PERFORMANCE AND SAFETY CHARACTERISTICS OF LITHIUM-MOLYBDENUM DISULFIDE CELLS

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I. INTRODUCTION

Moli Energy Limited (Moli) has, during the past five years, developed a technology base that is leading to the commercialization of a new family of electrochemical batteries. These batteries utilize the phenomenon of intercalation in a lithium-molybdenum disulfide system.

The molybdenum disulfide electrode, which had been examined by other investigators and rejected as being an unlikely candidate for practical use, has been thoroughly investigated by Moli. The underlying causes of the early failures were carefully analysed and the results utilized to create modifications in the molecular structure of the material. The consequent results are dramatic improvements in the utility of the material as an electrode active material. In addition Moli has developed a practical lithium electrode, which vastly reduces the problem of limited reversibility encountered in other developmental secondary lithium cells.

The first product under development is a C cell, utilizing a sprially wound 'jelly roll' electrode configuration. The C cell, in its non-optimized developmental form, has demonstrated attractive characteristics. These include:

1. High Rate Capability

Sustained drain rates of several amperes at a cell voltage above 1.3 volts have been demonstrated.

2. Inherent Safety Below 180°C

A wide variety of electrical and thermal abuse tests have been conducted which show that the cells are resistant to venting or rupture, provided that the cell temperature does not exceed 180°C.

3. Wide Ambient Temperature Operating Range

Sustained drain rates of at least 1 ampere at a cell voltage above 1.3 volts can be maintained over the temperature range from -15°C to +75°C. Lower drain rates can still be maintained at temperatures below -15°C.

4. Very Low Self-Discharge

Microcalorimetric measurements indicate a charge retention time in excess of 5 years.

5. Moderately High Energy Density

Energy densities range from 72 watt-hours per kilogram for a C cell to 150 watt-hours per kilogram for larger cells scheduled for future development.

6. State of the Art Cycle Life for Lithium Batteries

A cycle life in excess of 100 cycles with an 80% depth of discharge has been demonstrated. Cycle life testing on smaller cells indicates that 600 cycles with a similar depth of discharge will be achievable with optimization of the cell design.

7. Intrinsically Low Materials and Manufacturing Costs

Cost analysis has indicated that Moli cells will ultimately be cost competitive with currently marketed rechargeable cells.

II. EXPERIMENTAL CELLS

Extensive data has been collected on small-scale, starved-electrolyte cells. Figure 1 shows a schematic representation of the cell construction. These cells were fabricated with electrode capacities per unit area and electrode spacings representative of those contemplated for full-size large cells. Cycle life tests were conducted in such a manner as to demand constant average power from a cell during every useable cycle.

A single cycle sequence entails charging a cell at constant current to a preset voltage value and then discharging it at constant current to a lower preset voltage value. Based on these tests, the cycle life is defined as the number of successive cycles that can be obtained using the defined cycle sequence until the discharge time is reduced to one-half of that of the first discharge. The depth of discharge is determined by an appropriate choice of cycle sequence parameters. Figure 2 shows charge and discharge profiles for a typical small-scale cell. Figure 3 shows discharge curves as a function of cycle number. Figure 4

shows how the defined cycle life varies as a function of depth of discharge. Finally, Figure 5 shows the realizable capacity at various, uninterrupted, constant current drain rates.

III. DEVELOMENTAL CELLS

Initial developmental work at Moli was directed towards fabrication and performance evaluation of jelly roll cells in 1/2C-size cans. These cells were fabricated using machine-produced electrodes. Figure 6 shows the delivered charge from one of these cells over 320 cycles.

More extensive data has been obtained on developmental C cells. These cells were dry-room-fabricated using machine-produced electrodes in batches of 5 to 10 cells. Considerable quantities of performance and testing data have been accumulated.

1. Performance Data

A number of performance tests on non-optimized C cells have been conducted. The jelly roll construction of these cells is shown schematically in Figure 7. Figure 8 shows typical charge and discharge curves for C cells. Figure 9 shows the cell capacity available as a function of drain rate at temperatures of 22 ^{0}C (72^{0}F) and -12^{0}C (+10^{0}F). Figure 10 shows the cycling performance of a batch of consecutively fabricated cells. The cells functioned for 115 cycles and 145 cycles with an 85% depth of discharge. The limited cycle life, as compared to that obtained for the small-scale, flat-plate cells, can be attributed to specific shortcomings in the C cell design and fabrication procedure. It is anticipated that cycle life can be extended substantially through improvements in the electrode design.

2. Abuse Testing Data

To date a variety of electrical abuse tests have been conducted.

Figure 11 shows the evolution with time of the current and cell surface temperature for a C cell subjected to a short-circuit test. The cell was initially at an ambient temperature of 22 ^{0}C and the short resistance was 20 mΩ. The

cell delivered current until the cell temperature reached approximately 140°C, at which time the current dropped substantially and the cell temperature began to fall again. No venting of the cell occurred.

The drop in cell current is not associated with a complete discharge; rather it is attributed to the separator porosity being substantially reduced at 140°C. Tests on other cells have revealed that the sharpness of the current reduction at 140°C is increased if the cells are insulated to minimize heat loss and at the same time reduce the temperature gradient within the cells.

The resistance of the C cells to forced discharge and to overcharge is summarized in Table 1. The tests were conducted at constant current using a fully charged cell as a reference point. Thus, a 300% overcharge is defined as that condition where a cell has received a charge equal to three times its nominal capacity beyond the normal, fully charged state. A 400% forced discharge is defined as a constant current drain until the charge extracted from the cell exceeds the nominal capacity of the cell by 300%.

The results presented in Table 1 are for cells deep cycled 10 times before they were overcharged or force-discharged. As these results show, for overcharge rates of C/3 or less and for forced discharge not exceeding 250% there was no venting with flame or ejection of cell contents. For abuse outside of these limits, ejection of cell contents or venting with flame sometimes occurred.

Table 2 shows similar overcharge and forced discharge results for cells which were first deep cycled until they lost 50% of their deliverable capacity. In this case the overcharge results were unchanged over those obtained after 10 cycles, but the cells could not be force-discharged to 250% without venting with flame. However, it was noted that venting did not occur until the cells were driven into voltage reversal to about -4 volts. A silicon diode (such as 1N4005) connected across the cells so as to limit voltage reversal to less than -1 volt was found to reliably prevent venting in these cases.

Connection of a C cell to an AC mains circuit with a 15-ampere circuit breaker caused the circuit breaker to open. Additionally, tabs within the cell vaporized to cause the cell to be open-circuited. However, there was no visible deformation of the cell.

IV. CONCLUSIONS

The lithium-molybdenum disulfide system offers attractive characteristics including high rate capability, successful operation up to 75°C, a very low self-discharge rate, a good cycle life, and safety characteristics which compare favourably to those of other lithium cells. Moreover, the materials and manufacturing costs for the system can be effectively controlled, so the cells should ultimately be competitive with currently marketed rechargeable cells.

Table 1

DEVELOPMENTAL C CELLS
(NON-OPTIMIZED)

ELECTRICAL ABUSE TESTS
CONDUCTED ON CELLS AFTER 10 CYCLES AT 20°C

	C/100 RATE	C/10 RATE	C/5 RATE	C/3 RATE	C RATE
OVERCHARGE--150%	0	0	1	1	X
OVERCHARGE--300%	0	0	1	1	X
FORCED DISCHARGE--250%	0	0	0	0	0
FORCED DISCHARGE--400%	0	X	X	X	X

0 = NO CELL DEFORMATION

1 = SLIGHT DEFORMATION OR MILD VENTING

X = VENT WITH FLAME OR EJECTION OF CELL CONTENTS

INC. = TEST INCOMPLETE

Table 2

DEVELOPMENTAL C CELLS
(NON-OPTIMIZED)

ELECTRICAL ABUSE TESTS
CONDUCTED ON CELLS CYCLED TO ½ CAPACITY AT 20°C

	C/10 RATE	C/5 RATE	C/3 RATE	C RATE
OVERCHARGE--150%	0	0	0	INC.
OVERCHARGE--300%	0	0	0	INC.
FORCED DISCHARGE--250%	X	X	X	INC.
FORCED DISCHARGE--400%	X	X	X	INC.
FORCED DISCHARGE*--250%	0	INC.	0	INC.
FORCED DISCHARGE*--400%	0	INC.	0	INC.
*WITH DIODE PROTECTION (1N4005 SI DIODE)				

0 = NO DEFORMATION
X = VENT WITH FLAME OR EJECTION OF CELL CONTENTS
INC. = TEST INCOMPLETE

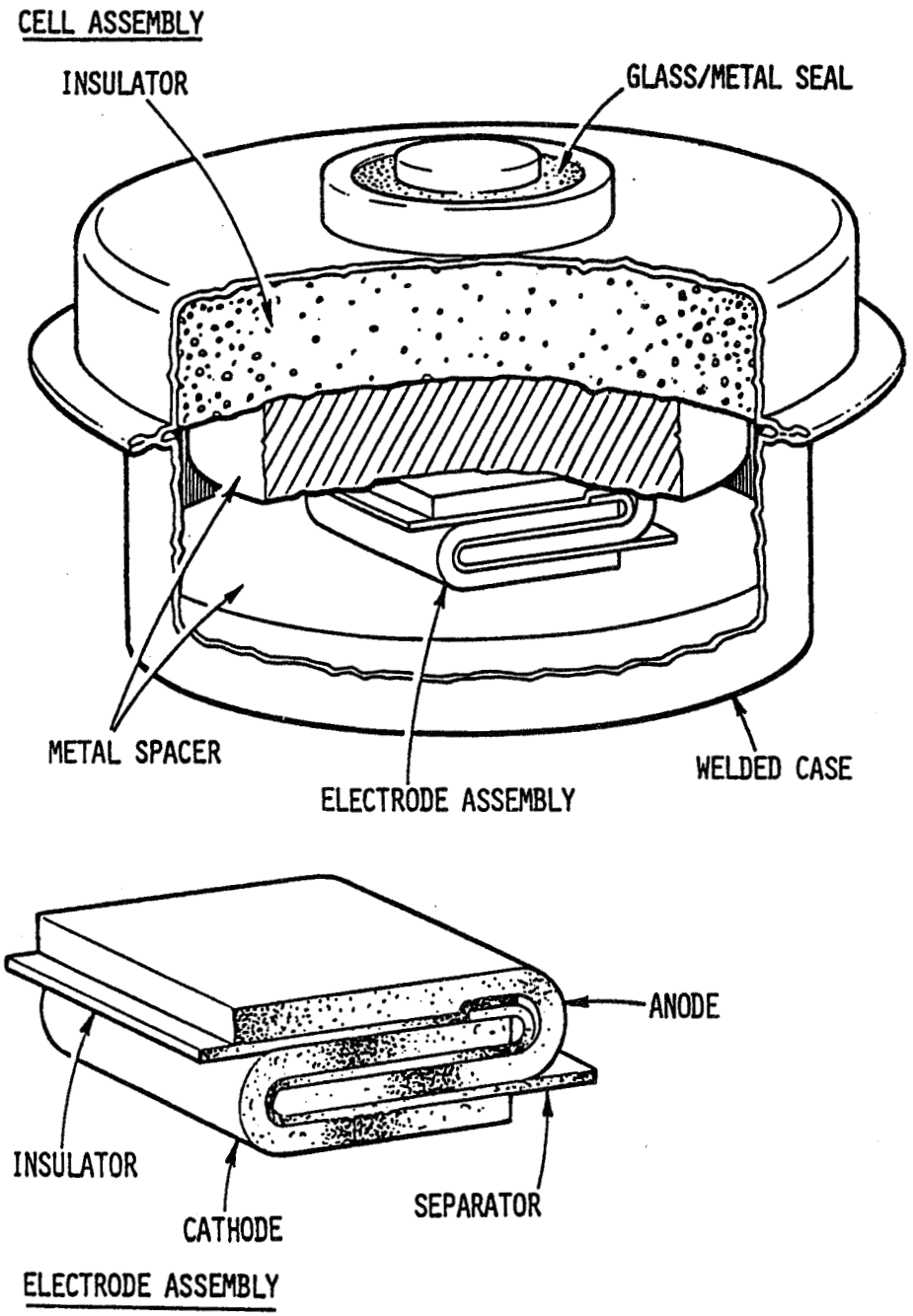
CELL ASSEMBLY
INSULATOR
GLASS/METAL SEAL
METAL SPACER
ELECTRODE ASSEMBLY
WELDED CASE
ANODE
INSULATOR
CATHODE
SEPARATOR
ELECTRODE ASSEMBLY

Figure 1.

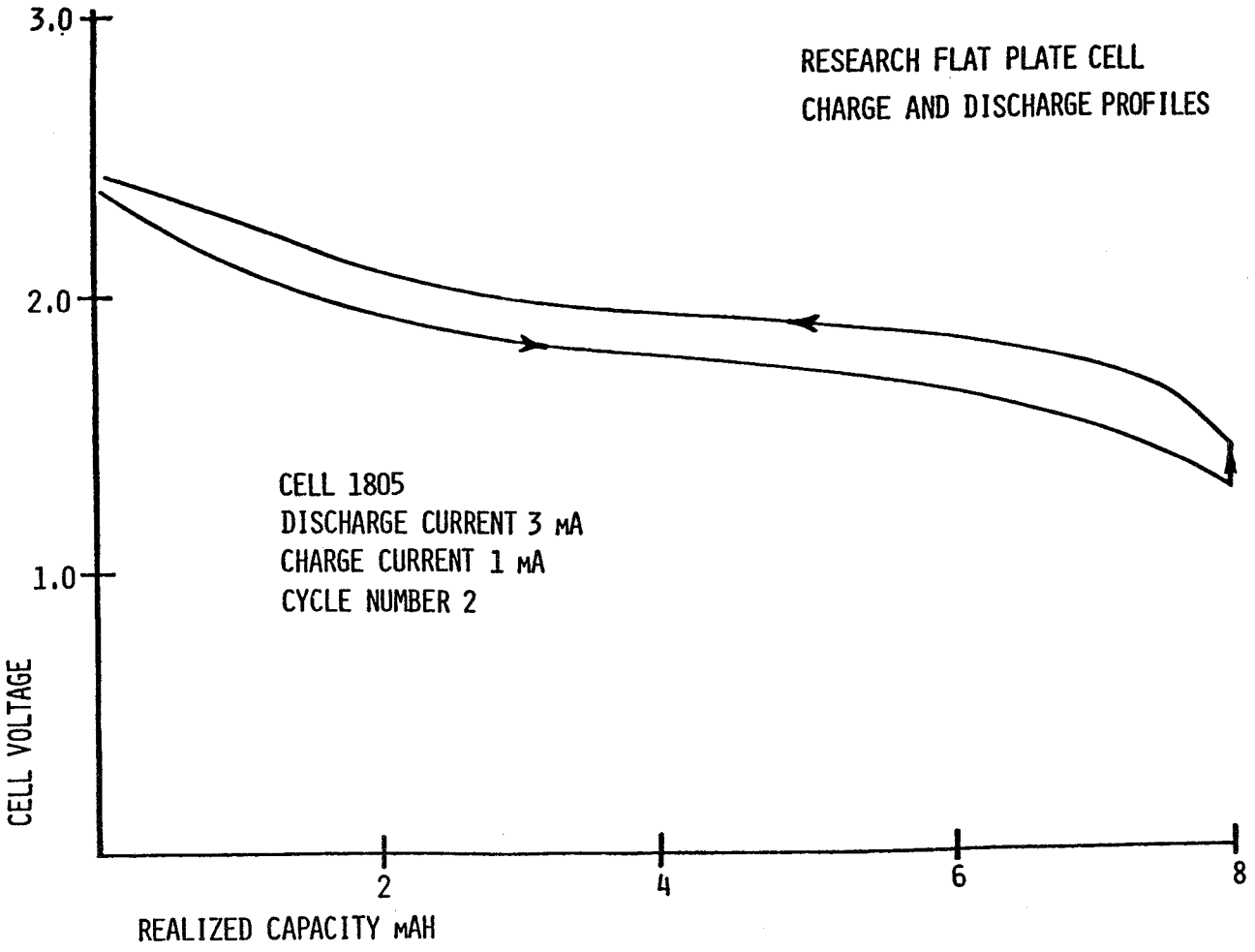
RESEARCH FLAT PLATE CELL
CHARGE AND DISCHARGE PROFILES
CELL 1805
DISCHARGE CURRENT 3 mA
CHARGE CURRENT 1 mA
CYCLE NUMBER 2
3.0
2.0
1.0
CELL VOLTAGE
2
4
6
8
REALIZED CAPACITY mAH

Figure 2

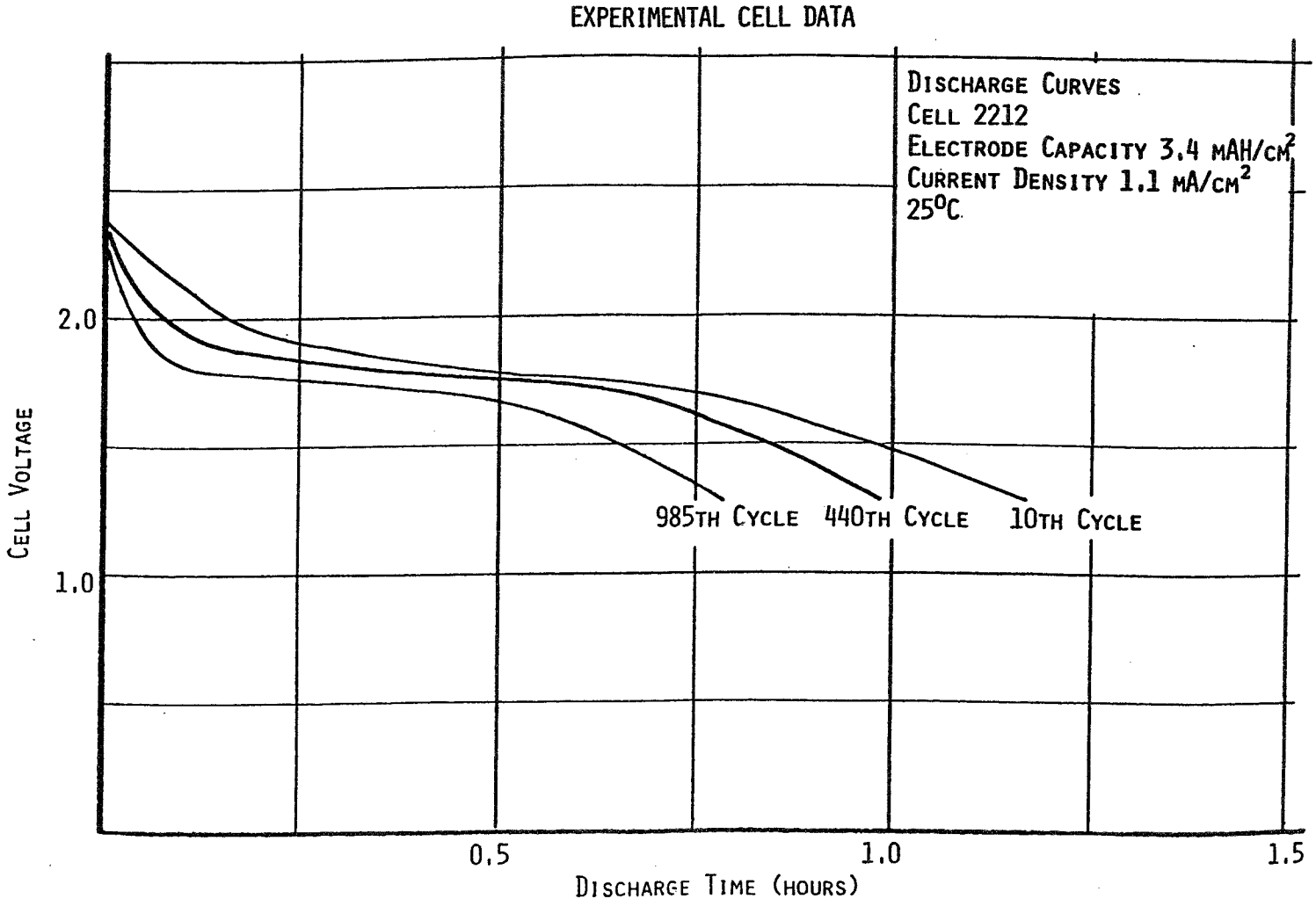
EXPERIMENTAL CELL DATA
DISCHARGE CURVES
CELL 2212
ELECTRODE CAPACITY 3.4 MAH/CM²
CURRENT DENSITY 1.1 MA/CM²
25°C
985TH CYCLE
440TH CYCLE
10TH CYCLE
CELL VOLTAGE
2.0
1.0
0.5
1.0
1.5
DISCHARGE TIME (HOURS)

Figure 3

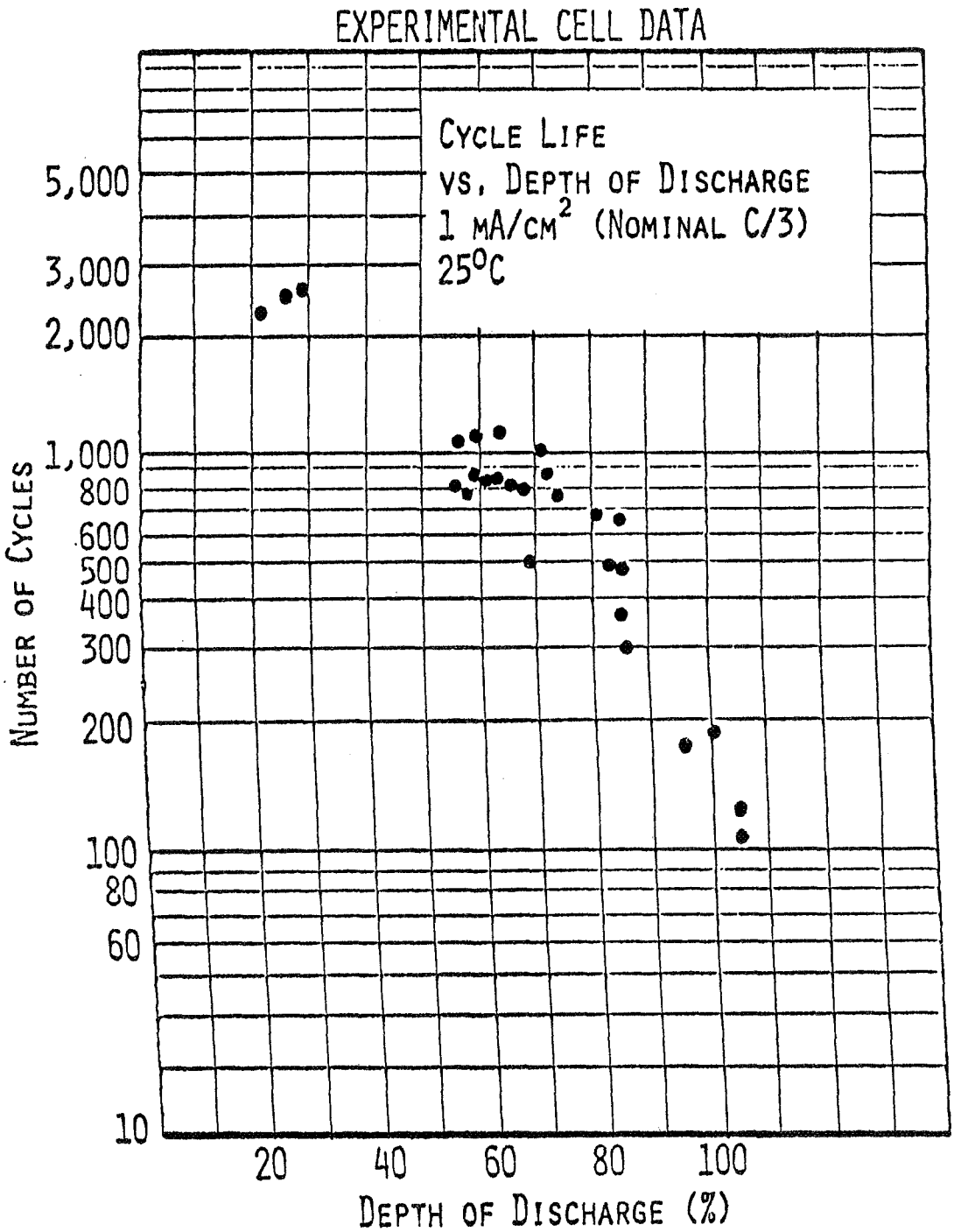
EXPERIMENTAL CELL DATA
CYCLE LIFE
VS. DEPTH OF DISCHARGE
1 mA/cm² (NOMINAL C/3)
25°C
NUMBER OF CYCLES
5,000
3,000
2,000
1,000
800
600
500
400
300
200
100
80
60
10
20
40
60
80
100
DEPTH OF DISCHARGE (%)

Figure 4

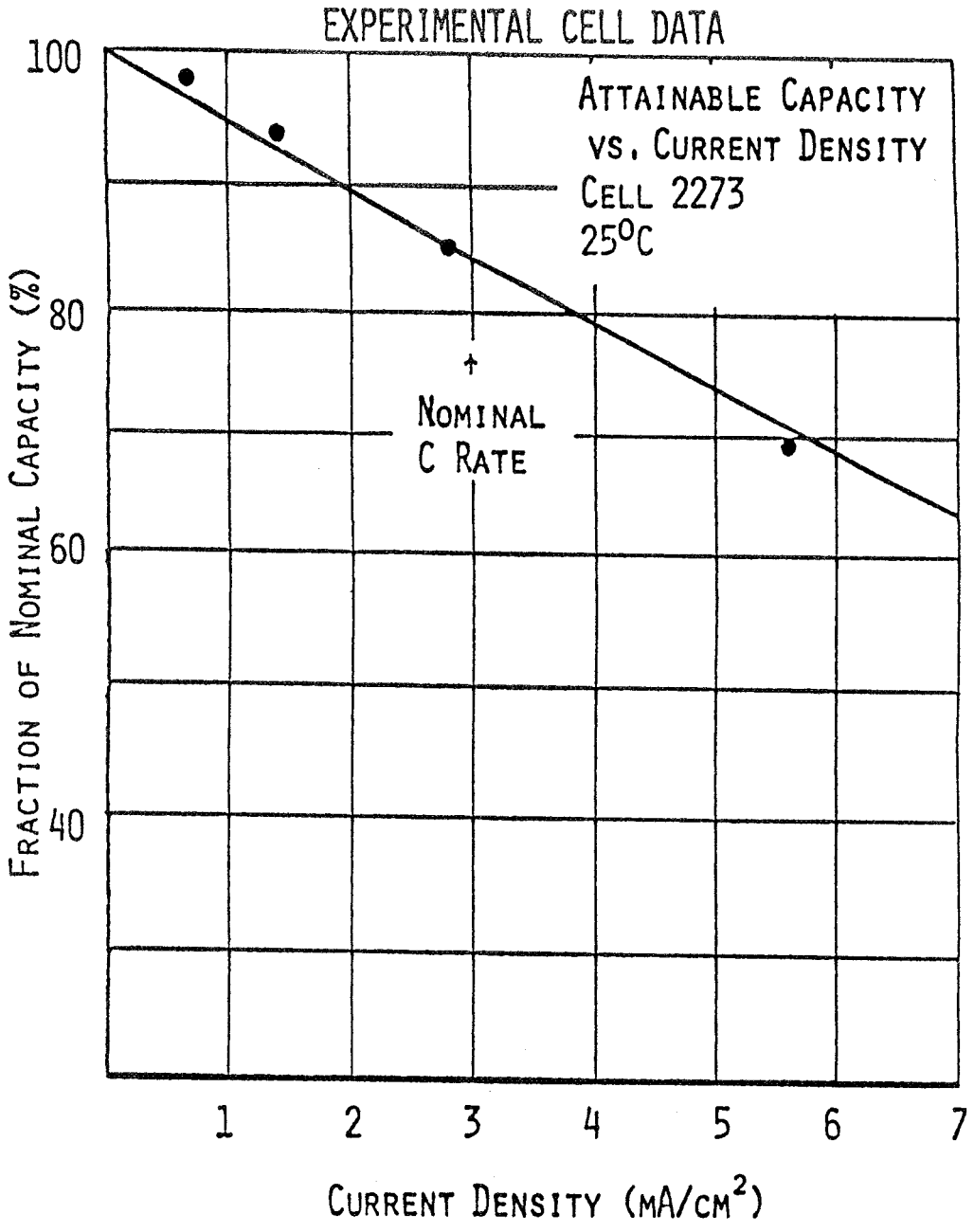
EXPERIMENTAL CELL DATA
ATTAINABLE CAPACITY
VS. CURRENT DENSITY
CELL 2273
25°C
NOMINAL
C RATE
FRACTION OF NOMINAL CAPACITY (%)
100
80
60
40
1
2
3
4
5
6
7
CURRENT DENSITY (mA/cm²)

Figure 5

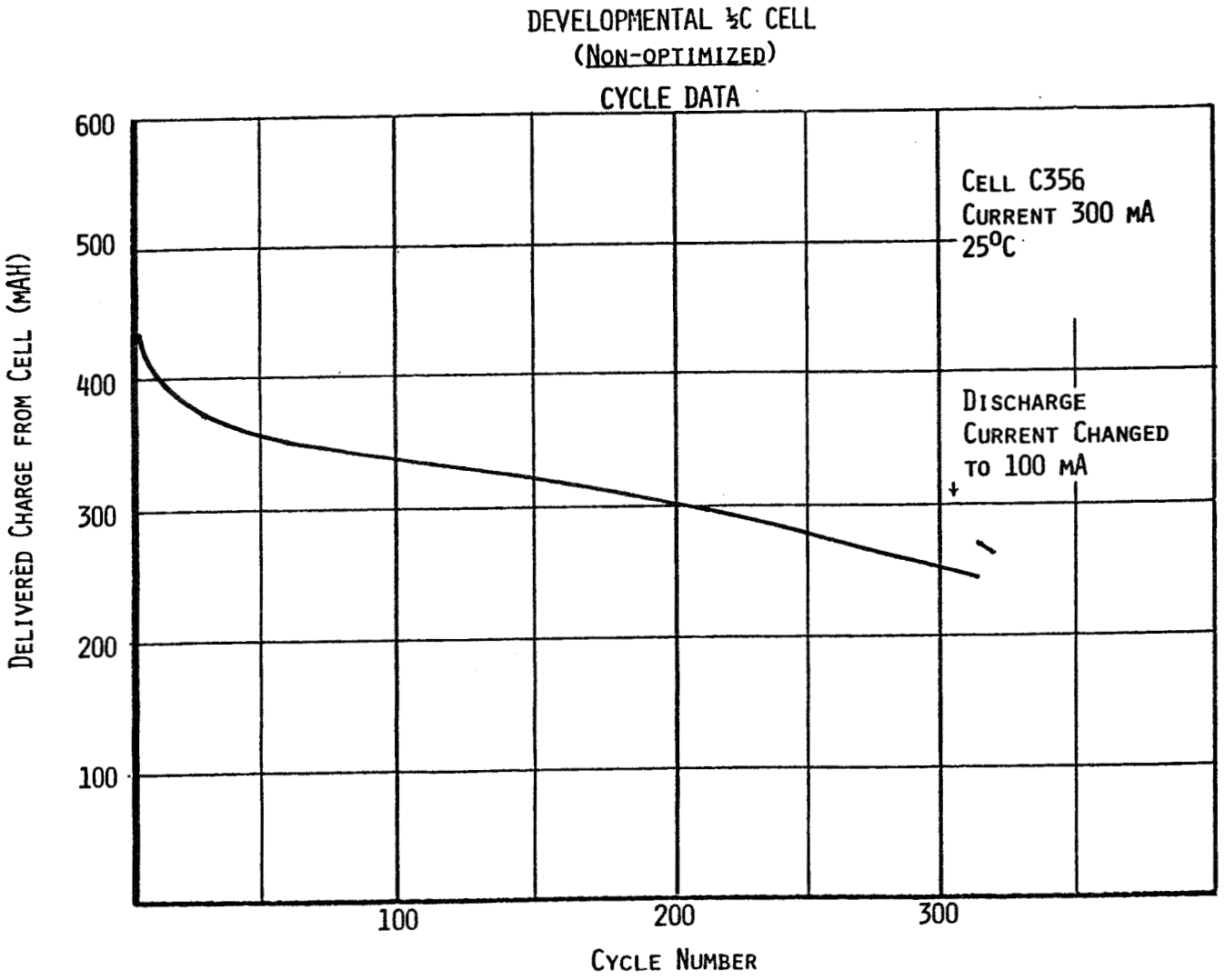
DEVELOPMENTAL ½C CELL
(NON-OPTIMIZED)
CYCLE DATA
DELIVERED CHARGE FROM CELL (MAH)
600
500
400
300
200
100
100
200
300
CYCLE NUMBER
CELL C356
CURRENT 300 MA
25°C
DISCHARGE
CURRENT CHANGED
TO 100 MA

Figure 6

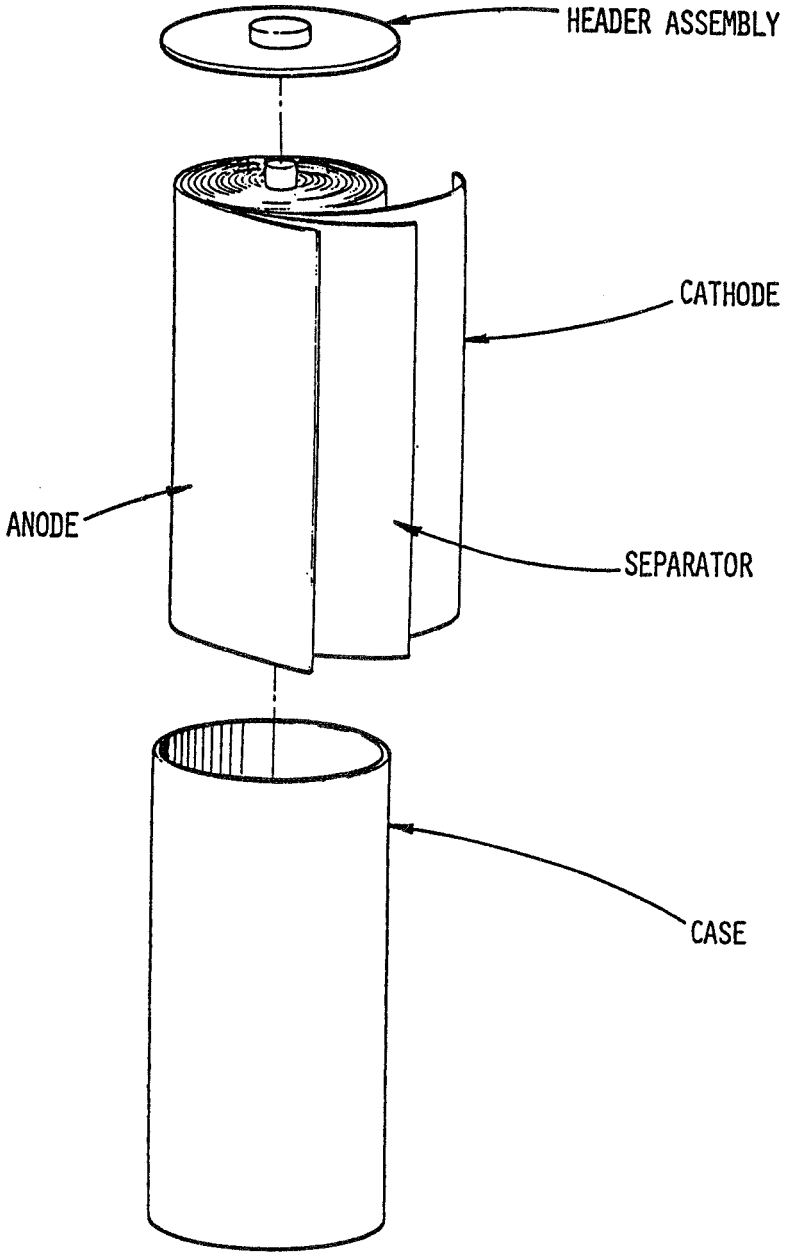

Figure 7

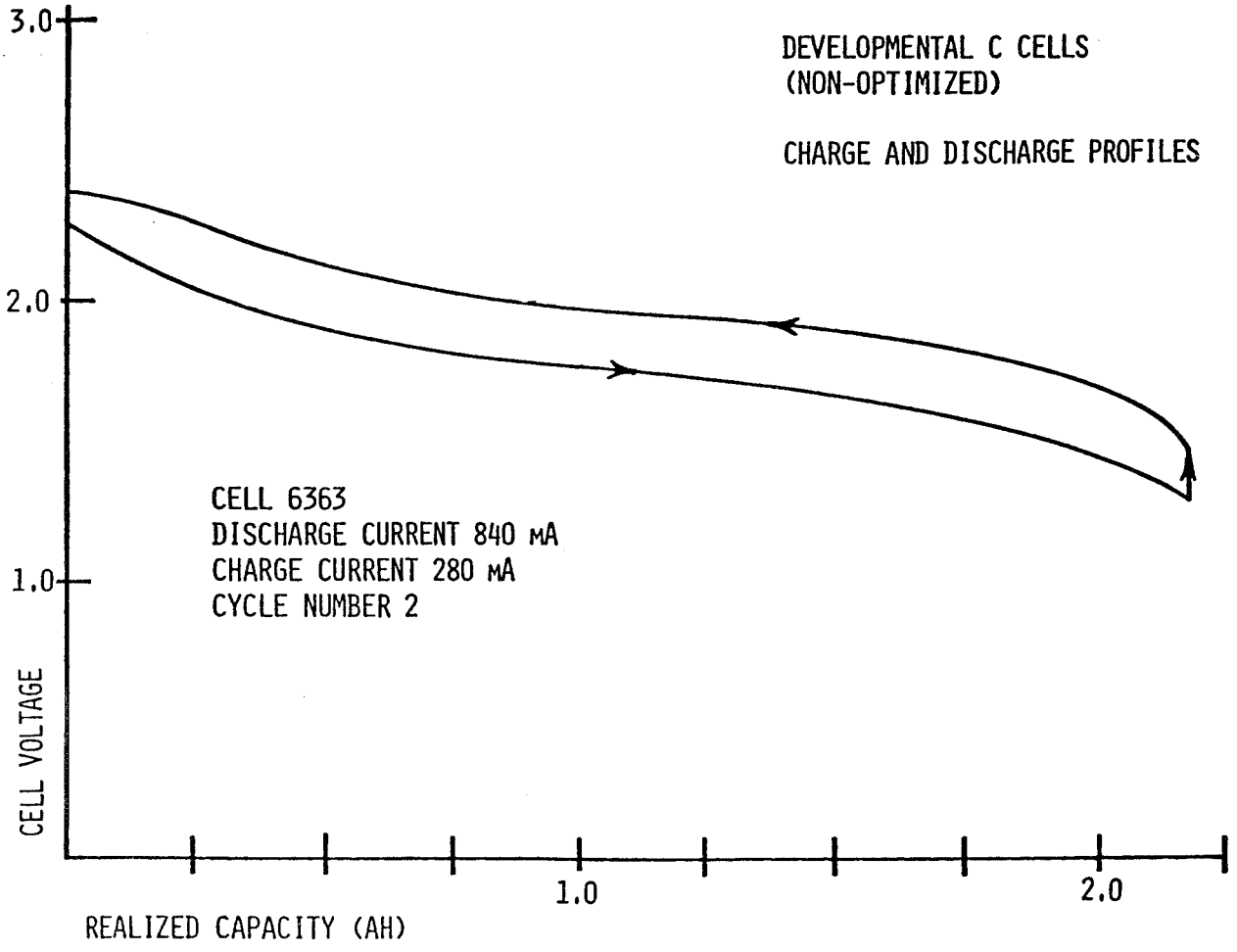
3.0
2.0
1.0
DEVELOPMENTAL C CELLS
(NON-OPTIMIZED)
CHARGE AND DISCHARGE PROFILES
CELL 6363
DISCHARGE CURRENT 840 mA
CHARGE CURRENT 280 mA
CYCLE NUMBER 2
CELL VOLTAGE
1.0
2.0
REALIZED CAPACITY (AH)

Figure 8

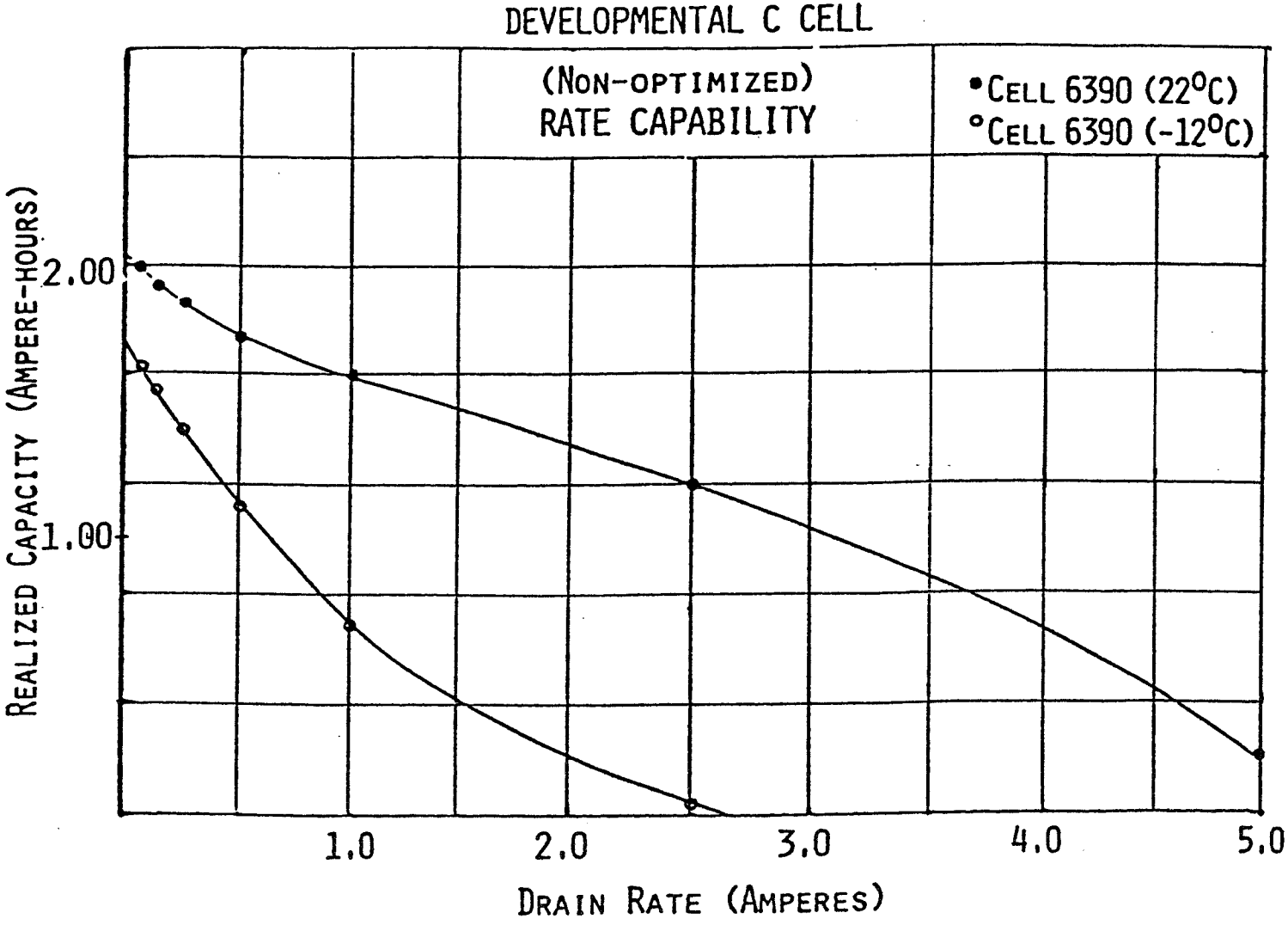
DEVELOPMENTAL C CELL
(NON-OPTIMIZED)
RATE CAPABILITY
•CELL 6390 (22°C)
°CELL 6390 (-12°C)
REALIZED CAPACITY (AMPERE-HOURS)
2.00
1.00
1.0
2.0
3.0
4.0
5.0
DRAIN RATE (AMPERES)

Figure 9

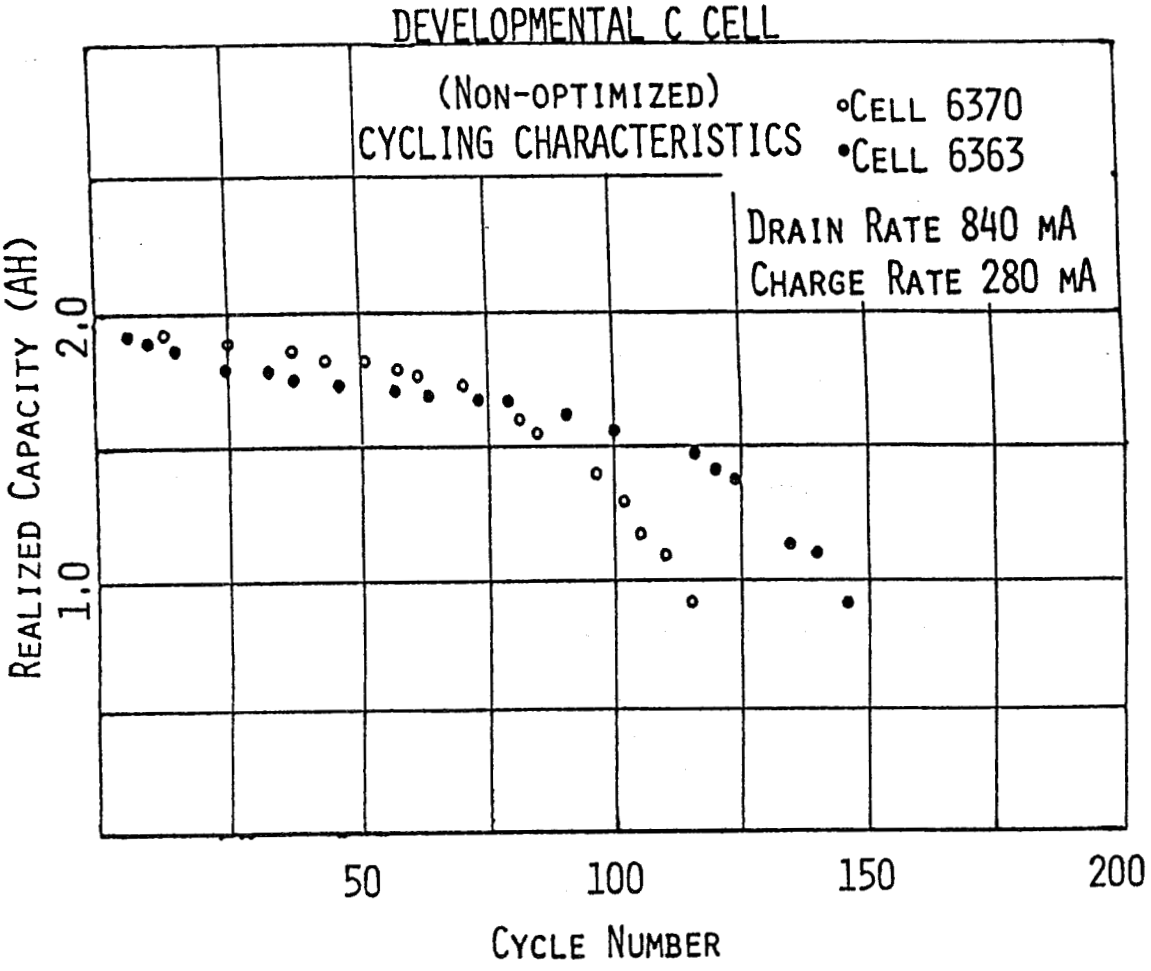
DEVELOPMENTAL C CELL
(NON-OPTIMIZED)
CYCLING CHARACTERISTICS
•CELL 6370
•CELL 6363
DRAIN RATE 840 mA
CHARGE RATE 280 mA
REALIZED CAPACITY (AH)
2.0
1.0
50
100
150
200
CYCLE NUMBER

Figure 10

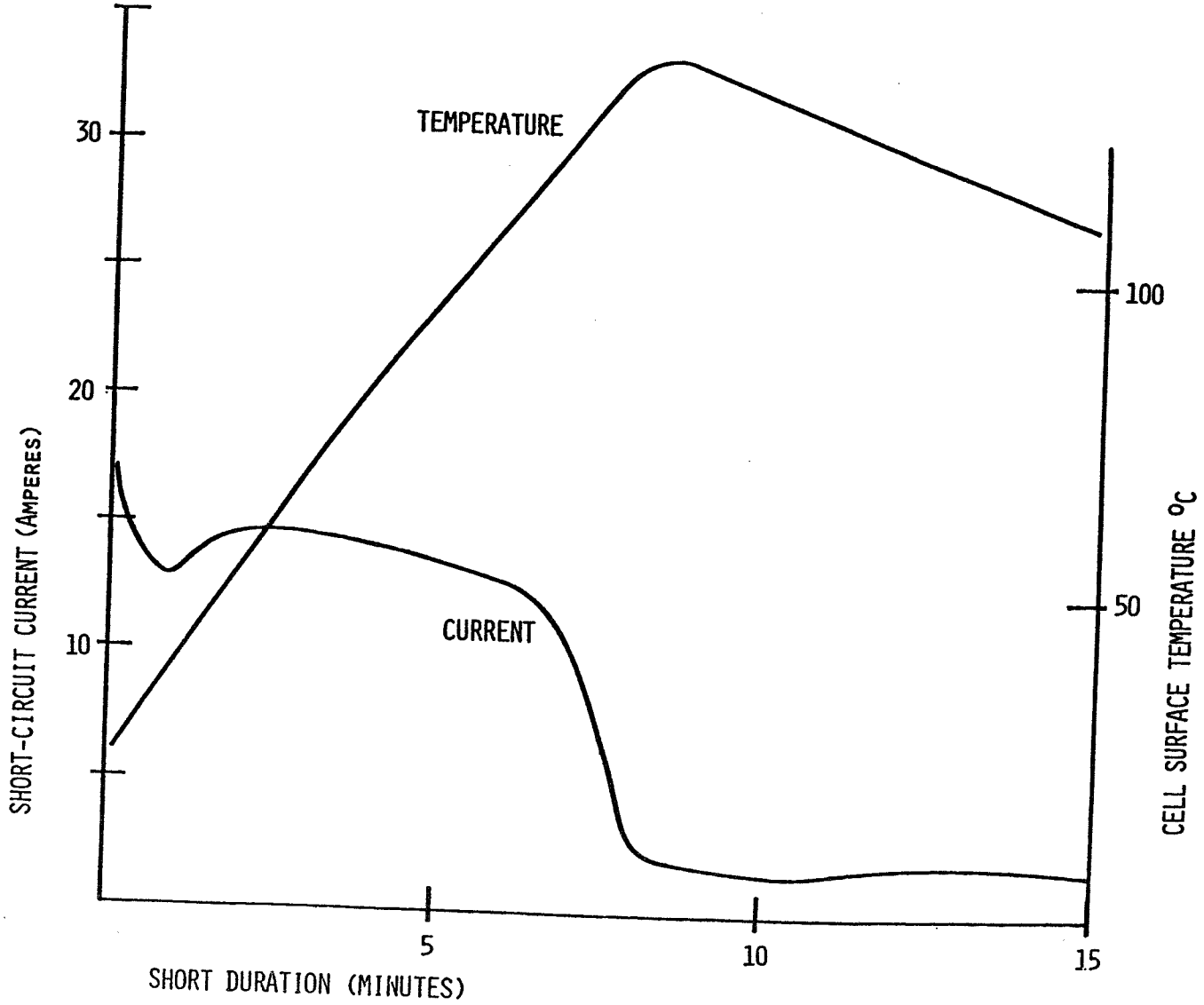
TEMPERATURE
CURRENT
30
20
10
100
50
5
10
15
SHORT-CIRCUIT CURRENT (AMPERES)
CELL SURFACE TEMPERATURE °C
SHORT DURATION (MINUTES)

Figure 11

Q. Somoano, JPL: I'd like to commend you on the progress you've made. That's some very encouraging data. Two questions: (1) Could you describe the nature of the electrolyte you used? (2) Tell us what the theoretical energy density is in terms of watt hours per kilogram and number of lithiums per many-sulfide.

A. Stiles, NPLI Energy, Ltd.: The first question I can't answer for you unfortunately. The second question - the energy density as quoted here is based on the intercolation of .6 electrons per molybdenum. It is possible to intercolate more molybdenum than that. That's rather an arbitrary figure. One could achieve a higher energy density by incorporating a larger fraction of lithium per molybdenum. However one does so at the sacrifice of cycle life and also with a wider voltage range during the discharge. One can, for example, charge all the way up to 2.7 volts and have it discharged down to 1.1 volts. If you did that you would enjoy approximately 25% increased energy density. But, as I say, you then have to accommodate the larger voltage variation and you have a penalty in cycle life.

Q. Sullivan, APL: There's two questions: (1) I'm wondering how you discharge a cell 400 percent. Is it with an external power supply? (2) You showed a slide where the short-circuit current of the battery dropped dramatically as the temperature went up and I'm wondering what the mechanism is that causes that to happen?

A. Stiles, NPLI Energy, Ltd.: The separator loses its porosity. The fusion of ions from the anode to the cathode is impeded at that temperature.

Q. Sullivan, APL: And that's designed to happen?

A. Stiles, NPLI Energy, Ltd.: Yes.

Q. Sullivan, APL: And the first one - how do you force discharge?

A. Stiles, NPLI Energy, Ltd.: With a power supply in series with the cell. With a very large voltage component so that, no matter what happens you maintain constant current.

Q. Sullivan, APL: What kind of a negative voltage do you get when you do that?

Q. Stiles, NPLI Energy, Ltd.: On the forced discharge?

A. Sullivan, APL: On the forced discharge.

A. Stiles, NPLI Energy, Ltd.: You can go up to about - 4 volts before you get a venting.

Q. Sullivan, APL: Per cell?

A. Stiles, NPLI Energy, Ltd.: The cell has a peculiar characteristic, actually. You don't actually get voltage reversal until you've discharged the cell to approximately 200-300% beyond the nominal end of discharge. So the property of the cathode prevents voltage reversals when you get out there.

Q. Yen, JPL: I have 3 questions. (1) Is your cell a lithium limited cell or cathode limited cell? (2) Do you add combative additive in your cathode? (3) I saw your cell configuration. What material is the mendral made of? Is that the cathode current collector? You know the C cell.

A. Stiles, NPLI Energy, Ltd.: I will answer the first question for now. As far as the lithium is concerned I'll just tell you that the mol ratio of lithium to molybdemum in the cell is 2½ to 1 - 2½ mols lithium to 1 molybdemum. I would rather not comment on the composition of the cathode at this stage. We do have a means of providing adequate connectivity but I'd rather not discuss how that's done. As far as the manderal materials are concerned - a wide variety of materials. It's not crucial to the operation of the cell.

Q. Yen, JPL: That is your current collector, I assume - the mandral?

A. Stiles, NPLI Energy, Ltd.: Yeah, the mandral is connected by a strip to the center terminal of the battery. The cathode is at the center terminal, potentially.

A. Yen, JPL: Well, I think even though you mentioned that there's a variety of material you can use probably some of the material may affect.

A. Stiles, NPLI Energy, Ltd.: Oh yes, you can't just use anything.

Q. Yen, JPL:: Yes, that's what I was asking. What type of current collector materials?

A. Stiles, NPLI Energy, Ltd.: I'd rather not comment right now.

Q. Kunigahalli, Bowie State College: In one of the viewgrafts I saw 3 discharge curves, depending on the number of cycles. Could you tell me whether the cells experienced the voltage degradation on the capacity degradation by virtue of increasing the number of cycles?

A. Stiles, NPLI Energy, Ltd.: When we cycled we charged at constant current and then terminated the charge when we reached 2.4 volts. Now the 2.4 volts was unchanged during the whole cycle life task.

A. Stiles, NPLI Energy, Ltd. (Con't): And we discharge the cell until the end voltage goes down to 1.3 volts. And, again, that 1.3 volts was unchanged during the entire cycle life task. So we're forcing just by the nature of the cycling regime. We're using, we're forcing the average voltage to remain constant during the test. So, in this test, there is no voltage degradation. One could cycle a cell in a different way. If you were to terminate the discharge on the basis of time, for example, rather than on voltage, one would see a lower average voltage as you increase the cycle number. But the second region we used just doesn't allow for a voltage droop.