LBL-18287
UC-94cc c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
OCT 9 1984
LIBRARY AND
DOCUMENTS SECTION

APPLIED SCIENCE DIVISION

SUPPORTED LIQUID MEMBRANE BATTERY SEPARATORS
Final Report

J.P. Pemsler and M.D. Dempsey

July 1984

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.

APPLIED SCIENCE
DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-18287 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-18287

SUPPORTED LIQUID MEMBRANE BATTERY SEPARATORS

Final Report

J. Paul Pemsler
and
Michael D. Dempsey

Castle Technology Corporation
52 Dragon Court
Woburn, MA 01801

Prepared for

Lawrence Berkeley Laboratory
University of California
Berkeley, California
Purchase Order No. 4521910

July 10, 1984

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, subcontract no. 4521910 with the Lawrence Berkeley Laboratory.

PROJECT SUMMARY

This study was performed to explore the feasibility of using a supported liquid membrane (SLM) as a separator in the nickel-zinc battery. In particular, SLM separators should prevent zinc dendrite growth from shorting out the cell and might also alleviate capacity loss due to zinc electrode shape changes.

A number of ion exchange/solvent modifier systems for incorporation into SLMs were developed under a previous LBL contract. SLMs prepared with these reagents exhibited resistances in the range of 0.4-10 ohm cm^2, selectively transported hydroxyl ions over zincate ions by a factor of 10^6-10^7, and possessed electrochemical and chemical stability in alkaline electrolytes.

In order to evaluate these SLM separators under conditions closely resembling a commercial Ni-Zn cell, an accelerated cycle life test was devised using commercial electrodes. Previous experimental studies indicated that cell hardware needed to be specially designed to accommodate the SLM separator. The new cell design was tailored to allow for the total thickness of the electrodes, wicks and SLM without placing excess mechanical pressure on the electrode package which could cause excess electrode gassing, localized heating, or electrolyte wick dry out.

Cycle life for the two SLM systems that perform best in 5M KOH electrolyte consistently exceeded cycle life for control cells containing one, two or three layers of Celgard 3501 separators. No evidence of dendrite "hot shorting" was found in any SLM-containing

cell. Results in 7M KOH electrolyte also indicate improved cycle life with the new cell design where the cycle life of cells containing a single layer SLM exceeded those of single and double layers of Celgard 3501. However, one control cell containing three layers of Celgard 3501 achieved 375 cycles, surpassing SLM cells. Once again the SLM-containing cells remained free of dendrite shorting. Studies were conducted to establish failure modes of cycled cells. Cells were also studied at rapid discharge rates and cells with multiple-layer SLMs were examined. Some possible causes were found for capacity loss in SLM cells; however, zinc electrode shape change may remain a major factor.

Recent Publications

1. J. P. Pemsler and M. D. Dempsey, "The Application of Supported Liquid Membrane Separators to Alkaline Secondary Batteries" in Proceedings of the Symposium on Advances in Battery Materials and Processes, Washington, DC, October 9-14, 1983, Electrochemical Society Proceedings.

2. J. P. Pemsler and M. D. Dempsey, "Supported Liquid Membrane Battery Separators", Extended Abstract #569, Electrochemical Society Meeting, San Francisco, CA, May 8-13, 1983.

TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	EXPERIMENTAL METHODS	2
	2.1 Improved Cell Container Design	2
	2.2 Cell Components and Test Description	4
	2.3 Battery Cycler and Data Collection	6
3.	MEMBRANE RESISTANCE STUDIES	7
4.	TESTING OF SUPPORTED LIQUID MEMBRANES IN NI-ZN CELLS	10
	4.1 Cycle Life Tests	10
	4.2 Accelerated Rate Study	28
	4.3 Multi-layer SLM Study	28
	4.4 Analysis of Failure Modes	31
5.	ACKNOWLEDGEMENT	35
6.	REFERENCES	35
7.	APPENDIX	36

1. INTRODUCTION

A fundamental component of many battery systems is the separator. Alkaline batteries, particularly Ni-Zn, have rigorous requirements for the separator and microporous or membrane films are generally used. Considerable effort has been expended in solving the problems of dendrite shorting and zinc electrode shape change in Ni-Zn batteries, particularly through the use of improved separators. The work reported here is directed toward the development of a new type of battery separator using supported liquid membranes. The initial studies of the concept of supported liquid membrane (SLM) battery separators were performed under LBL Contract No. 4512210 and reported in the First and Second Year Final Reports. SLMs consist of a liquid ion exchange/solvent system infused into the pores of a hydrophobic microporous membrane. Transport through SLMs is the result of a chemical and/or electrochemical activity gradient established between the aqueous phases on either side of the membrane. The specific liquid complexing agent within the membrane provides the opportunity for selective ion transport and presents a chemical barrier to the intrusion of zinc dendrites.

A separator for any alkaline battery must possess certain properties that include chemical and electrochemical stability, low resistivity, mechanical and dimensional stability and low cost. Ni-Zn cells also require a separator that prevents the migration of soluble zinc species between the two opposite electrodes. Supported liquid membranes possess both the necessary chemical and electrochemical stability for use in alkaline systems. SLM separators can be routinely made with resistances of 0.4-1.4 ohm cm^2, and offer the excellent mechanical stability of their inert polypropylene support. Costs for SLM separators are only slightly higher than that of the microporous support alone. Most importantly, SLMs are ion selective and transport hydroxyl ions about 10^6 times more rapidly than zincate ions. These properties may enable the SLM to alleviate separator-related problems in the Ni-Zn battery.

2. EXPERIMENTAL METHODS

2.1 Improved Cell Design

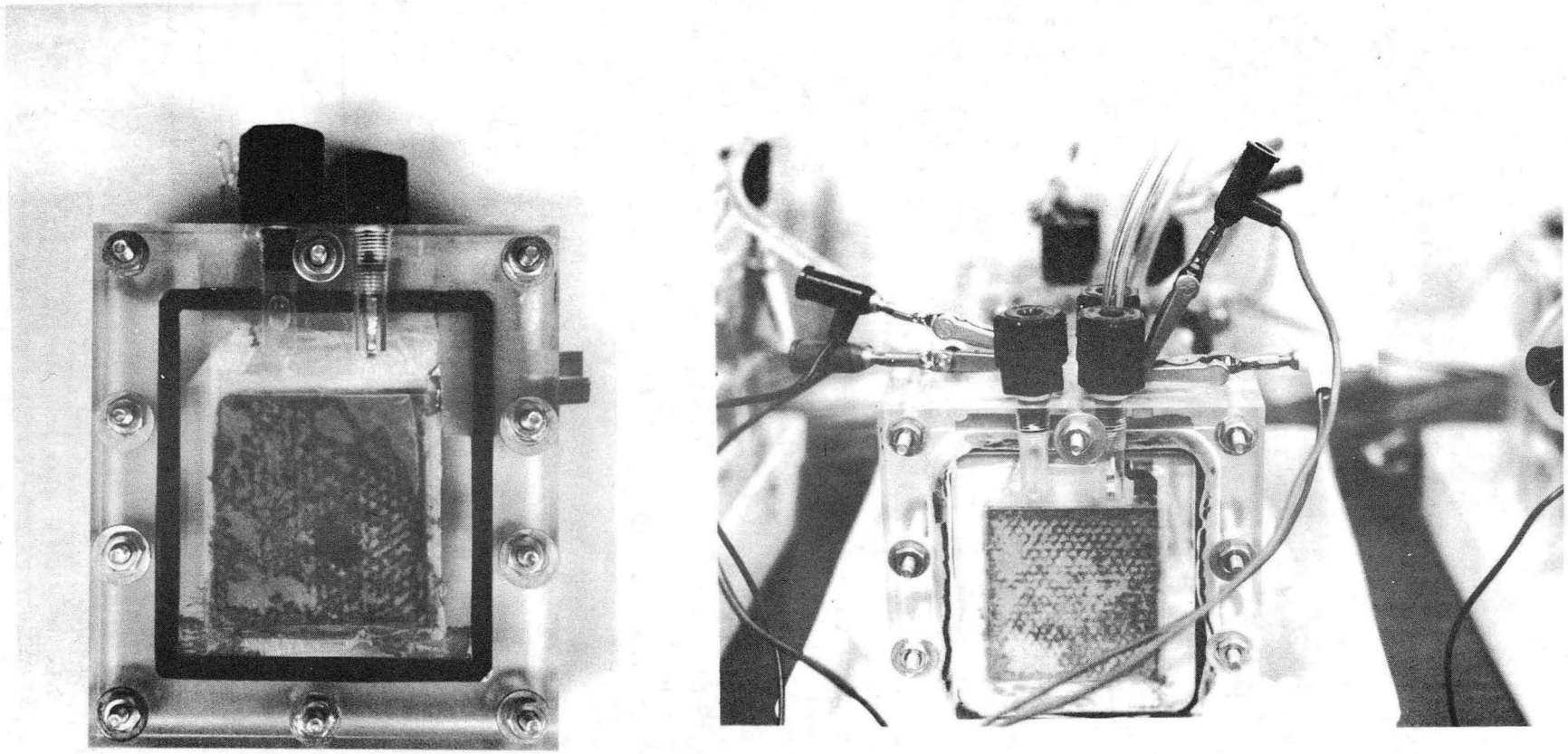
In our previous study (1) we showed that the use of supported liquid membrane battery separators in Ni-Zn cells required redesign of the cell hardware. Post mortem examination of failed cells from this program indicated SLM life was limited by the loss of the organic from the SLM in small areas. This was believed to be the result of one or more factors such as excess electrode gassing, absorption of the material into the wick layer, or localized heating. Another problem found in some dismantled cells was that the zinc electrode wick was drying out thereby resulting in a lack of electrode wetting. These problems were believed to be caused by exerting excessive pressure on the electrode package during cell assembly which forced electrolyte out of the SLM envelope.

Two new designs this year incorporated the ability to control the thickness of the electrode compartment. This was accomplished by using either a) a combination of a machined recess in the cell container and thin plastic shims or b) an adjustable removable electrode compartment. Both cell designs also included measures to alleviate excess electrode gassing and localized heating by providing ample venting channels in the cell to prevent pressure build-up. The cells also contained reference electrode compartments to allow the continuous monitoring of individual electrodes thereby preventing damaging overpotentials.

The total thickness of each electrode package was measured before assembly. A thicker wick material, Pellon FS2108 with an electrolyte adsorption capacity of 500 g/m^2, was used. The depth of the cell electrode compartment was then adjusted to the total thickness of the package either by using plastic shims or by separately machining a central electrode compartment. Using these cell designs, no excess pressure was exerted on the SLM separator or zinc electrode.

Two sample cells were assembled using the two new designs. One cell contained an LT1-M2 SLM separator and 7M KOH electrolyte while the other cell used an LT17-M2 SLM separator and 5M KOH electrolyte. Extended cell cycle life tests demonstrated the beneficial effect of the new cell designs which lasted significantly longer than comparable cells without dimensional control that were used last year. The cell design that incorporated a recess for the electrode package and adjusted the thickness with plastic shims was easier to use and was chosen as the standard configuration for the remainder of the program. Nine additional cell containers using the new design, as shown in Figure 2-1, were

Figure 2-1 NEW CELL HARDWARE DESIGN



Two assembled SLM cells showing the use of new acrylic cell containers

machined from clear acrylic plastic to allow visual observation of the cell electrodes and electrolyte levels. Cells were sealed with an ethylene-polypropylene rubber o-ring gasket.

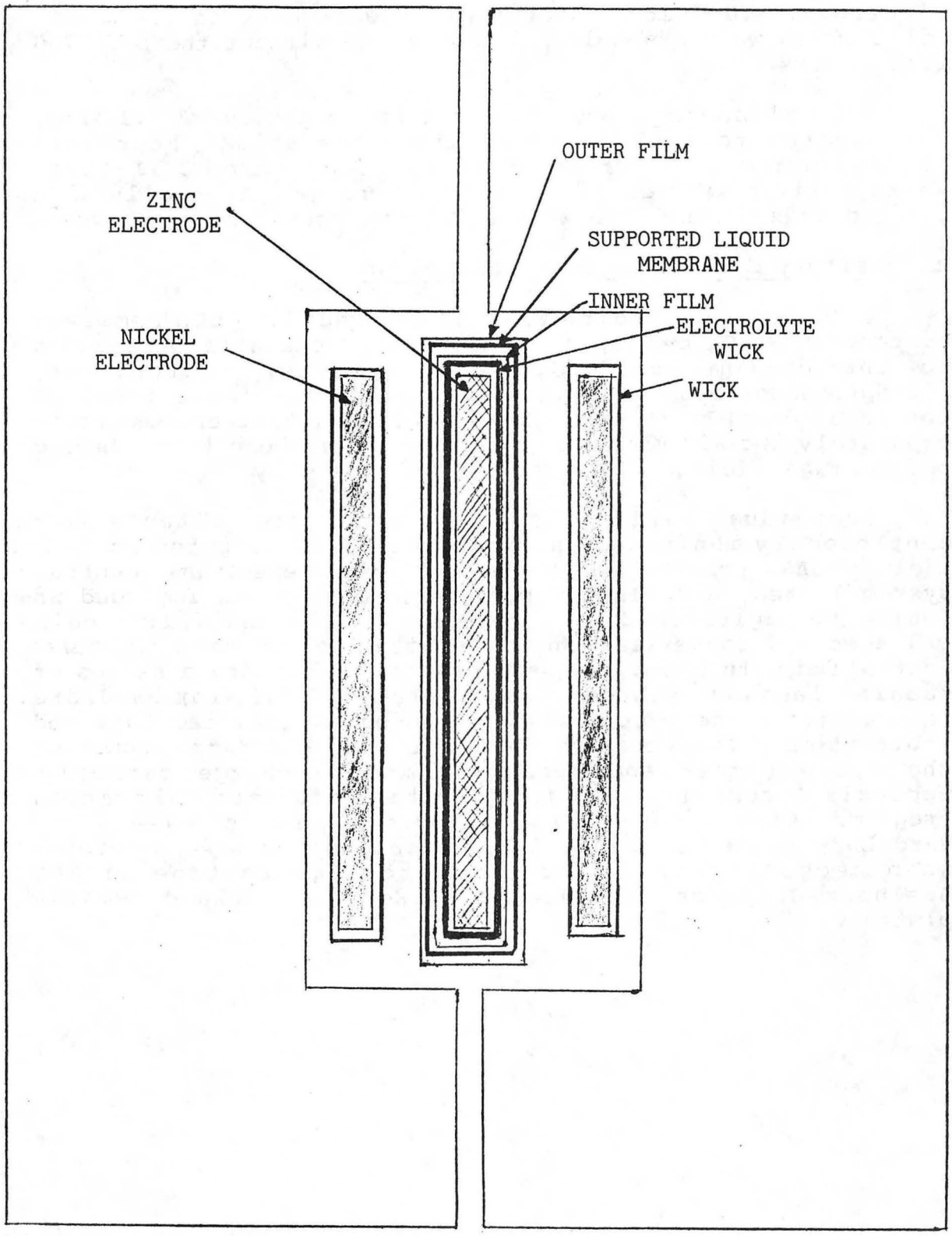
Due to machining errors, some of the new cells developed electrolyte leakage during cycling. This problem was later corrected by using PTFE tape and foam gaskets at the appropriate locations.

2.2 Cell Components and Test Description

SLM separators were evaluated under conditions resembling commercial cell testing by using an accelerated cycle life test. PTFE bonded zinc oxide electrodes and roll bonded nickel electrodes were obtained from Energy Research Corporation of Danbury, CT. The zinc electrode allowed for a three-fold excess of capacity over the two nickel electrodes used in each cell. Dimensions of both electrodes were 6 cm X 5 cm for a total usable area of 60 cm^2 per electrode. The cell had a flooded flat plate configuration, as shown in Figure 2-2, with a single zinc electrode sandwiched between the two nickel electrodes. The electrolyte in all cases was either a 5M or 7M KOH with 1% LiOH solution presaturated with very small amounts of the organic constituents of the SLM. This prevented leaching of aqueous-soluble constituents from the SLM. Cells containing SLM separators were assembled in the following manner: the zinc electrode was enclosed in a heat-sealed Pellon FS2108 non-woven polypropylene envelope which acted as an electrolyte wick (Pellon Corporation, Chelmsford, MA). This was wet with the alkaline electrolyte and placed inside an envelope of RAI P700 ion exchange film obtained from RAI Research Corporation, Hauppauge, NY. The film was placed on the inside and outside of the SLM in order to protect the SLM from localized heating and any loss of organic constituent due to excess gassing in the cell. The RAI film had a very low electrical resistance, on the order of a 0.12 ohm cm^2, but little resistance to zinc dendrite penetration. The film served only as buffer between the electrolyte wick and the SLM separator. The SLM consisted of a heat-sealed Celgard 2500 membrane filled with the appropriate organic constituents. The zinc electrode and accompanying wick and separators were placed between two nickel electrodes each wrapped in a thin Pellon FS2121 non-woven polypropylene wick envelope. This package was placed in the cell container, sealed and filled with electrolyte.

Several cells without SLM separators were assembled for comparison purposes. These cells used aqueous wettable Celgard 3501 membranes as separators either as a single layer

Figure 2-2: EXPANDED VIEW OF NI-ZN CELL CONTAINING A SUPPORTED LIQUID MEMBRANE SEPARATOR



or triple layer heat-sealed envelope around the zinc electrode. Identical Pellon wicks were used in the blank cells which were assembled both with and without the RAI P700 film layers.

The cells, which had a theoretical capacity of 1.2 Ahrs, were cycled to 100% depth of discharge at a 2 hour rate corresponding to a current density of 7.3 mA/cm^2. A lower voltage limit was set to 1.00V on discharge. The cells were charged at a 4 hour rate with a 20% overcharge on each cycle.

2.3 Battery Cycler and Data Collection

In order to expedite testing of candidate SLM membrane systems in Ni-Zn cells, five additional channels were added to the custom built Starbuck Systems, Newton, MA, microprocessor-controlled battery cycler, giving a total of ten individual stations. The cycler monitors each station separately and allows cells to be cycled in both time-limited and voltage-limited cycle modes simultaneously.

Individual cell voltages and reference voltages were continuously monitored and all cycle data computed using a Kiethly DAS, Boston, MA, Series 500 measurement and control system linked to an IBM-PC computer. The system included an analog to digital module for measuring the individual cell voltages and converting them to digital form. The system was controlled with BASIC language programs including a series of machine language subroutines, called Soft500, for hardware interaction. The system was programmed to read the data and store it on a diskette, while tabulating the data, counting the cycle number and measuring the discharge capacity. Appendix A contains a listing of the main data collection program. Also included is an example of the processed data. Hard copy plots of the cell potential curves were generated when necessary with a data interchange routine of BPS Business Graphics software and a Hewlett Packard HP7470A plotter.

3. MEMBRANE RESISTANCE STUDIES

In any battery, it is desirable for the separator to have as low a resistance as possible while providing the necessary separation of electrolytes in the positive and negative electrode compartments. In an SLM we seek the best compromise between high degrees of ion specificity and resistance. In our previous studies we identified many possible transport agents, solvents and modifiers that exhibited low resistance when used as an organic constitutent of an SLM. This year four low resistance systems were chosen as candidates and tested extensively in Ni-Zn cells. The composition of these candidate systems and their separator resistances are listed in Table 3-1. The two separator systems that perform best in 5M KOH electrolyte can be routinely made with resistances in the 0.4-1.4 ohm cm^2 range. Several new combinations were tested for adequate separator resistance using the DC method or an AC resistance bridge. Results for these new systems, which were not tested in Ni-Zn cells, are listed in Table 3-2.

TABLE 3-1

Examples of SLM Separator Resistances

Transport Agent	Concentration, Wt%	KOH Molarity	Separator Resistance ohm cm^2
LT-17	20	5	1.3
	75	5	1.8
LT-8	10	7	54
	20	7	3.0
LT-18	20	5	0.4
LT-1	20	7	3.0

TABLE 3-2

Summary of New SLM Separator Resistance Tests

	ohm cm^2	KOH electrolyte
75% LT17 - 25% M2	1.5	5M
50% LT2 - 50% M2	1.2	5M
20% LT8 - 10% LT17 - 70% M2	3.0	5M
100% M6	64	7M
20% LT8 - 10% LT17 - 70% M2	104	7M
20% LT8 - 80% M6	36	7M
20% LT19 - 80% M2	114	7M
20% LT20 - 80% M2	240	7M
50% LT2 - 50% M2	1.7	3.5M
20% LT2 - 80% M2	1.0	5M
20% LT2 - 80% M2	38	7M

4. TESTING OF SUPPORTED LIQUID MEMBRANES IN NI-ZN CELLS

4.1 Cycle Life Tests

Cycle life tests in Ni-Zn cells were performed on only four candidate SLM systems in order to establish sufficient statistically meaningful data. One system, LT1-M2, was later dropped from testing after it was found that the generically similar LT8-M2, a less aqueous-soluble derivative, performed better in cell cycle tests.

The performance of Ni-Zn cells containing three of the SLM systems, LT8, LT17, and LT18, has improved during the last two years. Cycle life performance is charted over time in Figure 4-1 where results for the longest cycling cell are plotted for each change in cell hardware design. Results for December of 1982 were obtained with an initial cell design that did not specifically accommodate the SLM separator. Excess pressure on the cell package caused wick dry-out, poor venting and localized heating. Also unrestricted edges on the zinc electrodes allowed excess zinc plating on the outside surfaces during cycling. This lead to mechanical breakage of separators and poor electrode reversibility. As a result, cells cycled for a maximum of only 40 cycles to 60% of their original capacity level. By April of 1983 improvements in cell assembly technique had increased cycle life to 100-175 cycles. A thicker wicking material was used on the zinc electrode along with protective films on both sides of the SLM to guard against localized heating and excess mechanical pressure. The cell containers themselves remained a problem however, because they could not be adjusted to the thickness of the cell package. Excessive mechanical pressure, poor venting and the need for excess electrolyte resulted from the poor design.

At the beginning of this year's contract, the cell hardware design changes outlined in Section 2.1 were implemented. The new cell containers allowed for the use of thicker wicking material, variable electrode package thickness and protective films without necessitating excessive mechanical pressure. Advances were also made in controlling the "edge effect" by coating zinc electrode edges with PVC cement, better restricting the edges of the cell package in the cell container by the use of an electrode compartment, and lessening electrolyte convective forces by minimizing the amount of electrolyte in the cell. After some initial problems with cell container leakage were solved, cycle life had risen to 200-300 cycles. With further improvements in gas venting, final cell life to 60% capacity for the best cells containing SLM separators were in the range of 250-450 cycles.

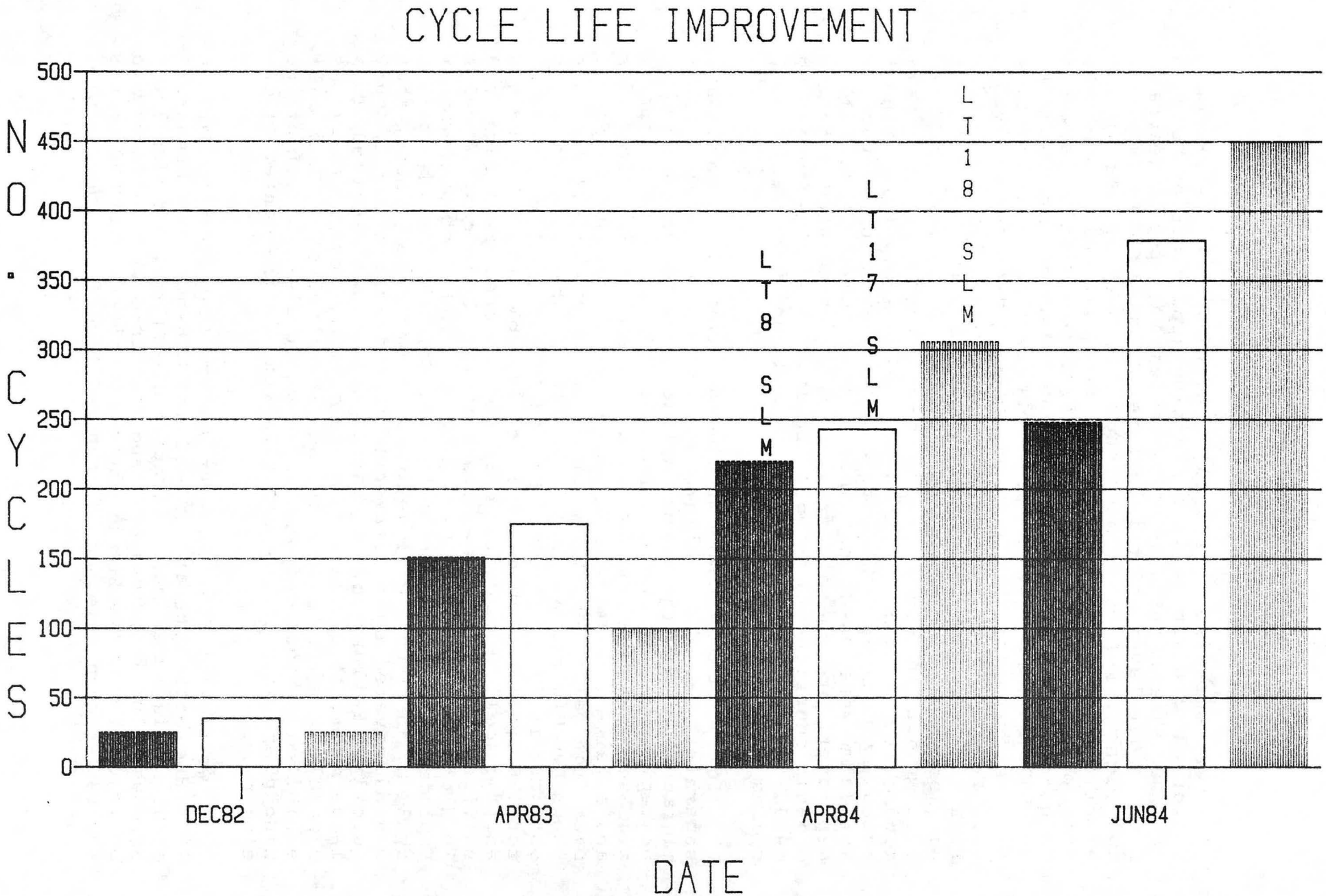


Figure 4-1: Progress made in cycle life improvement in Ni-Zn cells for three different SLM sysstems.

For comparison purposes, control cycling tests were performed on Ni-Zn cells containing separators of Celgard 3501, an aqueous wettable polypropylene microporous membrane. Both single layer and triple layer Celgard were used, with and without RAI outer membranes, in both 5M and 7M KOH electrolyte. Results shown in Figures 4-2 and 4-3 show the poor performance of cells containing a single layer of Celgard 3501 as separator. In Figure 4-2, cell numbers 407 and 501, both containing 7M electrolyte and no protective film, shorted out at 17 cycles and 96 cycles respectively. Cell No. 502, which contained two layers of the protective film with a single layer of Celgard 3501, did not short out but lost capacity quickly, cycling only 77 cycles. Cell No. 802, shown in Figure 4-3 was an attempt to simulate conditions in an SLM cell as closely as possible without actually using an SLM separator. Two layers of protective RAI film were used surrounding the single Celgard 3501 separator, and the electrolyte was presaturated with the organic constituent, as would be done in an SLM-containing cell. The cell lost capacity rapidly and achieved only 42 cycles in the test.

In all cases where a single layer of Celgard 3501 separator was used, failure was due to excessive zincate migration through the separator which resulted in cell shorts or rapid capacity loss. Examination of failed cells showed zinc shorts located on the mating surfaces of the electrodes and a large amount of zinc metal was throughout the cell. Data from cells containing three layers of Celgard 3501 are shown in Figures 4-4 and 4-5. The best performance was obtained in 7M KOH for Cell No. 261 (Figure 4-4) which lasted for 375 cycles. Reproducibility is, however, not good and another cell (Cell No. 408) lost capacity earlier and survived only 246 cycles. The behavior of the control cells in 5M KOH, shown in Figure 4-5, also show a lack of reproducibility with the best cell, No. 309, lasting for 255 cycles. Cell No. 704 developed a short at 70 cycles, that was discovered upon disassembly, and lost capacity very quickly. Failure in all control cells that survived for a large number of cycles was due to capacity loss, probably as a result of shape change in the zinc electrode. Each cell exhibited various changes in the macro distribution of the zinc plate with excess accumulations in the center of the electrode.

Two similar SLM separator systems that function well in 7M KOH electrolyte are LT1-M2 and LT8-M2. The transport agent LT8 is a chemical derivative of LT1 that has mich lower aqueous solubility than LT-1 and therefore is less likely to be leached from the SLM by the electrolyte. The LT8 system was tested extensively this year and Figure 4-6 shows a plot

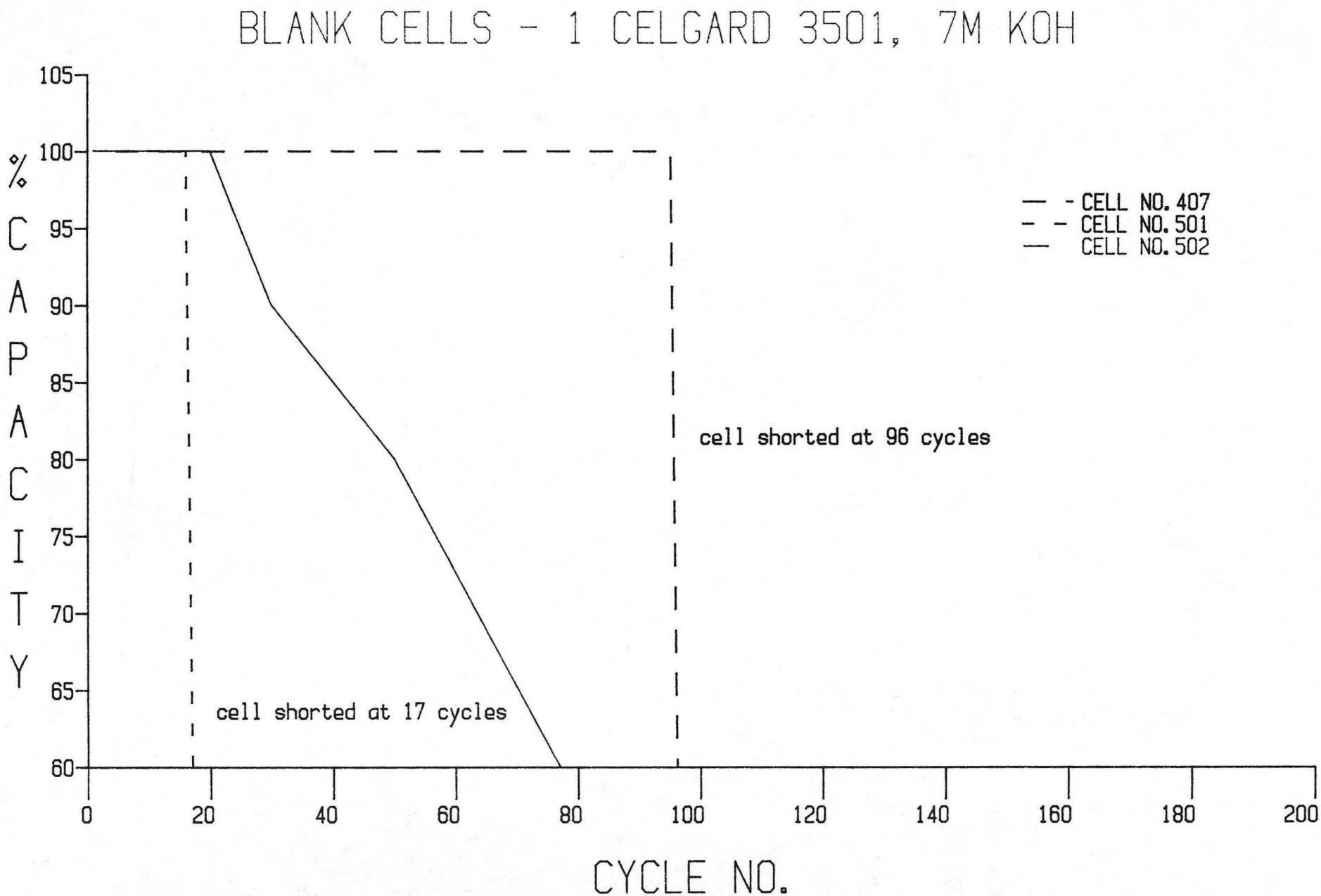


Figure 4-2: Cycle life results for three control cells with 7M KOH electrolyte containing a single layer Celgard 3501 separator.

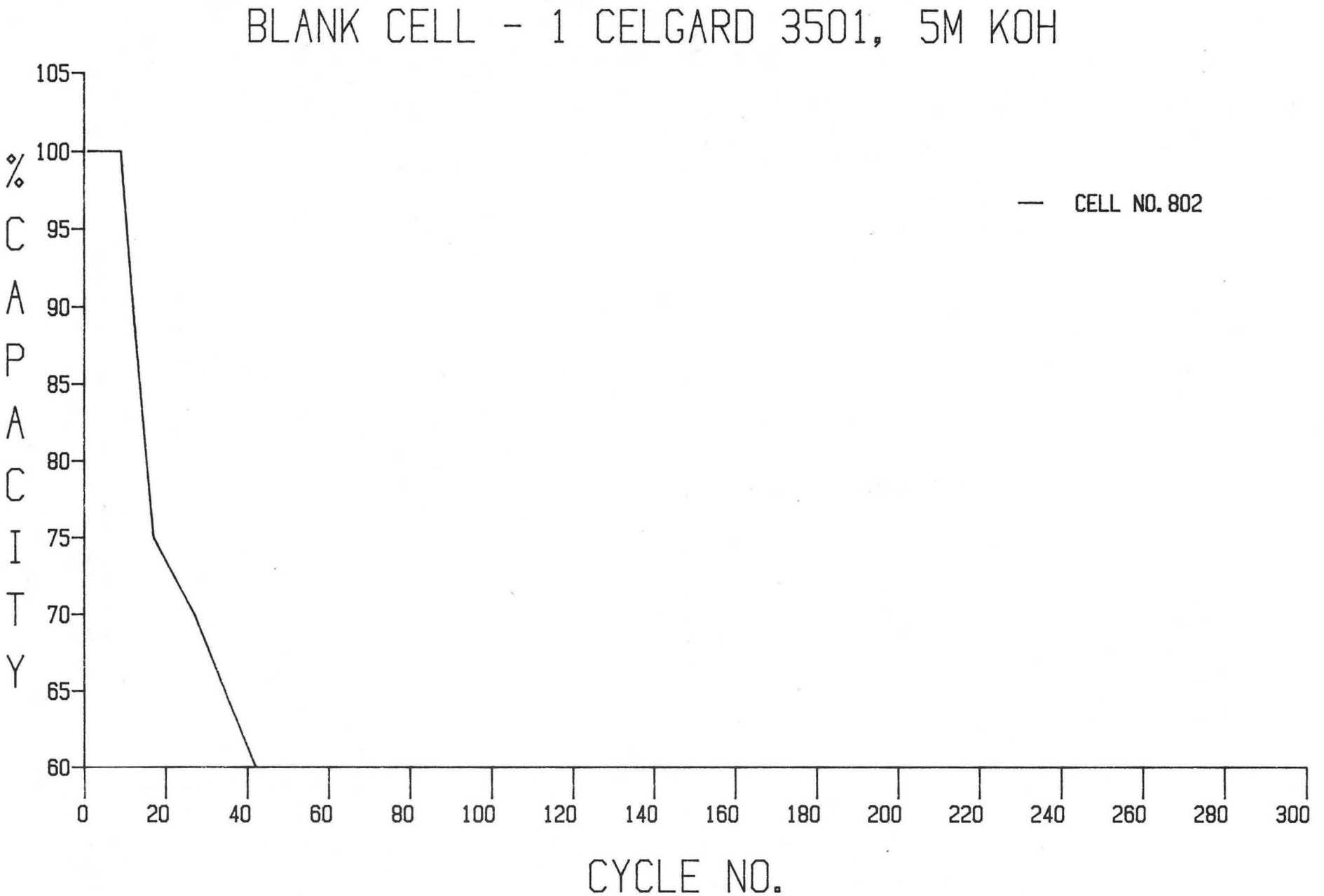


Figure 4-3: Cycle life results for a control cell with 5M KOH electrolyte containing a single layer Celgard 3501 separator.

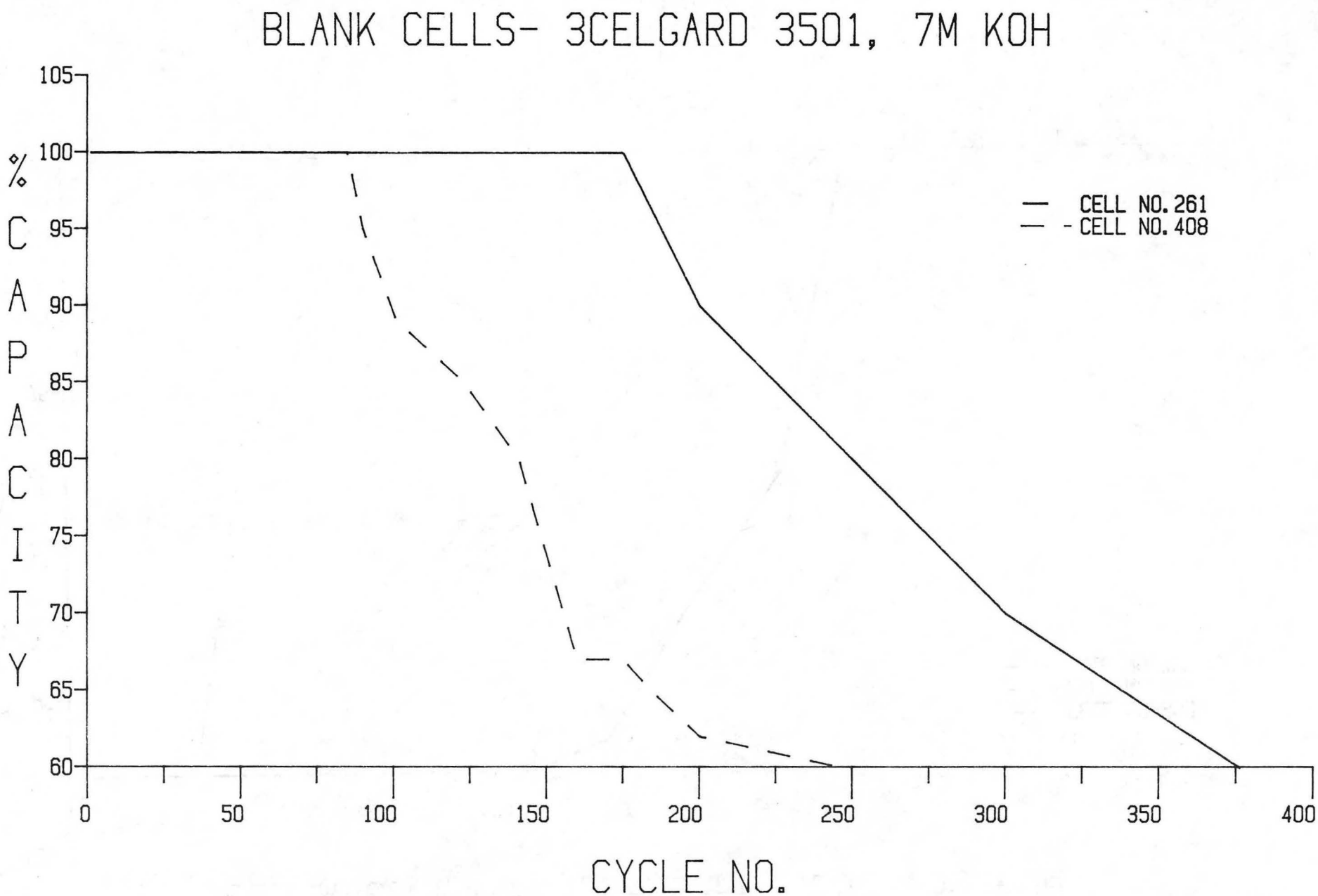


Figure 4-4: Cycle life results for two control cells with 7M KOH electrolyte containing a triple layer Celgard 3501 separator.

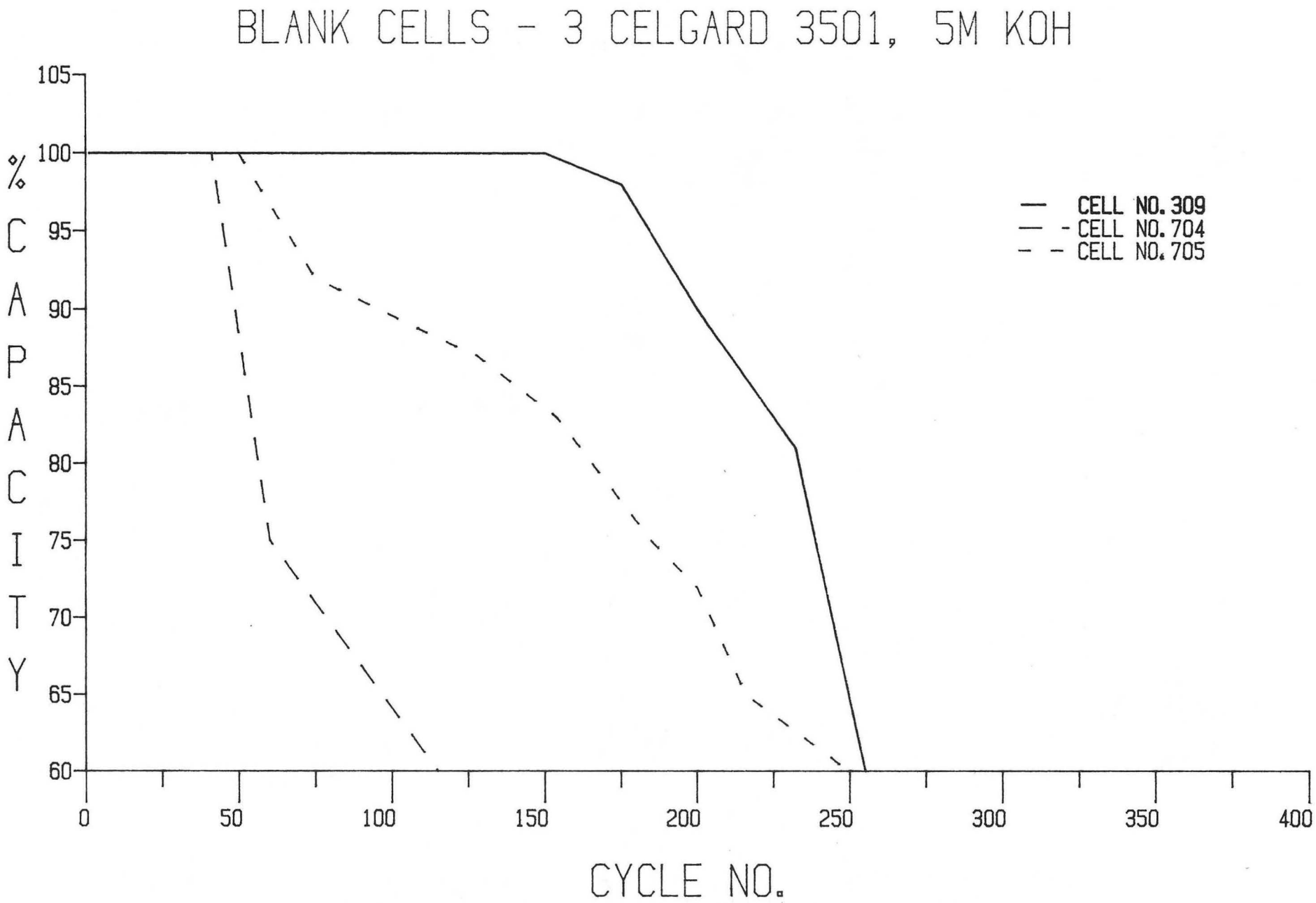


Figure 4-5: Cycle life results for three control cells with 5M KOH electrolyte containing a triple layer Celgard 3501 separator.

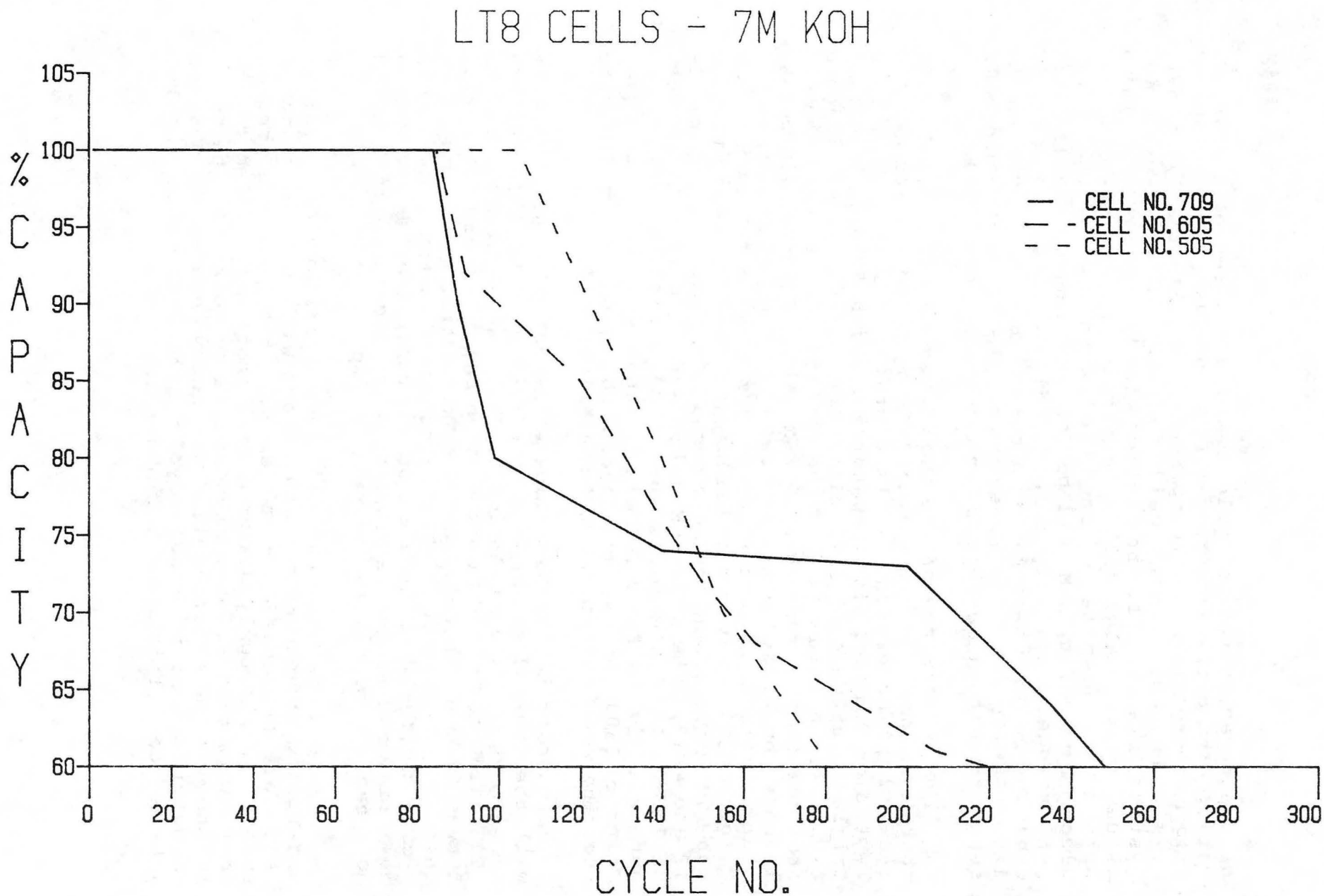


Figure 4-6: Cycle life results for three Ni-Zn cells with 7M KOH electrolyte containing a single LT8 SLM separator.

of the capacity versus cycle number for three different LT8 cells. The cycle life ranges from 190-248 cycles to 60% of original capacity. For comparison purposes, the cycle data of the longest running cell for each of the two 7M KOH systems, LT8 and LT1, are plotted with the best results for a three layer Celgard 3501 control. Figures 4-7 and 4-8 show that, despite cycle life improvements in 7M KOH electrolyte cells, SLM cell performance cannot match the best performance of the triple layer Celgard 3501. No cases of dendrite shorting were found in the cells containing a single layer SLM LT1 or LT8. However, single layer Celgard 3501 separators in 7M KOH shorted in two out of three cells.

The performance of the two SLM systems, LT17 and LT18, that function in 5M KOH electrolyte equalled or exceeded the cycle life of control cells containing single or triple layers of Celgard 3501 separators. With 5M KOH, the best triple layer Celgard 3501 blank ran for 255 cycles. Figure 4-9 shows the cycle life of the control cell as well as data from the longest running LT17 SLM cell. Figures 4-10 and 4-11 show comparison plots for two LT18 SLM cells versus the blank. Both SLM systems outperform the blank triple layer Celgard 3501. Several cells were tested for each of these two SLM systems, and the best results are shown in Figures 4-12 and 4-13. The LT17 SLM cells survived 240-380 cycles, while the LT18 SLM cells survived to 270-450 cycles. In general, the 5M KOH SLM cells outperform the three layer Celgard 3501 cells, and again no evidence of dendrite shorting was found in any SLM-containing cell.

In order to further compare the behavior of SLM cells with the control cells, typical cell potential curves are displayed in Figure 4-14 for the 5th and 100th cycle for an LT17 cell, an LT18 cell and a three layer Celgard 3501 cell. Curves for the SLM cells are not substantially different from those of the control. Throughout the program, SLM cells cycled similarly to the best of the control cells and showed no evidence of excessive gassing, unusual cell voltage or any noticeable effect on the overall cell potential.

Cycle life data for all four candidate SLM systems undergoing extensive testing, along with data for control cells are summarized in Table 4-1. Early in the program several of the newly designed cell containers failed due to poor seals that allowed electrolyte to leak from the cell. In some cases electrolyte loss was excessive and caused premature capacity loss. Cycle test where this problem affected cell life are noted in the table.

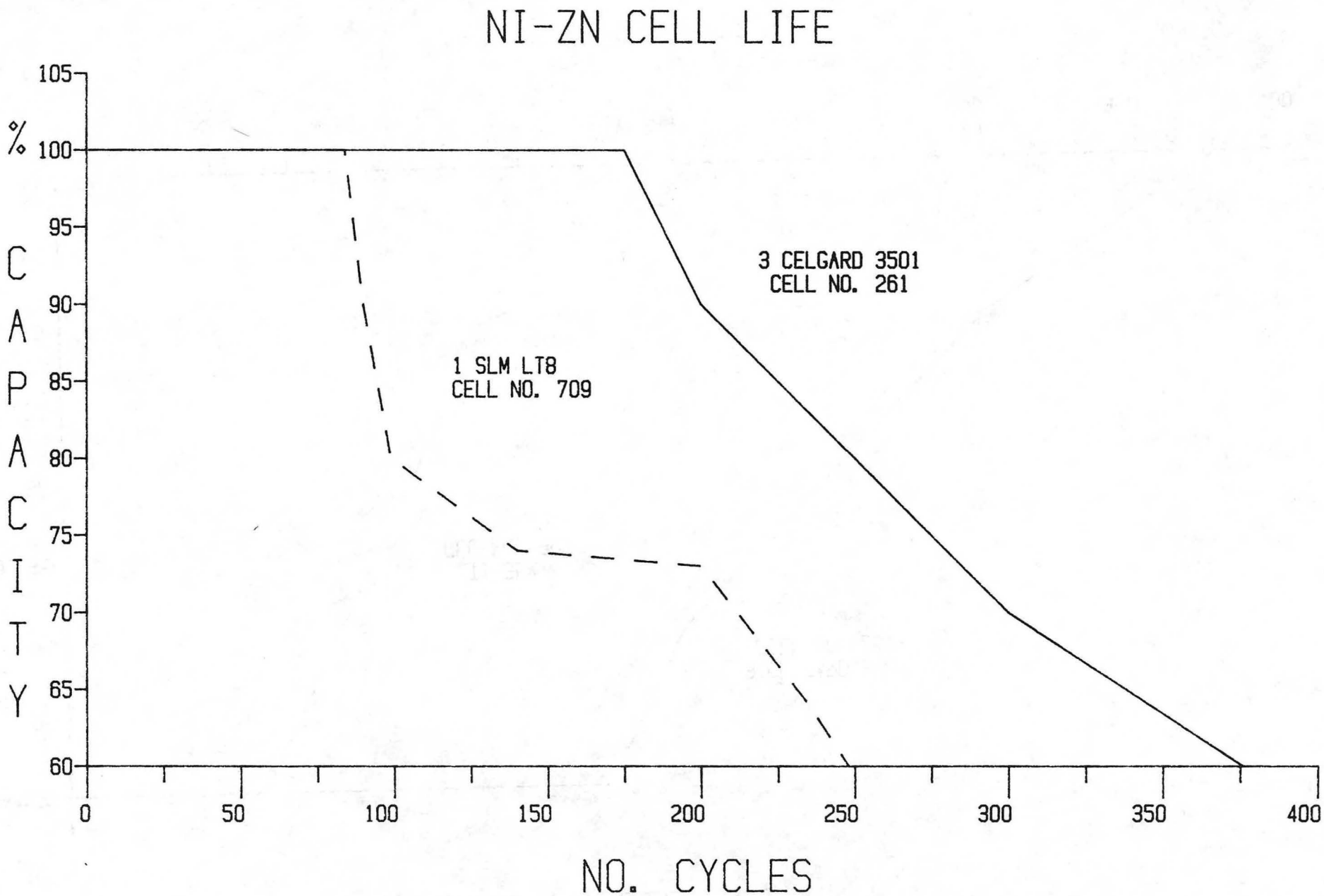


Figure 4-7: Cycle life comparison for an LT8 SLM cell versus a triple layer Celgard 3501 control cell both with 7M KOH electrolyte.

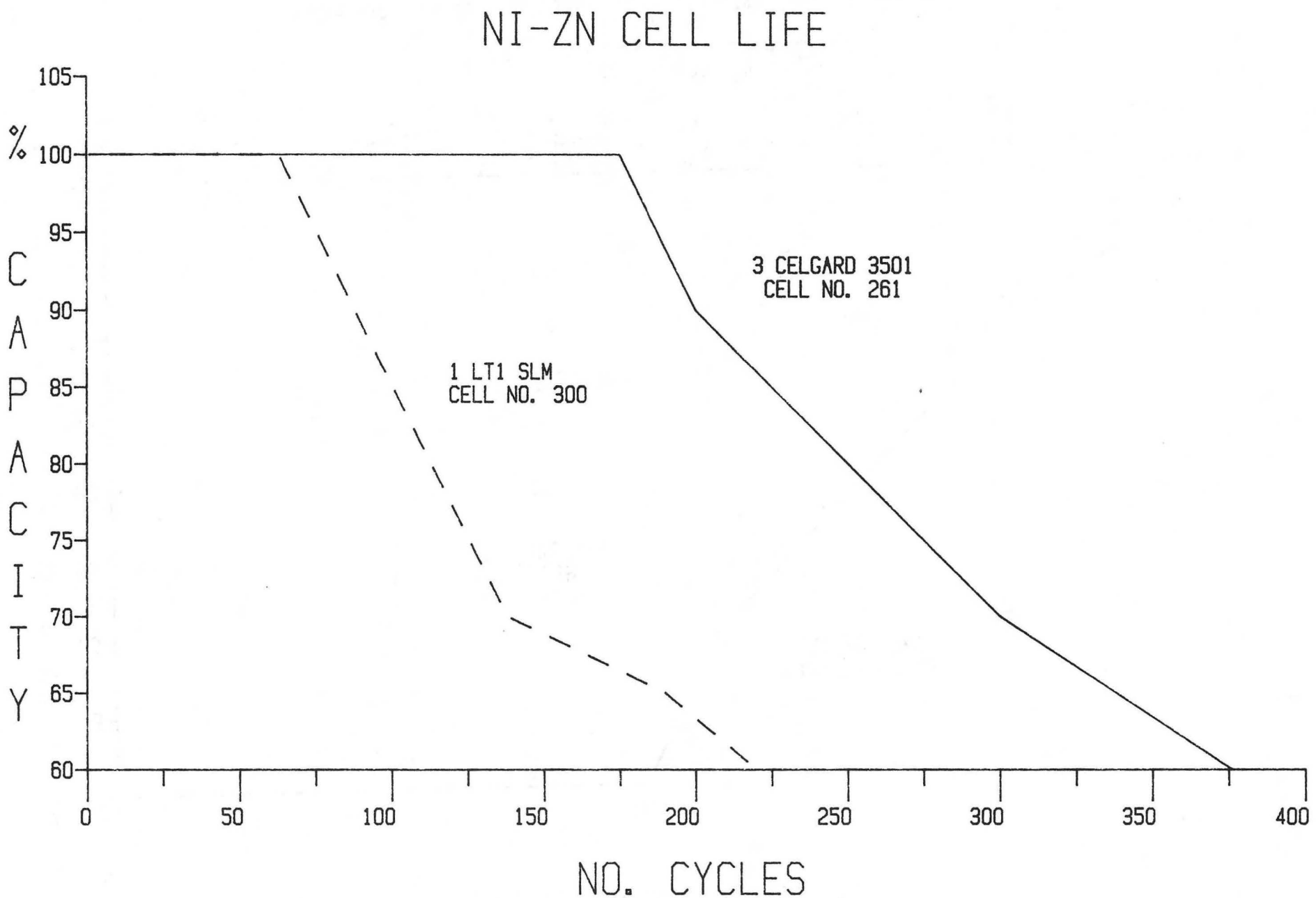


Figure 4-8: Cycle life comparison for an LT1 SLM cell versus a triple layer Celgard 3501 control cell both with 7M KOH electrolyte.

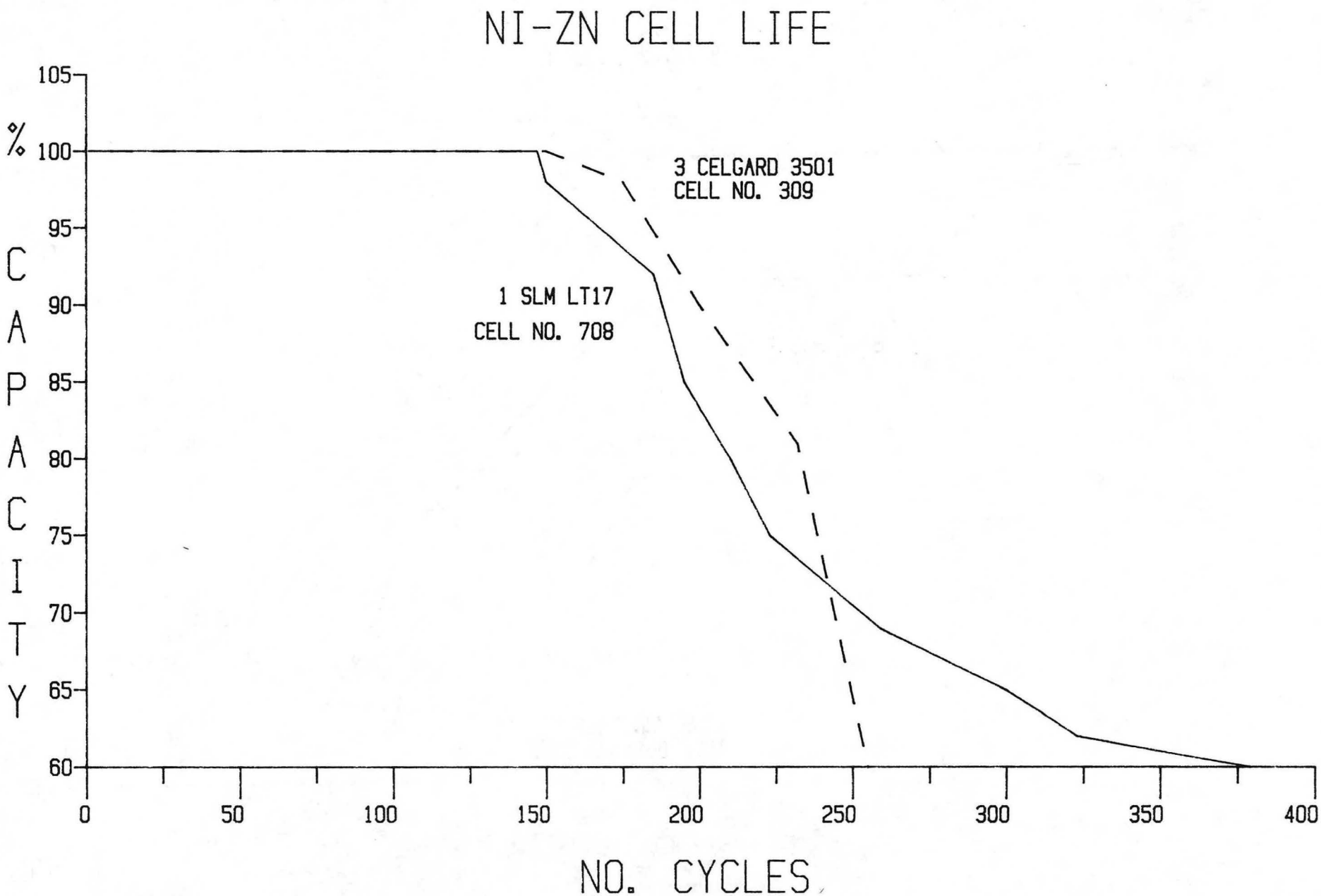


Figure 4-9: Cycle life comparison for an LT17 SLM cell versus a triple layer Celgard 3501 control cell both with 5M KOH electrolyte.

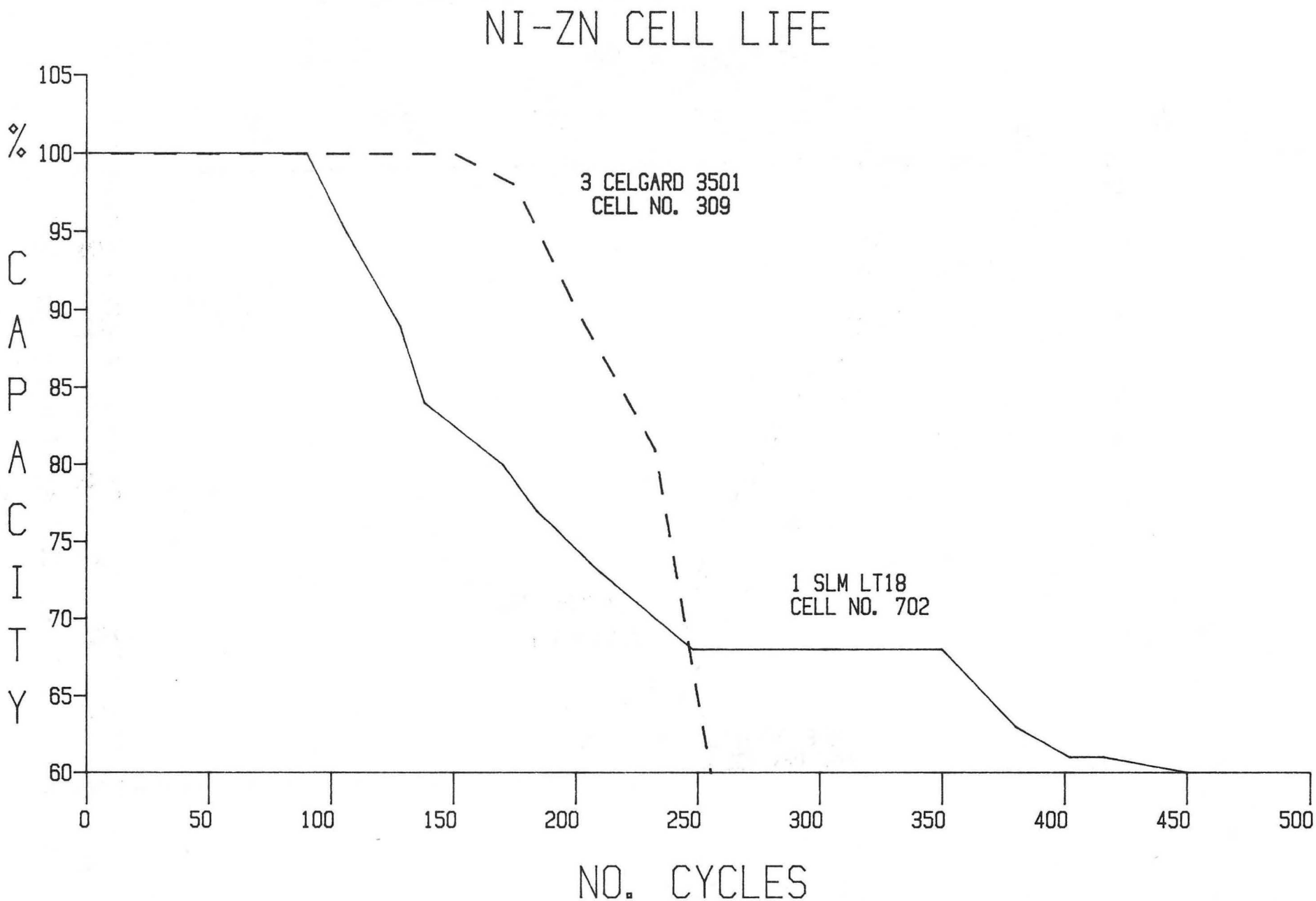


Figure 4-10: Cycle life comparison for an LT18 SLM cell versus a triple layer Celgard 3501 control cell both with 5M KOH electrolyte.

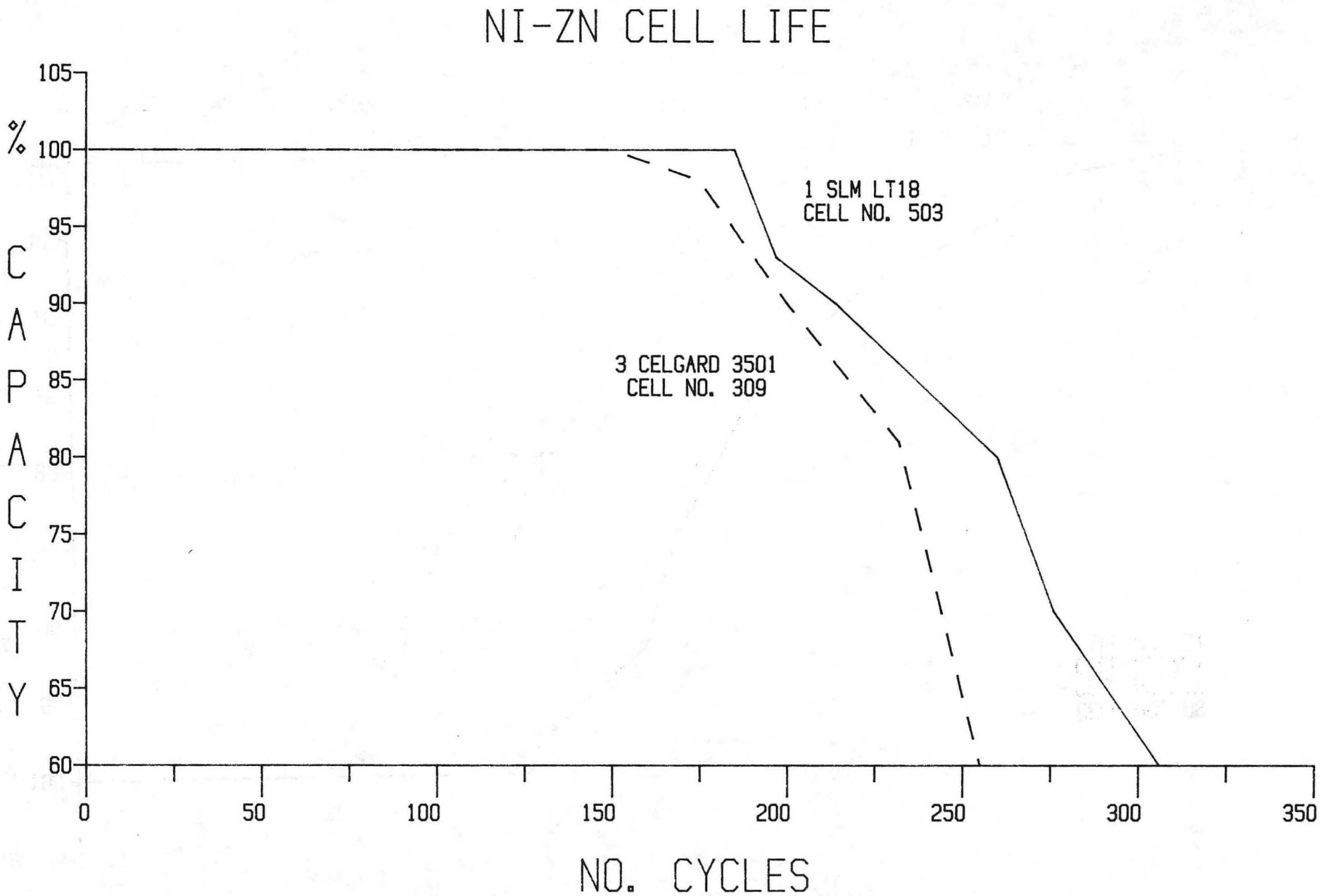


Figure 4-11: Cycle life comparison for an LT18 SLM cell versus a triple layer Celgard 3501 control cell both with 5M KOH electrolyte.

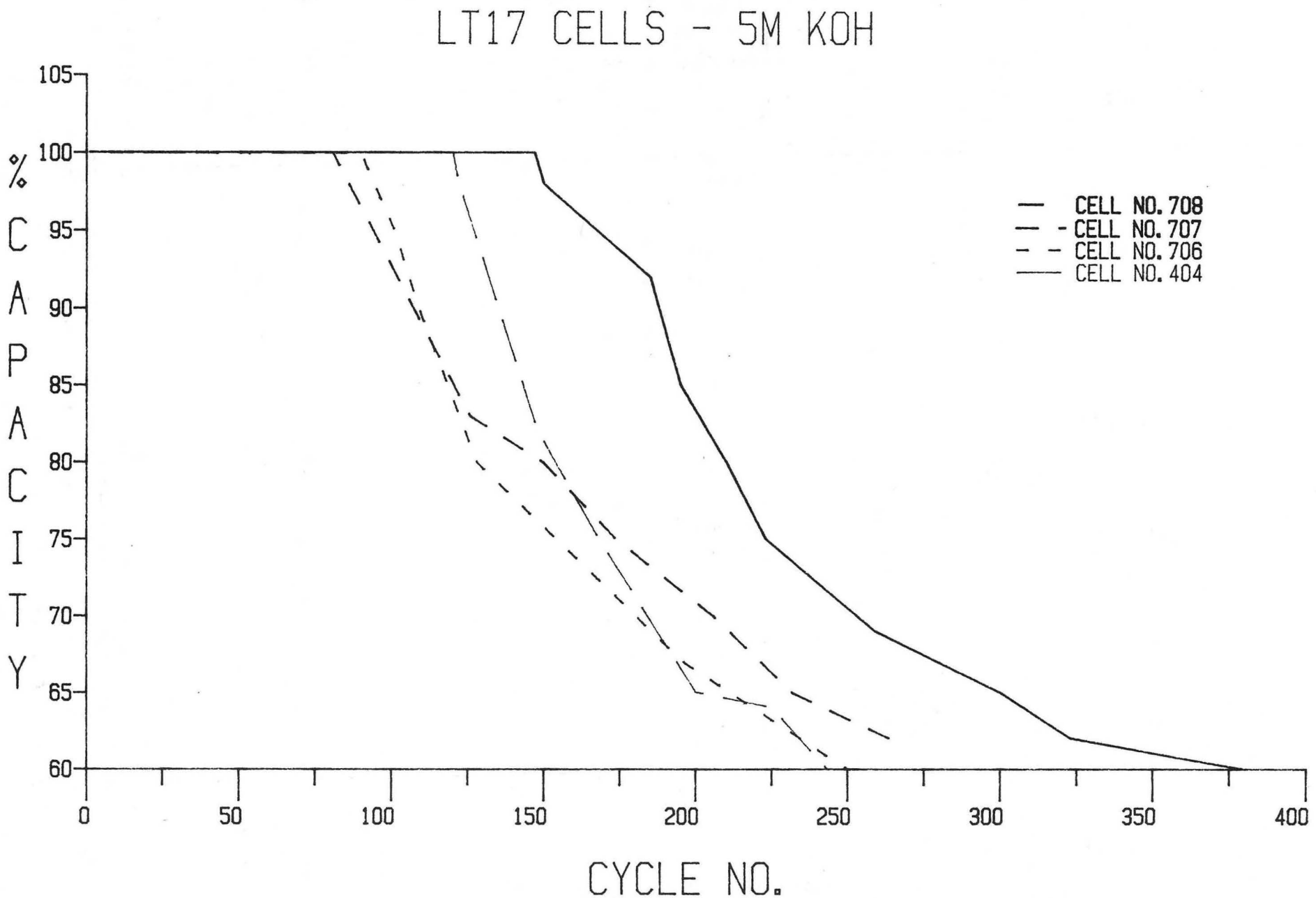


Figure 4-12: Cycle life results for four Ni-Zn cells with 5M KOH electrolyte containing a single LT17 SLM separator.

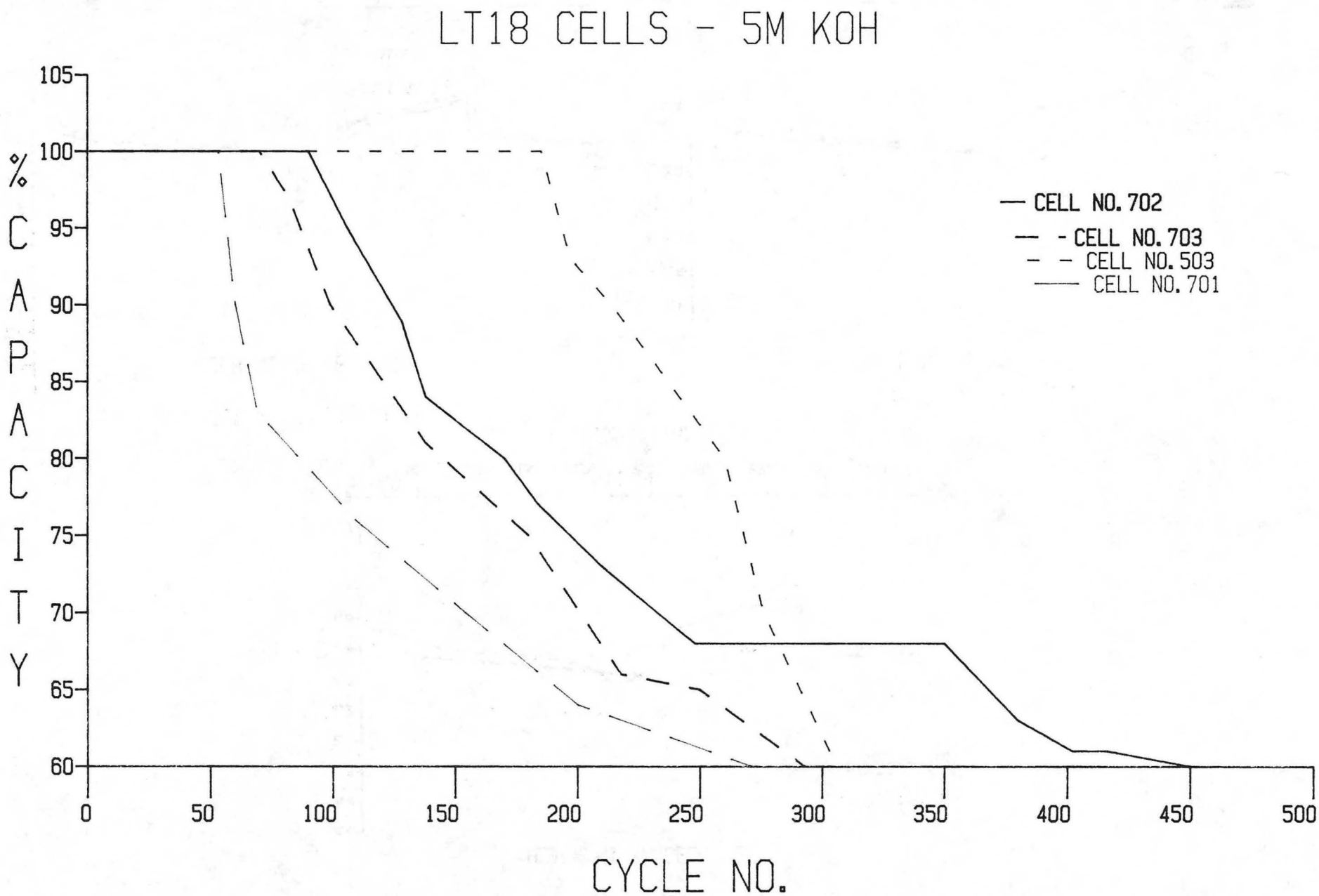


Figure 4-13: Cycle life results for four Ni-Zn cells with 5M KOH electrolyte containing a single LT18 SLM separator.

Figure 4-14: Comparison of potential curves for cycles 5 and 100 of a three layer Celgard 3501 control cell and 2 single layer SLM cells.

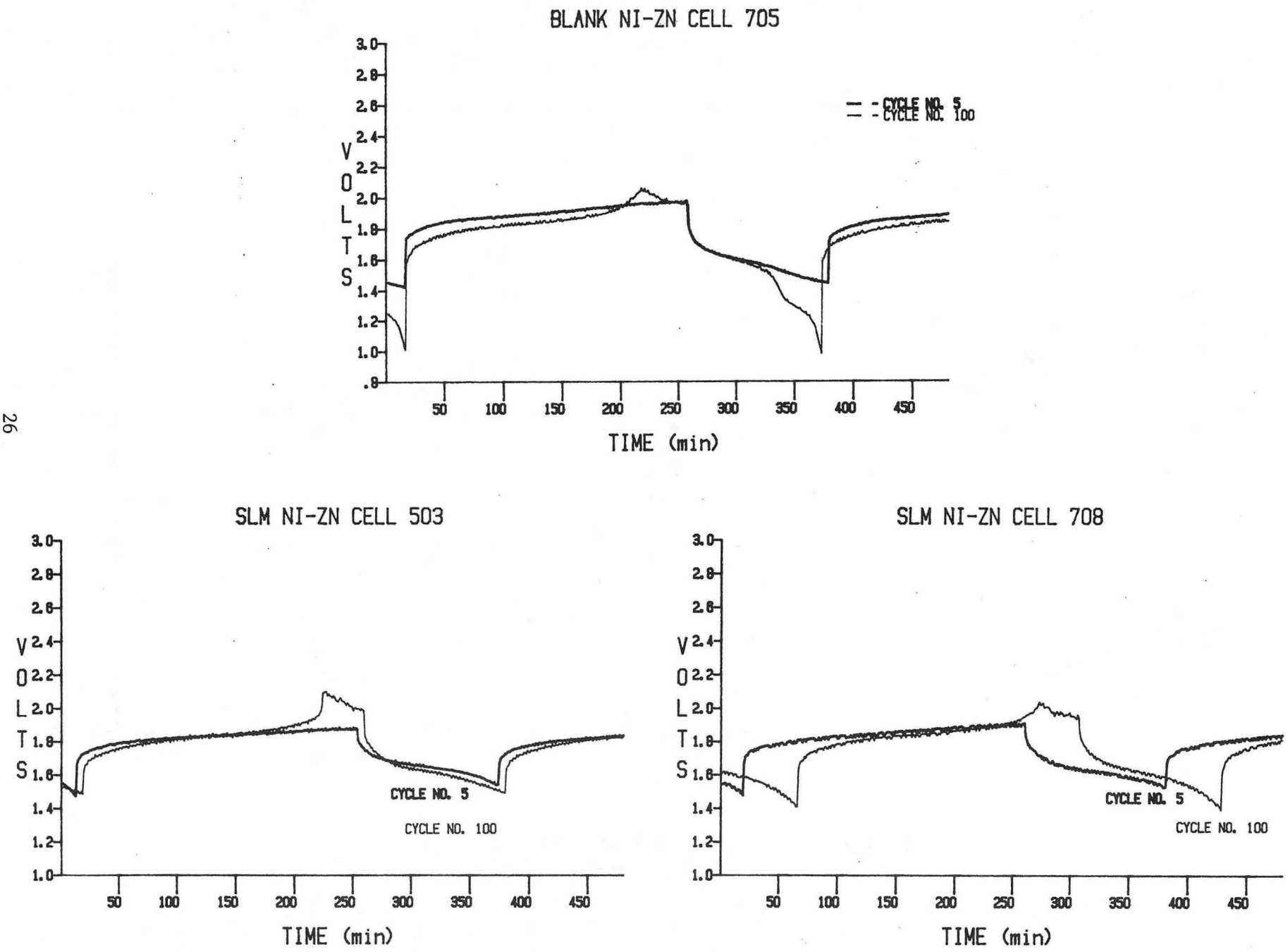


TABLE 4-1

Summary of Ni-Zn Cell Data
(No. of Cycles 60% Capacity)

LT17 SLM 5M KOH		
Cell		Cycles
#404		243
#409	L	164
#504		198
#601		170
#604		230
#607	L	158
#609	L	153
#706		250
#707		285
#708		379
#803		214+

LT18 SLM 5M KOH		
Cell		Cycles
#503		306
#507	L	117
#603		181
#606		203
#610	L	141
#611	L	134
#701		271
#702		450
#703		293
#804		223+

LT8 SLM 7M KOH		
Cell		Cycles
#410	L	152
#505		190
#602	L	99
#605		220
#608		113
#709		248
#805		207+

LT1 SLM 7M KOH		
Cell		Cycles
#405	L	150
#300		220

3 Celgard 3501 Control 5M KOH		
Cell		Cycles
#704	S	115
#705		250
#309		255
#801		204+

3 Celgard 3501 Control 7M KOH	
Cell	Cycles
#408	246
#261	375

1 Celgard 3501 Control 7M KOH		
Cell		Cycles
#407	S	95
#501	S	16
#502		77

1 Celgard 3501 Control 5M KOH	
Cell	Cycles
#802	42

Multi-layer SLM 5M KOH	
Cell	Cycles
#506 (2 LT18)	82
#710 (2 LT17)	60

L - excess electrolyte leakage affected capacity
S - zinc dendrite shorted cell through separator
+ - continued cycling after program ended

4.2 Accelerated Rate Study

In order to determine the effect of SLM resistance on the internal cell resistance and capacity, a rapid rate discharge study was conducted. Fresh test cells containing either an LT17 or LT18 SLM were cycled 3-5 cycles at the normal 2 hour discharge rate (7.3 mA/cm^2) to establish 100% capacity. Both cells were then discharged at the C rate, recharged and discharged at the 2C rate. Table 4-2 shows the results of this test which demonstrated the ability of cells with SLM separators to perform under current load. Figures 4-15 and 4-16 show the C and 2C rate discharge curves compared with a typical C/2 rate discharge cut off after 2 hours. The data indicated that the use of an SLM separator does not adversely effect the ability of Ni-Zn cells to perform well when fully discharged in one-half hour at the 2C rate.

TABLE 4-2

	C/2 rate 7.3 mA/cm^2	C rate 16.6 mA/cm^2	2C rate 29.3 mA/cm^2
LT17 SLM	1.25 Ahrs	1.16 Ahrs	0.8 Ahrs
LT18 SLM	1.25 Ahrs	1.23 Ahrs	1.0 Ahrs

Note: theoretical cell capacity - 1.3 Ahrs

4.3 Multi-Layer SLM Experiments

Since multi-layered Celgard outperformed single layers of Celgard 3501 in control experiments, we tested cells containing two layers of SLMs. The low resistance SLM systems, LT17 and LT18, were chosen. Each cell contained two SLMs interspersed between three layers of RAI P700 protective film. The cells both had to be cycled at low current density initially and quickly lost capacity, reaching 60% after 60 cycles for the LT17 cell and 82 cycles for the LT18 cell. We believe that the internal resistance of the cells were too high using this separator configuration, probably due to excess organic constituent that raised separator resistance above a usuable level. A different configuration of SLMs and protective films would be necessary to adequately test the use of multi-layered SLMs.

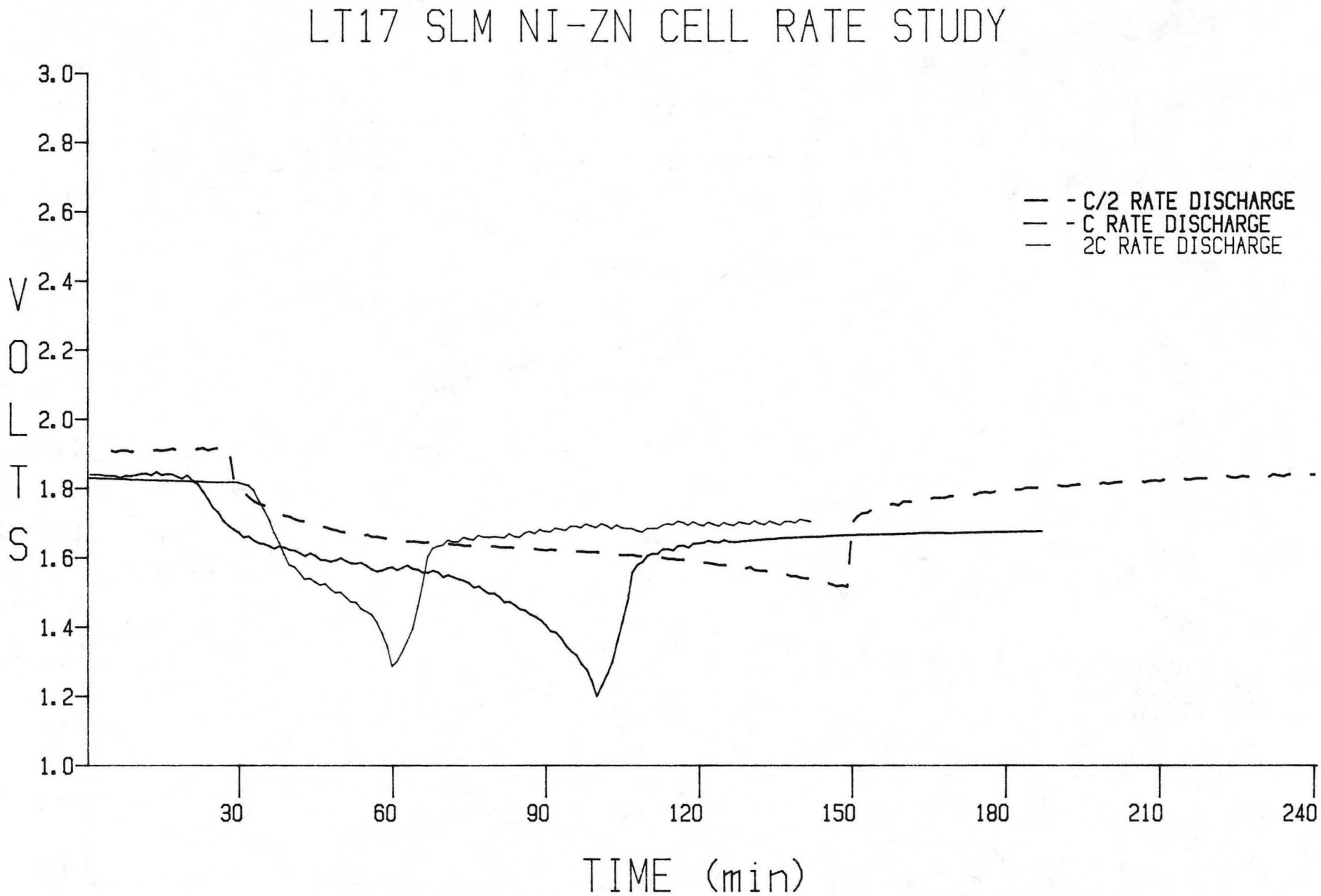


Figure 4-15: Comparison of potential curves for three different discharge rates of an LT17 SLM cell.

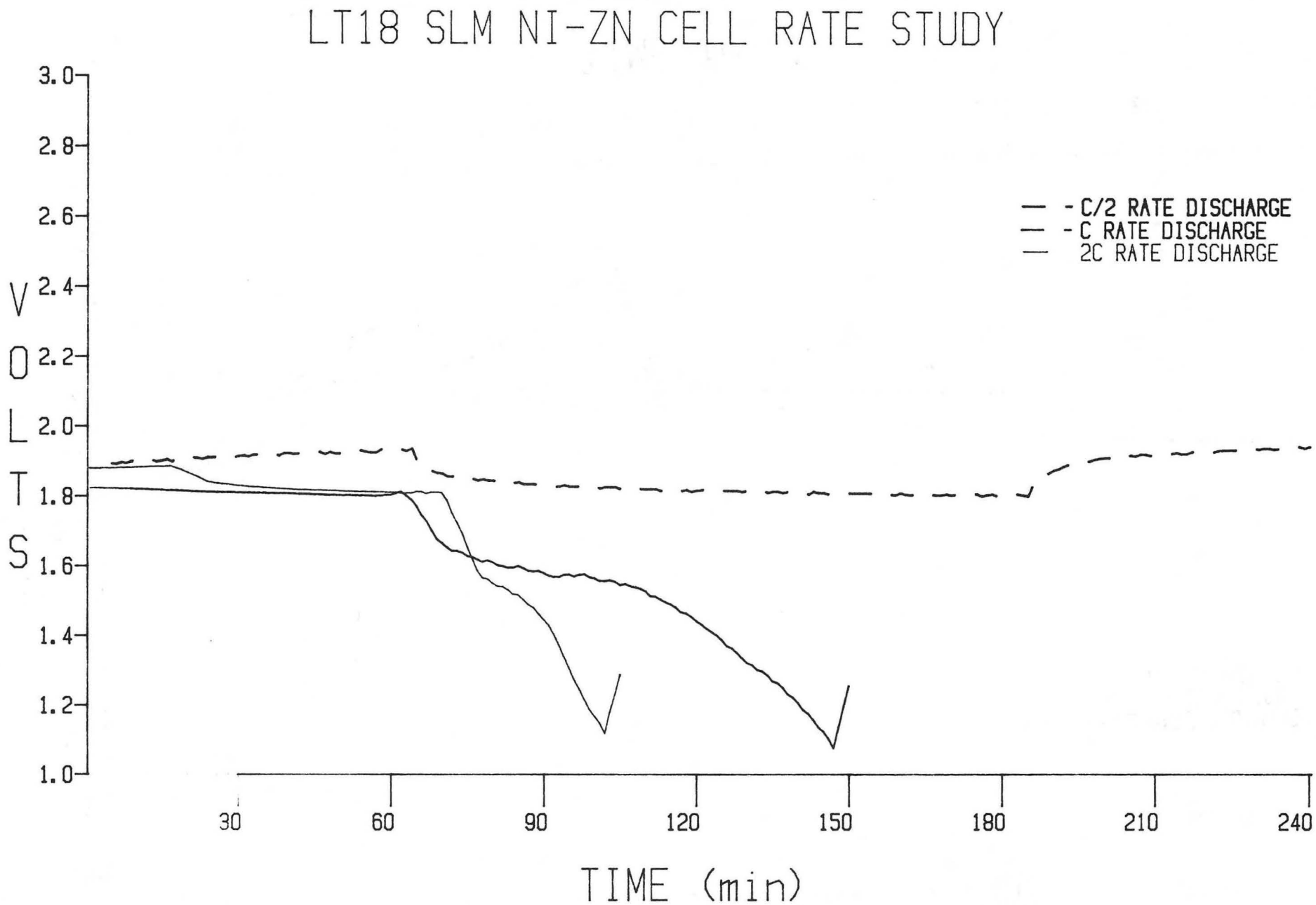


Figure 4-16: Comparison of potential curves for three different discharge rates of an LT18 SLM cell.

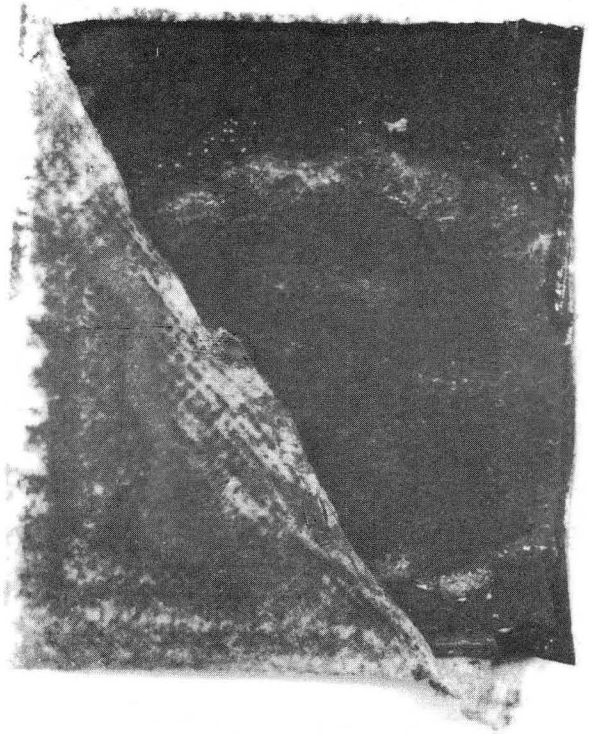
4.4 Analysis of Failure Mode

All Ni-Zn test cells, both with and without SLM separators, were examined after cycling for determination of failure mode. As described previously, control cells examined with one layer of Celgard 3501 failed primarily due to dead shorts through the separator from a zinc dendrite. Control cells with three layers of Celgard 3501 failed primarily due to capacity loss after long-term cycling. Upon disassembly, these cells were examined and a high degree of shape change was noted on the zinc electrode. Zinc metal was spread throughout the cell filling wicks and dispersed on the separator. It appeared that most of the cell reaction was taking place at the center of the electrodes. These results generally agree with previous work (2,3) on the Ni-Zn system where long-term cells with microporous separators cycled 100-300 cycles and failure was due to capacity loss. This capacity loss has been attributed to zinc electrode shape change (4), "soft shorts" (5) or poor gas management.

None of the many cells tested containing SLM separators failed due to dead shorts from zinc dendrites. The single layer SLM separator appears to adequately prevent the penetration of destructive zinc dendrites. As in the control triple layer Celgard 3501 cells, failure was due to capacity loss after long-term cycling. This capacity loss was determined to be due to the zinc electrode since the nickel electrode had the ability to be reused and functioned normally. In examinations of long-term cycled cells, microscopic zinc shape change noted in cells with SLM separators was observed to be less pronounced than with the control cells. Figure 4-17 shows a photograph of the zinc electrode surfaces from both an SLM cell and a control cell after each had cycled 250 cycles. The distribution of the plated zinc is more even in the SLM cell zinc electrode while a concentration of zinc in the center of the electrode is noted on the control electrode.

Capacity loss in long-term cycled SLM cells may have been caused by a combination of the zinc wick drying out, edge effects and "soft shorts" due to slight zincate passage as well as to some macro and micro shape change effects. In a few cases, disassembled cells contained wicks that were approaching dryness. Earlier in the program wick thickness was increased and this appeared to help increase cycle life. On long-term cycling the edges of the zinc electrode, although coated with plastic, continued to disintegrate and branch out mechanically breaking the seams of the separator envelope. This factor allowed zinc metal to be present near the nickel electrodes. "Soft shorts" can often develop due to excess zinc metal in the cell electrolyte and in the

Figure 4-17 COMPARISON OF ZINC SHAPE CHANGE



a. Zinc electrode from control cell after 250 cycles showing concentration at center.

b. Zinc electrode from SLM cell after 250 cycles showing even distribution of zinc plate.

separator. These form conducting paths between electrodes, thereby draining charge current from the nickel electrode. It is also possible that the SLM separator has minimal ability to alter zinc electrode morphology changes on a micro scale, and this eventually results in capacity loss to the cell.

A series of test cells were cycled in which the internal cell impedance was measured frequently throughout the cell life time to determine whether any significant electrical resistance changes occurred due to changes in the SLM separator, or as a result of drying of the zinc wick. A three layer Celgard 3501 blank was tested along with three cells each containing an SLM-LT8, LT17 and LT18. The SLM cells had a higher initial internal resistance before cycling began, probably due to the presence of excess organic constituent on the surface of the SLM. Once cycling had begun, the resistances all dropped to a level comparable to the control cell. Cell resistance values leveled off and stayed fairly constant for all the cells as shown in Figure 4-18. These results are consistent with the belief that no unusual changes occur to the SLM separator during cycling. Further detailed investigation would be necessary to determine the exact mode of capacity loss in cells containing SLM separators.

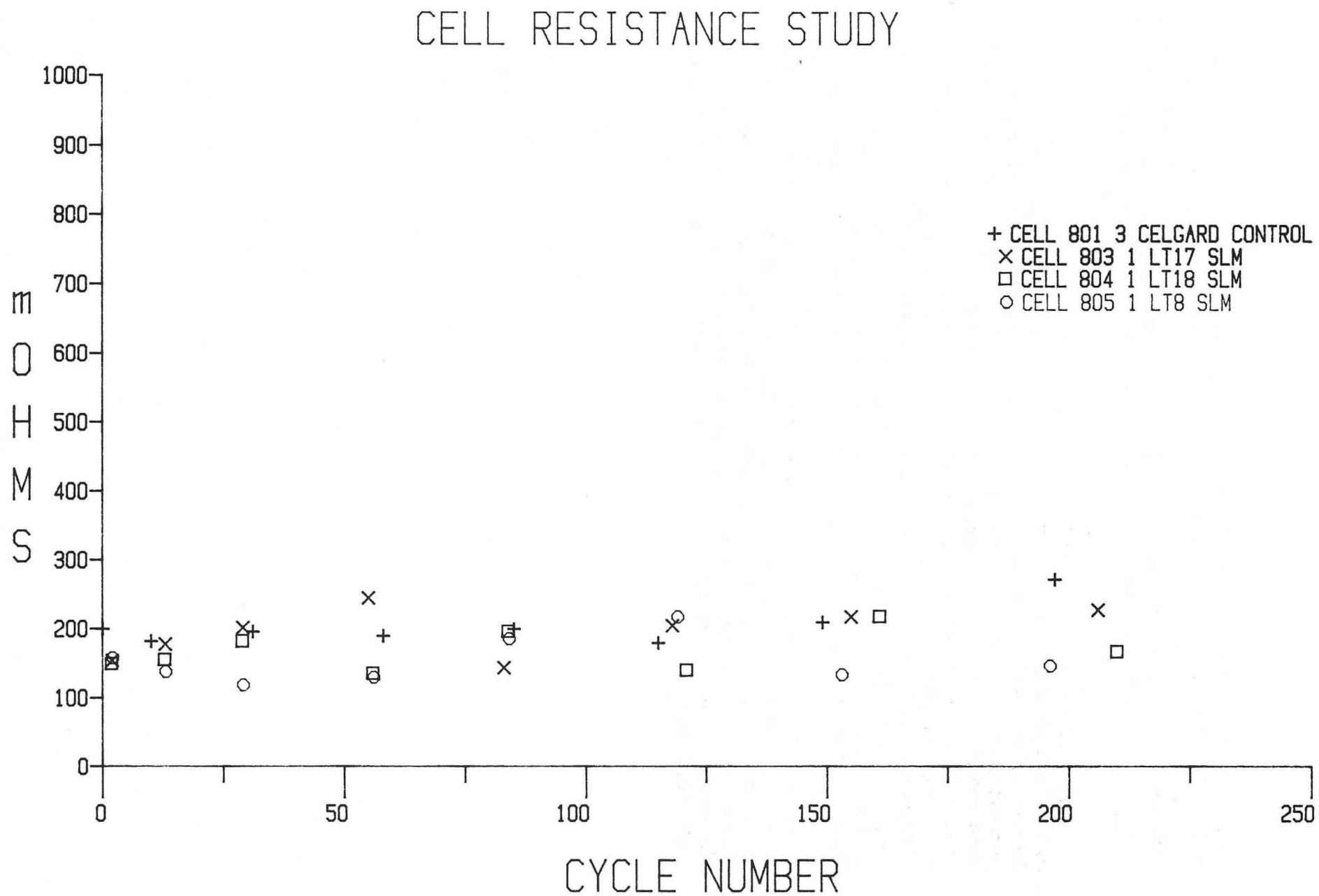


Figure 4-18: Cell resistance versus cycle number for 1 control cell with 3 Celgard 3501 and 3 SLM cells showing no substantial change in separator resistance.

5. ACKNOWLEDGEMENT

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

6. REFERENCES

1. J. P. Pemsler and M. D. Dempsey, Final Report of Supported Liquid Membrane Battery Separators, Lawrence Berkeley Laboratory Report LBL P.O. 4512210 (1983)

2. F. Hornstra, E. Berrill, P. Cannar, D. Cap, W. Deluca, D. Fredickson, L. Singer, C. Swoboda, C. Webster, C. Christianson, and N. Yao, Battery testing results at the national battery test laboratory, Fourth U.S. DOE Battery and Electrochemical Contractors Conference, Washington, DC, June 2-4, 1981

3. J.T. Lundquist, Jr., J. Membrane Science, 13 (1983) 337-347

4. J. McBreen, J. Electrochem. Soc. 119 (1972) 1620

5. G. D. Bucci, R. P. Fedora and R. R. Steiner, Research development and demonstration of a nickel-zinc battery for electric vehicle propulsion, DOE Battery and Electrochemical Contractors Conference Vo. 1, Arlington, Virginia, December 10-12, 1978

7. APPENDIX

A. Battery Cycler Data Acquisition Program Listing

B. Sample Data Output

```
10 REM************  BACKGROUND DATA AQUISITION PROGRAM  ***********
20 REM
30 REM     REVISION 12      `BKDAQCOM.12'
40 REM This program is used to take data from the battery cycler for 1-10
50 REM channels. Each block of data is stored in an array until filled then it
60 REM is stored on disk using the subroutine. The data is labeled with the date

70 REM it was stored on disk. The amount of space available on the disk is
80 REM checked and a warning given if necessary. During data collection
90 REM each channel and point is checked using subroutine 1000 to compile
100 REM cycle data. It is stored in a basic file as defined initially.
110 REM*************************************************************
120 REM
130 REM******************* WARNINGS ******************************
140 REM
150 CLS:LOCATE 1,13:PRINT "`BKDAQCOM' BACKGROUND DATA AQUISITION PROGRAM"
160 PRINT:PRINT "STOP!! BEFORE GOING FURTHER HIT CONTROL BREAK KEYS AND LIST "
170 PRINT "THE PROGRAM. CHECK FOR THE CORRECT NUMBER AND SPECS. OF IONAME "
180 PRINT "STATEMENTS (lines 450-540).ALSO CHECK ANIN AND INTON FOR THE "
190 PRINT "DESIRED INTERUPT SETTING AND TIME BETWEEN SAMPLES (lines 550-570)."
200 PRINT:PRINT "PRESS ANY KEY TO CONTINUE"
210 T$=INKEY$:IF T$="" THEN 210
220 REM*************************************************************
230 REM
240 REM******* INITIALIZATION OF VARIABLES ************************
250 REM
260 CLS: VA1=0
270 HR%=0:MIN%=0:SEC%=0:DATE%=0:MO%=0:YR%=0
280 BF$(1)="B:CELL701.DAT":BF$(2)="B:CELL702.DAT":BF$(3)="B:CELL703.DAT"
290 BF$(4)="B:CELL704.DAT":BF$(5)="B:CELL705.DAT":BF$(6)="B:CELL706.DAT"
300 BF$(7)="B:CELL707.DAT":BF$(8)="B:CELL708.DAT":BF$(9)="B;CELL709.DAT"
305 BF$(10)="B:CELL710.DAT"
310 INPUT "ENTER THE FIRST RECORD NUMBER (-x)",REC
320 INPUT "ENTER THE NUMBER OF CHANNELS ",N
330 FOR ASK = 1 TO N
335     ADV(ASK) = 200
340     PRINT ASK,BF$(ASK)
350     INPUT "ENTER THE CURRENT CYCLE NUMBER AND LAST CYCLE TRIP TIME (seperate
 by comma)                ",CYNO(ASK),PRELP(ASK)
360 NEXT ASK
370 INPUT "ENTER THE AMOUNT OF DISKSPACE USED THUS FAR ON DATA DISK ",DISKSPACE
380 PRINT:INPUT "ARE YOU READY TO BEGIN TAKING DATA Y/N ";Y$
390 IF Y$ <> "Y" AND Y$ <> "y" THEN 150
400 REM*************************************************************
410 REM
420 REM***************** MAIN PROGRAM ******************************
430 REM
440 CALL INIT
442 CALL WARNOFF
445 CLS
450 CALL IONAME' ("C1",3,1,12,1,128)
460 CALL IONAME' ("C2",3,2,12,1,128)
470 CALL IONAME' ("C3",3,3,12,1,128)
480 CALL IONAME' ("C4",3,4,12,1,128)
490 CALL IONAME' ("C5",3,5,12,1,128)
500 CALL IONAME' ("C6",3,6,12,1,128)
510 CALL IONAME' ("C7",3,7,12,1,128)
520 CALL IONAME' ("C8",3,8,12,1,128)
```

```
530 CALL IONAME' ("C9",3,9,12,1,128)
540 CALL IONAME' ("C10",3,10,12,1,128)
550 CALL ANIN' ("BATV%",120.,"C1,C2,C3,C4,C5,C6,C7,C8,C9,C10",60,1,)
560 REM turns on interupts at one per minute for 120 data points
570 CALL INTON' (1,"SEC")
580 LOCATE 1,1 : PRINT "DATA AQUISITION IN PROGRESS"
590 LP = 0
600 WHILE LP<120
610    FOR X =1 TO 3000 : NEXT X
620    CALL ARLASTP' ("BATV%",LP)
630    GOSUB 1000
640 WEND
650 CALL INTOFF
660 GOSUB 3000
670 REM after disk storage go back to taking data,add `PAUSE'here if needed
680 GOTO 550
690 REM*********************************************************
700 REM
710 REM
720 REM*********** SUBROUTINES ********************************
730 REM*************************************************************
960 REM
970 REM*********** VALUE TESTER SUBROUTINE *************************
980 REM  finds a cycle trip value between 1.61 and 1.59 volts
990 REM
1000 FOR J=1 TO N
1010    IF LP = NLP(J) THEN  GOTO 1070
1020    IF ADV(J) < 200
           THEN  ADV(J)=ADV(J)+1: GOTO 1060
           ELSE  J%=J
1030    CALL ARGETVAL ' ("BATV%",LP,J%,VA1,0)
1050    IF VA1 >1.59 AND VA1 < 1.61 THEN GOSUB 2000
1060    NLP(J)=LP
1070 NEXT J
1080 RETURN
1090 REM
1100 REM*************************************************************
1110 REM
1970 REM********* INCREMENT AND FILE WRITE SUBROUTINE ***************
1980 REM keeps track of cycle number,writes info to disk when called
1990 REM
2000 CYNO(J)= CYNO(J)+1
2005 CALL CLOCKREAD' (HR%,MIN%,SEC%,DATE%,MO%,YR%)
2010 LPTIME(J)=(REC* -120) + LP
2020 CYTIME(J) = LPTIME(J)- PRELP(J) - 240
2030 OPEN BF$(J) FOR APPEND AS #1
2040    WRITE #1, CYNO(J),CYTIME(J),LP,REC,VA1,HR%,MIN%,MO%,DATE%
2050 CLOSE
2060 ADV(J) = 0:     PRELP(J) = LPTIME(J)
2070 RETURN
2080 REM
```

```
2080 REM
2090 REM*************************************************************
2100 REM
2980 REM******* DATA STORAGE ON DISK SUBROUTINE *****************
2990 REM
3000 CALL CLOCKREAD'(HR%,MIN%,SEC%,DATE%,MO%,YR%)
3010 LAB$ = SPACE$(40)
3020 LAB$= "RECORD SAVED AT:"+STR$(HR%)+":"+STR$(MIN%)+":"+STR$(SEC%)+" ON"+STR$
(MO%)+"/"+STR$(DATE%)+"/"+STR$(YR%)    'label with time and date
3030 CALL ARLABEL' ("BATV%",LAB$)
3040 ROOM=0: FREE=0
3050 FIL$= "B:"+STR$(REC)+"REC.ARY"
3060 REM save the array to the disk
3070 PRINT "LAST RECORD SAVED ",FIL$ " AT "HR%":"MIN% " ON " MO% "/"DATE%
3080 PRINT "CELL","CYCLE NO.","TIME","LP","REC"
3090 FOR J=1 TO N
3095    T=LPTIME(J)/120
3100    PRINT:PRINT BF$(J),CYNO(J),CYTIME(J),(T - INT(T))*120,INT(T)
3110 NEXT J
3120 CALL ARSAVE' ("BATV%",FIL$)
3130 REC =REC -1
3140 REM check the amount of space on the disk
3150 CALL MEMFREE' (ROOM)
3160 CALL ARDEL' ("BATV%")
3170 CALL MEMFREE' (FREE)
3180 DISKSPACE = DISKSPACE + (FREE-ROOM)
3190 IF DISKSPACE >270000! THEN BEEP ELSE RETURN
3200 LOCATE 24,1: PRINT "REPLACE DISK SOON  270K AT REC NO. "REC
3210 RETURN
3220 REM
3230 REM*************************************************************
```

B. Sample Data Output from Computer Data Acquisition System

CELL DATA FOR CELL 805 FROM DISK 4.6

CYNO	CYTIME	CAP%	LP.REC		TIME	DATE
69	125	100 %	46	-3591	18 : 8	6 - 8
70	121	100 %	47	-3594	0 : 6	6 - 9
71	122	100 %	49	-3597	6 : 6	6 - 9
72	124	100 %	53	-3600	12 : 7	6 - 9
73	122	100 %	55	-3603	18 : 7	6 - 9
74	123	100 %	58	-3606	0 : 8	6 - 10
75	123	100 %	61	-3609	6 : 8	6 - 10
76	122	100 %	63	-3612	12 : 8	6 - 10
77	123	100 %	66	-3615	18 : 8	6 - 10
78	122	100 %	68	-3618	0 : 8	6 - 11
79	123	100 %	71	-3621	6 : 8	6 - 11
80	122	100 %	73	-3624	12 : 8	6 - 11
81	124	100 %	77	-3627	18 : 10	6 - 11
82	120	100 %	77	-3630	0 : 7	6 - 12
83	122	100 %	79	-3633	6 : 7	6 - 12
84	122	100 %	81	-3636	12 : 7	6 - 12
85	238	198 %	79	-3640	20 : 1	6 - 12
86	121	100 %	80	-3643	2 : 0	6 - 13
87	122	100 %	82	-3646	8 : 0	6 - 13
88	123	100 %	85	-3649	14 : 0	6 - 13
89	124	100 %	89	-3652	20 : 2	6 - 13
90	121	100 %	90	-3655	2 : 1	6 - 14
91	122	100 %	92	-3658	8 : 0	6 - 14
92	122	100 %	94	-3661	14 : 0	6 - 14
93	125	100 %	99	-3664	20 : 2	6 - 14
94	120	100 %	99	-3667	2 : 0	6 - 15
95	121	100 %	100	-3670	7 : 59	6 - 15
96	121	100 %	101	-3673	13 : 57	6 - 15

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720