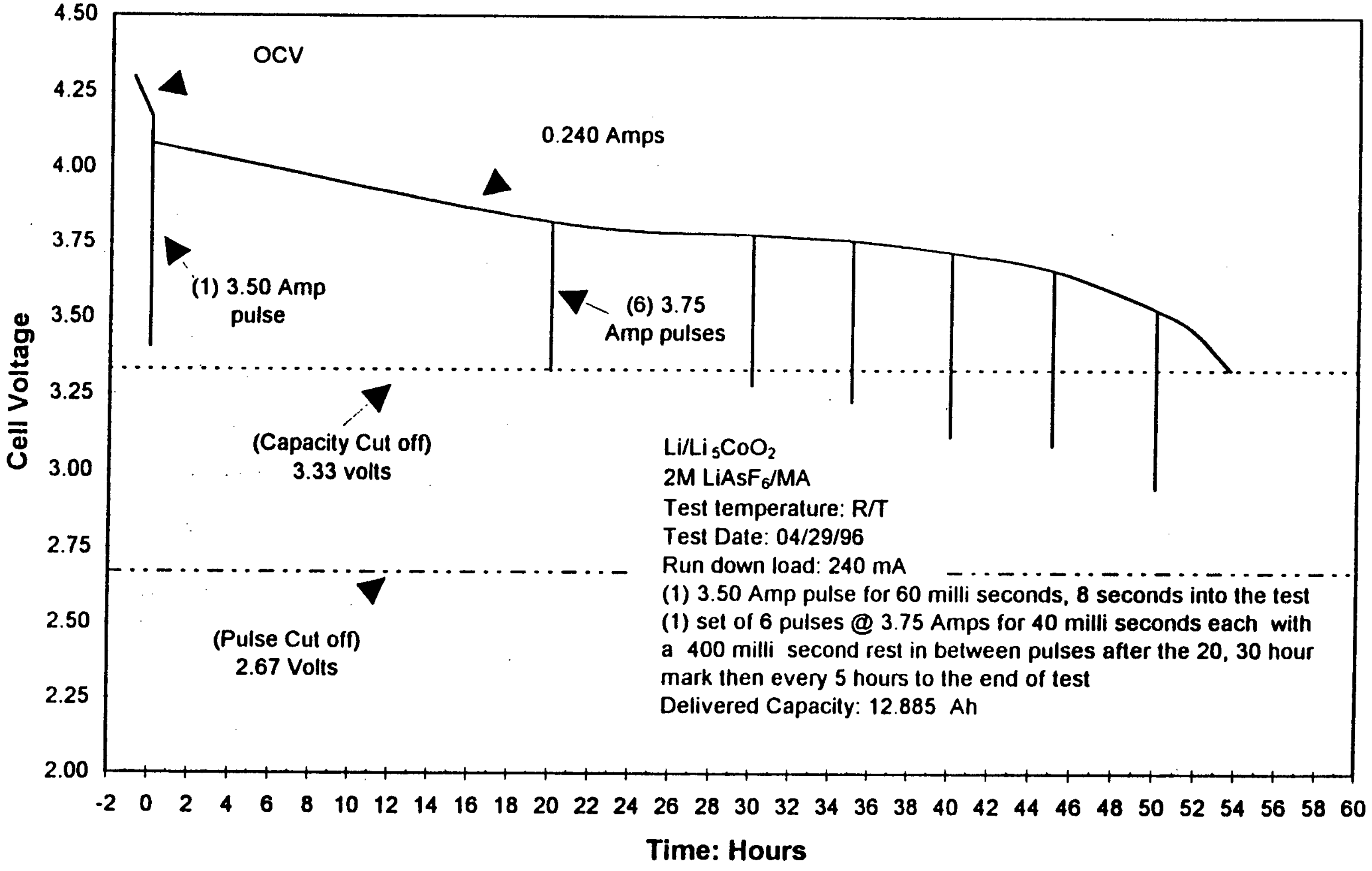
13. The method of claim 10 where $x \leqq 0.5$ after charging.

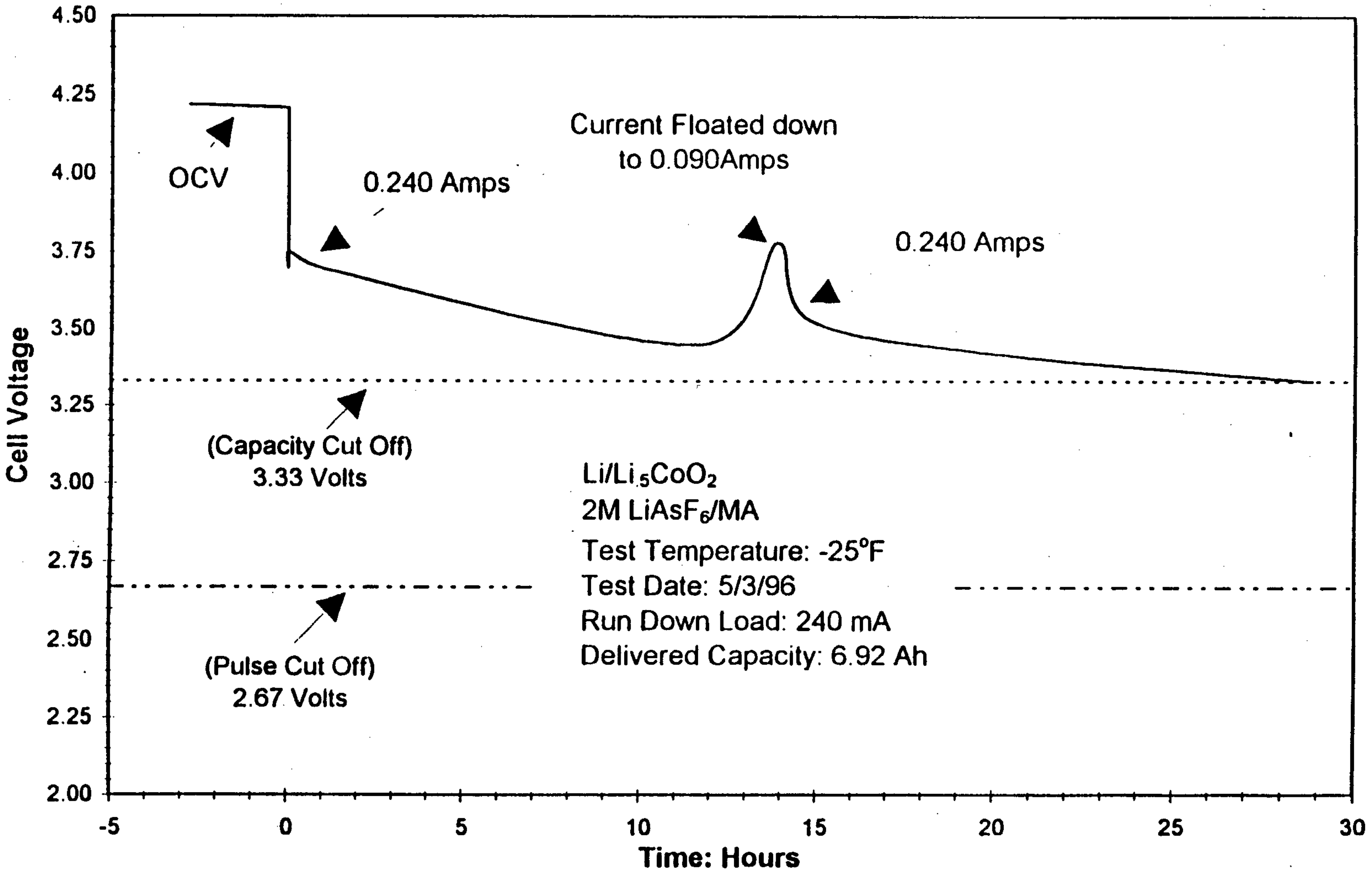
* * * * *

Appendix C

Compilation of Hermetic Cell Test Results

Pulse and Capacity Run Down Profile, Cell WAMH02

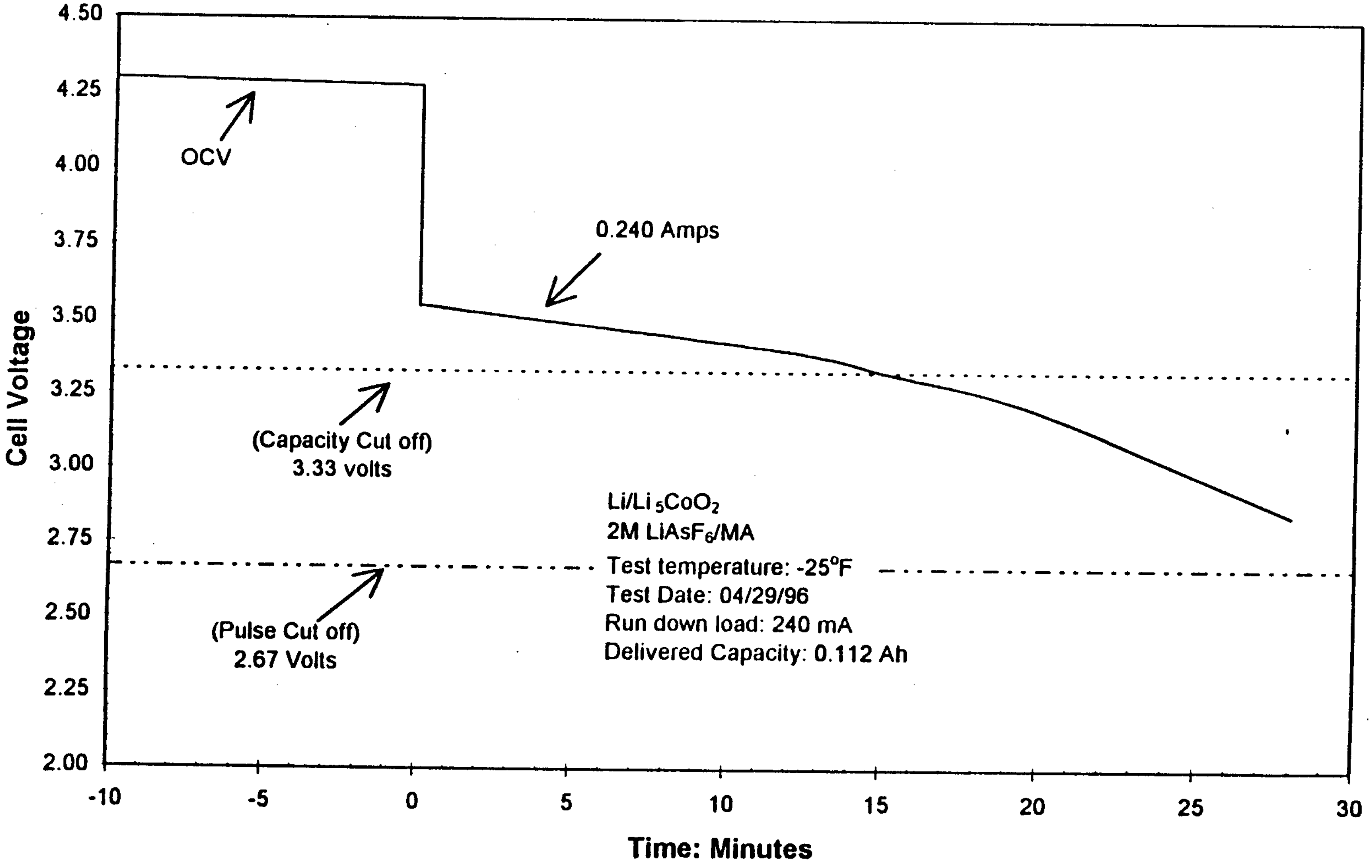




Pulse and Capacity Run Down Profile, Cell WAMH10

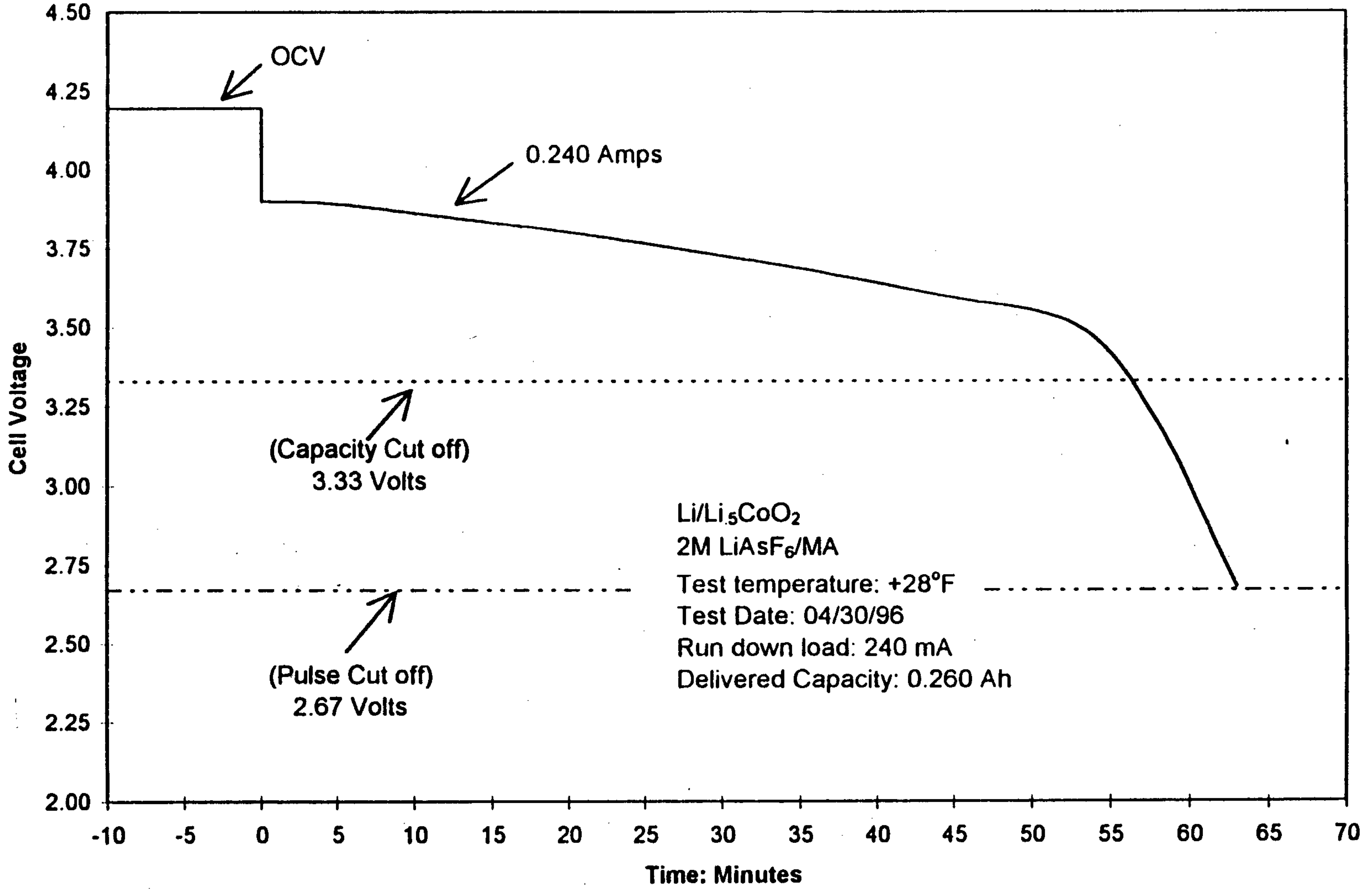
Pulse and Capacity Run Down Profile, Cell WAMH11

page 1 of 3



Pulse and Capacity Run Down Profile, Cell WAMH11

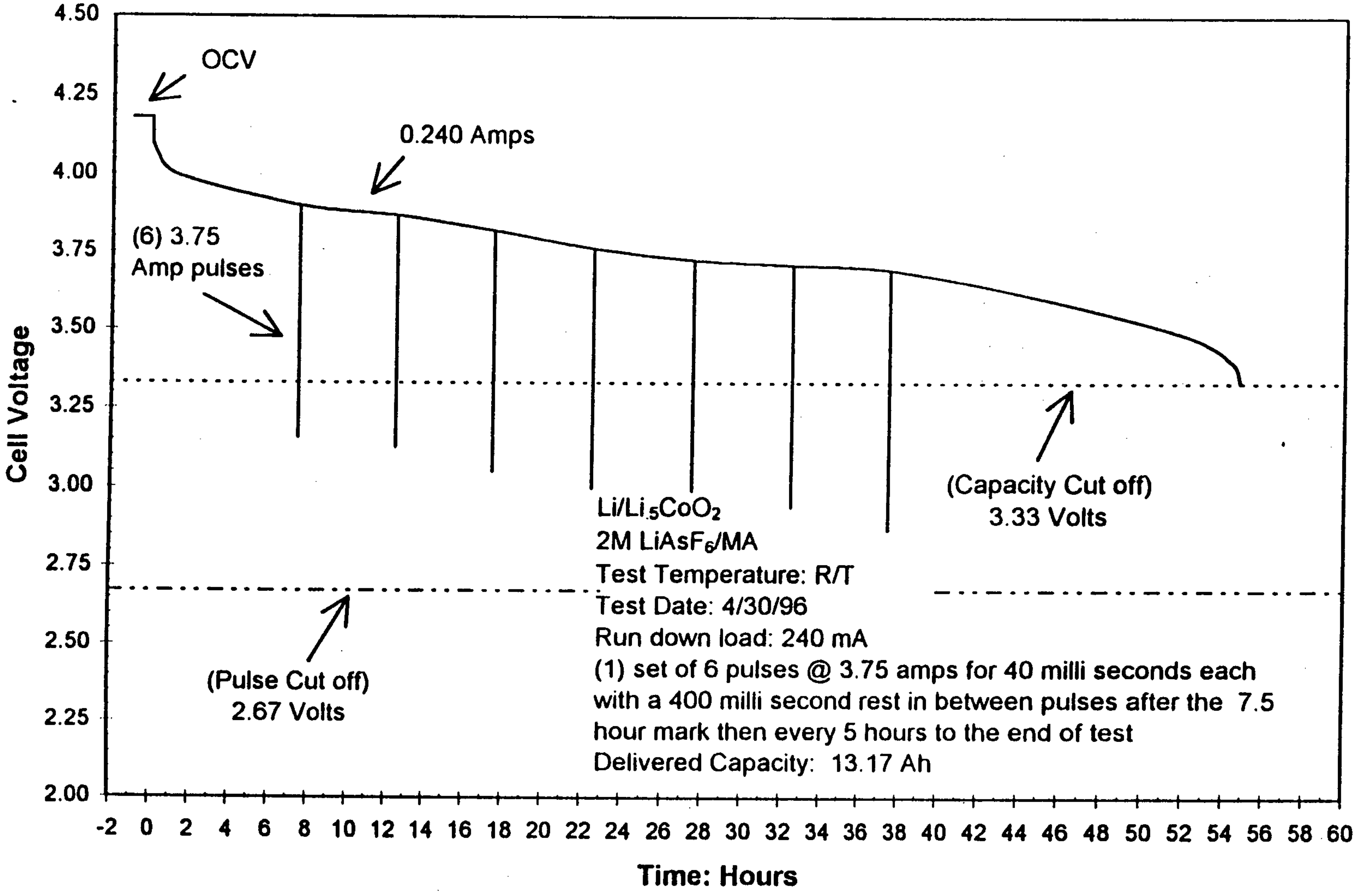
page 2 of 3



Li/Li$_{.5}$CoO$_2$
2M LiAsF$_6$/MA
Test temperature: +28°F
Test Date: 04/30/96
Run down load: 240 mA
Delivered Capacity: 0.260 Ah

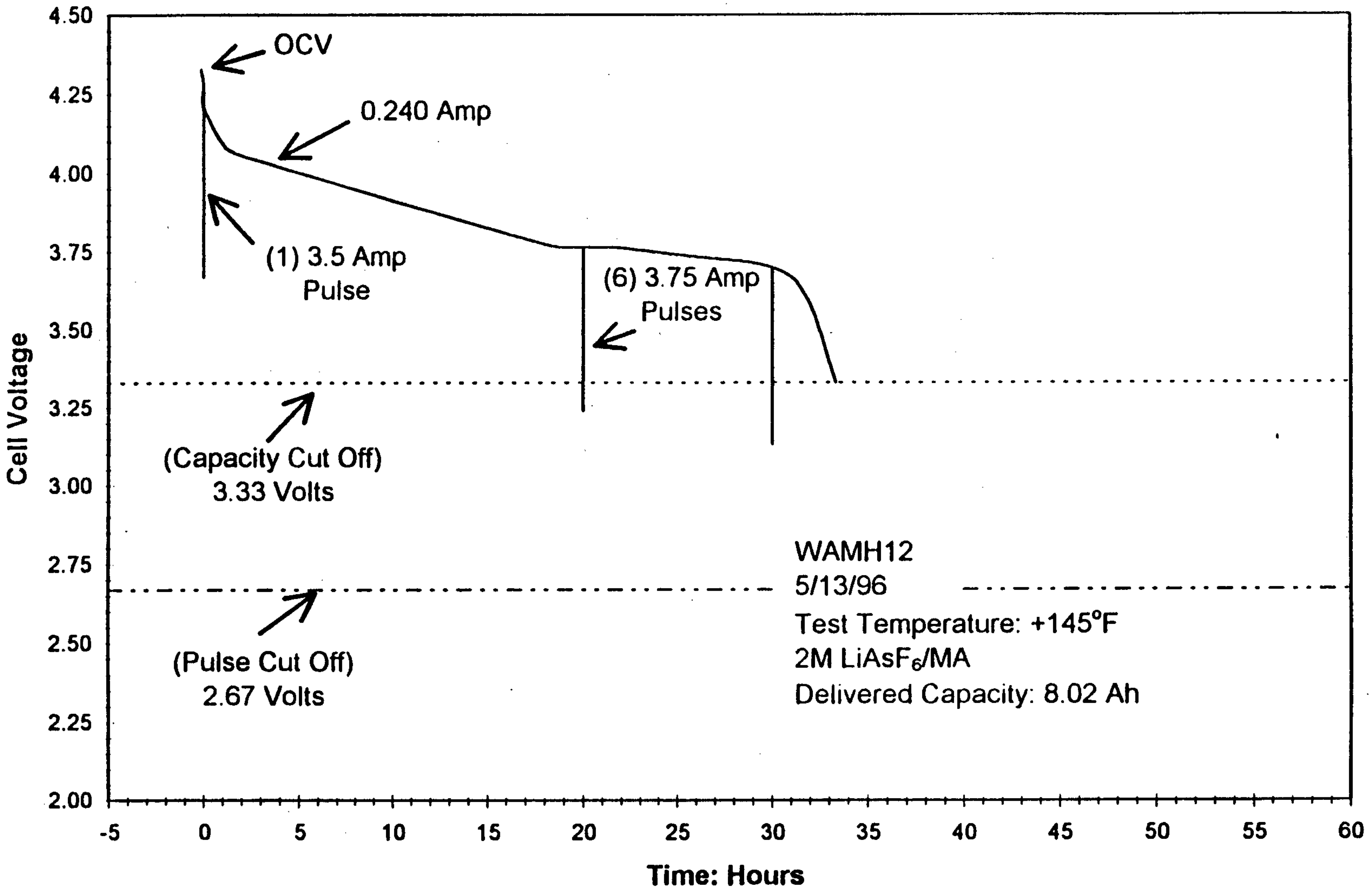
Pulse and Capacity Run Down Profile, Cell WAMH11

page 3 of 3

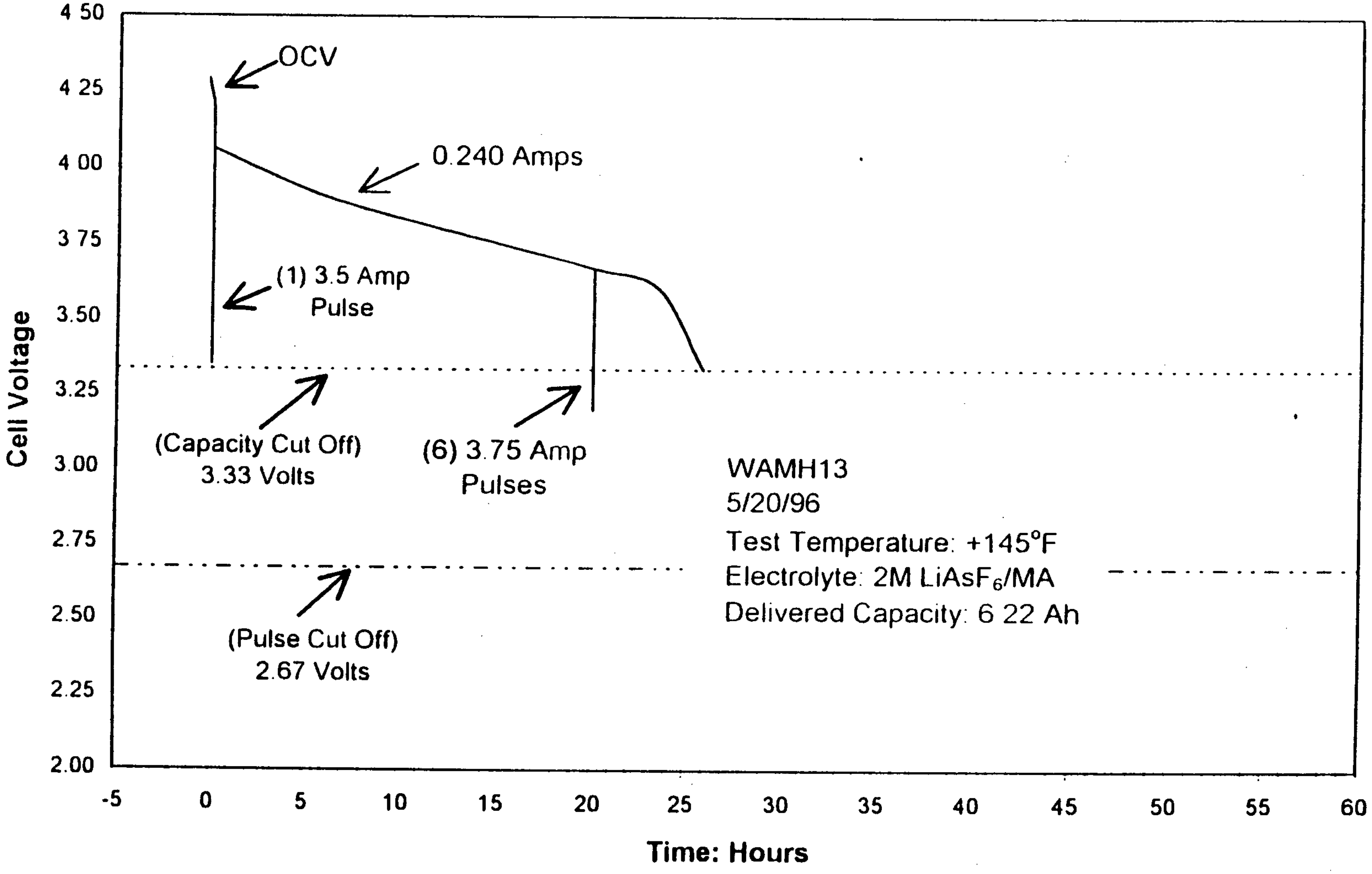


$Li/Li_{.5}CoO_2$
2M $LiAsF_6$/MA
Test Temperature: R/T
Test Date: 4/30/96
Run down load: 240 mA
(1) set of 6 pulses @ 3.75 amps for 40 milli seconds each with a 400 milli second rest in between pulses after the 7.5 hour mark then every 5 hours to the end of test
Delivered Capacity: 13.17 Ah

Pulse and Capacity Run Down Profile, WAMH12

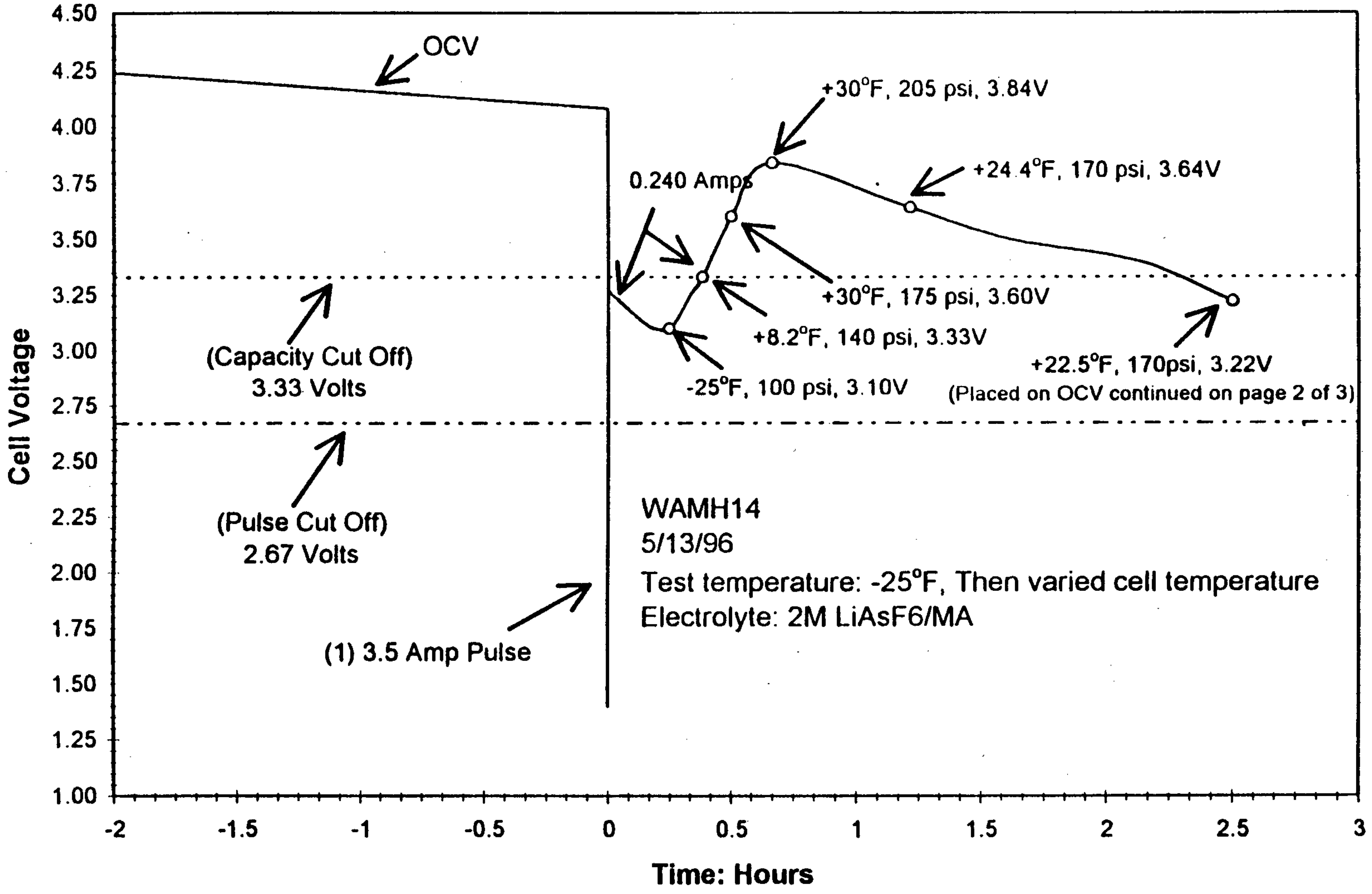


Pulse and Capacity Run Down Profile, WAMH13



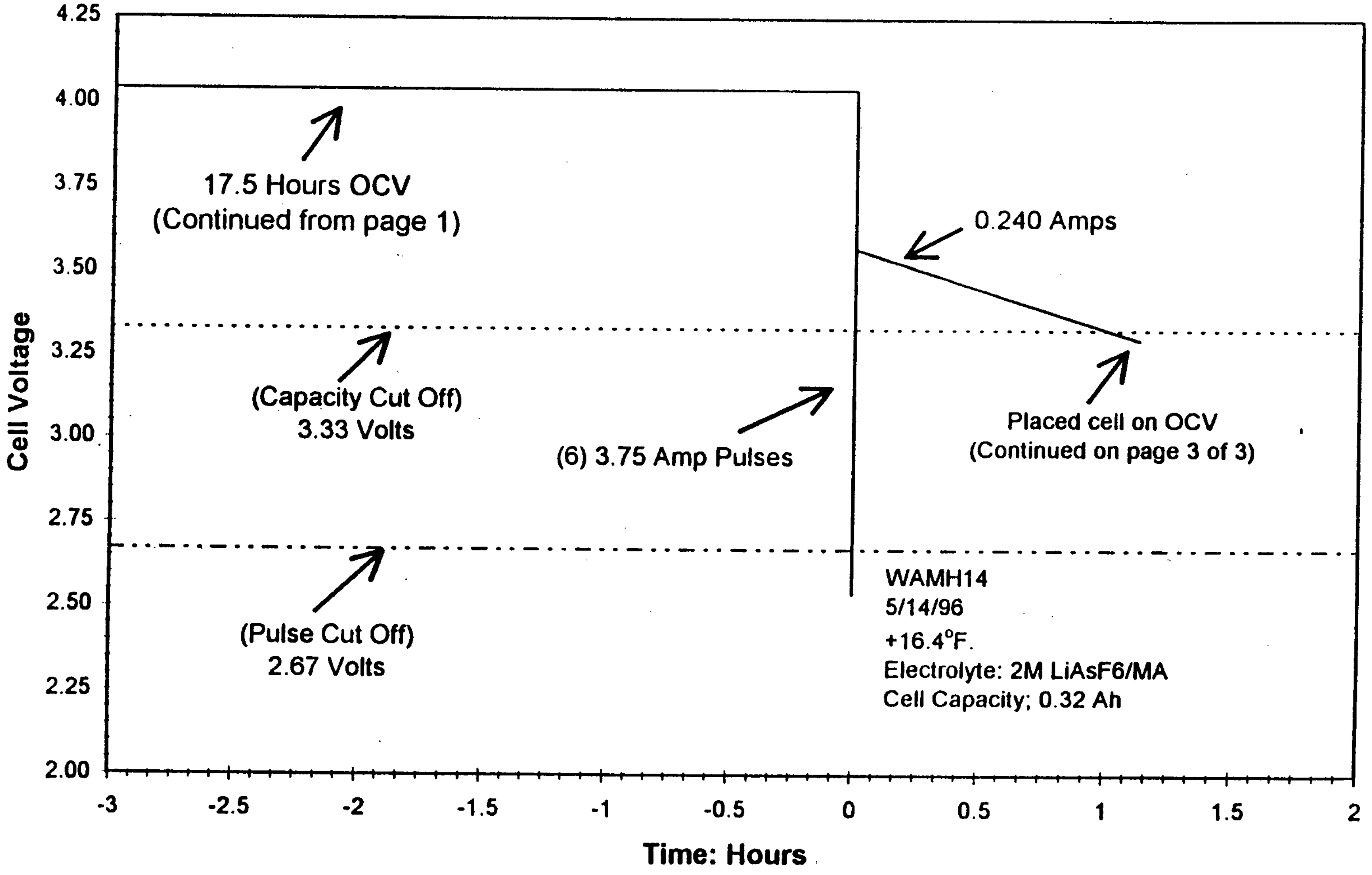
Pulse and Capacity Run Down, WAMH14

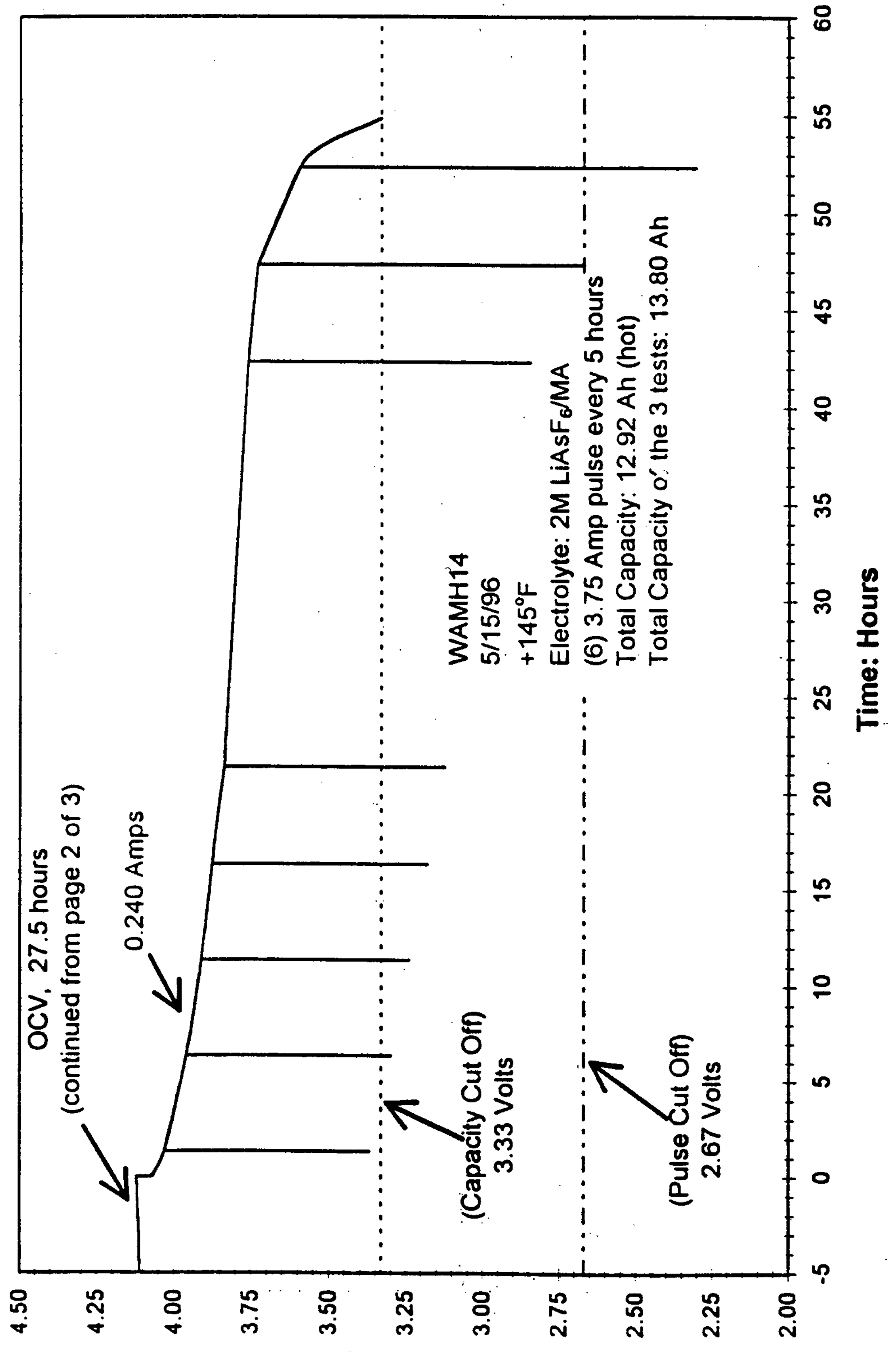
Page 1 of 3



Pulse and Capacity Run Down, WAMH14

Page 2 of 3





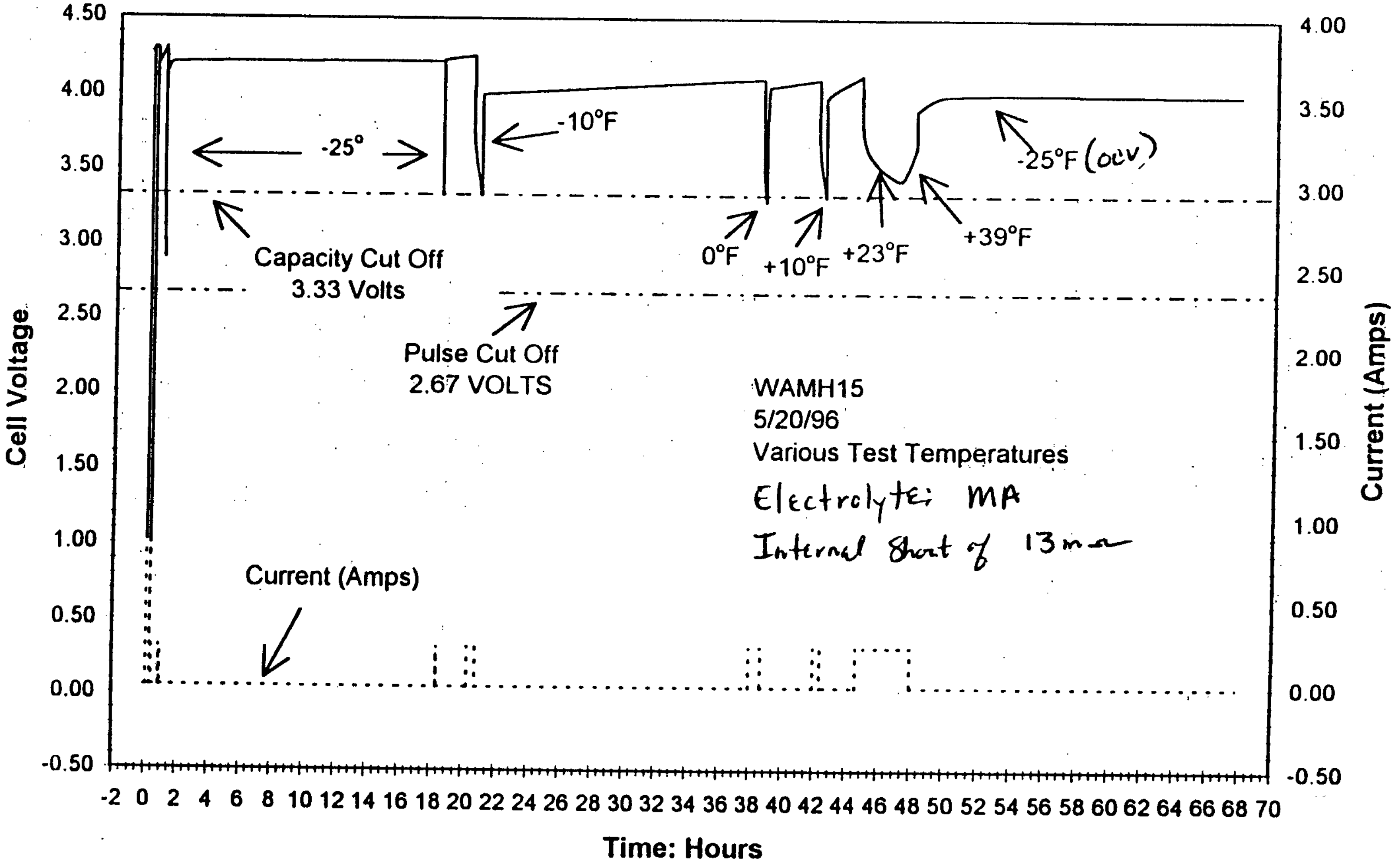
Pulse and Capacity Run Down Profile, WAMH14

Page 3 of 3

WAMH14
5/15/96
+145°F
Electrolyte: 2M $LiAsF_6$/MA
(6) 3.75 Amp pulse every 5 hours
Total Capacity: 12.92 Ah (hot)
Total Capacity of the 3 tests: 13.80 Ah

Pulse and Capacity Run Down Profile, WAMH15

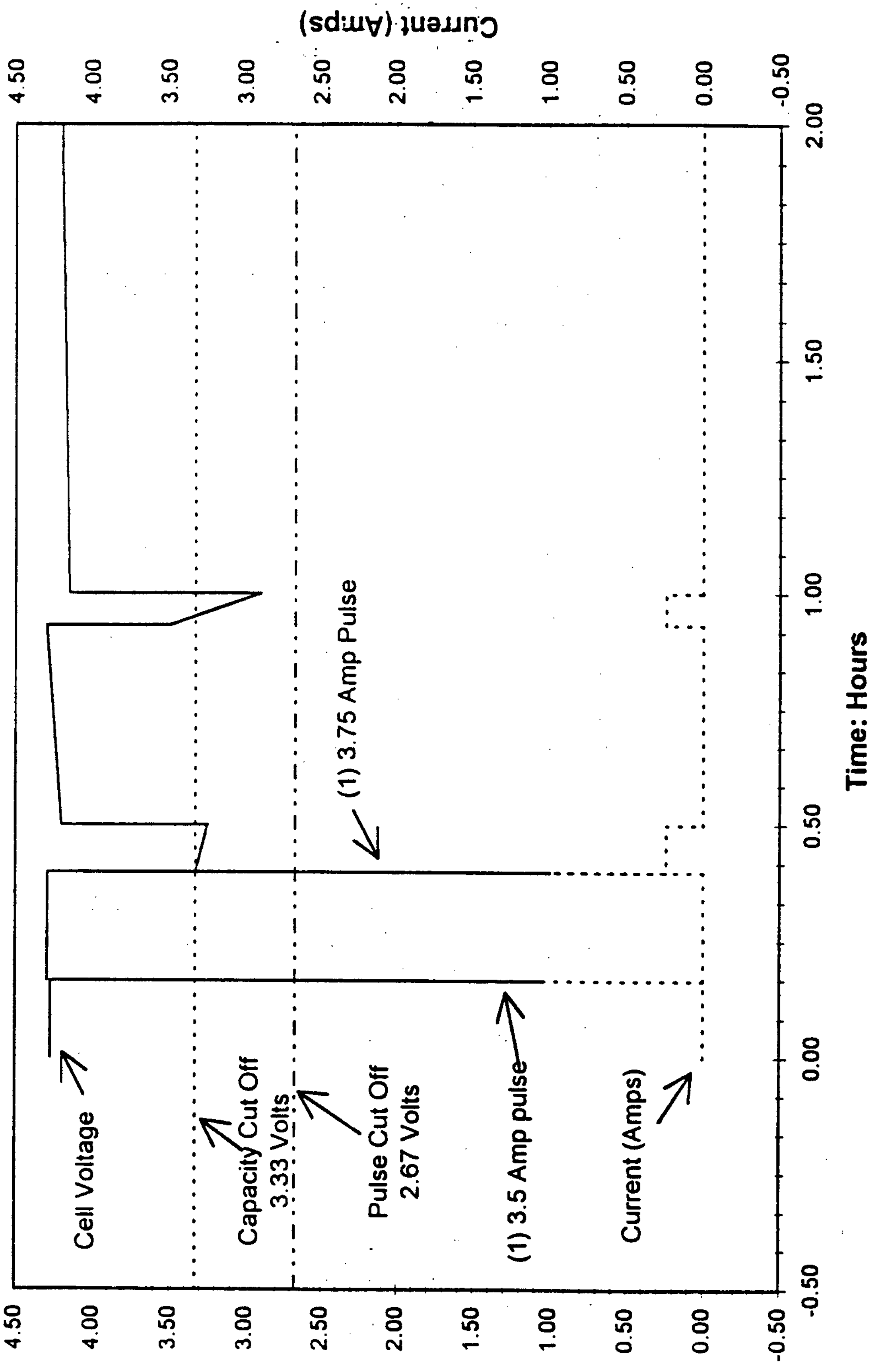
Page 1 of 5



WAMH15
5/20/96
Various Test Temperatures
Electrolyte: MA
Internal Short of 13 ma

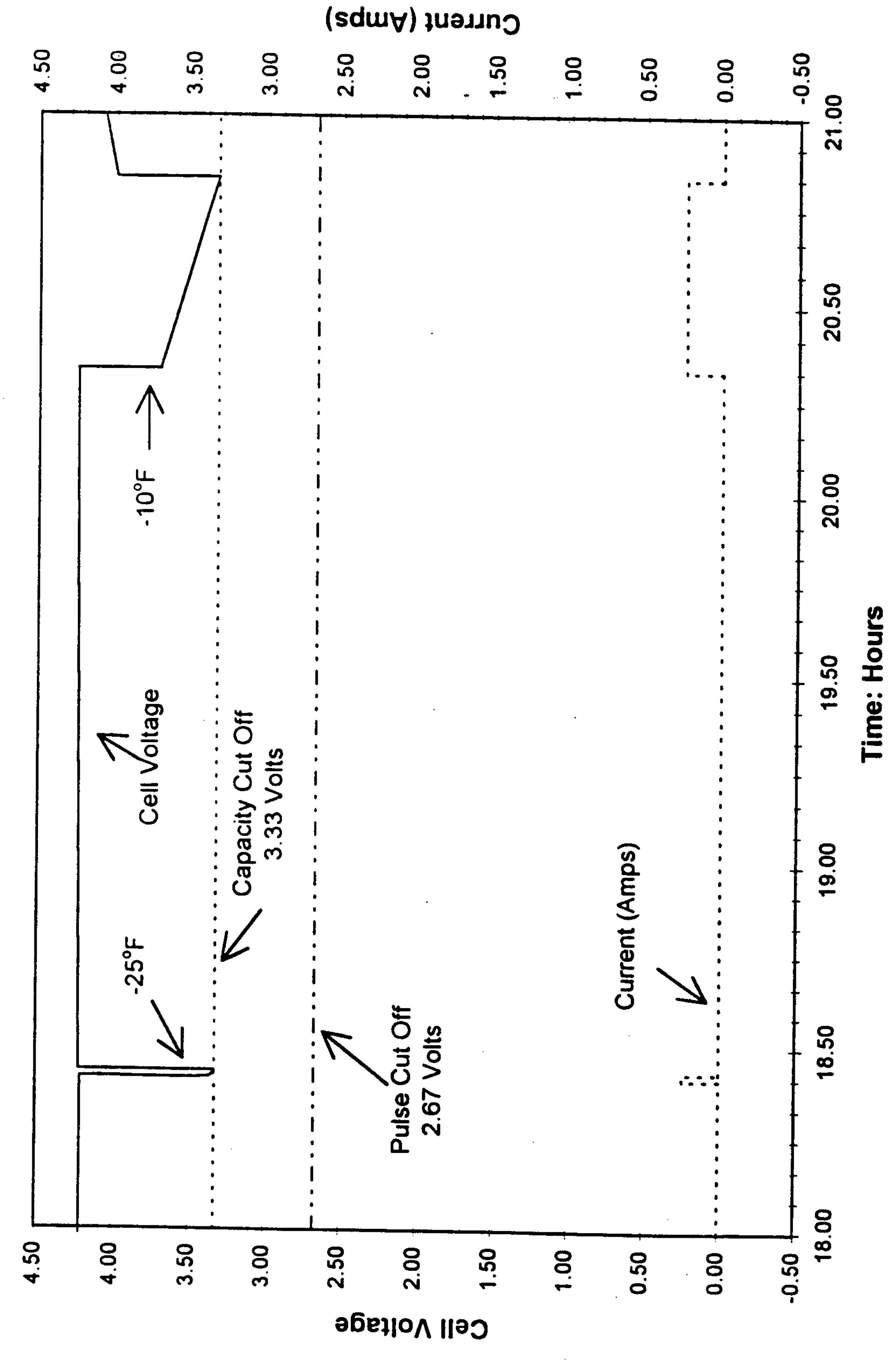
Pulse and Capacity Run Down Profile, WAMH15

page 2 of 5



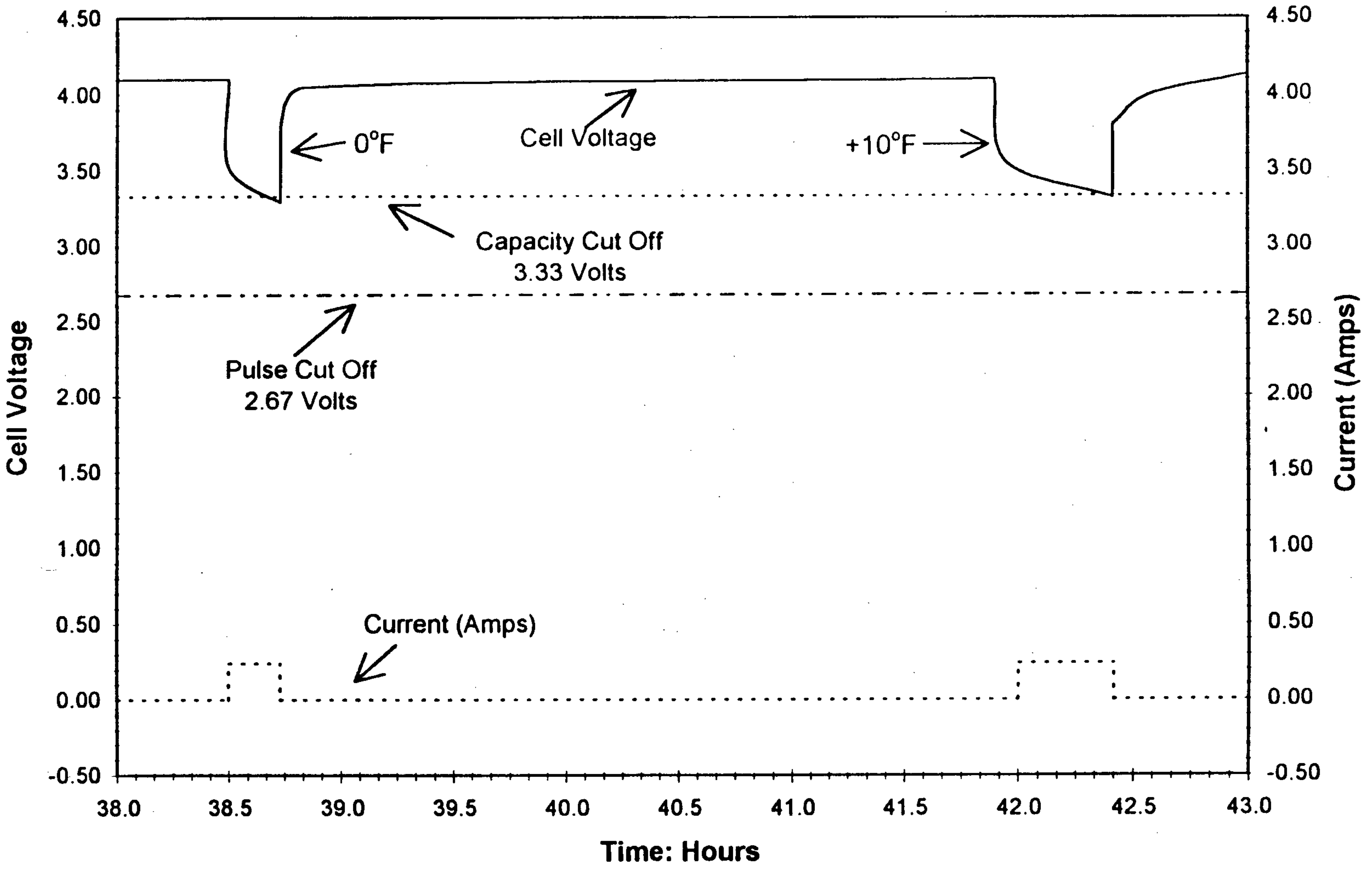
Pulse and Capacity Run Down Profile, WAMH15

page 3 of 5



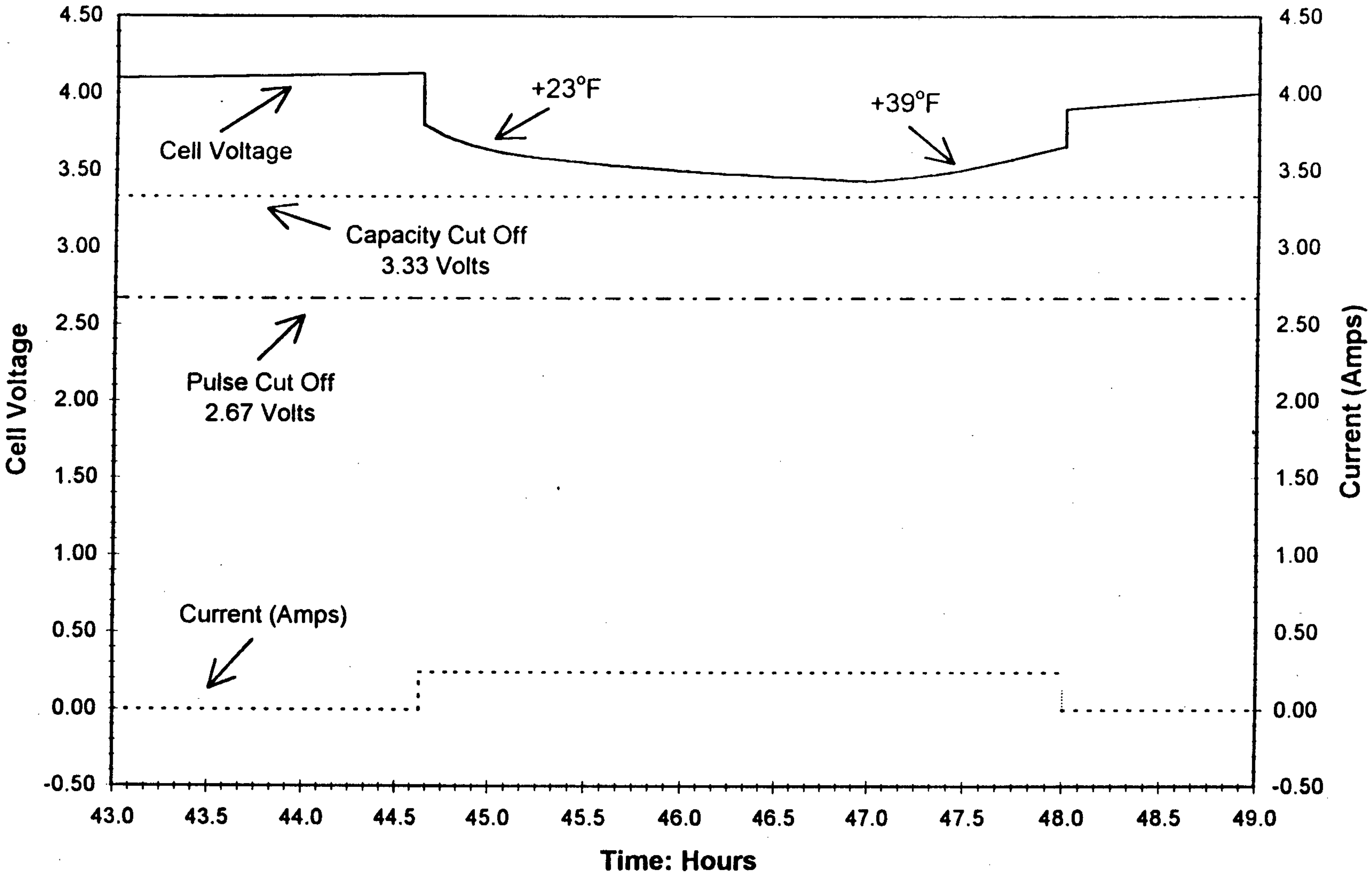
Pulse and Capacity Run Down Profile, WAMH15

page 4 of 5



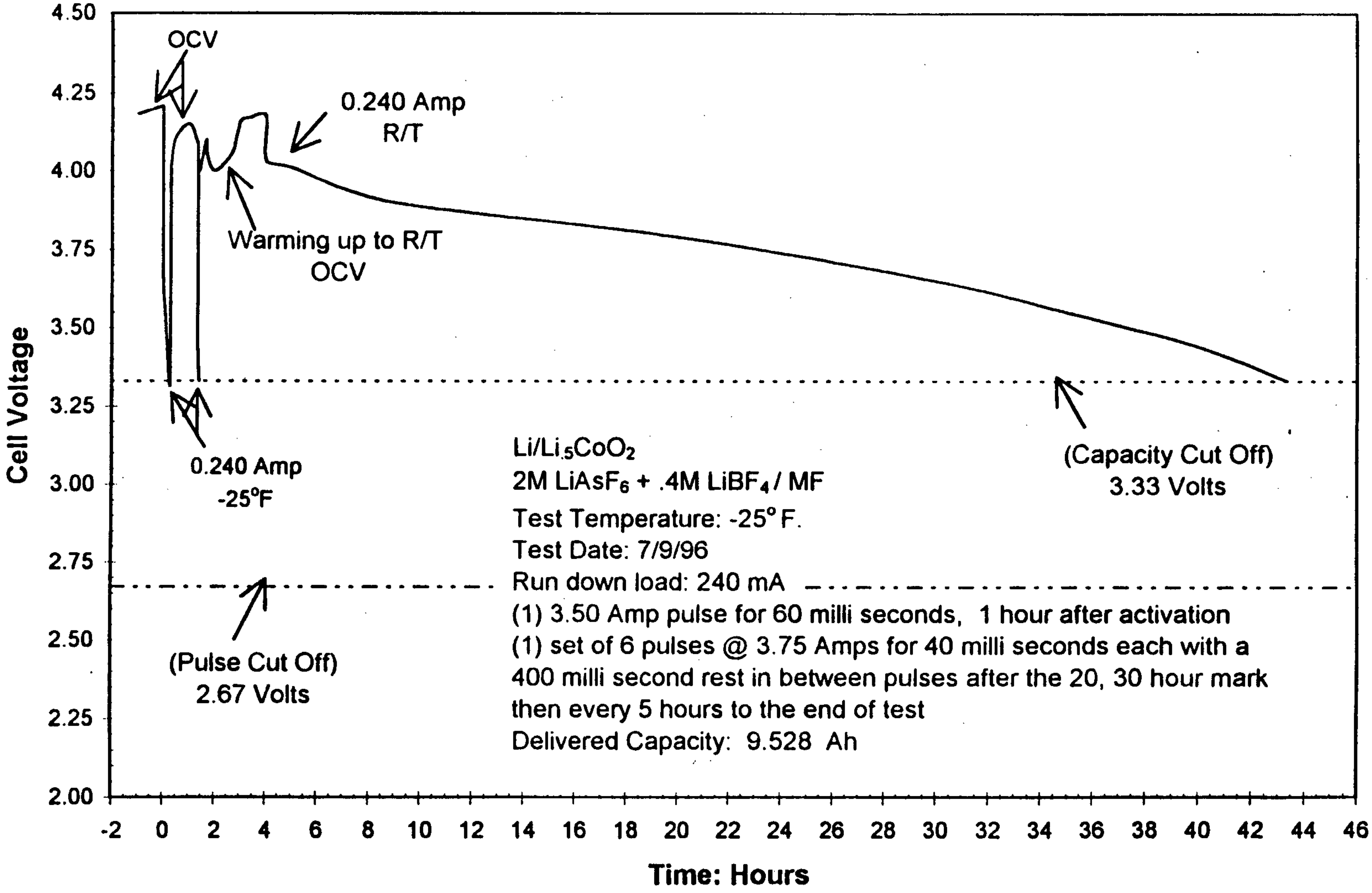
Pulse and Capacity Run Down Profile, Cell WAMH15

page 5 of 5



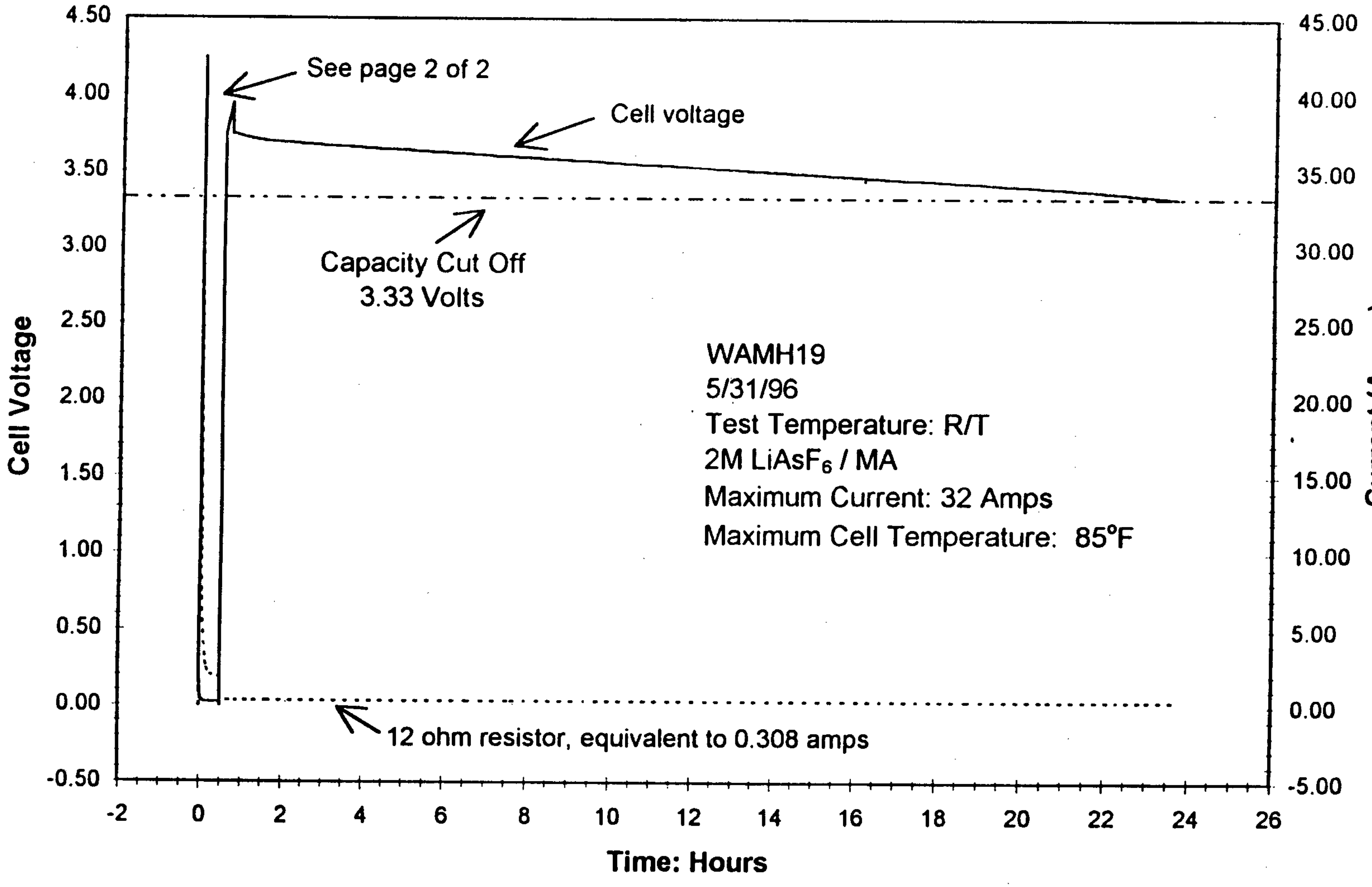
Pulse and Capacity Run Down Profile, WAMH16

3 Month Storage @ R/T



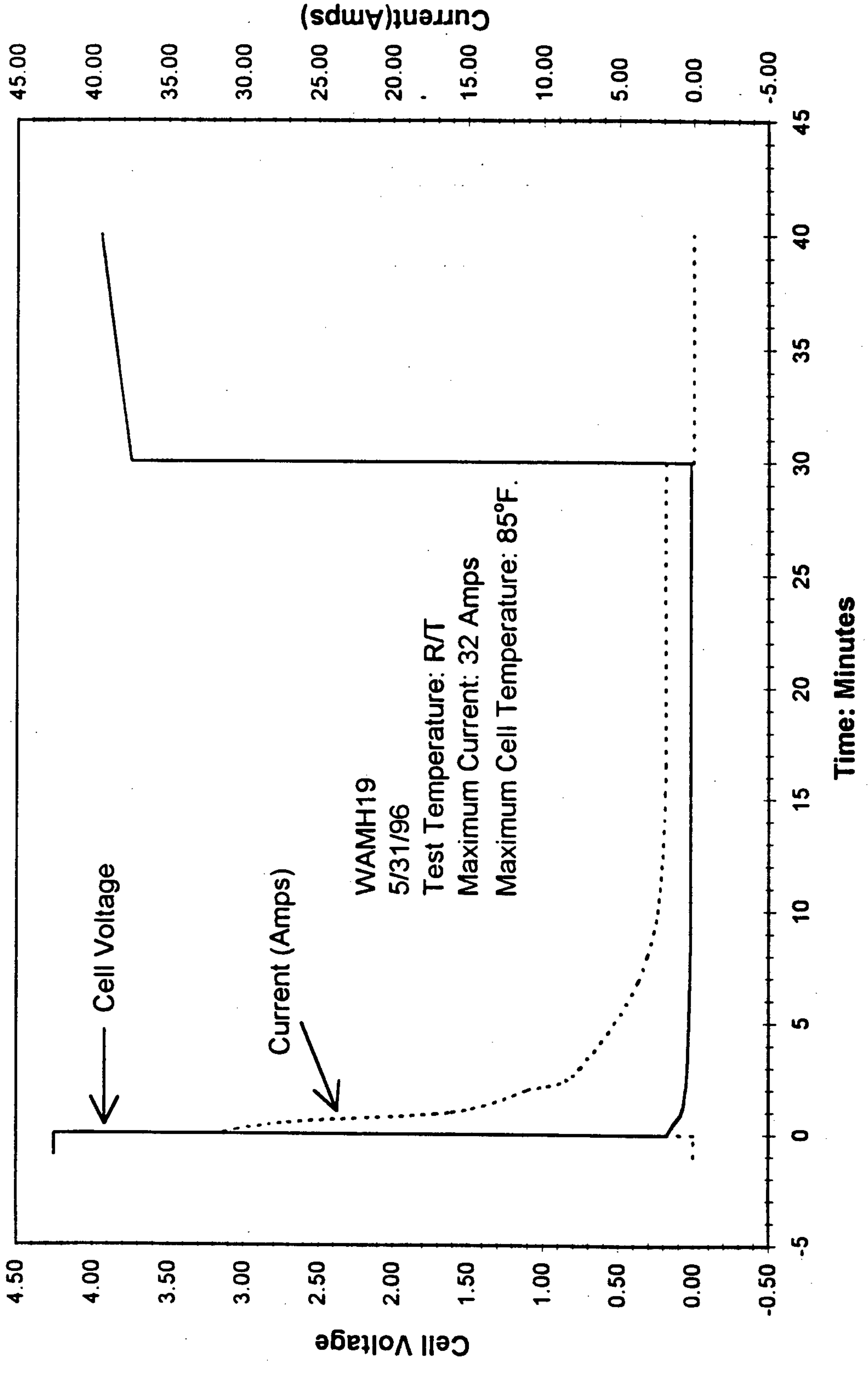
External Short Circuit Test, WAMH19

page 1 of 2



H-WAM External Short Circuit Test, WAMH19

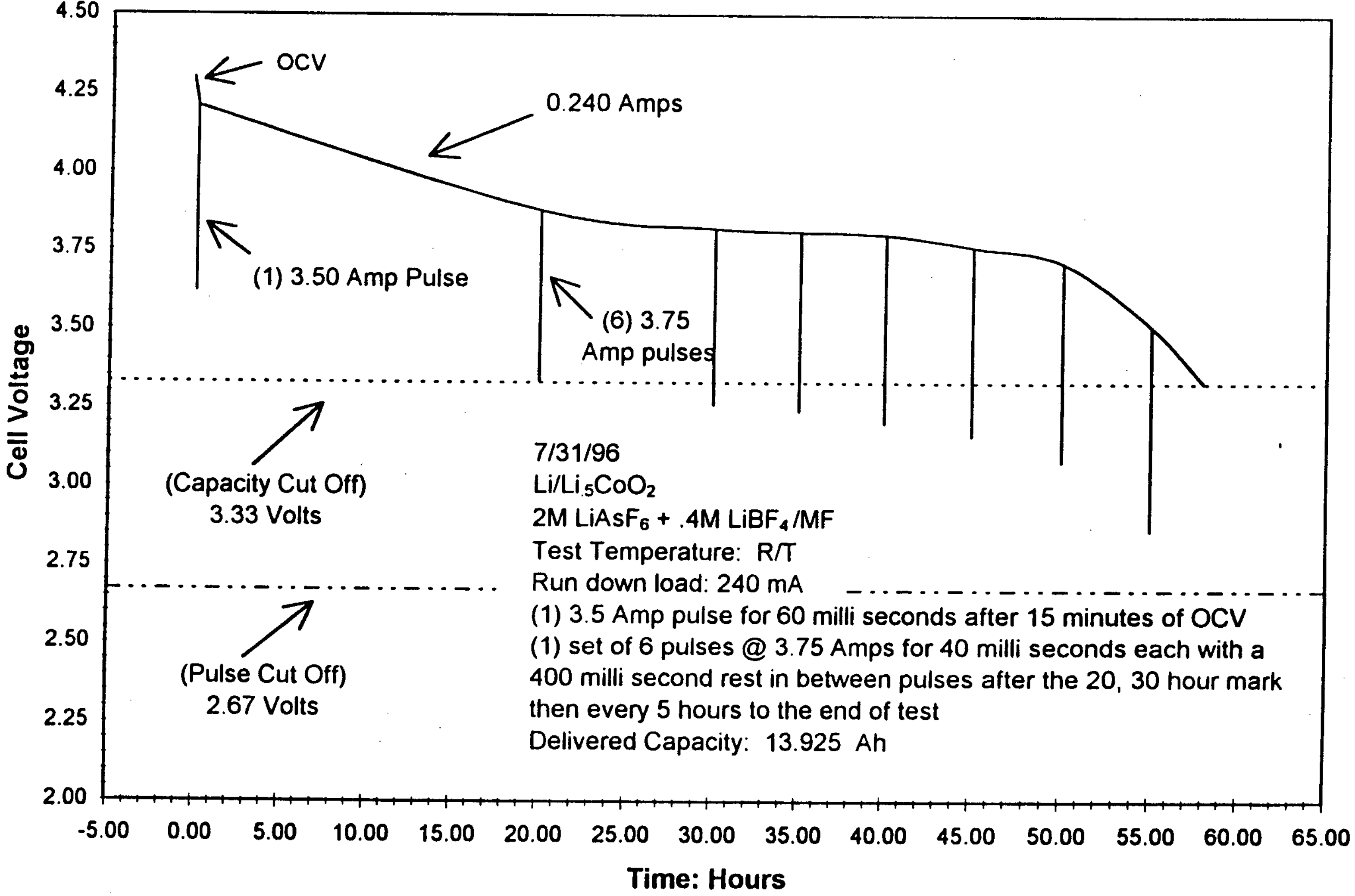
page 2 of 2



WAMH19
5/31/96
Test Temperature: R/T
Maximum Current: 32 Amps
Maximum Cell Temperature: 85°F.

Pulse and Capacity Run Down Profile, WAMH21

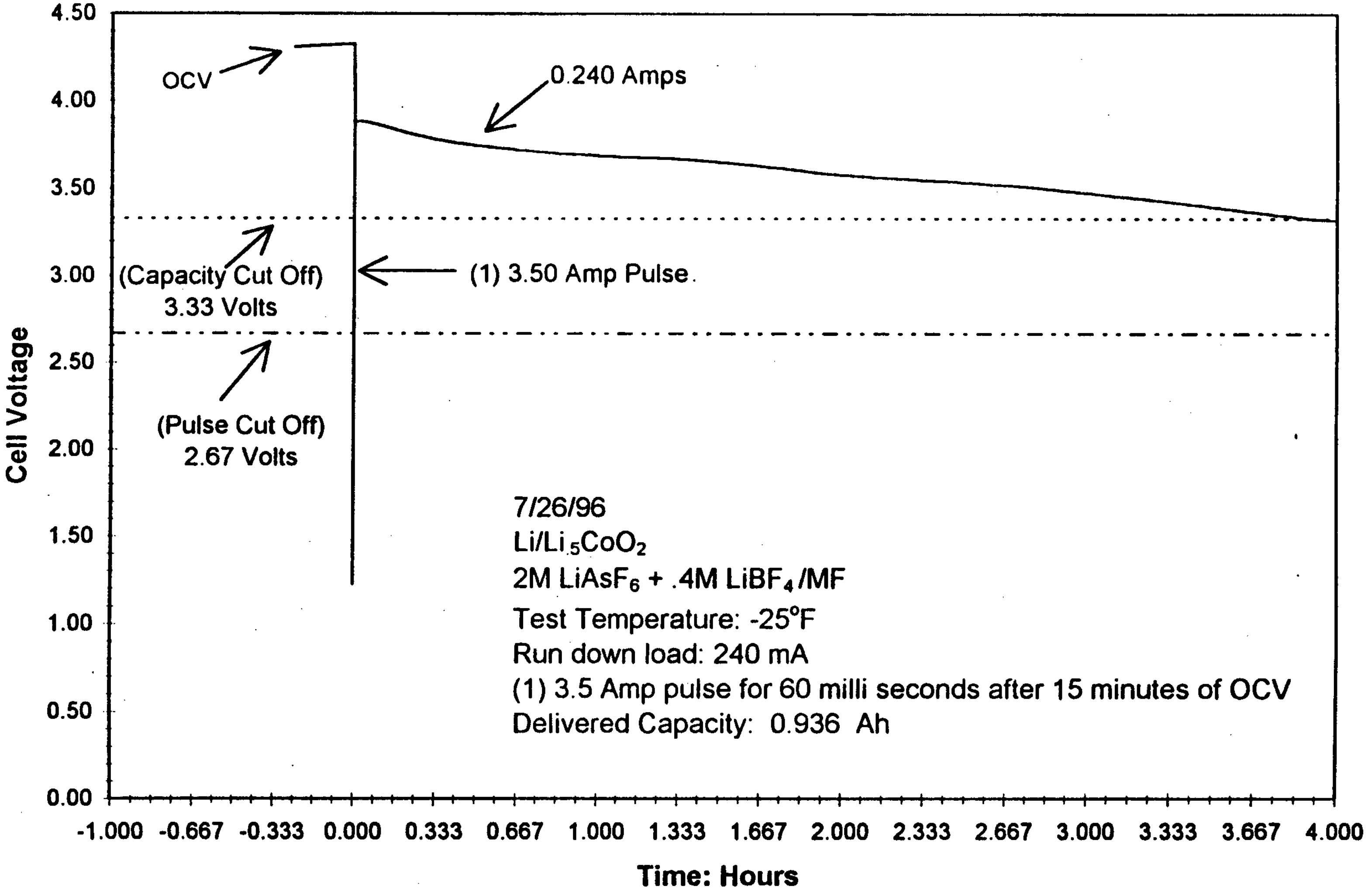
3 Month Storage @ -65°F



7/31/96
Li/Li$_5$CoO$_2$
2M LiAsF$_6$ + .4M LiBF$_4$/MF
Test Temperature: R/T
Run down load: 240 mA
(1) 3.5 Amp pulse for 60 milli seconds after 15 minutes of OCV
(1) set of 6 pulses @ 3.75 Amps for 40 milli seconds each with a 400 milli second rest in between pulses after the 20, 30 hour mark then every 5 hours to the end of test
Delivered Capacity: 13.925 Ah

Pulse and Capacity Run Down Profile, WAMH23

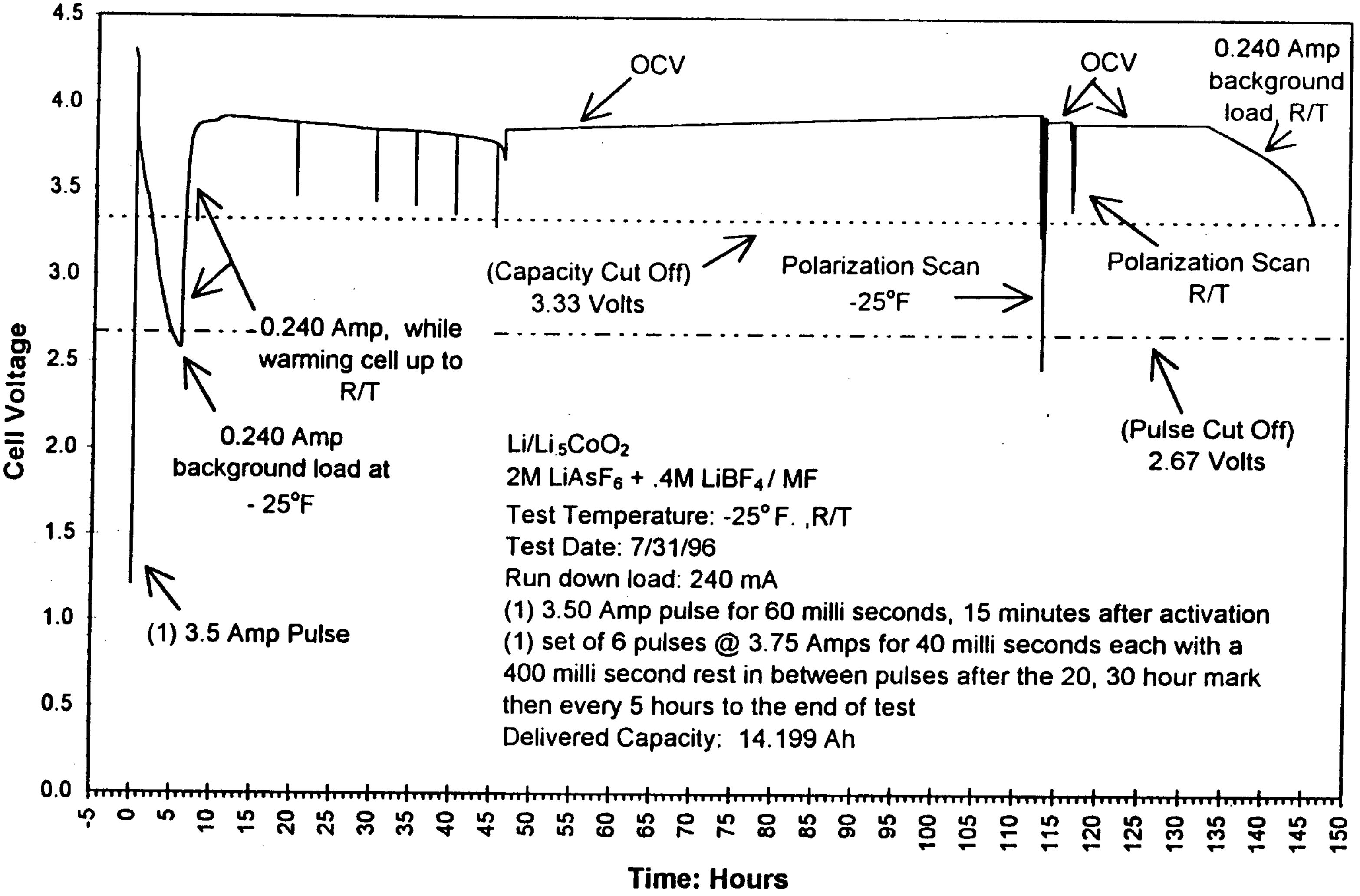
3 Month Storage @ +160°F



7/26/96
Li/Li$_{.5}$CoO$_2$
2M LiAsF$_6$ + .4M LiBF$_4$/MF
Test Temperature: -25°F
Run down load: 240 mA
(1) 3.5 Amp pulse for 60 milli seconds after 15 minutes of OCV
Delivered Capacity: 0.936 Ah

Pulse and Capacity Run Down Profile, WAMH24

3 Month Storage @ R/T



Li/Li_5CoO_2

$2M\ LiAsF_6 + .4M\ LiBF_4 / MF$

Test Temperature: -25° F. ,R/T

Test Date: 7/31/96

Run down load: 240 mA

(1) 3.50 Amp pulse for 60 milli seconds, 15 minutes after activation

(1) set of 6 pulses @ 3.75 Amps for 40 milli seconds each with a 400 milli second rest in between pulses after the 20, 30 hour mark then every 5 hours to the end of test

Delivered Capacity: 14.199 Ah

Appendix D

Safety Study Presentation of July 20, 1995

NSWC Option 7

$LiCoO_2$ H-WAM Battery

Safety Review

20 July 1995

Agenda

- Review electrochemical discharge comparing $SOCl_2$ and $LiCoO_2$ reactions
- Discuss hazard potential of the $LiCoO_2$ electrochemical system
- Compare the potential for energy release of $LiCoO_2$ battery with a Li/$SOCl_2$ battery
- Review of design and manufacturing characteristics relevant to safety
- Discuss a $LiCoO_2$ battery reaction to abusive external conditions
- Open Discussion

REVIEW ELECTROCHEMICAL DISCHARGE COMPARING $SOCl_2$ AND $LiCoO_2$ REACTIONS

Thionyl Chloride

$$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$$

- $SOCl_2$ is both electrolyte solvent and the active cathode material (solvent/oxidant).
- Moderate build-up of pressure from SO_2 during discharge.
- Sulfur crystallizes (rhombic form) in the product solution.
- Reacted electrolyte is a volatile substance[1]
- Amount of elemental sulfur is proportional to depth of discharge.

Lithium Cobalt Dioxide

$$yLi + Li_xCoO_2 \rightarrow Li_{x+y}CoO_2$$

- Cell is manufactured with cathode in a fully precharged state.
- Ester based solvent for electrolyte solution (methyl acetate) in combination with $LiAsF_6$ and $LiBF_4$ salts.
- There are no reaction products which contribute to increasing volatility with discharge.

---

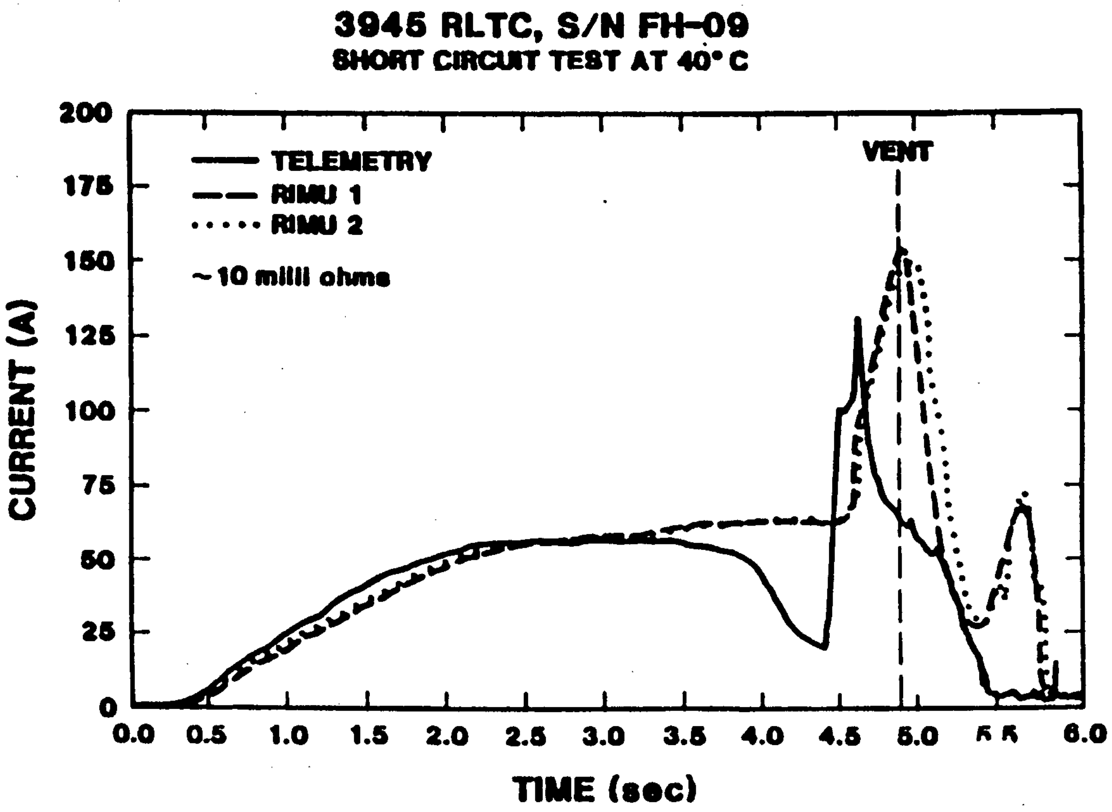
[1] C.R. Schlaikjer, F. Goebel, N. Marincic, J. Electrochem. Soc., 126, 513-522 (1979).

SOCl$_2$ Intentional Abuse

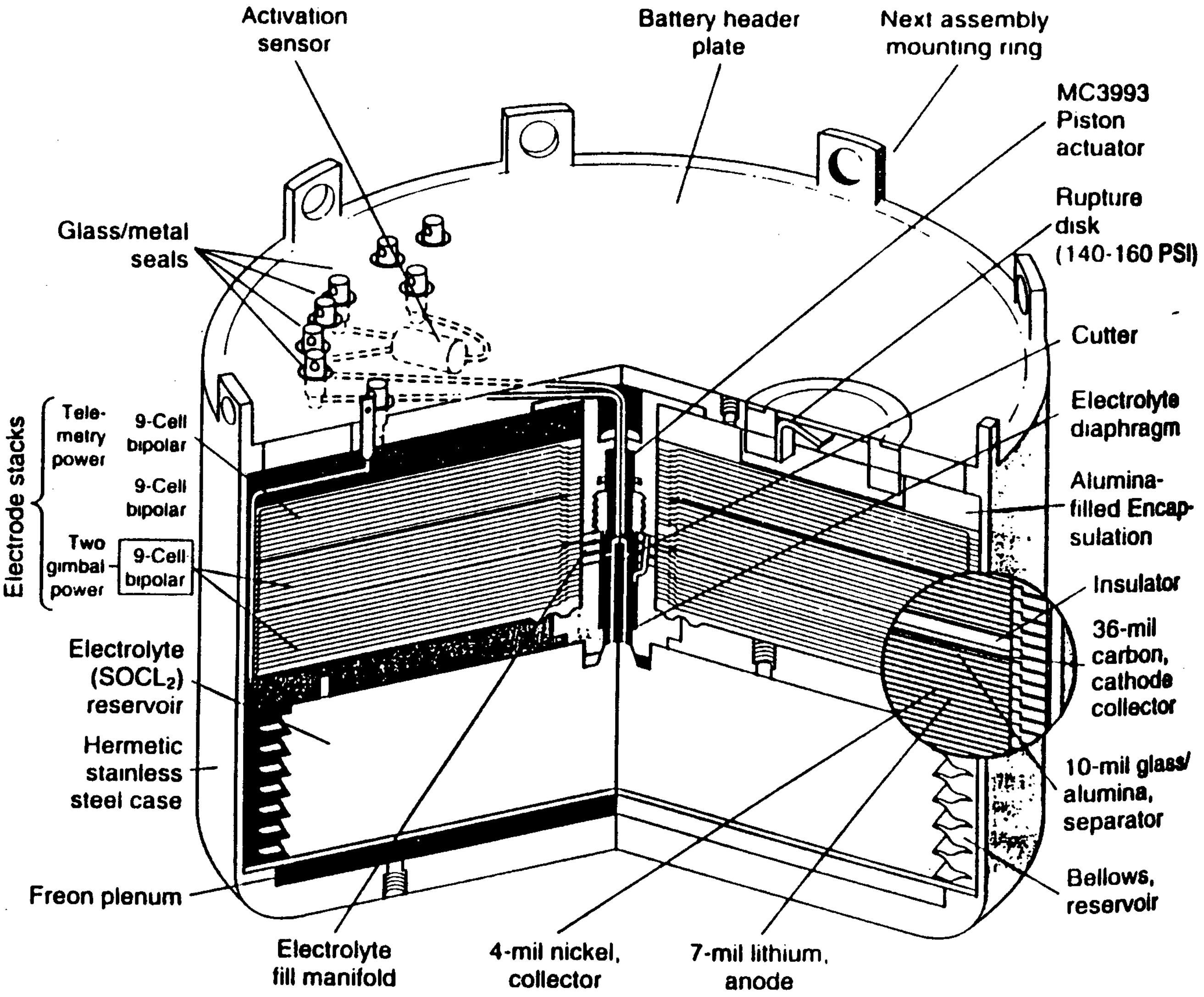
Test Item: MC3945 Reserve Li/SOCl$_2$ Battery

Test Conditions: External Short (≈ 10 mΩ) before activation

Results: Violent case rupture ≈ 4 seconds after activation. Total current exceeded 400 amps (≈1000 mA/cm^2).


3945 RLTC, S/N FH-09
SHORT CIRCUIT TEST AT 40° C

MC3945 Reserve Battery



NSWC Option 7 $LiCoO_2$ H-WAM
Battery Safety Review
20 July 1995

[M50720-1.wp]*paw

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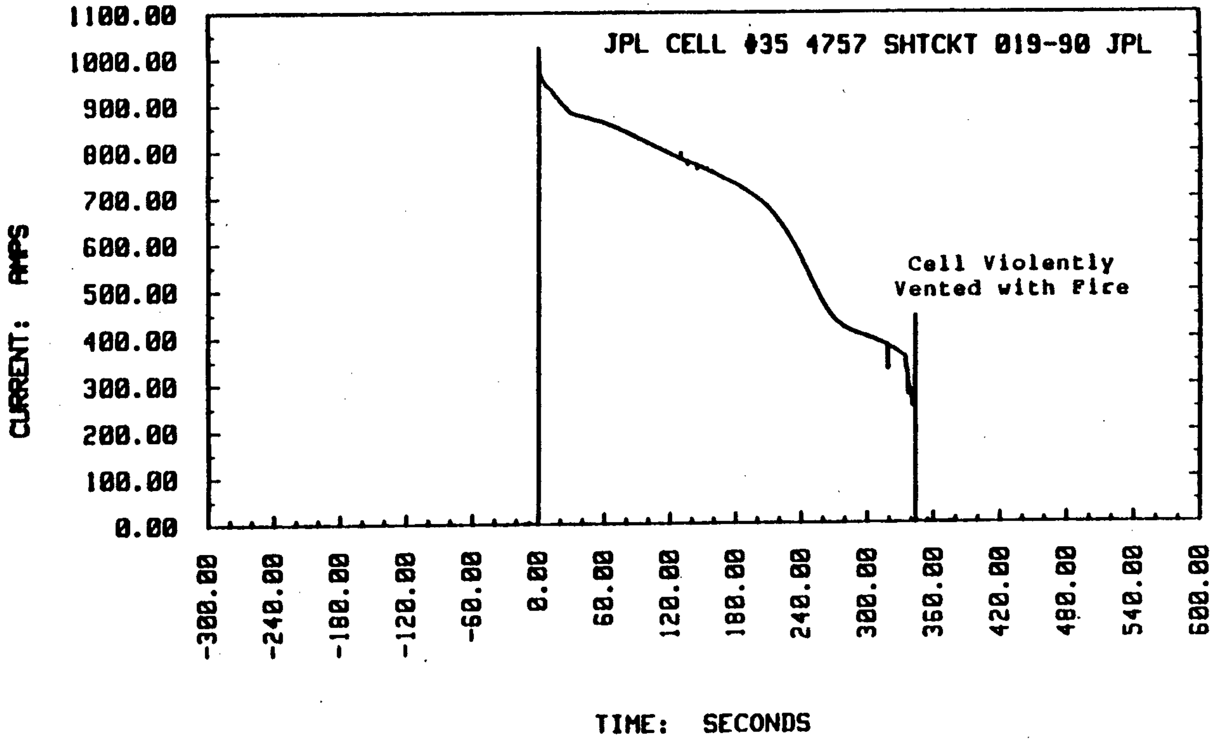
$SOCl_2$ Intentional Abuse

Test Item:	JPL 250 Ah (320 Ah) $SOCl_2$ Active Cell
Test Conditions:	Externally shorted fresh cell (≈ 2 mΩ)
Results:	Violent venting/case rupture ≈ 5 minutes after shorting



EXTERNAL SHORT CIRCUIT TEST AT +75°F

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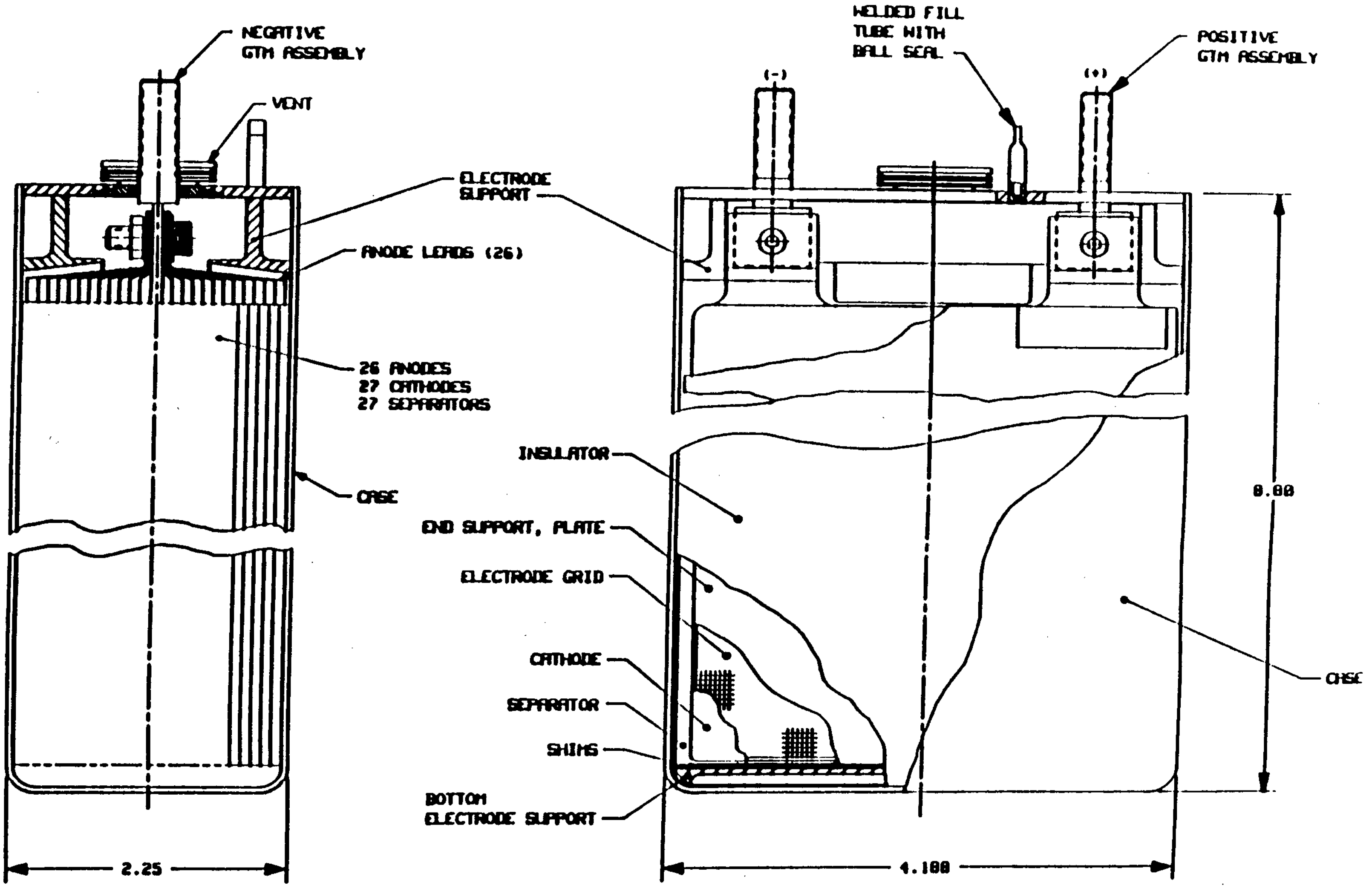
JPL 250 Ah Cell



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Battery Safety Review
20 July 1995

[M50720-1.wp]*paw

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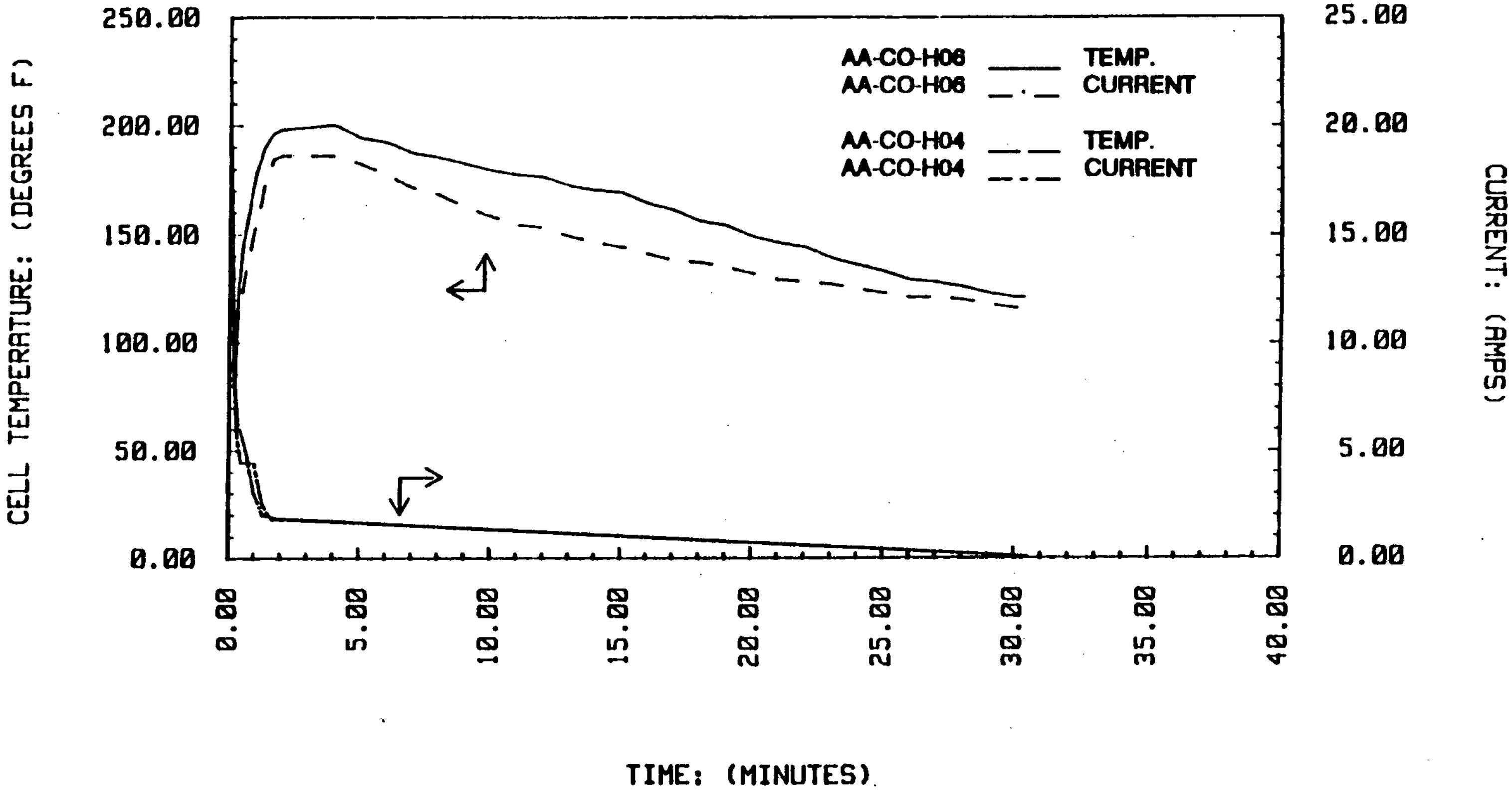
Ziegler Seal "AA" Cells

Test Item:	$LiCoO_2$ "AA" Cell (0.8 Ah)
Test Conditions:	Externally shorted charged cell
Results:	Measured peak current 20A (328 mA/cm^2). Case temperature did not rise above 200°F. Cell remained intact. Vent did not open.



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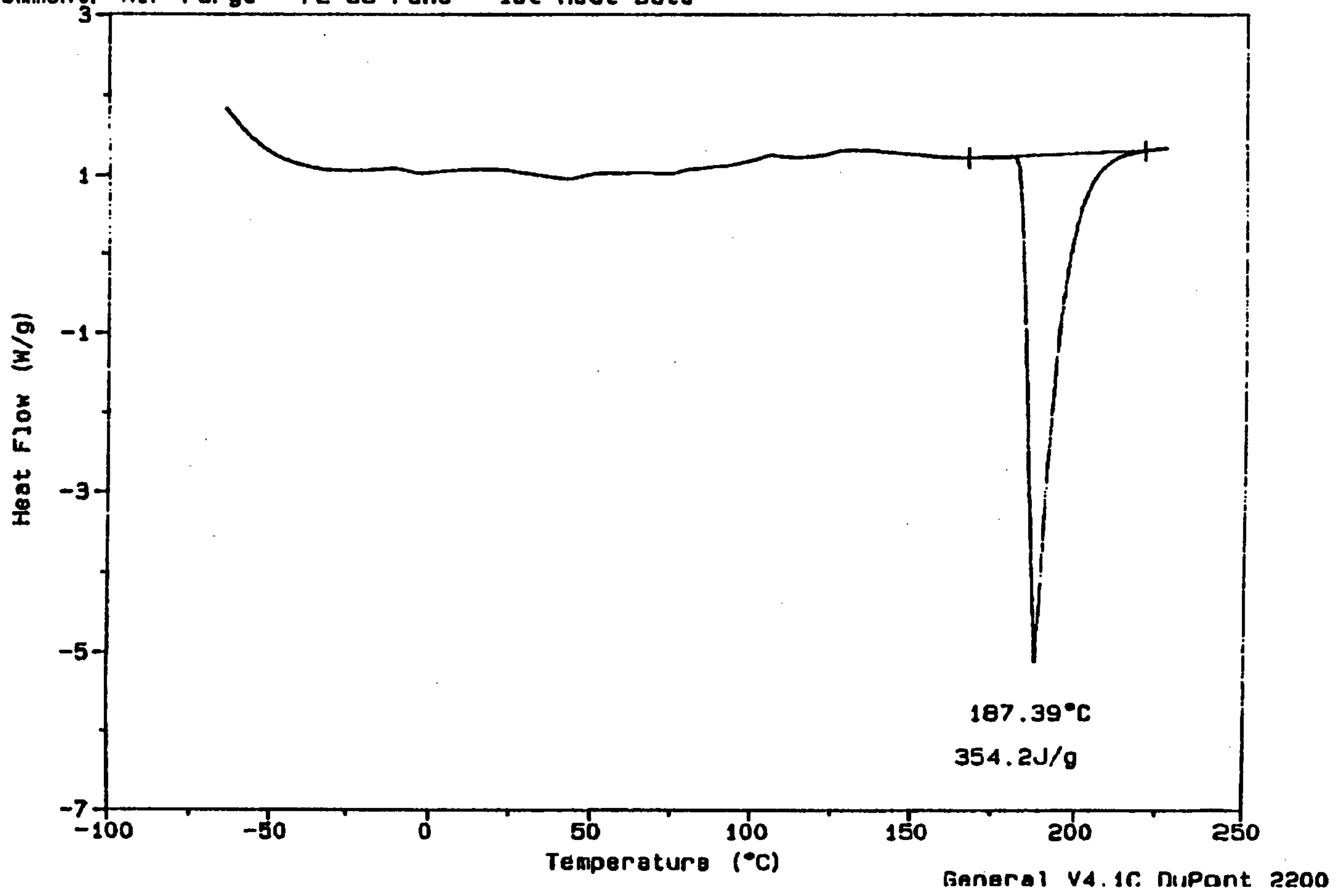
Differential Scanning Calorimetry

Lithium Sample

Sample: Lithium alone as received
Size: 5.4600 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE SS Pans - 1st Heat Data -

DSC

File: C: HMDSCLI.100
Operator: J.Sosnowik MDSC 2910
Run Date: 7-Jul-95 09: 02



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Battery Safety Review
20 July 1995

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Differential Scanning Calorimetry

$LiCoO_2$ Sample

Sample: LiCoO2 As Received
Size: 9.7500 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE Sealed SS Pans - Sealed in glove box -

DSC

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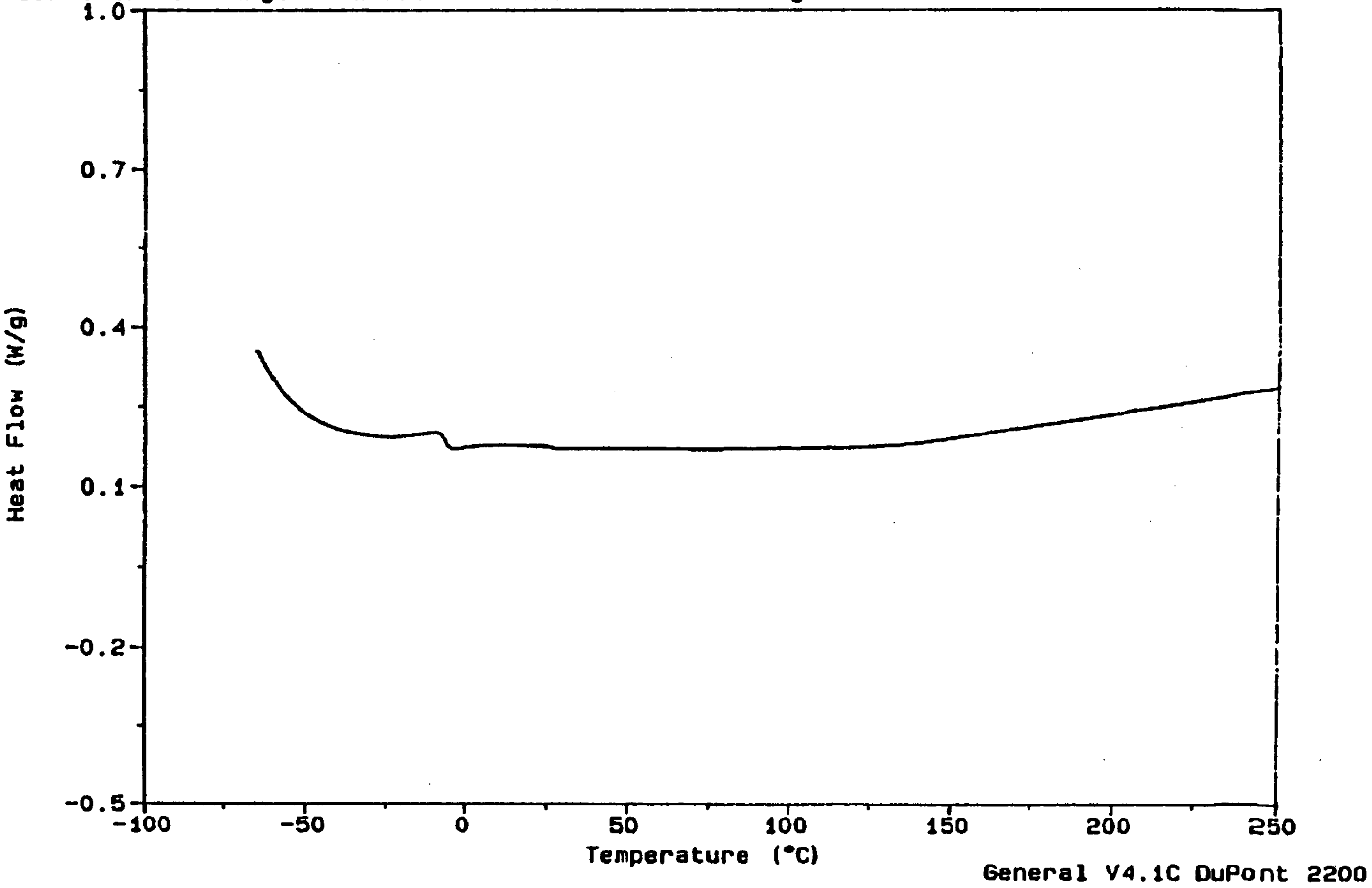
Operator: J.Sosnowik MDSC 2910
Run Date: 6-Jul-95 11: 04



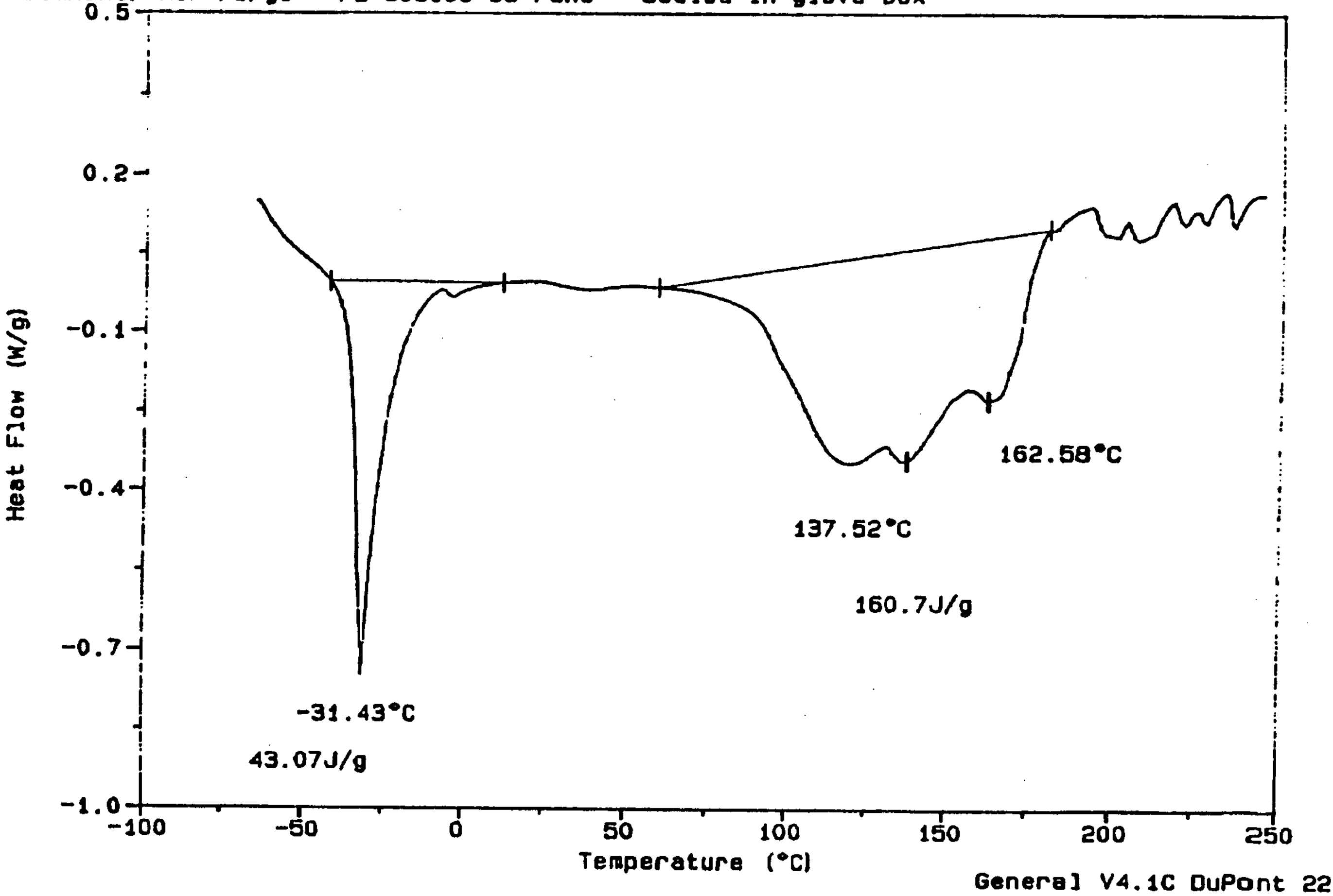
Differential Scanning Calorimetry

Methyl Acetate Electrolyte

Sample: MeAc/LiAsF6 As Received
Size: 10.3100 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE Sealed SS Pans - Sealed in glove box -

DSC

File: C: HMDSCMEAC.100
Operator: J.Sosnowik MDSC 2910
Run Date: 6-Jul-95 09: 57



General V4.1C DuPont 2200

NSWC Option 7 $LiCoO_2$ H-WAM
Battery Safety Review
20 July 1995

[M50720-1.wp]*paw

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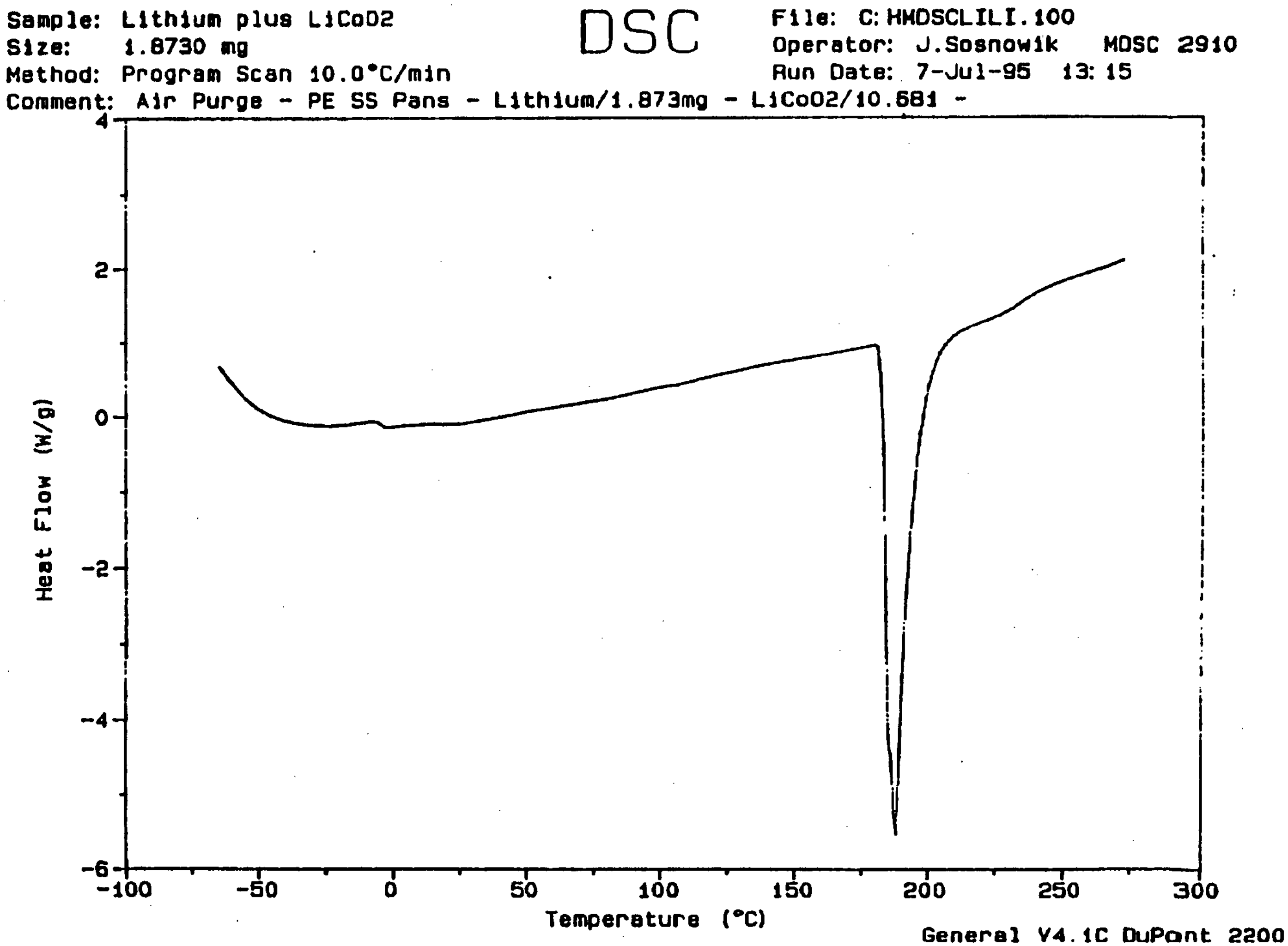
Differential Scanning Calorimetry

Lithium/$LiCoO_2$ Sample



Sample: Lithium plus LiCoO2
Size: 1.8730 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE SS Pans - Lithium/1.873mg - LiCoO2/10.681 -

File: C:HMDSCLILI.100
Operator: J.Sosnowik MDSC 2910
Run Date: 7-Jul-95 13:15

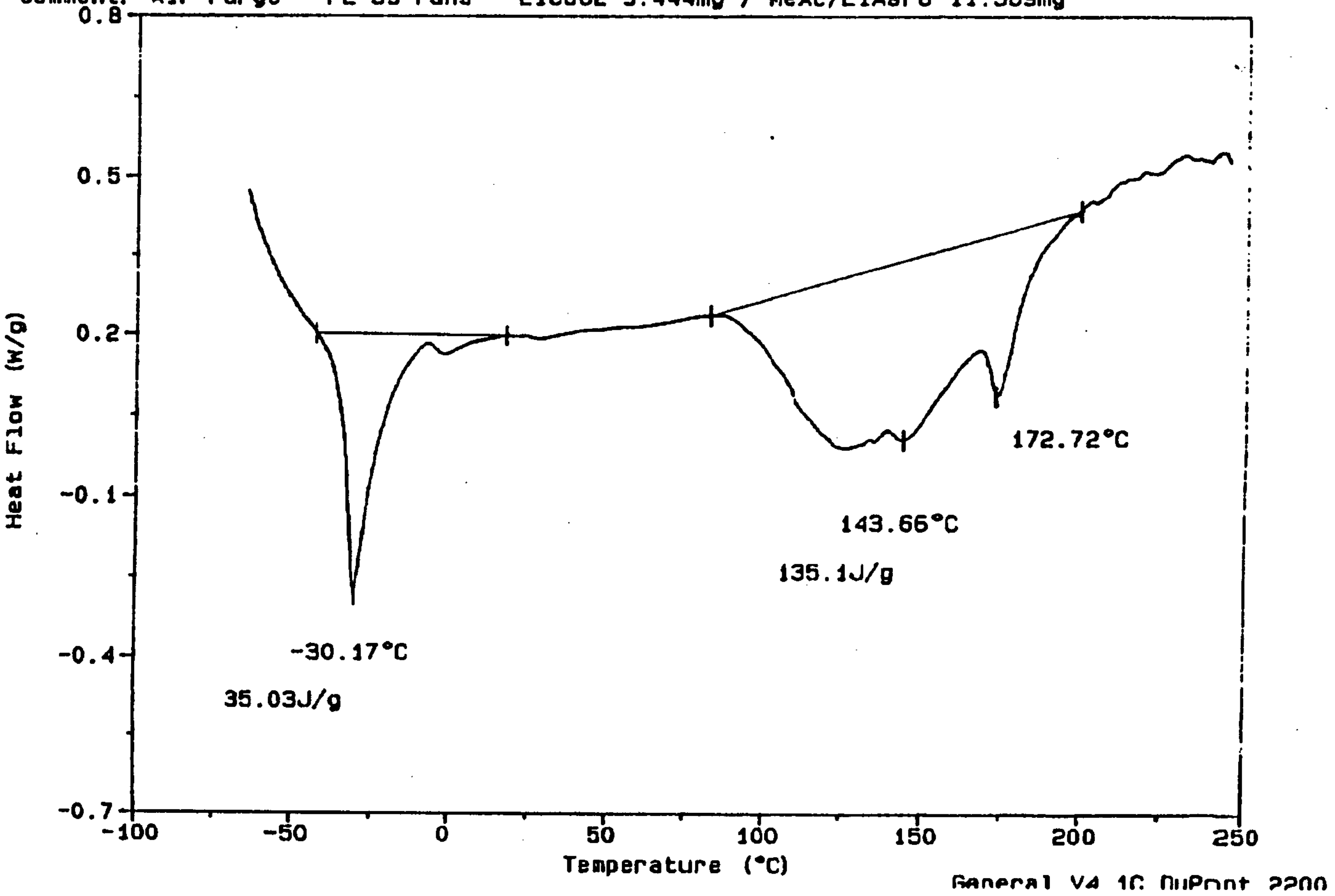
Differential Scanning Calorimetry

$LiCoO_2$/Methyl Acetate Electrolyte

Sample: LiCoO2 \ MeAC/LiAsF6 Mix
Size: 11.5690 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE SS Pans - LiCoO2 3.444mg / MeAc/LiAsF6 11.569mg -

DSC

File: C: HMDSCMIXA.100
Operator: J.Sosnowik MDSC 2910
Run Date: 6-Jul-95 12: 23



NSWC Option 7 $LiCoO_2$ H-WAM
Battery Safety Review
20 July 1995

[M50720-1.wp]*paw

Differential Scanning Calorimetry

Lithium/Methyl Acetate Electrolyte

Sample: Lithium plus MeAc/LiAsF6
Size: 15.8700 mg
Method: Program Scan 10.0°C/min
Comment: Air Purge - PE SS Pans - Lithium/1.750mg - MeAc/15.870mg -

DSC

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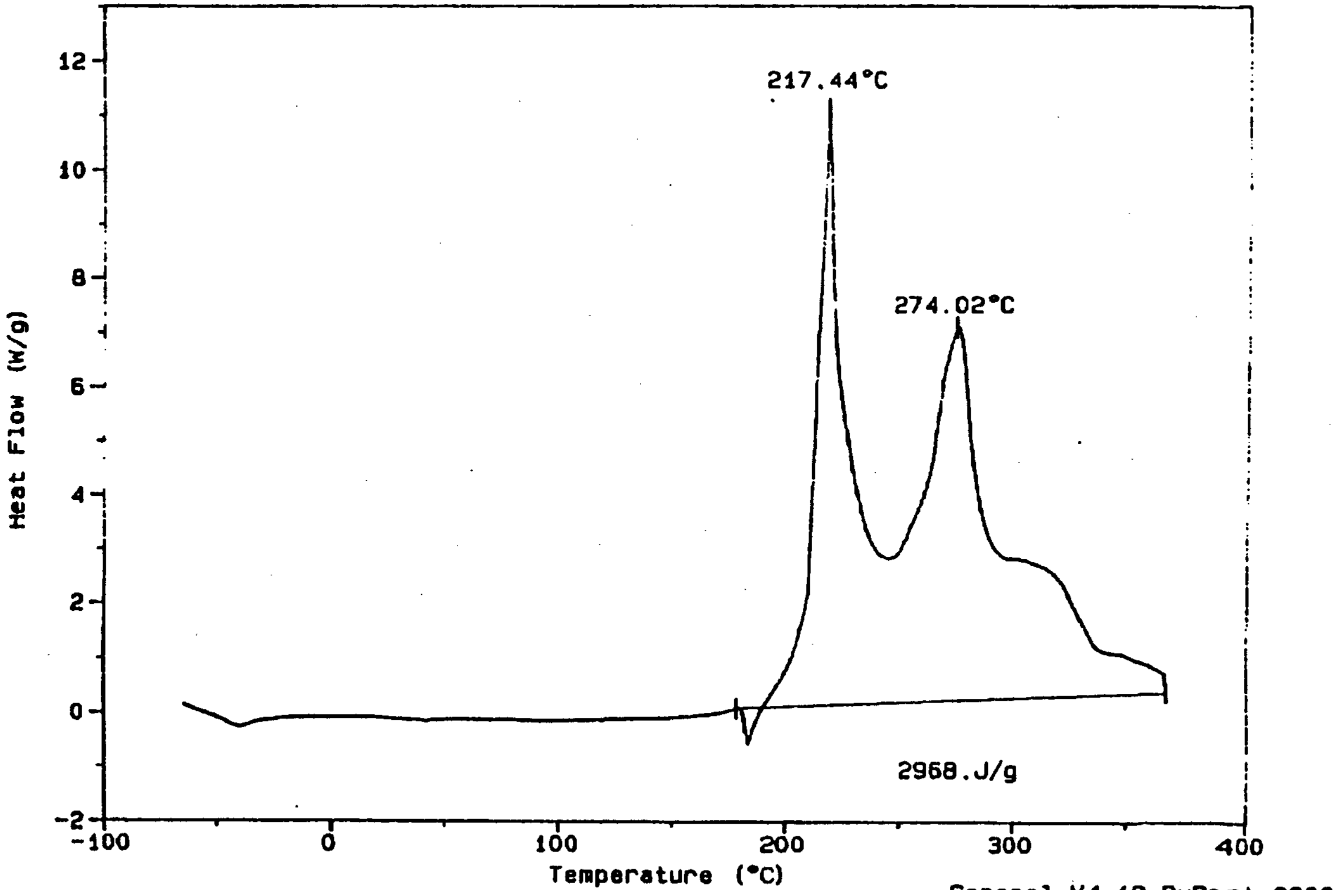
Operator: J.Sosnowik MDSC 2910
Run Date: 7-Jul-95 10:07



General V4.1C DuPont 2200

NSWC Option 7 $LiCoO_2$ H-WAM
Battery Safety Review
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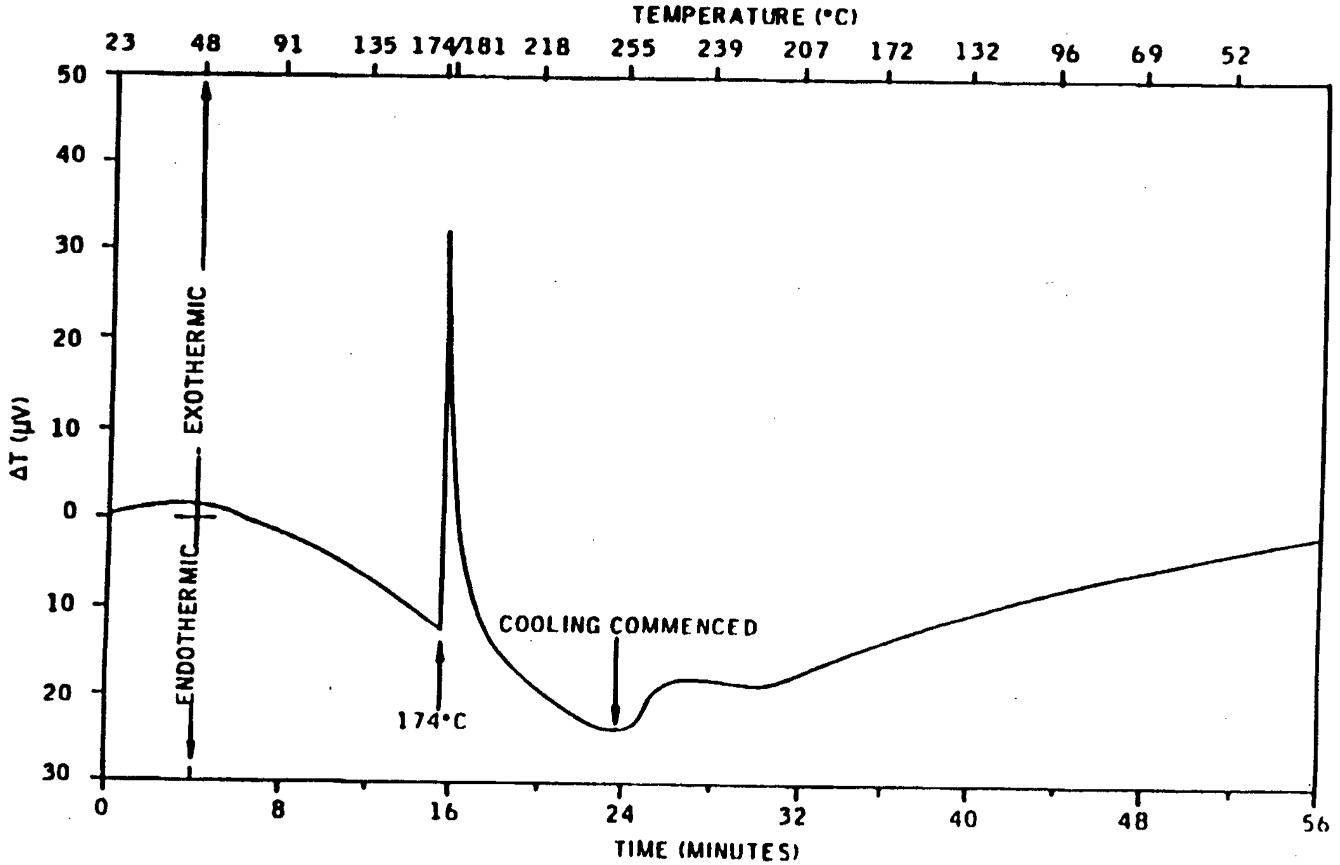
Part of a Thermogram from DTA of a Sample Containing Li (0.8 mg) and S (2.30 mg)



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Battery Safety Review
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Differential Thermal Analysis Results

Sample (mg)	Temperature of lithium fusion endotherm (°C)	Temperature and description[a] of exotherms			
		Under 300°C	300-360°C	360-380°C	Over 380°C
Li (0.8) + S (2.3)	--	174, 1, sh	--	--	--
Li (5.8) + $SOCl_2$ (2.1)	179	--	356, 1, sh	--	--
Li (4.8) + SO_2Cl_2 (6.6)	178	252, s, b	357, 1, sh	362, 1, sh	408, s, b
Li (4.8) + S_2CL_2 (14.0)	180	Upward drift	357, m, sh	370, s, sh	390, 1, sh
Li (3.5) + S (6.5) + $SOCl_2$ (12.0)	180	Upward drift, started 280°C	334, 1, sh	--	--
Li (8.0) + S (12.8) + SO_2Cl_2 (16.0)	179	293, 1, sh	334-348 four s, sh	--	--
Li (3.4) + S (11.3) + S_2Cl_2 (11.8)	178	250, s, b	--	--	390, 1, sh
Li (2.0) + Cathode Mix (5.0)	174	--	--	--	429, 1, sh
Li (10.3) + Glass (4.1)	176	--	--	--	587, s, sh

[a] Size: s = small, m = medium, l = large
Shape: b = broad, sh = sharp

DESIGN FEATURES AND MANUFACTURING CHARACTERISTICS ENHANCING BATTERY SAFETY

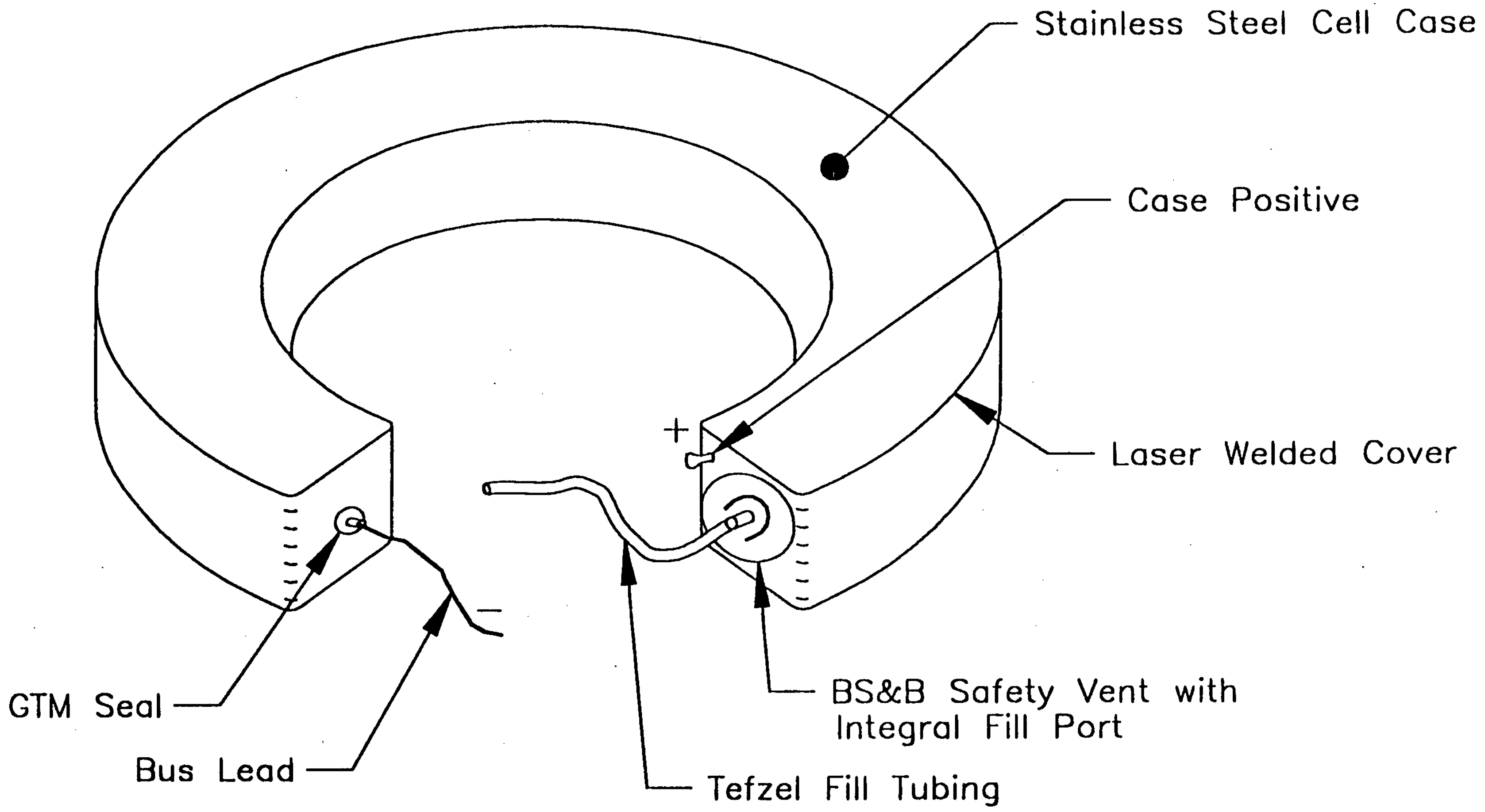
Design

- Safety vents (scored diaphragm type)
    - one per cell
    - one per battery housing
- Shut down separator - microporous PP/PE/PP
    - Not glass as used in $SOCl_2$. Lithium and glass reacts at 207°C.
- Fused links in cell leads.
- Electrolyte flooded cells.
- Independent electrolyte reservoirs for each cell. No intercell leakage. Hermetic metal bellows reservoirs.
- Flame arrestor matting outside safety vents.
- Current collector grids are chemically etched - no burrs.

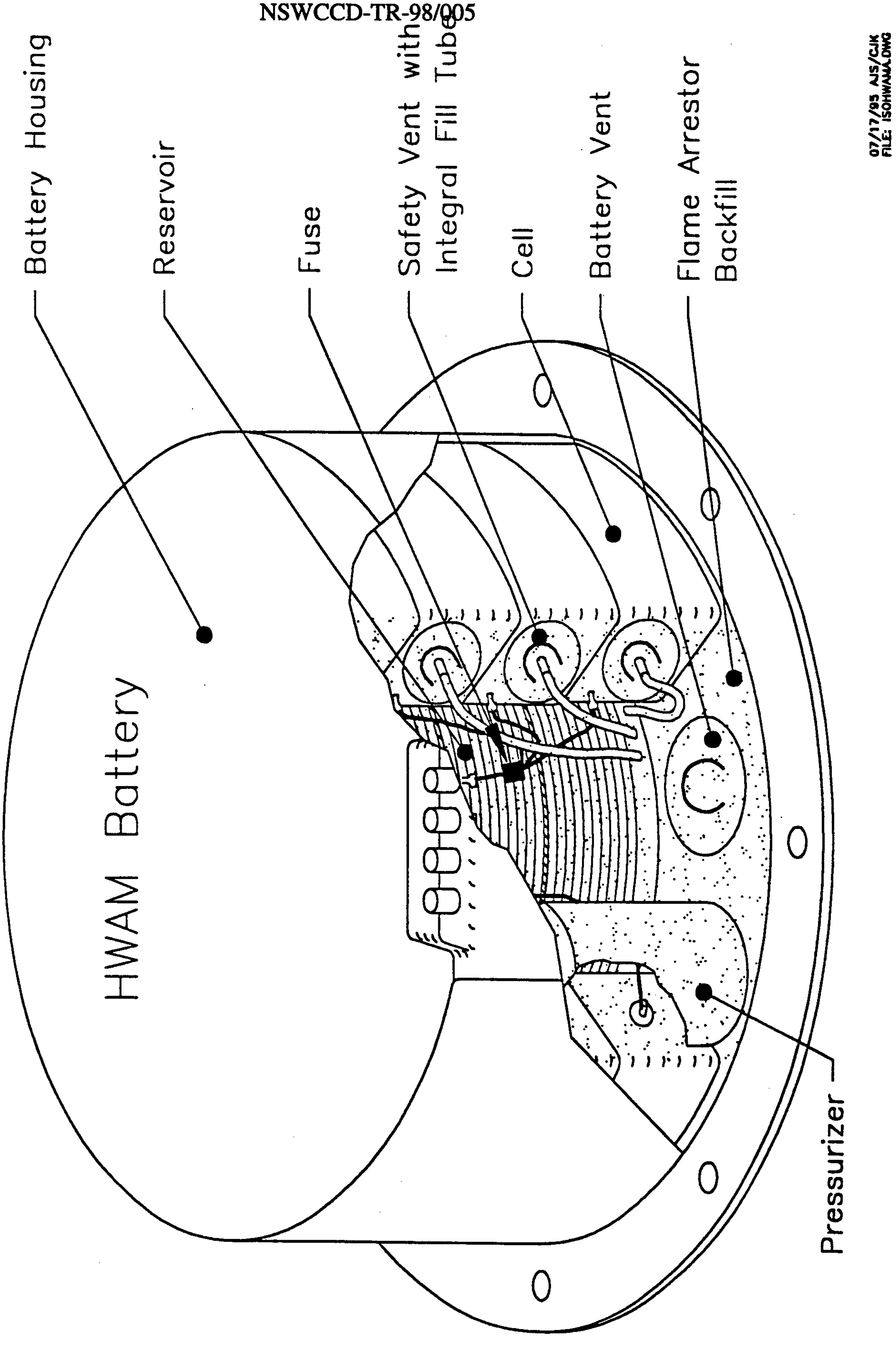
Manufacturing

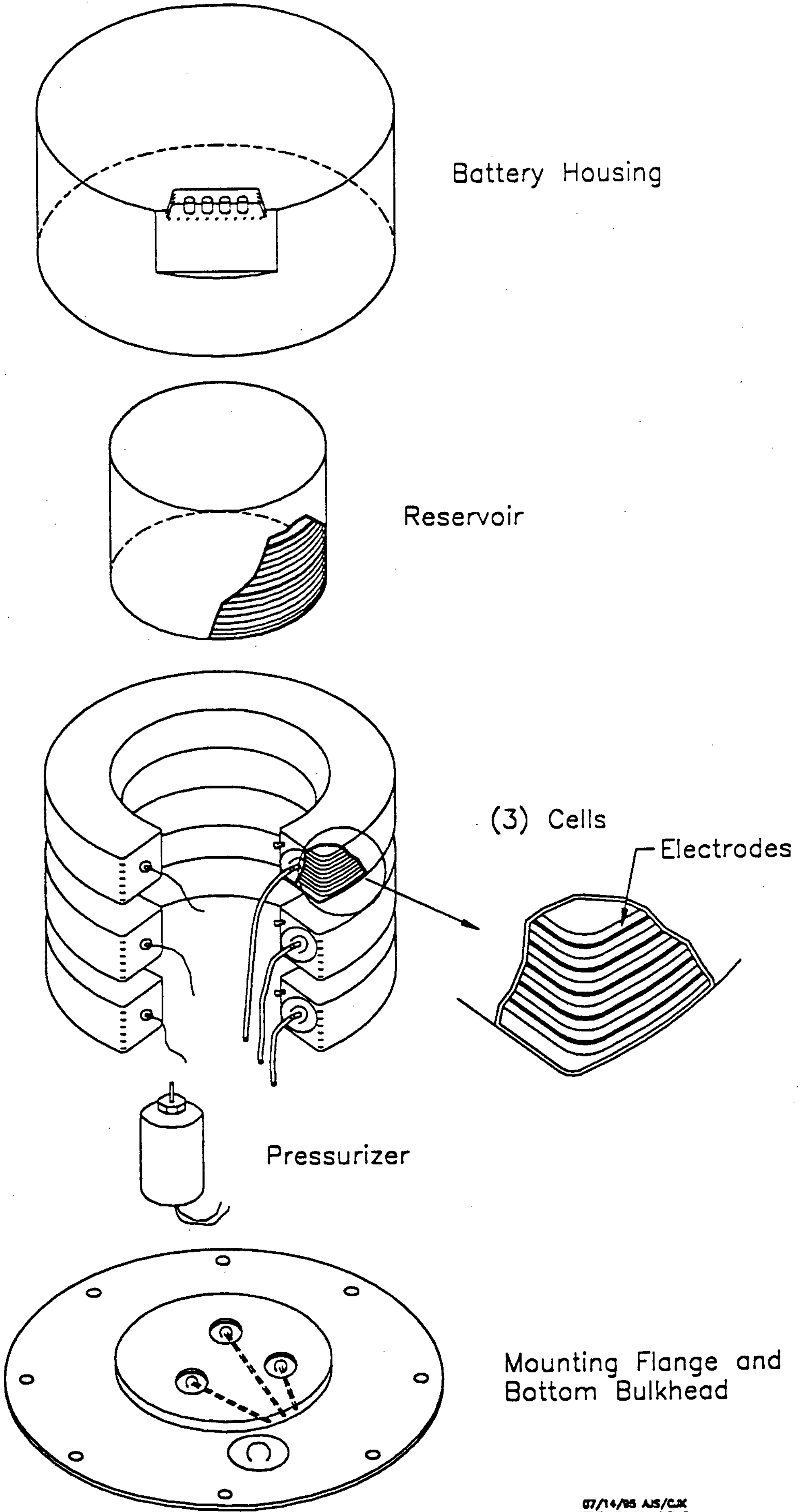
- Offset electrode edges with separators enveloping and heat sealed around every electrode plate.
- Stack alignment keyed to solid separator edges via assembly tooling.
- No dendrites in reserve state because cathode is precharged before assembly, new lithium metal anodes are assembled in reserve cell.

Individual Cell Case



07/14/95 AJS/CJK
FILE: ISOHWAM2.DWG


Battery Housing
Reservoir
Fuse
Safety Vent with Integral Fill Tube
Cell
Battery Vent
Flame Arrestor
Backfill
Pressurizer
HWAM Battery
07/17/95 AJS/CJK
FILE: ISOHWAMA.DWG



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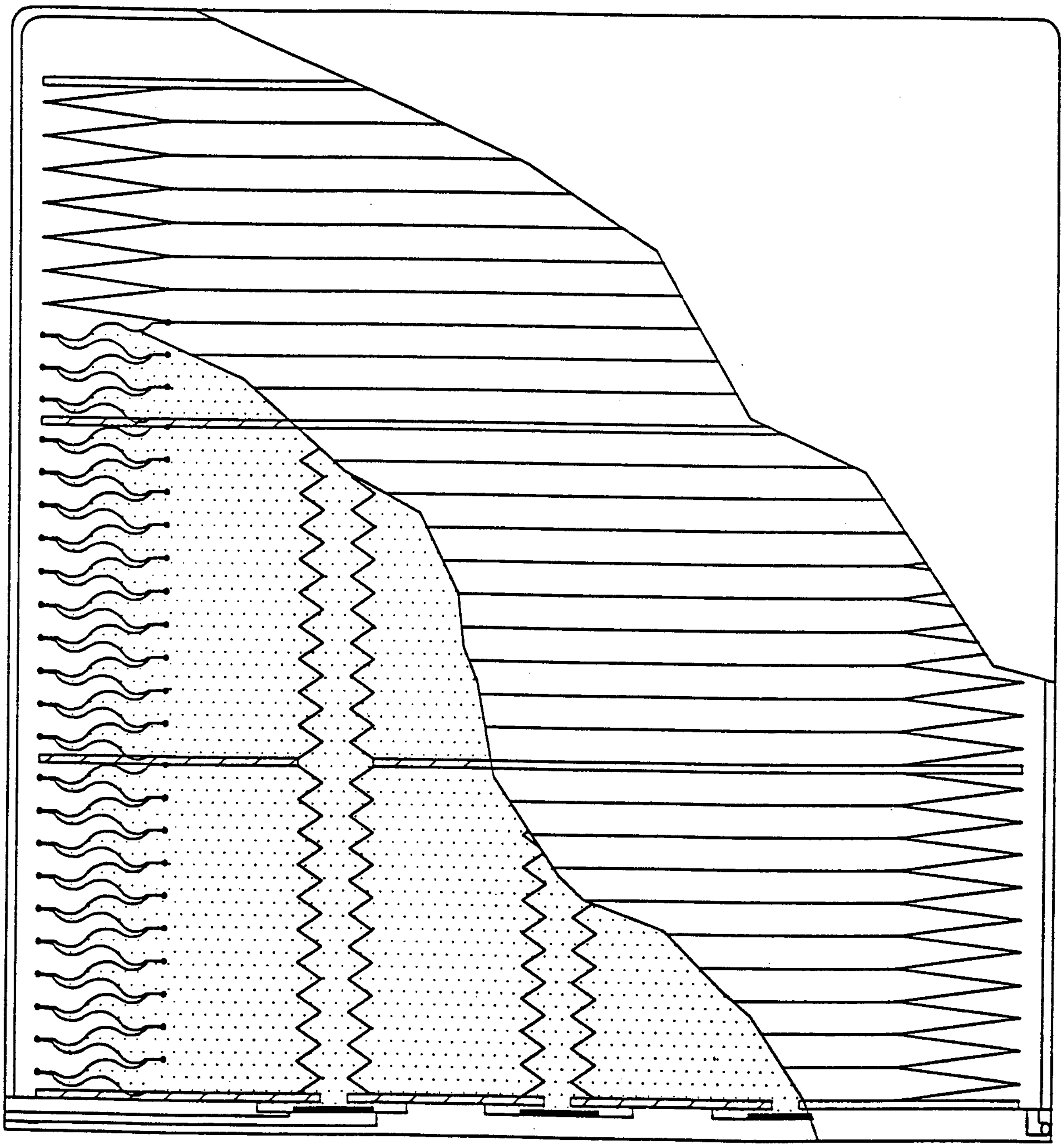
FILE: ISCHWAN3.DWG

Cross Section of HWAM Reservoir



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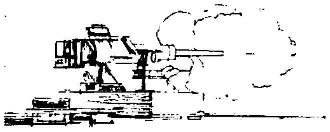
FILE: HWAM4.DWG

Appendix E

Specification Sheets for Ordnance Batteries



Ordnance Batteries

Electrochemical Variations Give Two Dimensionally Similar Batteries Vastly Different Capacities

Electrochemical flexibility has allowed PSC to produce two electrically and physically interchangeable batteries with very different capacities for the U.S. Army's FASCAM (Family of Scatterable Mines) project. Both reserve batteries are small and low-rate, and they offer long life relative to their size.

In both batteries, electrolyte is held in reserve in a glass ampul until a mechanical, electrical, or explosive impulse fractures the glass to release the electrolyte and activate the battery. This system gives an ambient shelf life of more than 20 years, yet allows rapid rise to full power and fresh cell capacity.

The first of the two, the G2666, has been in high-volume production at Honeywell since 1978. It offers a capacity of 100 mAh, and is based on Li/V$_2$O$_5$ electrochemistry. Product reliability is greater than .9993 at 98 percent confidence.

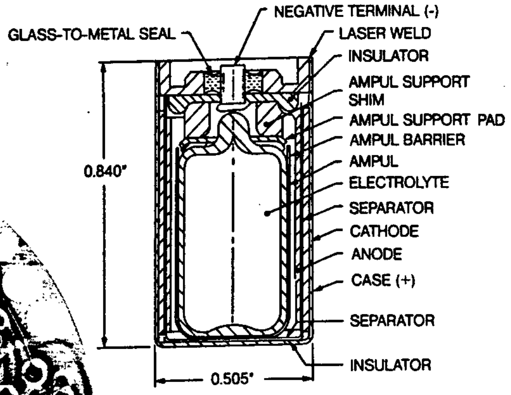
More recently designed and now in pilot production, the G2666B1 uses Li/SOCl$_2$ electrochemistry to produce a capacity of 280 mAh. Together, the two batteries prove the versatility of the variety of electrochemical configurations available from PSC's design teams.

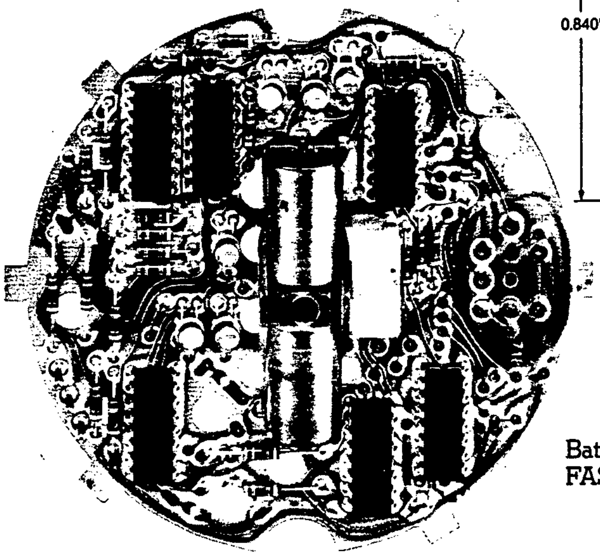
Specifications

	Model No. G2666 Chemistry Li/V$_2$O$_5$	Model No. G2666B1 Chemistry Li/SOCl$_2$
Performance		
Open circuit voltage:	3.4 volts	3.6 volts
Voltage under load:	3.3 volts at 0.5 mA/plateau #1 3.1 volts at 0.5 mA/plateau #2	3.6 volts with 65,000 ohm load
Rated capacity:	100 mAh to a 2.5 volt cutoff at 0.5 mA load at 72°F	280 mAh to a 2.5 volt cutoff at 0.49 mA load at 72°F
Energy density (at rated load):	2.06 Whr/in^3, 0.122 Whr/cc 27.5 Whr/1b, 0.061 Whr/g	6.13 Whr/in^3, 0.37 Whr/cc 89.1 Whr/1b, 0.20 Whr/g
Physical Characteristics		
Diameter:	0.50 inches	0.50 inches
Length:	0.84 inches	0.84 inches
Weight:	0.18 oz	0.18 oz
Volume:	0.16 inches^3	0.16 inches^3
Positive terminal:	Glass-to-metal seal with 52 alloy pin	Glass-to-metal seal with 52 alloy pin
Case material:	316L Stainless Steel	316L Stainless Steel
SAFETY FEATURES		
Reserve:	Electrolyte stored in glass ampul. Both cells inactive during storage.	

G2666 Cells and Ampuls

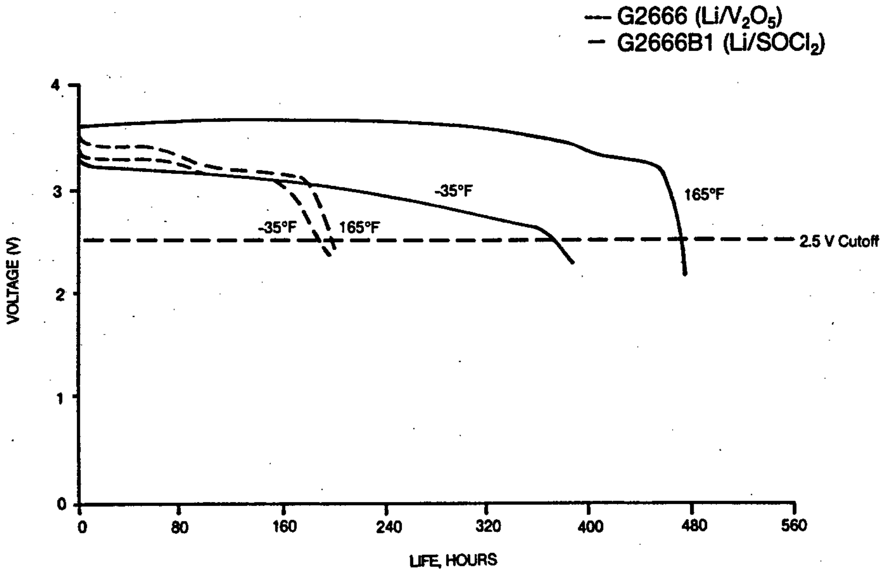
Lithium/Thionyl Chloride Reserve Cell Model G2666B1

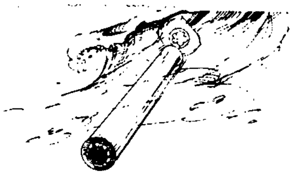




Batteries mounted on FASCAM pc board.

Output Capacity Comparison for G2666 and G2666B1 Cells at .5 mA





Underwater Mines/ Buoy Batteries

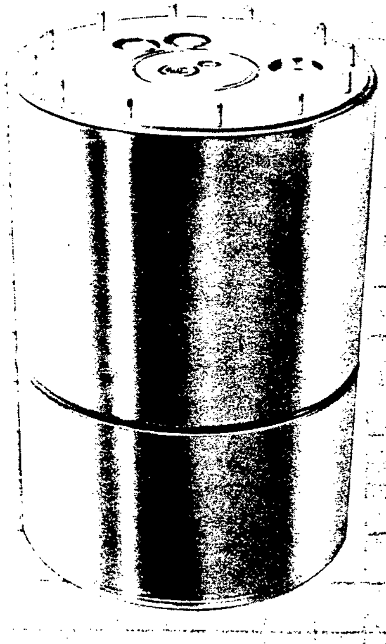
4000 Watt Battery Employs Standard Technology

The Model G3070A2 is an expendable, high power, remotely activated multicell lithium battery, containing two electrically isolated voltage sections. The low power section operates continuously at 71 watts, while the high power section operates at 4000 watts. Testing has demonstrated the battery can operate at pulses to 200 amps, providing pulse power outputs of 10,000 watts.

Maintaining the battery's reserve integrity is a major safety feature. Until it is electrically initiated, the battery will not activate during handling, shipping, or storage. For test purposes, the battery was activated and allowed to stand on open circuit for 90 days. During the test there were no safety related episodes, and the battery retained 85% of fresh discharge capacity. In the event the battery is subjected to an abusive condition, it contains a series of venting mechanisms.

PHYSICAL CHARACTERISTICS

Diameter:	11.5 inches
Length:	17.0 inches
Weight:	140 pounds
Activation Method:	Electrically initiated Squib assembly
All Fire Current –	5 amps, 10 msec pulse
No Fire Current –	1 amp-1 watt 5 minutes at 225°F
Oper. Temp. Range:	−40°C to +60°C
Case Material:	Stainless Steel



G3070A2 Battery

Specifications

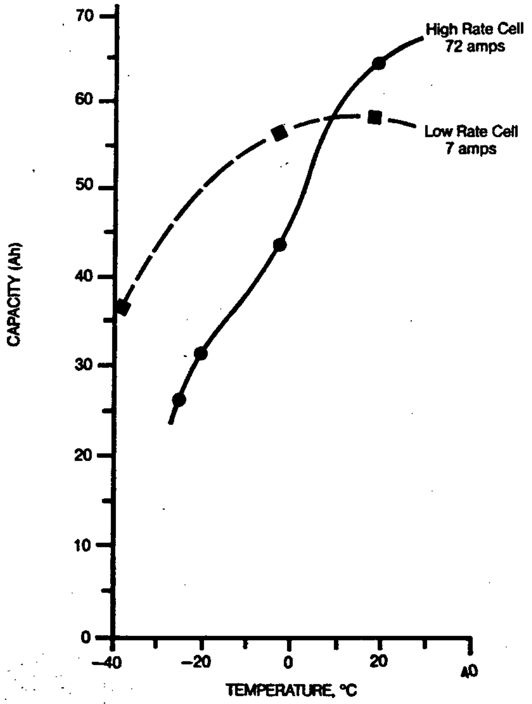
Model No. G3070A2 Battery	Low Power Section Li/$SOCl_2$ Reserve/Series Connected Multiplate Cells	High Power Section Li/$SOCl_2$ Reserve/Series Connected Multiplate Cells
Performance		
Number of Cells	3 cells	18 cells
Open Circuit Voltage: (Activated)	11.0 volts	66.0 volts
Voltage under load:	10.2 volts 7 amps at 20°C	55.8 volts 72 amps at 20°C
Rated Capacity:	57 Ahr at 7 amps to 8.0 volts at 20°C	65 Ahr at 72 amps to 47.3 volts at 20°C
Power:	71.4 watts continuous	4018 watts, pulses to 200 amps

Safety Features

Reserve:

- —Electrolyte stored in stainless steel reservoir
- —Battery case and reservoir vents
- —Temperature monitoring sensor
- —Cell and cell stack voltage monitoring leads
- —Fully shielded actuator firing leads

G3070A2 Cell Capacity at Various Temperatures



Physically Similar, High Power, Reserve Cells, Offer Performance Alternatives

The Low and High Power performance of the G3070A2 Reserve Battery sections (pages 4 and 5) demonstrate the wide current carrying capability of its cells.

These two physically similar, remotely activated cells are tailored for low rate (7 amps) or high rate (200 amp pulses) performance. Differing only in cell height and capacity, as a result of one less set of electrodes, the two cells offer corresponding rate carrying ability.

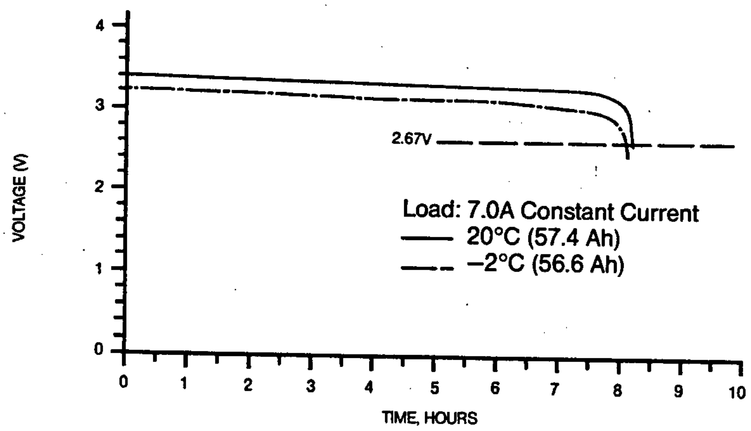
They are the baseline cells for the G3070A2 battery and allow for flexibility in battery design through series/parallel configurations.

As presented in the specifications, the two cells have the same inside and outside diameters. However, they differ in height (0.06 inches), which results in a corresponding decrease in rate carrying ability of the low rate cell.

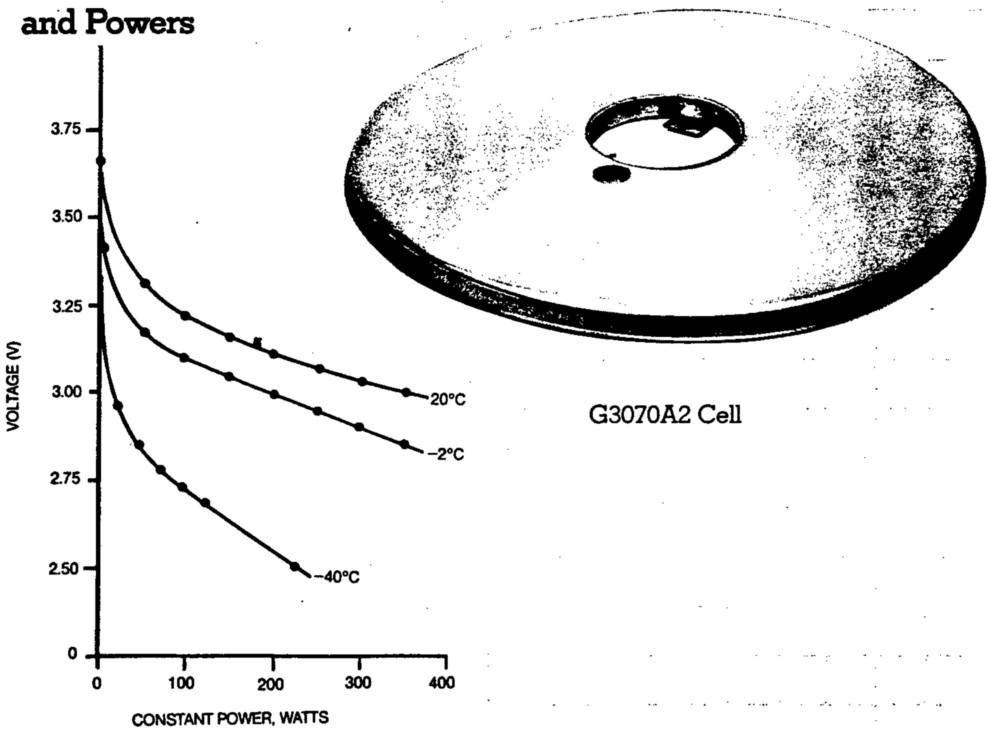
Specifications

	Model No. G3070A2 Low Rate Reserve Cell Chemistry Li/SOCl$_2$	Model No. G3070A2 High Rate Reserve Cell Chemisty Li/SOCl$_2$
Performance		
Open Circuit Voltage:	3.67 volts (activated)	3.67 volts (activated)
Voltage under load:	3.40 volts 7 amps at 20°C	3.10 volts 72 amps at 20°C
Rated Capacity:	57 Ahr at 7 amps to 2.67 volts at 20°C	65 Ahr at 72 amps to 2.63 volts at 20°C
Physical Characteristics		
Max Diameter: OD	11.22 inches	11.22 inches
Max Diameter: ID	2.65 inches	2.65 inches
Max Height:	0.35 inches	0.41 inches
Cell Weight w/electrolyte:	1310 grams 2.89 lbs	1485 grams 3.27 lbs
Case Material:	Stainless Steel	Stainless Steel

G3070A2 Low Rate Cell Discharge Profile

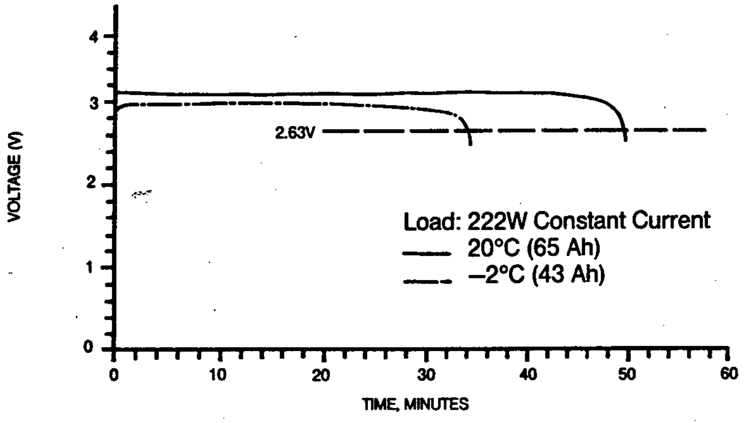


Voltage Characteristics of G3070A2 High Rate Cell at Various Temperatures and Powers



G3070A2 Cell

G3070A2 High Rate Cell Discharge Profile



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