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IMPROVED THERMAL BATTERY PERFORMANCE.(U)
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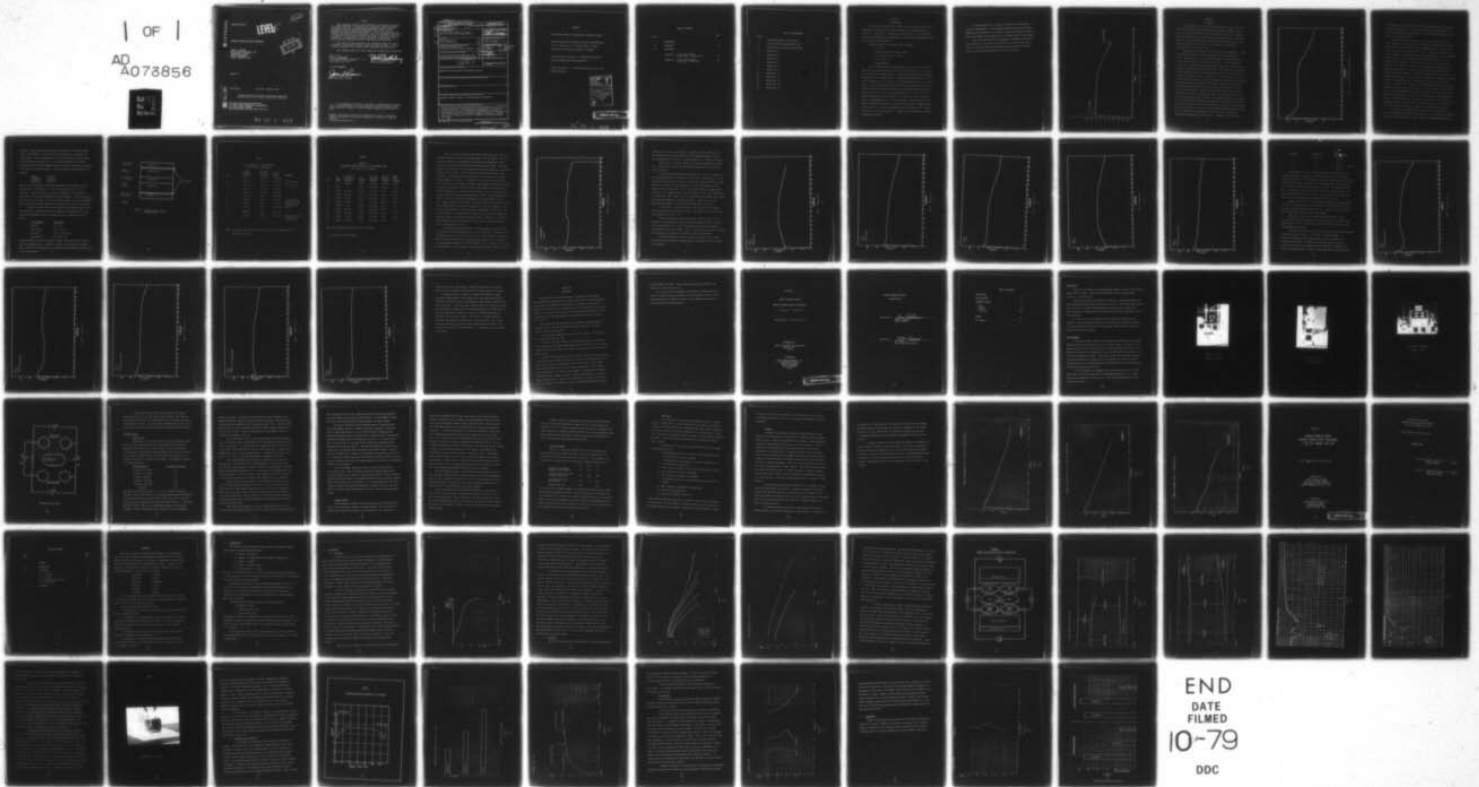
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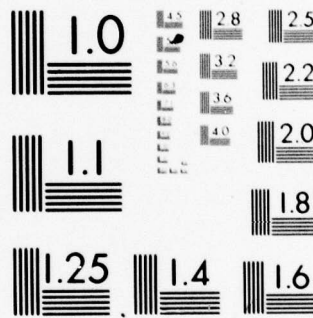
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IMPROVED THERMAL BATTERY PERFORMANCE

JAMES A. DeGRUSON
EAGLE-PICHER INDUSTRIES, INC.
ELECTRONICS DIVISION
COUPLES DEPARTMENT
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Final Report

June 1976 - February 1979

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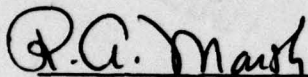
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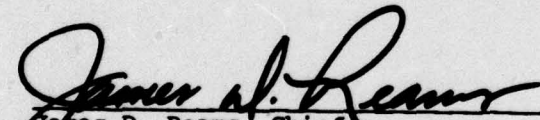


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) During the course of this program, Eagle-Picher Industries, Inc. has developed a thermal battery which has demonstrated an energy density in excess of 17 watt-hours per pound. This advancement of approximately three times the energy density of thermal batteries was accomplished with the lithium aluminum iron disulfide system. The technology necessary to manufacture a thermal battery which will produce 28 volts at 30 amperes for 30 minutes has been achieved.			

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PREFACE

Eagle-Picher wishes to acknowledge the following people:

Wright-Patterson Air Force Base technical representatives,
Mr. R. A. Marsh, Mr. W. S. Bishop and Mr. S. Cloyd --
assistance and guidance throughout the program.

Argonne National Laboratory -- technology pertaining to
lithium aluminum-iron sulfide batteries.

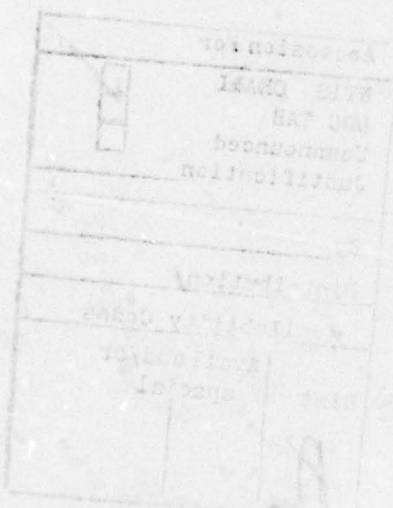
Sandia Laboratories -- technology pertaining to long life
thermal batteries.

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SECTION I

INTRODUCTION

Since June 1976, Eagle-Picher Industries, Inc. has been pursuing the improvement of thermal batteries under contract with Wright-Patterson Air Force Base. Specifically, a design which would be four to five times better than existing thermal battery performance to allow the use of thermal batteries in a wider range of applications.

The design goals of the contract were as follows:

28 \pm 4 volts

30 minutes life under 30 amp loading

1 second activation to 26 volts

140 in³ maximum

17 pounds maximum

Since a thermal battery's nominal density is less than .1 lb/in³, the volume goal and not the weight goal was the restricting factor in the design of a 15 ampere-hour thermal battery. Considering the volume and the optimum configuration for a thermal battery, a battery having the dimensions of 5.625 inches in diameter and 5.625 inches in length was identified as the final test vehicle. Using these dimensions and relying on previous work with long life thermal batteries dictating the amount of necessary peripheral insulation, an active surface area of the cell was determined to be 17.7 in². The 5.625" length would allow two stacks in parallel, so the active surface area was doubled to approximately 35 in². Thus, the nominal current density for the "Improved Thermal" was arrived at by dividing the specified 30 amperes by the surface area of 35 in² giving a current density of .86 amperes/in². Because of this logic, the current density of 1 ampere/in² was used as basic loading throughout the program.

A considerable amount of single cell testing was accomplished to evaluate a large number of electrochemical systems and the many different parameters of each system. At the current density dictated by the program goals, the LiAl/FeS_2 cell produced the most favorable results (see Figure 1).

Since the interim reports (see summaries in appendix) detailed the single cell tests, this report picks up where the second interim report ended so that a more detailed and definitized description of the final concept of the Improved Thermal Battery could be presented.

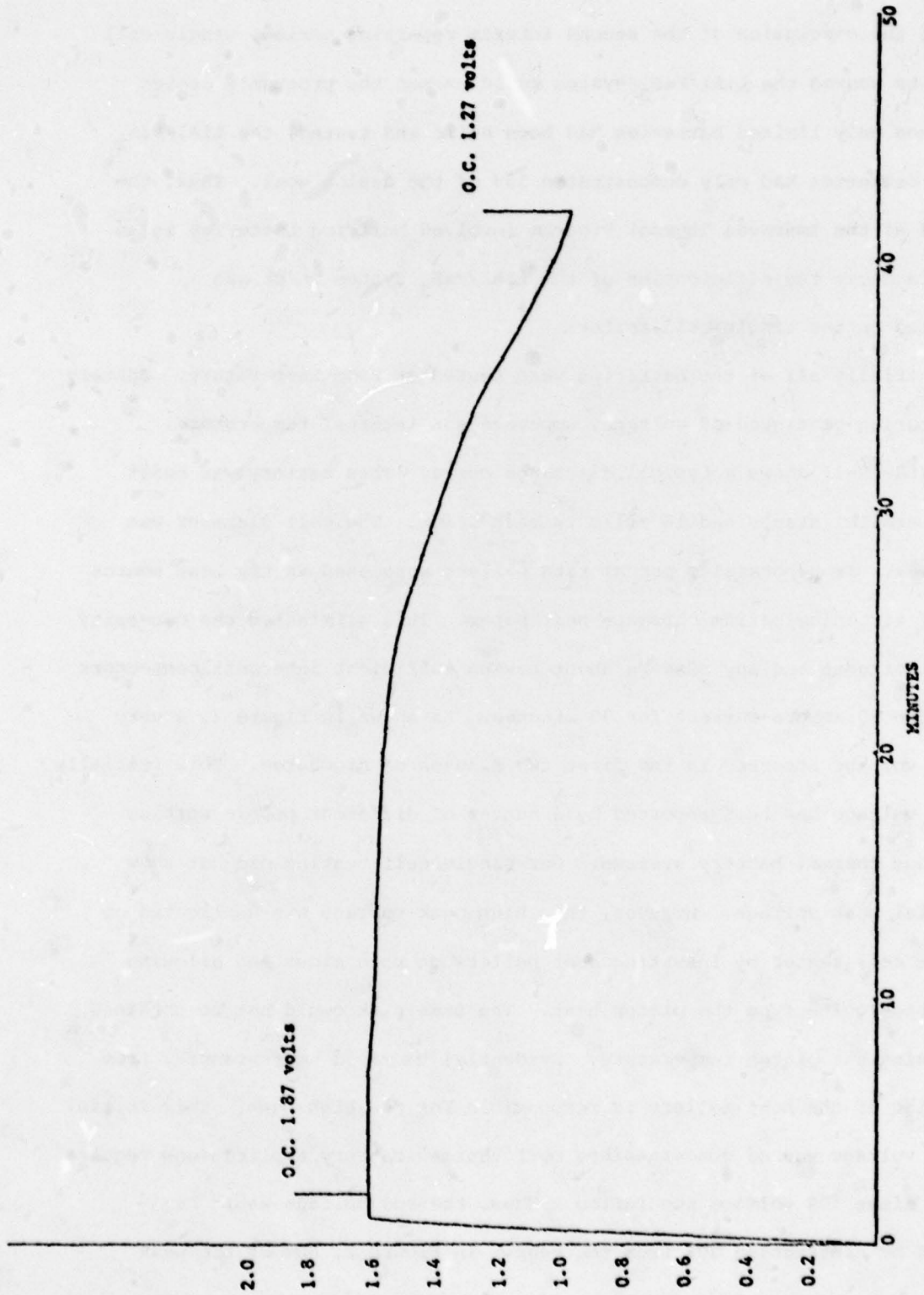


Figure 1. LiAl/FeS₂ Cell, 1A/in² Constant Current

SECTION II

DISCUSSION

At the conclusion of the second interim reporting period, single cell test results showed the LiAl/FeS_2 system would exceed the program's design goal. Since only limited batteries had been built and tested, the LiAl/FeS_2 system in batteries had only demonstrated 33% of the design goal. Thus, the last phase of the Improved Thermal Program involved building batteries in an effort to achieve the efficiencies of the LiAl/FeS_2 system which was demonstrated on the single cell tester.

Initially all of the batteries were tested at room temperature. Battery test monitoring consisted of voltage, amperage and internal temperature. Figure 2 (L8-12-1) shows a typical discharge curve. This battery was built with two parallel stacks and 16 cells in each stack. The cell diameter was 2.625 inches. Iron/potassium perchlorate pellets were used as the heat source instead of zirconium/barium chromate heat paper. This eliminated the necessity of dual electrodes and any concern about having sufficient intercell connectors to carry the 30 ampere current for 30 minutes. As shown in Figure 2, a very high peak voltage occurred in the first two minutes of discharge. This initially high peak voltage has been reported by a number of different people working with various thermal battery systems. Our single cell testing did not show this initial peak voltage. However, this high peak voltage was duplicated on the single cell tester by inserting heat pellets on both sides and allowing them to auto-ignite from the platen heat. The same peak could not be obtained by increasing the platen temperature. Evidently, the rapid heat transfer from the ignition of the heat pellets is responsible for the high peak. This initial high peak voltage was of concern since most thermal battery applications require a plus or minus 10% voltage regulation. Thus, the end voltage would be determined by subtracting 20% from the peak. In Figure 2, 80% of the peak

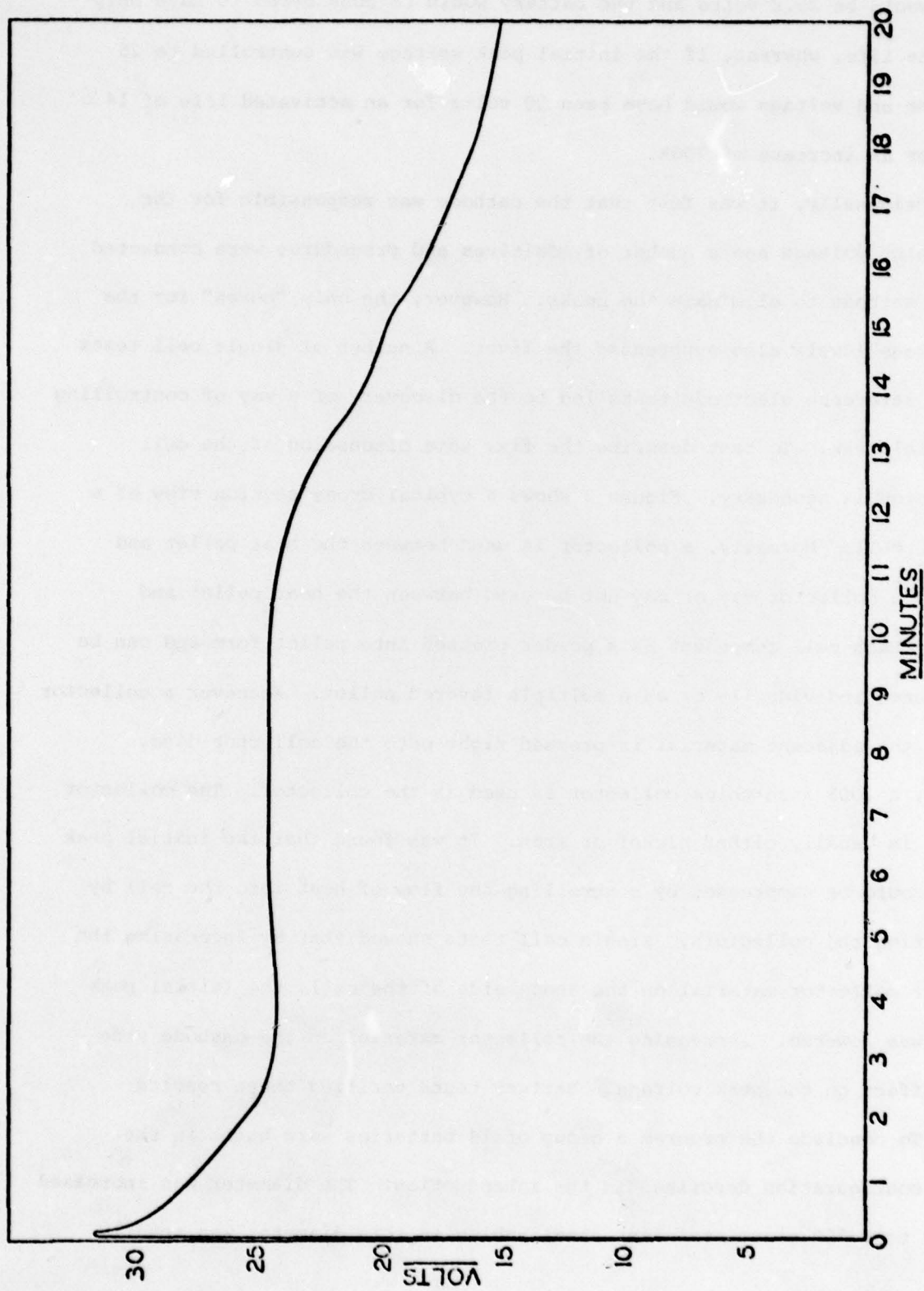


Figure 2. LiAl/FeS₂ Battery Graph (SN L8-12-1)

(31.5V) would be 25.2 volts and the battery would be considered to have only a 2-minute life, whereas, if the initial peak voltage was controlled to 25 volts, the end voltage would have been 20 volts for an activated life of 14.5 minutes or an increase of 700%.

Originally, it was felt that the cathode was responsible for the initial high voltage and a number of additives and procedures were conducted with the cathode to eliminate the peaks. However, the only "cures" for the high voltage levels also suppressed the lives. A number of single cell tests and some reference electrode tests led to the discovery of a way of controlling the initial peak. To best describe the fix, some discussion of the cell construction is necessary. Figure 3 shows a typical cross section view of a LiAl/FeS₂ cell. Normally, a collector is used between the heat pellet and anode and a collector may or may not be used between the heat pellet and cathode. Each cell component is a powder pressed into pellet form and can be manufactured individually or as a multiple layered pellet. Whenever a collector is used, the adjacent material is pressed right onto the collector disc. Normally, a .005 inch thick collector is used as the collector. The collector material is usually either nickel or iron. It was found that the initial peak voltage could be suppressed by controlling the flow of heat into the cell by manipulating the collectors. Single cell tests showed that by increasing the amount of collector material on the anode side of the cell, the initial peak voltage was lowered. Increasing the collector material on the cathode side had no effect on the peak voltage. Battery tests verified these results.

To conclude the program a group of 14 batteries were built in the outline configuration described in the introduction. The diameter was increased slightly to 5.75" since stainless steel tubing in this diameter was readily

available. Keeping with optimum thermal configuration, the length was made equal to the diameter. Min-K insulation was used both as a peripheral and end insulator. The cell diameter was 4.75" which presented a slight problem in the manufacture of the pellets. Due to press capabilities, the same densities used on the small diameter batteries could not be obtained. Instead of the densities listed in Figure 3, the 4.75" diameter cell had densities as follows:

Anode	1.15 g/cc
Electrolyte	1.75 g/cc
Cathode	2.10 g/cc
Heat Pellet	3.25 g/cc

With the extra thicknesses of the large diameter cell, the number of cells necessary for a 28-volt battery could not be contained in the 5.75" tall container. Rather than order 1-inch taller containers, it was decided to build 20-volt batteries and extrapolate the data obtained. The batteries were not built all at one time, but in seven different groups so that the performance data could be analyzed and improvements incorporated into the next build group.

It should be stated that all work with the LiAl powder was done outside of glove boxes in dry rooms with relative humidity of approximately 3%. Some general build parameters were held constant for all 14 batteries as listed below:

<u>Cell Component</u>	<u>Composition</u>
Fe-KClO ₄	86% - 14%
LiAl-KCl-LiCl	80% - 11% - 9%
KCl-LiCl-B	49.5% - 40.5% - 10%
FeS ₂ -KCl-LiCl	60% - 22% - 18%

Changes were made in the seven groups to achieve a lower initial peak voltage and a flat discharge curve. Success was achieved in both areas as described herein. Tables 1 and 2 summarize build parameters and performance characteristics of the final batteries.

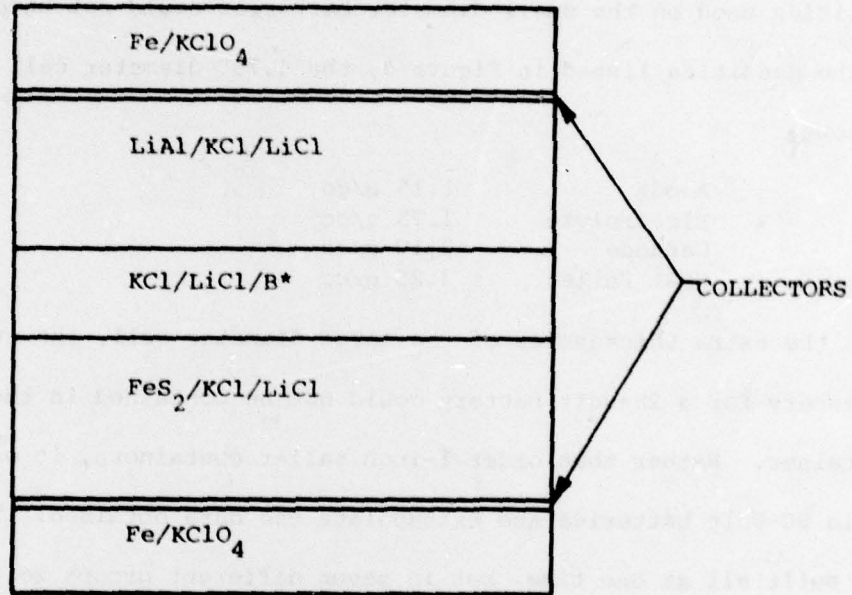
HEAT PELLETT
3.50 g/cc

ANODE
1.35 g/cc

ELECTROLYTE
1.90 g/cc

CATHODE
2.5 g/cc

HEAT PELLETT
3.50 g/cc



* Binder

Figure 3. Cross Section of Typical
LiAl/FeS₂ Cell

TABLE 1

BUILD PARAMETERS OF FINAL BATTERIES
(5.75" DIA. X 5.75" HEIGHT)

<u>S/N</u>	<u>Collector Adjacent to Anode</u>	<u>Collector Adjacent to Cathode</u>	<u>Battery Weight</u>	<u>Comments</u>
1	.005" Fe	.005" Fe	11.25 lbs	
4	.005" Fe	.005" Fe	11.25 lbs	1% Mg in anode
5	.005" Fe	.005" Fe	11.25 lbs	1% Mg in anode
7	.005" Fe	.005" Fe	11.25 lbs	
8	.005" Fe	.005" Fe	11.25 lbs	
9	.005" Fe	None	11.25 lbs	
10	.007 Ni	None	12.10 lbs	30% increase in cathode material
11	.007 Ni	None	12.10 lbs	and 15% increase in heat pellet
12	.010 Fe	None	12.10 lbs	weight
13	.005 Fe .007 Ni	None	12.10 lbs	
14	.014 Ni	None	12.39 lbs	Additional increase in heat pellet weight of 10%

NOTE: All batteries were built identically except for the comments mentioned above and in the text.

TABLE 2

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PERFORMANCE CHARACTERISTICS OF FINAL BATTERY TESTS

(5.75" DIA. X 5.75" HEIGHT)

<u>S/N</u>	<u>Test Temp.</u>	<u>Rise Time to 80% Peak Voltage</u>	<u>Peak Voltage</u>	<u>Life to 80% Peak Voltage</u>	<u>Life to 75% Peak Voltage</u> *	<u>WH/lb Total Battery</u>
1	R.T.	2.44 sec	19.8V	18.5 min	19 min +	14.8
4	-40°F	--	17.6V	16.0 min	18 min	12.0
5	+160°F	1.73 sec	21.9V	12.2 min	14.5	11.6
7	+160°F	1.88 sec	23.2V	12.0 min	13.5	13.0
8	-40°F	3.0 sec	19.2V	18.5 min	20.5	16.5
9	+160°F	2.1 sec	22.1V	17.5 min	20.0	16.1
10	+160°F	1.3 sec	24.0V	16.0 min	17.0	16.5
11	-40°F	1.87 sec	22.0V	16.5 min	20.0	13.3
12	+160°F	1.51 sec	23.1V	18.0 min	19.5	16.5
13	-40°F	2.23 sec	20.2V	18.0 min	21.0	15.4
14	+160°F	2.08 sec	22.3V	21.0 min	24.0	17.2

NOTE: All batteries were tested into a .67 ohm load.

* Lead burned in half internally

The first group consisted of six batteries with three units built as a baseline and to be tested at room temperature, -40°F and $+160^{\circ}\text{F}$. Two other units were built with 1% magnesium in the anode since preliminary testing showed that a reduction in the initial peak voltage might result. The sixth battery was built with a .005 iron collector against the anode and no collector adjacent to the cathode. Figure 4 shows the first battery tested at room temperature. The battery was discharged into a .67 ohm load so the current was approximately 29 amperes. It appeared that the battery had an internal short initially, but it evidently cleared itself between six and seven minutes. The battery voltage was starting to decline when suddenly at 19 minutes, the voltage dropped to zero. After allowing the unit to cool, it was opened and it was found that the negative lead was burnt in half. The lead material was .010" X .25" flat iron lead and evidently was not heavy enough to sustain the 29 ampere current for 20 minutes. Five other batteries were built with the same lead material and nothing could be done to correct the problem, so they were tested as planned to obtain as much data as possible. Battery No. 2 was tested at $+160^{\circ}\text{F}$. No information was obtained since the elevated temperature caused the leads to burn through within 30 seconds. Battery No. 3 tested at -40°F showed very little peak voltage initially and the voltage dropped to zero at approximately six minutes.

After these discouraging results, not much hope was held in obtaining any information from the remaining three units. Battery No. 6 resulted in no information, but Nos. 4 and 5 did not short or fall off abruptly to zero volts. These two units were built with 1% magnesium in the anode and were tested at the two temperature extremes of -40°F and $+160^{\circ}\text{F}$. No. 4, tested at -40°F , rose to approximately 15 volts, dropped 1.4 volts and then slowly climbed to a peak

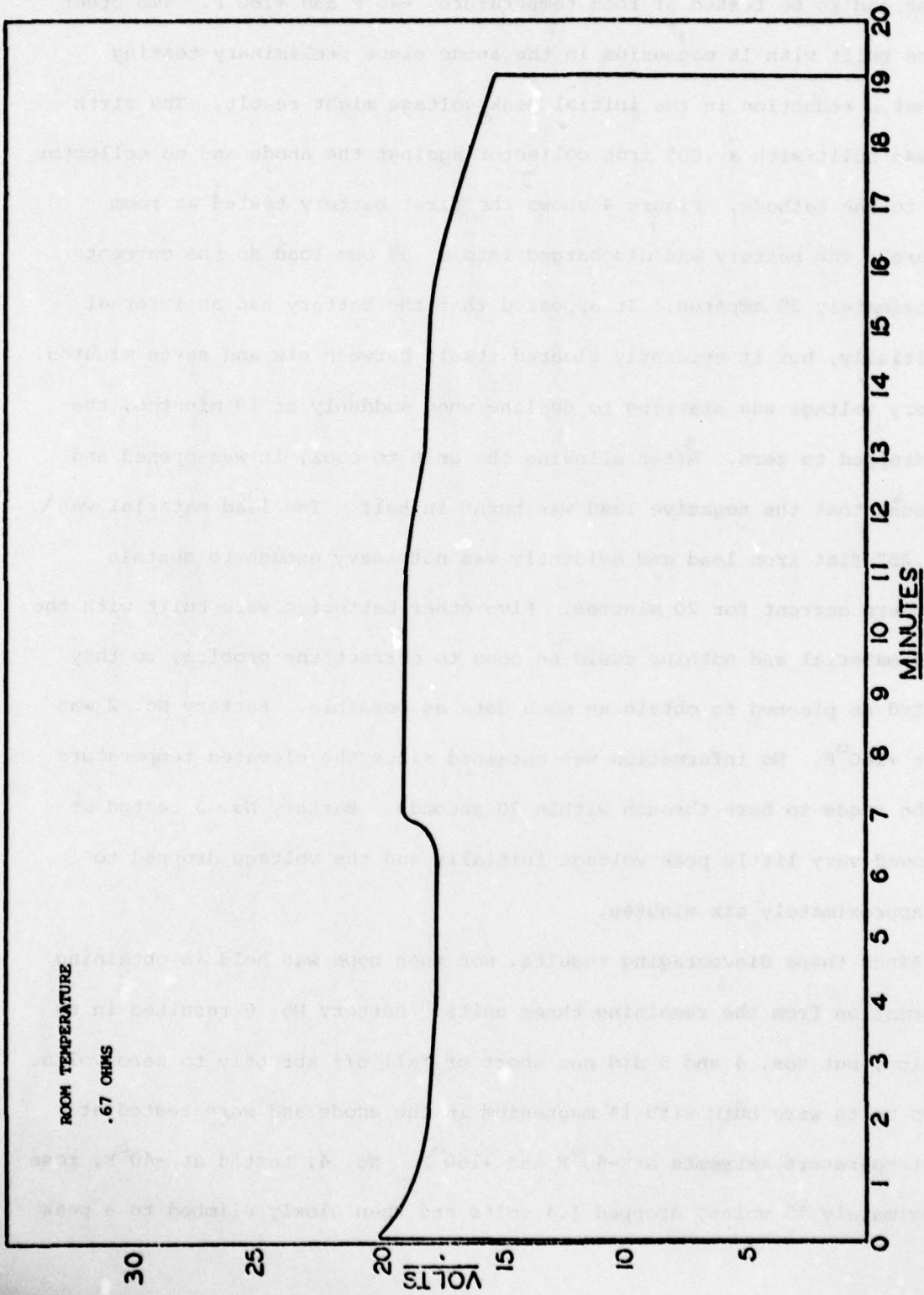


Figure 4. Battery No. 1

voltage of 17.6 volts at six minutes. Evidently, complete ignition of the heat pellets had not occurred causing a high internal impedance initially. The impedance at 30 seconds was .35 ohm as compared to .13 ohm at six minutes.

Battery No. 5, tested at +160°F, had no ignition problems and peaked at 21.9 volts initially with the peak voltage dropping two volts within the first two minutes.

The second group of batteries were built with .020" X .25" leads with no problems experienced in burning the leads in half. Batteries Nos. 7 and 8 were built the same as Nos. 2 and 3 to obtain test results at -40°F and +160°F. Battery No. 7 tested at +160°F peaked at 23.2 volts and dropped two volts during the first two minutes. Life to 80% of peak voltage was approximately 13 minutes. The companion battery (No. 8), tested at -40°F, again demonstrated a very slow rise time. However, once the peak voltage was reached, the voltage trace was very comparable to the +160°F battery. Both the hot and cold batteries had declined to about the same voltage level at 13 minutes.

To decrease the ignition time on the -40°F batteries, the number of fuse trains were increased from two to four. The width of the fuse trains was also increased from .5" to .75".

The third group was a single battery (No. 9) built with a .005 iron collector on the anode and no collector with the cathode. Tested at +160°F, this battery peaked at 22.1 volts with the initial peak voltage dropping 1.4 volts within the first two minutes. After the initial voltage drop, the voltage stabilized with a run time of 17.5 minutes to 80% of peak voltage.

Since this performance looked very good, the remaining four groups of batteries were arranged with varying types of collectors against the anode as shown below:

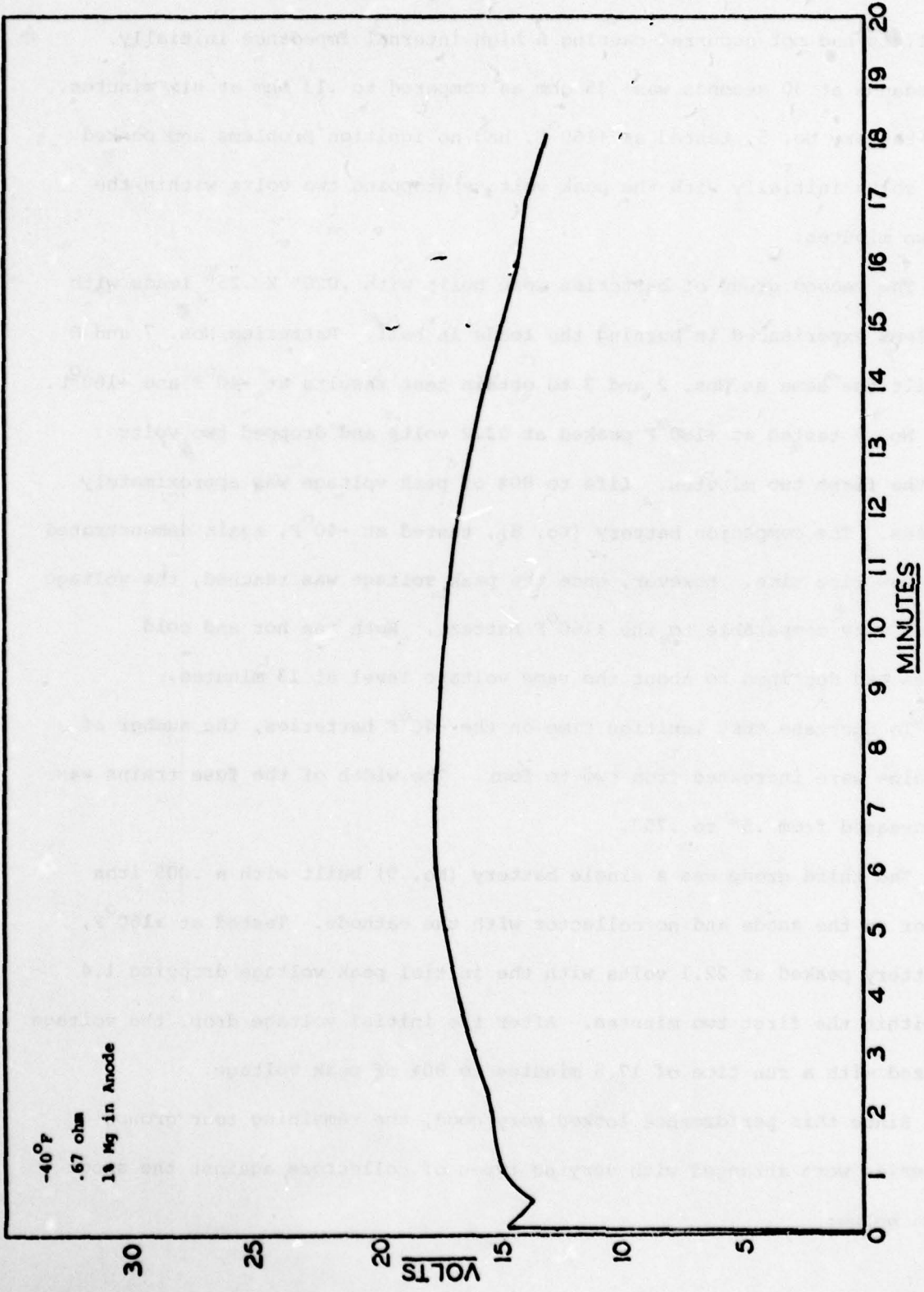


Figure 5. Battery No. 4

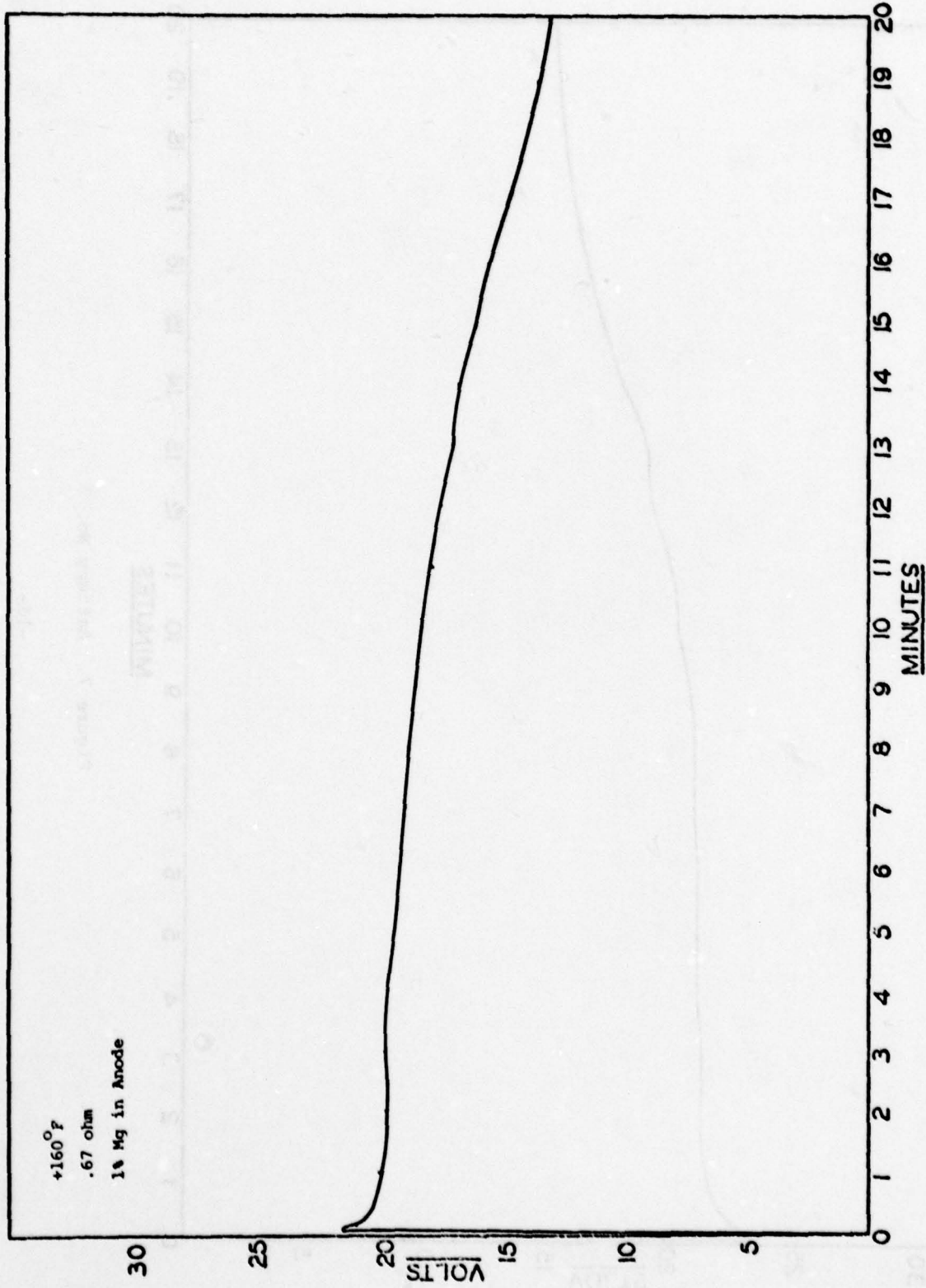


Figure 6. Battery No. 5

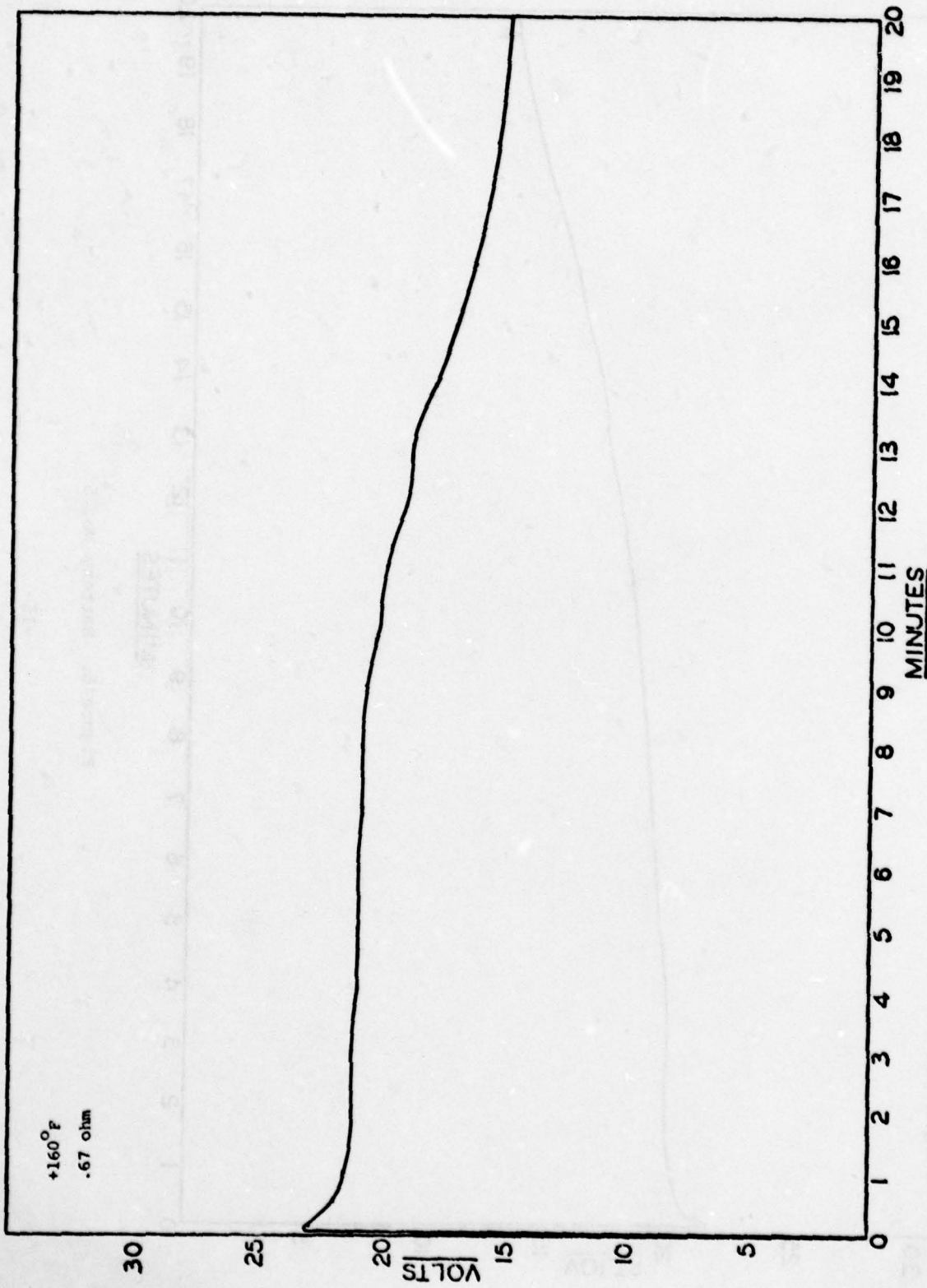


Figure 7. Battery No. 7

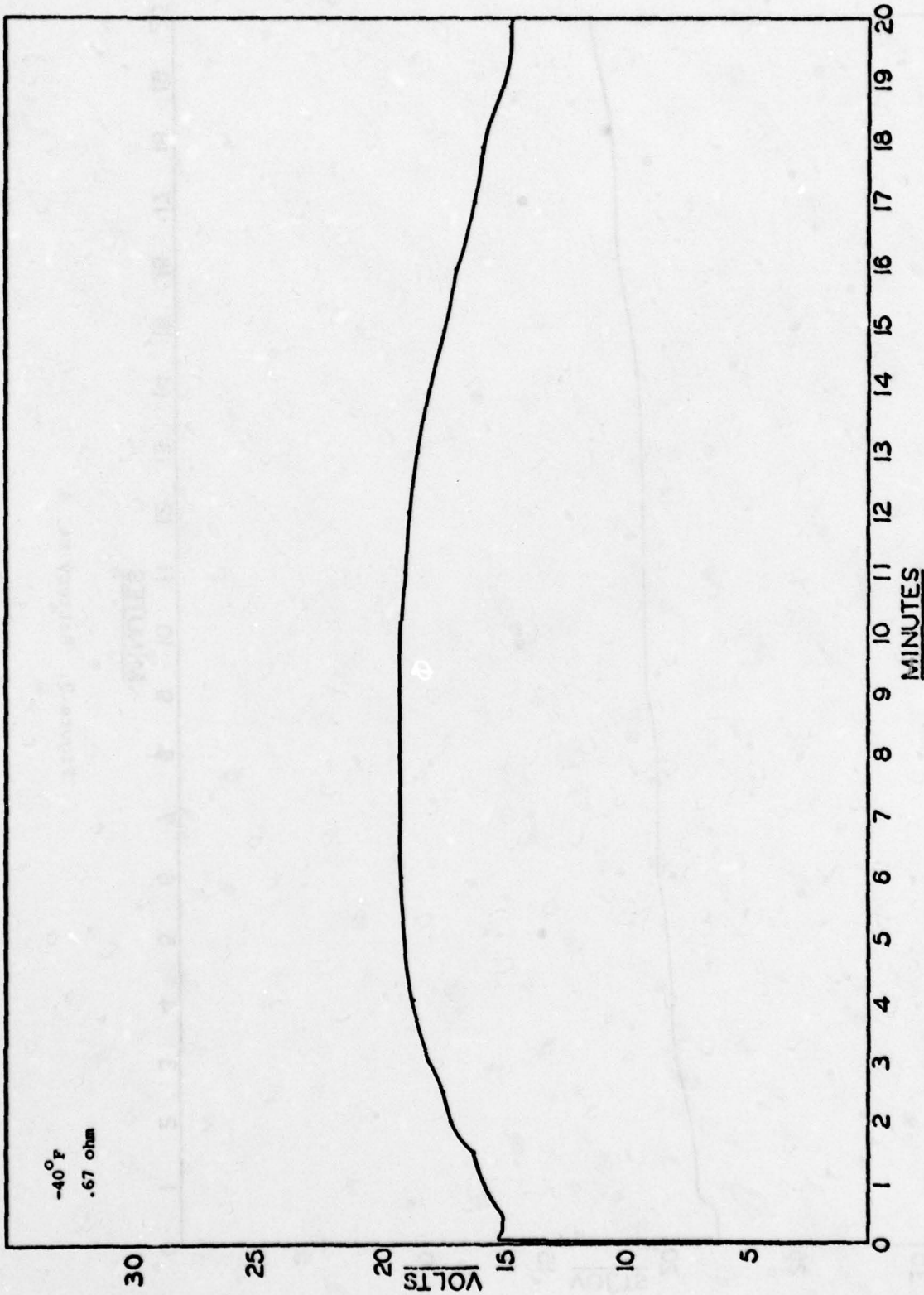


Figure 8. Battery No. 8

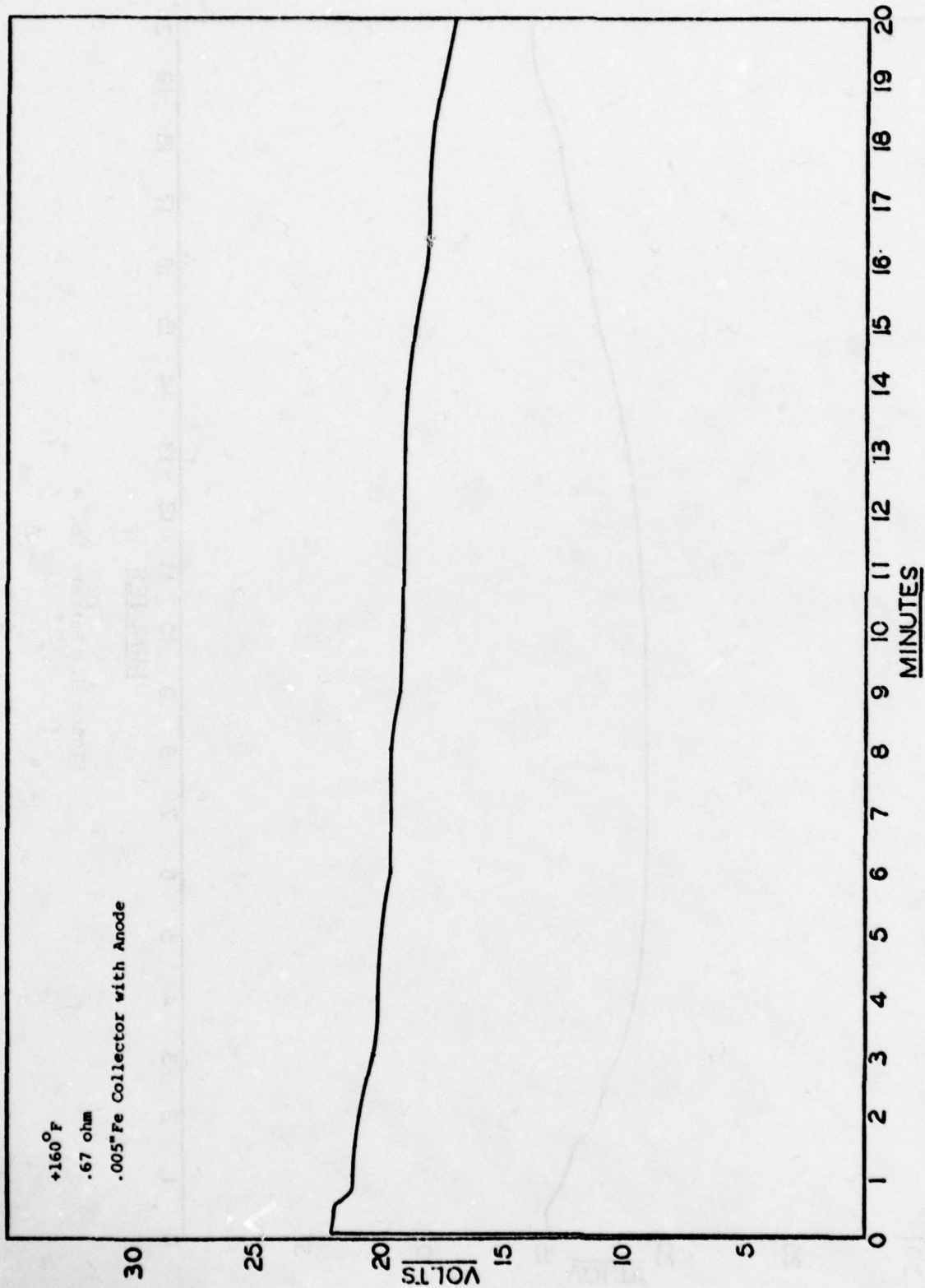


Figure 9. Battery No. 9

<u>Group No.</u>	<u>Battery No.</u>	<u>Anode Collector Type</u>
4	10 and 11	.007" Ni
5	12	.010" Fe
6	13	.005" Fe .007" Ni
7	14	.014" Ni

Batteries Nos. 10 and 11, built identically, were tested at the two temperature extremes. Battery No. 10, tested at 160°F, had a very large voltage drop during the first two minutes, but the voltage came back up slightly and carried better than 30 amperes for 16 minutes above 80% of peak voltage. The rise time to 80% of peak voltage was 1.3 seconds. The companion battery (No. 11), tested at -40°F, had a similar curve but at a lower voltage. The -40°F battery reached 80% of peak voltage in 1.9 seconds. Its voltage drop during the first two minutes was fairly large also at 3.3 volts.

Battery No. 12 with .010 iron collectors against the anode was tested at +160°F. The discharge trace was very smooth and the voltage drop during the first two minutes was just under two volts. Life to 80% of peak voltage was 18 minutes when the slope of the curve changed.

Battery No. 13 with a .005 iron collector was tested at -40°F. The initial voltage drop during the first two minutes was very sharp and was approximately two volts. The battery remained above 80% of the peak voltage for approximately 18 minutes.

The final battery (No. 14) was built with .014 nickel collectors against the anode and also an increase in the amount of cathode material. A proportional increase in heat pellet weight was made to accommodate the increased cathode weight. No additional height was necessary as filler insulation at the top of the battery stack was removed to accommodate the thicker cathode/heat pellets. Figure 14 shows the graph of the battery with

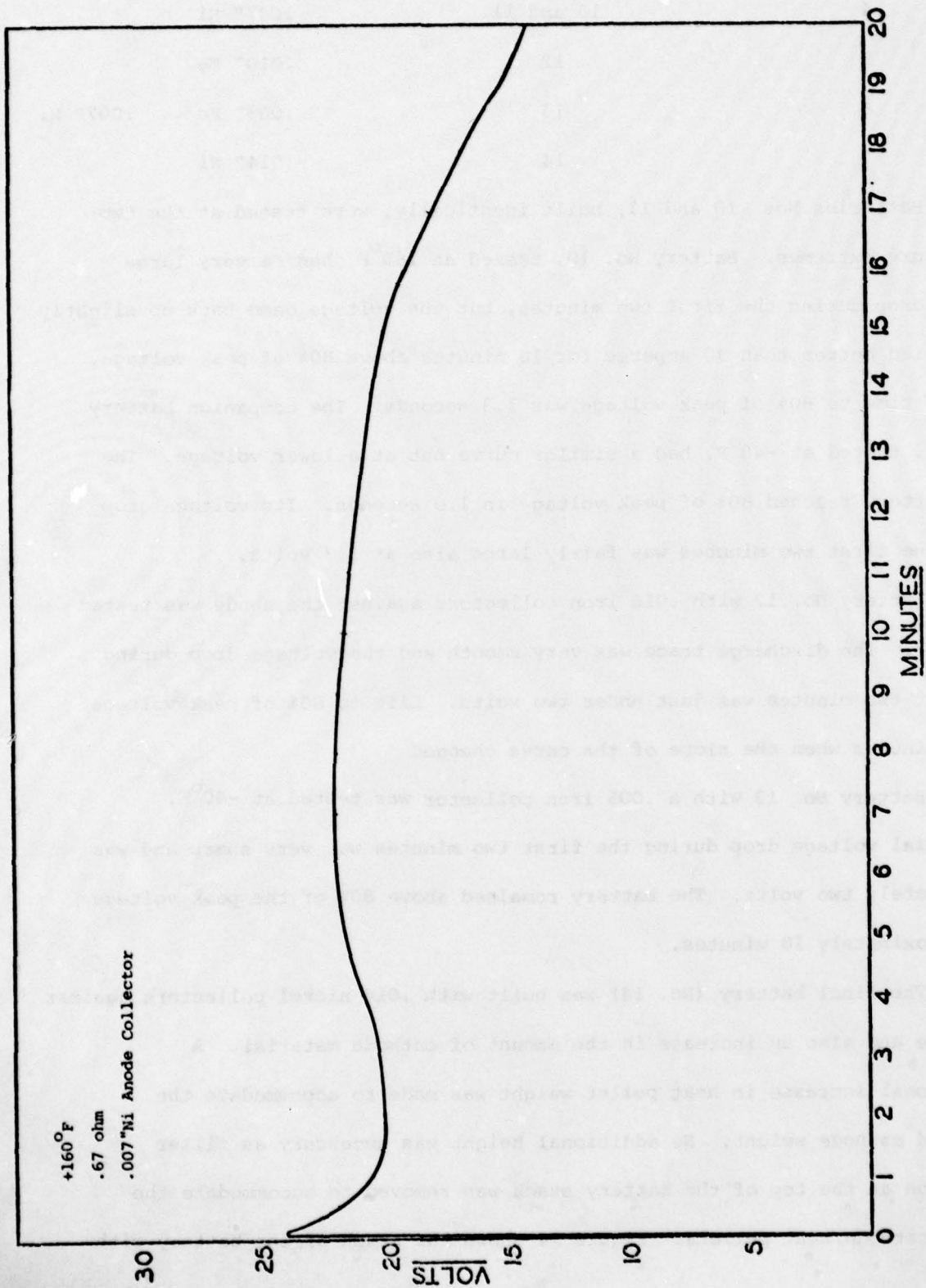


Figure 10. Battery No. 10

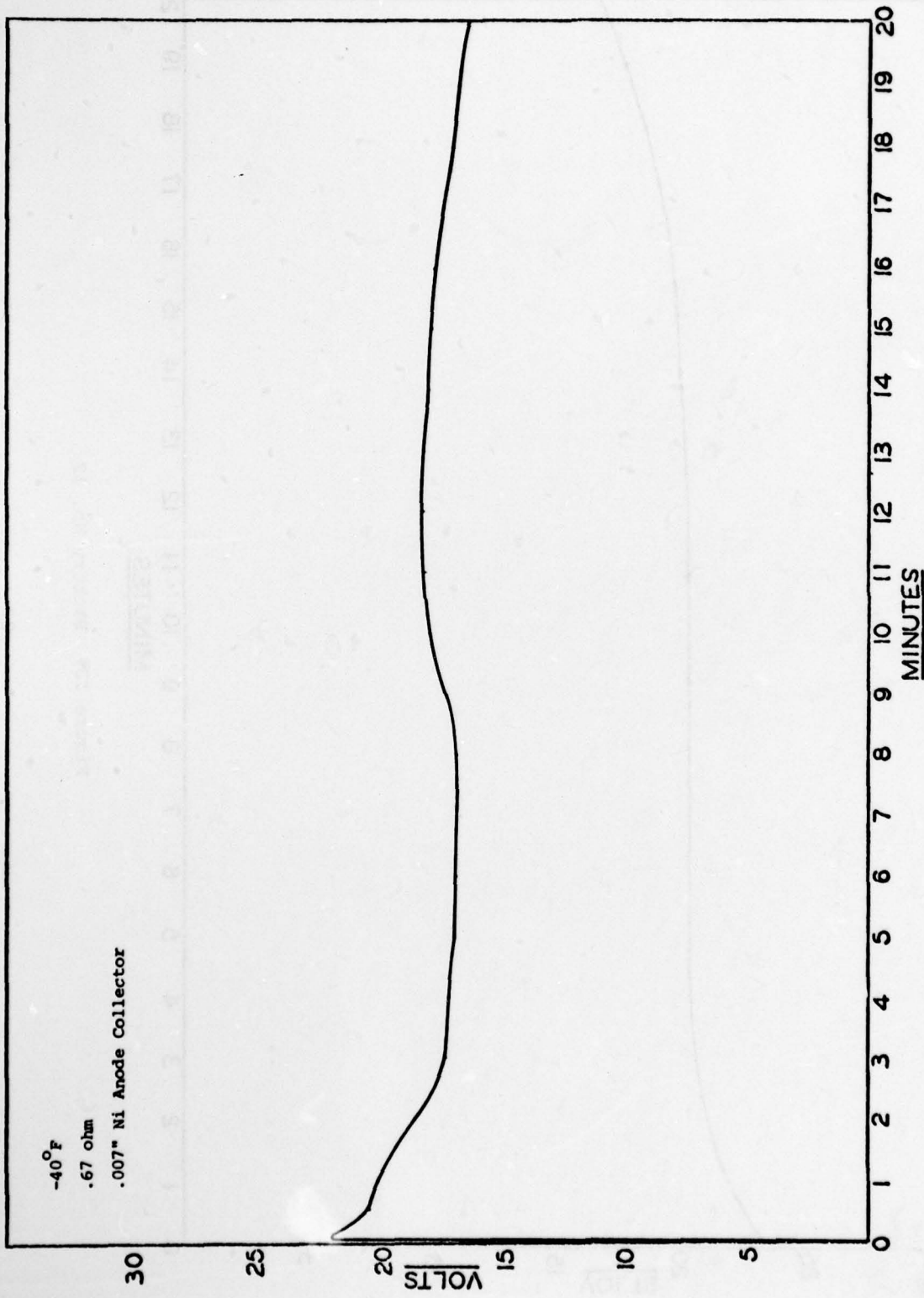


Figure 11. Battery No. 11

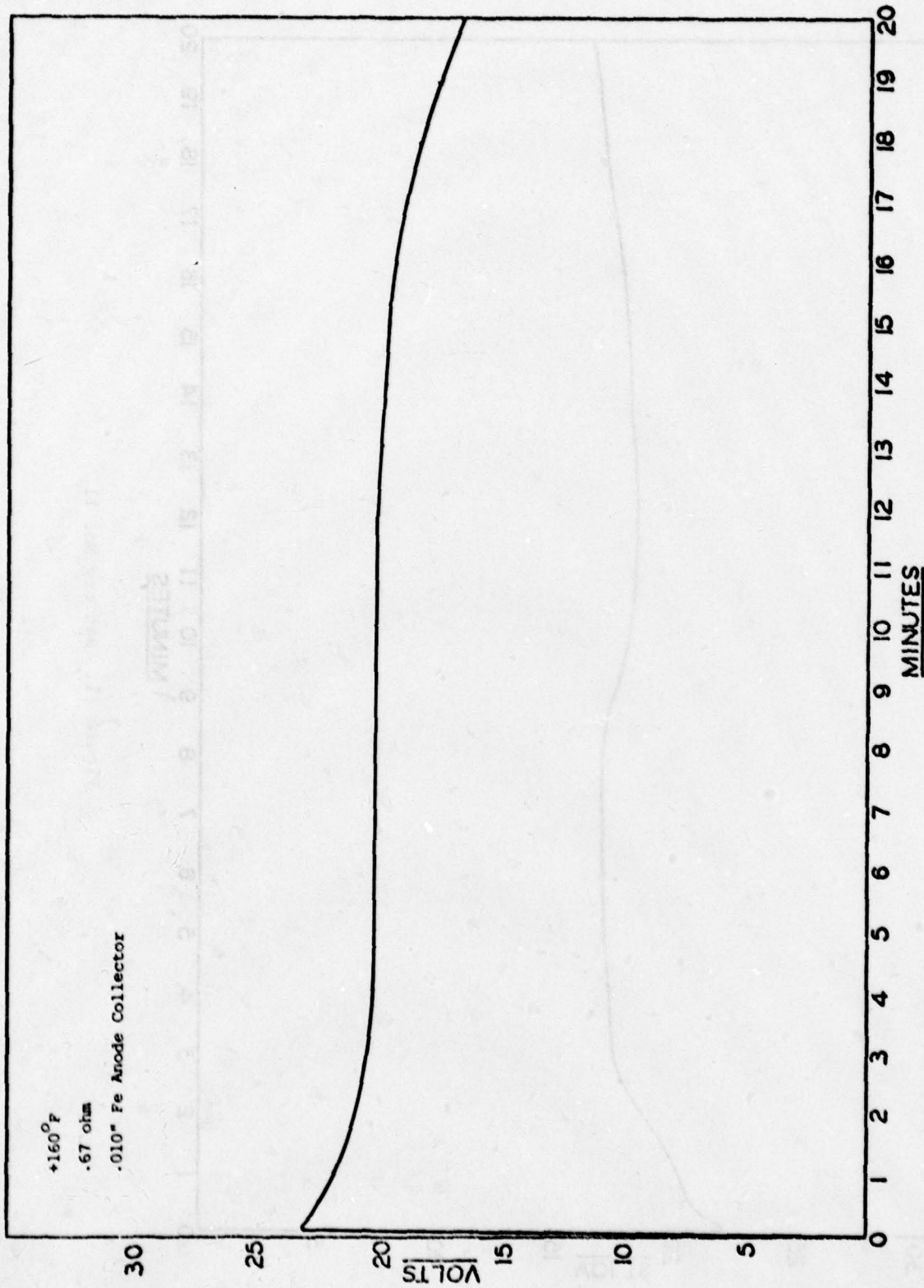


Figure 12. Battery No. 12

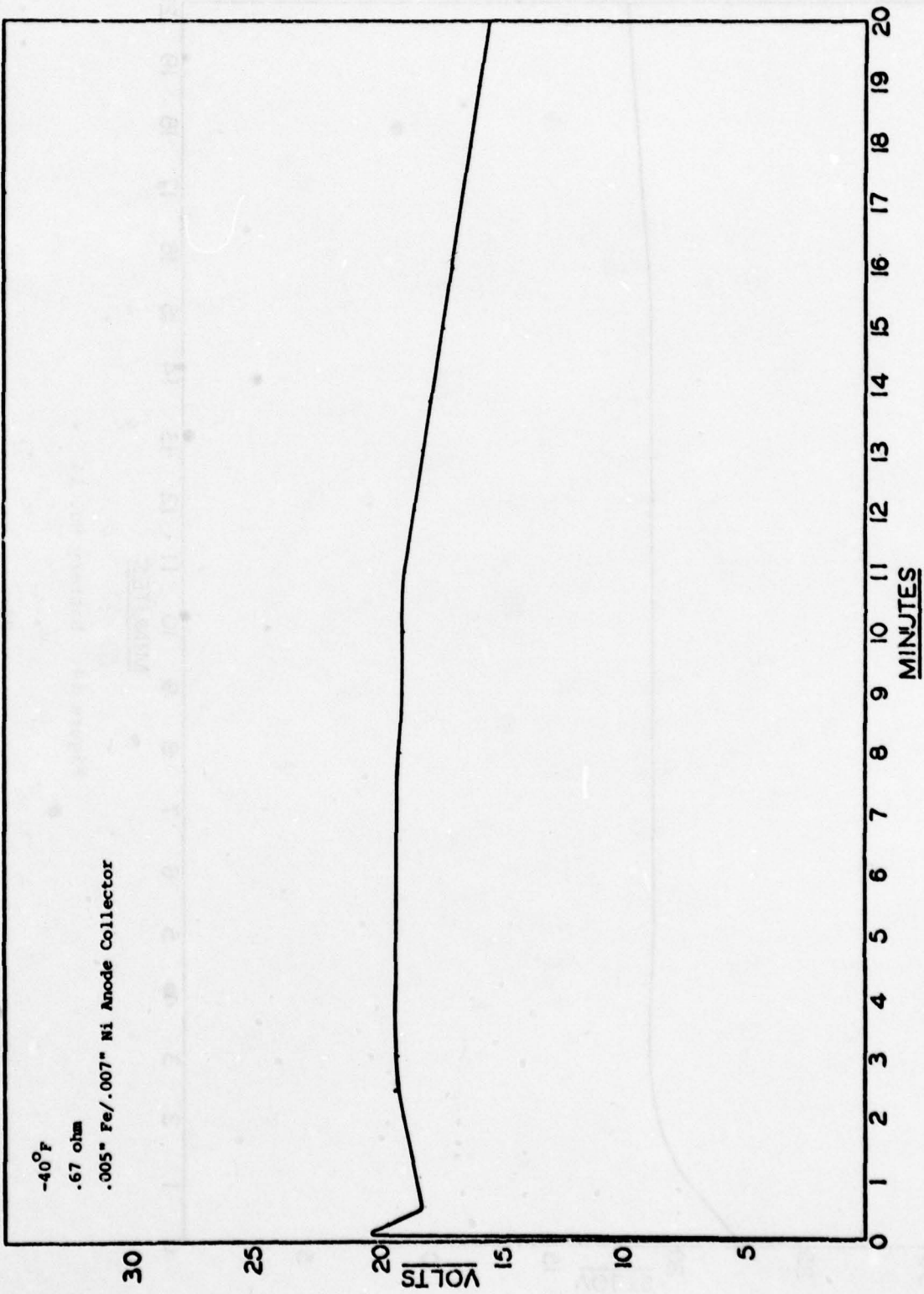


Figure 13. Battery No. 13

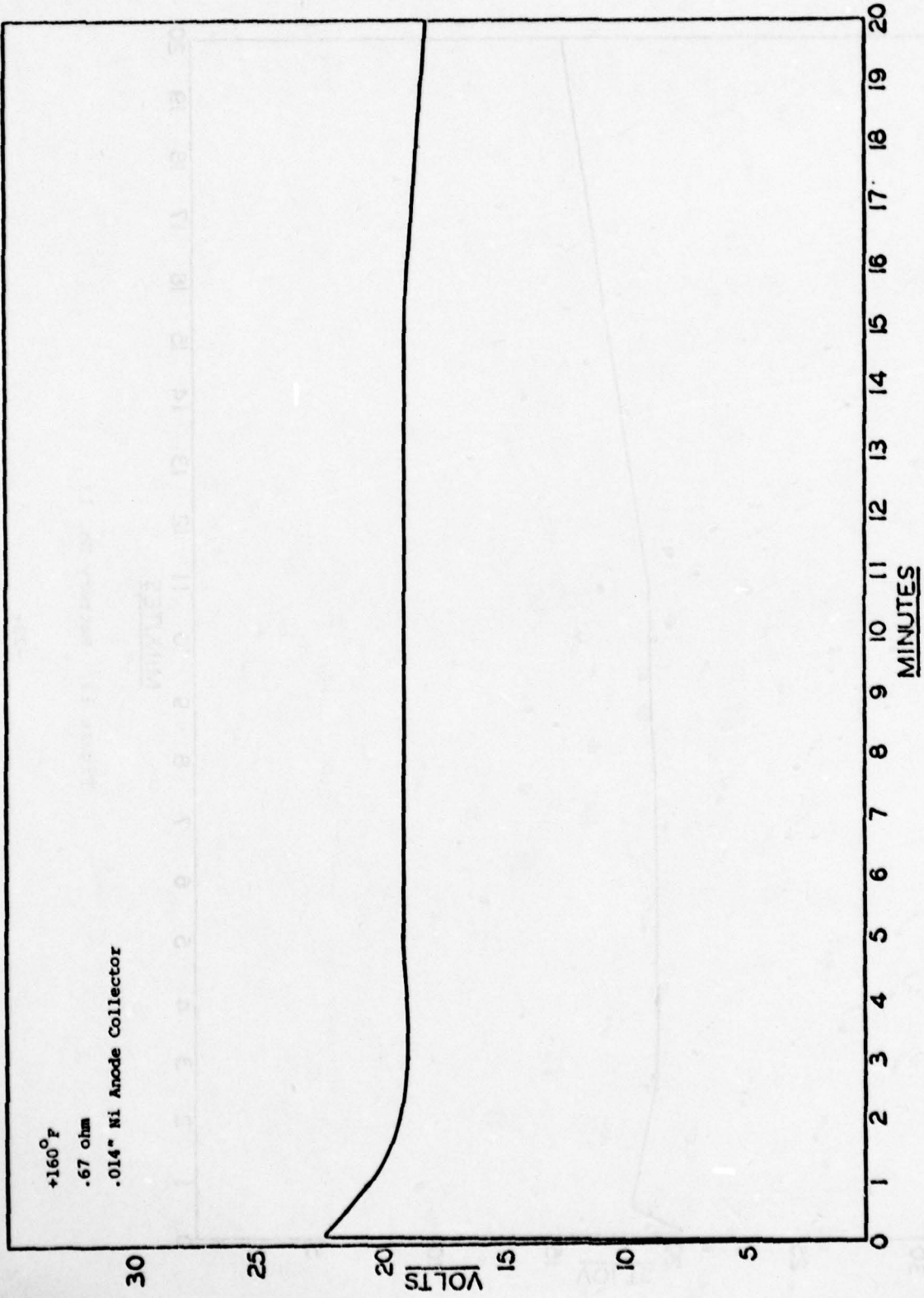


Figure 14. Battery No. 14

a fairly high initial peak voltage. However, the balance of the trace is very flat which increased the life above 80% of peak voltage to 21 minutes.

In analyzing the test results, it appears that whenever a nickel collector is used adjacent to the anode, a very large peak voltage occurs initially. This may be due to the difference in the thermal conductivity of the two materials. All of the results indicate that the initial peak voltage can be altered by changing the heat transfer mechanism of the anode; that is, by either buffering the anode with a collector or adding magnesium, the performance of the battery changed. The increase in cathodic material definitely flattened the discharge curve. The last battery test verified the single cell polarization tests which showed that the LiAl/FeS_2 cell is cathode limited until the cathodic material is increased to twice the amount of the anode.

SECTION III

CONCLUSION

The single cell test results (Figure 1) showed that the LiAl/FeS_2 system achieved 20.25 watt-hours per pound. (The single cell energy densities were ratioed to include heat source material, insulation and container.) If the data from battery No. 14 is extrapolated to a 28 volt battery, the energy density is 19.5 watt-hours per pound. The LiAl/FeS_2 battery results are very predictable and as just described can be correlated very nicely to single cell tests.

Even though the LiAl/FeS_2 system has a lower cell voltage than the Ca/CaCrO_4 system, its high energy density figure lends itself into high current, long life applications.

The two systems complement each other with Ca/CaCrO_4 being better for high current and short lives.

All of the LiAl/FeS_2 batteries tested displayed little or no bulging of the container. No thermal runaways were experienced and, since the calcium-lithium alloy does not form in this system, no noise was noted at low current density tests.

With the success achieved on this program, the LiAl/FeS_2 system warrants further activity to finalize the design. The use of nickel collectors on the anode has been shown to increase the initial peak voltage. Other buffer materials which would alter the heat transfer mechanism of the cell needs to be investigated. Even though a large number of cathodes were evaluated, a better cathode is needed. A better cathode could be defined as one which would increase the cell voltage or one which would not polarize as badly as the iron sulfide. Only limited battery tests were conducted with zirconium/

barium chromate heat paper. These tests showed quicker activation times and better initial peak voltages.

With the low internal impedance of this battery, many applications closed to thermal batteries previously are now attainable. The low cost of thermal batteries will make this system in great demand for replacing the more sophisticated primary batteries.

APPENDIX A

INTERIM TECHNICAL REPORT

IMPROVED THERMAL BATTERY PERFORMANCE

1 JUNE 1976 - 30 APRIL 1977

USAF Contract No. 33615-76-C-2074

Prepared For

WRIGHT PATTERSON AIR FORCE BASE
DAYTON, OHIO
45433

Prepared By

EAGLE-PICHER INDUSTRIES, INC.
ELECTRONICS DIVISION
COUPLES DEPARTMENT
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INTERIM TECHNICAL REPORT

APPROVAL PAGE

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INTRODUCTION

This report represents the accomplishments achieved to date on the "Improved Thermal Battery Program" sponsored by Wright-Patterson Air Force Base under contract no. 33615-76-C-2074.

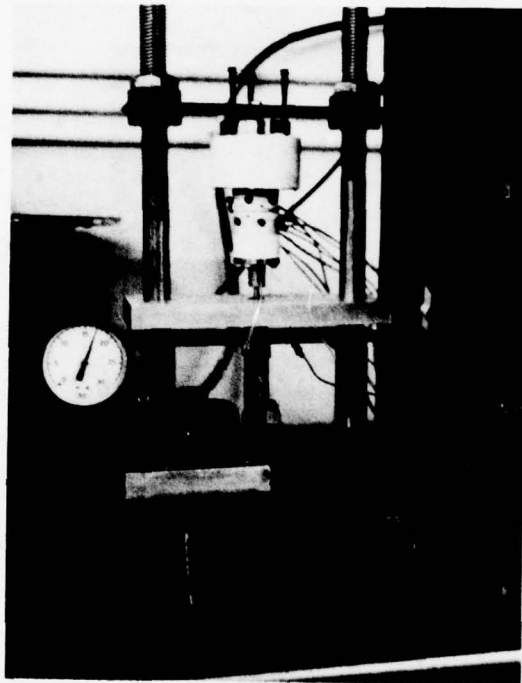
Principal effort has been directed at individual component studies of the Calcium/Calcium Chromate system as directed by contract. In assessing other thermal battery systems, the 48/A% Lithium Aluminum anode has received a major effort due to the greater coulombic efficiency realized along with its more stable operating performance.

The first part of the program was spent constructing single-cell test equipment, acquiring necessary dies for cell fabrication and literature searching of new materials with the balance of the work period being used for single cell testing and material evaluation.

TEST EQUIPMENT

A single-cell tester similar to the Sandia tester described in SLA73-0896, December 1973, was constructed at the start of this program. It consists of two heated platens (2" Dia.) of boron nitride with the upper platen stationary. All single-cell tests have been performed on this unit maintaining the pressure at 2.5 psi and the temperature at 500°C. Each test was conducted in duplicate with the test being repeated if any disparity was noted between the two tests. Unless otherwise stated all of the data herein was obtained using a 4.0 ohm load with the voltage being monitored to 1.0 volt.

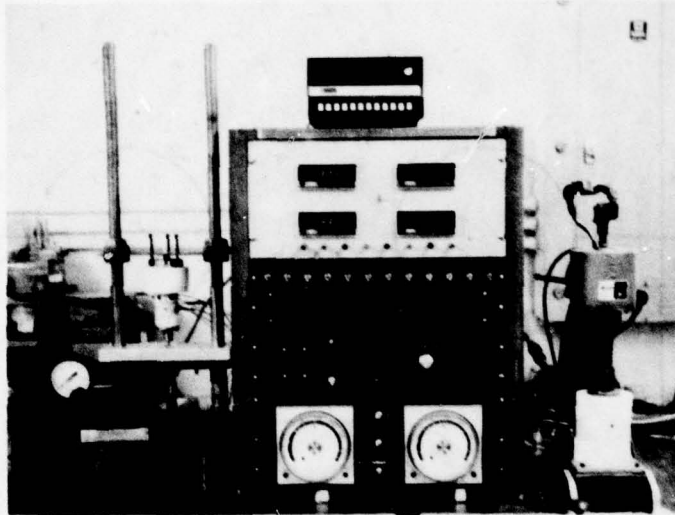
All of the powder cell components were pressed into pellets on a 20 ton hand press. The die was constructed to accommodate materials up to 1.5 inches thick with the diameter of the die set at 1.129 inches representing exactly one square inch of area.



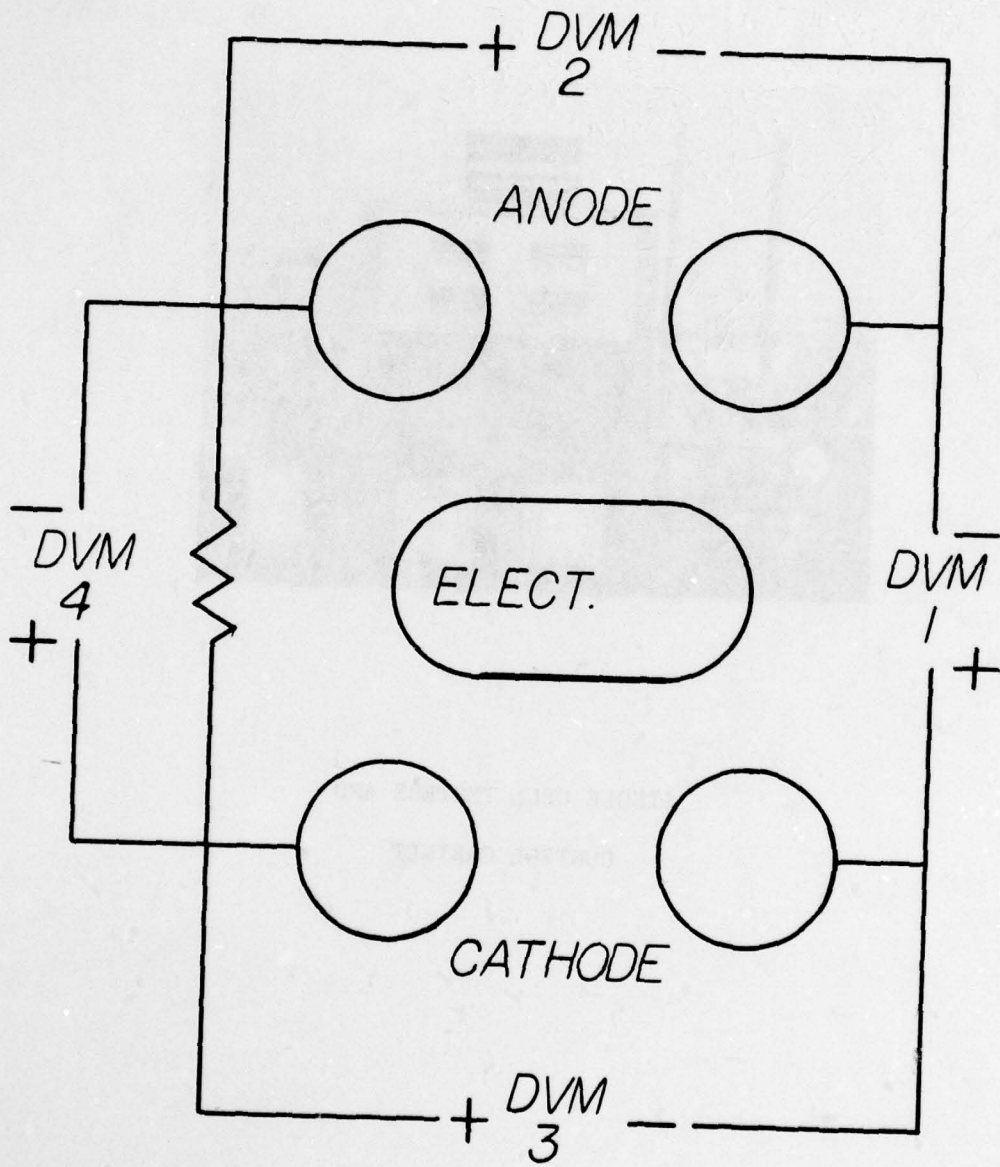
SINGLE CELL TESTER
2" DIAMETER PLATENS



SINGLE CELL TESTER
4" DIAMETER PLATENS



SINGLE CELL TESTERS AND
CONTROL CABINET



POLARIZATION TEST SETUP

A second single-cell tester utilizing four (4) inch diameter platens was utilized for all reference electrode testing. This tester was constructed with the lower platen stationary and the upper platen attached to a Mead pneumatic cylinder. The large platens eliminated the need for the one-square-inch cells to be sectioned to perform the reference electrode testing.

COMPONENT STUDIES

Anode Studies

Historically, calcium in sheet form of various thicknesses (.003", .005", .010" and .020") has been used as the anode material with vacuum deposited calcium being used to a lesser degree. Both of these forms of calcium have been investigated along with powdered calcium. After failing to reduce granular calcium (6 mesh) to powder by grinding, powdered calcium produced by atomizing was obtained for evaluation. The powdered calcium had the following properties:

<u>Tyler Designation</u>	<u>Percentage of Material</u>
-16 mesh to + 20 mesh	1.3
-20 mesh to + 30 mesh	3.3
-30 mesh to +50 mesh	25.7
-50 mesh to +100 mesh	46.8
-100 mesh to +200 mesh	20.2
-200 mesh	3.0

The purity was 90-95 per cent with 3 - 4% Mg, 1.50 ppm Mn, 320 ppm Fe, 700 ppm Al, 3 ppm Si and 23 ppm Cu. One problem experienced with the powdered calcium is that the small particles tend to oxidize very easily. The best cells to date have produced lives of forty-five (45) minutes to 1.0 volt under 60 mA/cm² loading. However, in considering the amount of anode material necessary to obtain a good pellet, the efficiency is low at approximately

fifteen (15) percent. By making the calcium pellets as thin as possible, the highest efficiencies realized have been seventeen (17) percent. All testing shows that the most coarse powdered calcium produces the longest lives. The more coarse material does not compact as smoothly as the fine powder allowing a greater surface area for reaction. A typical discharge curve of the powdered calcium is attached in the appendix. (Page 15)

In evaluating sheet calcium, three different suppliers' calcium have been used. All produced similar results with the only difference being in the activation times to peak voltage. The best efficiencies obtained remained at thirty percent for the .020" thick calcium and up to 44% for .005" thick calcium. Attached in the Appendix (Page 16) is a typical discharge curve of the sheet calcium anode with a life to one (1) volt of forty-one (41) minutes at approximately 75 mA/cm².

The vacuum deposited calcium produced the shortest lives of any anode material used. This is partly due to the small amount of cells tested to date. The effort has been directed to a higher utilization by using different substrates. These substrates have included nickel, stainless steel, iron, expanded metal, steel wool and honeycomb. By use of the latter three substrates, a gain in active surface area was achieved but the efficiency still remained low at 6 - 8 percent.

With all forms of calcium anodes, calcium-lithium alloy beads have been noted to appear around the periphery of the cells. In most of the cells these beads did not get large enough to short out the cell. In tests to determine why these alloy beads form on some of the cells, it was found that the alloy beads are temperature-sensitive. That is, with cells tested with different temperatures around the periphery, more alloy beads formed at the low temperature edge than at the high temperature edge.

Thus, with calcium anodes, the two main problems identified are: 1) the calcium oxide layering which inhibits life and, 2) the excessive calcium-lithium alloy

which causes shorting and noise. Reference electrode testing has established that the Ca/CaCrO₄ cell is primarily anode limited. By using powdered calcium, with CaCrO₄, some cells have been constructed which are cathode limited.

By using 48 atom percent lithium-aluminum anodes in conjunction with the calcium chromate cathode, a cathode limited cell is produced. Cells with lives of eighty (80) minutes to 1.0 volt under 60 mA/cm² loading have been produced giving approximately twice the capacity achieved with the calcium anodes (see typical discharge curve of LiAl/CaCrO₄ cell, Page 17). By using the 48% LiAl, the melting point of the anode is above 700°C so no problems have been experienced in melting the anodes. It has been determined that electrolyte containing forty (40) percent binder and pressed at the lowest density (1.50 g/cc) produce the longest lives. However, by substituting yttrium oxide for the kaolin at a 50 percent by weight amount, the lives have been extended. Unlike the calcium anodes, the particle size and pellet forming pressure of the LiAl do not significantly affect cell performance.

One of the biggest obstacles in meeting the goals of the contract is the allowable volume. Both the powdered calcium and lithium aluminum result in thicker anodes than the sheet and vacuum deposited calcium. Since the lithium aluminum anode's performance is not hampered by particle size or pressure, thinner anodes can be achieved with this material. Due to the brittleness of the alloy, rolling into sheet form cannot be accomplished. Casting of the alloy into thin sheets is currently being investigated in an effort to reduce the thickness even further.

Cathode Studies

Calcium chromate coulombic efficiencies have typically been from thirty (30) to forty (40) percent maximum in thermal batteries. This efficiency has usually been achieved at the higher current densities of 140 - 160 mA/cm².

Based on the assumption that CaCr_2O_4 forms rapidly at the surface interface between the metallic current collector and the depolarizer with the reaction sites being progressively removed farther from the metallic collector as the cell discharge proceeds, an effort has been aimed at reducing the resultant resistance. To reduce this depolarizer to collector resistance, studies have been conducted using honeycomb structure and expanded metal as an integral part of the collector so that the depolarizer material could be pressed into it resulting in a metallic conductor throughout the depolarizer pellet. The use of powdered metals, specifically iron and nickel, have also been used in attempts to improve the electrical conductivity of the cathode. The powdered iron oxidized very rapidly causing the cathode to burst into flame. The powdered nickel appears to improve the electrical conductivity somewhat as indicated by the reference electrode testing. Carbon black and graphite have been used in previous studies, but the high bulking and relatively low conductivity result in thick low density pellets which nullify any gain in efficiency.

The expanded metal improves the efficiency of the cathode better than the honeycomb, although neither structure improves the efficiency substantially. Thus, the only real benefit derived from the use of these structures is in the physical attachment of the pellet to the collector allowing thinner and less dense pellets to be used than would be possible otherwise.

Various cathode materials including PbCrO_4 , NaCuCrO_4 , V_2O_5 , TiS_2 and FeS_2 have been used in attempts to gain greater cathode efficiencies. Only the FeS_2 has demonstrated a better performance than that achieved with CaCrO_4 . By using an overabundance of FeS_2 , the LiAl/FeS_2 cell will become anode limited. Even with twice the amount of CaCrO_4 as LiAl , the LiAl/CaCrO_4 cell has remained cathode limited.

Density studies for the cathode in a two-layer pellet have shown that a less dense pellet produces a longer life for the LiAl/CaCrO_4 cell. Densities of 1.75 - 2.00 gm/cc produced optimum lives for the Ca/CaCrO_4 cells while a density of 1.50 gm/cc produced optimum lives for the LiAl/CaCrO_4 cells. Lower density pellets (less than 1.50 gm/cc) could not be evaluated due to their fragileness and poor handling characteristics.

Collector Studies

Nickel in a flat plate configuration is the most commonly used electrode material for thermal batteries. Iron is also widely used as a collector while stainless steel has been used only in a few instances. The properties of the metals which are important to battery performance are:

	<u>Ni</u>	<u>SS</u>	<u>Fe</u>
Coefficient of Thermal Expansion (10^{-6} in/in $^{\circ}$ F)	5.8	9.6	6.7
Thermal Conductivity (BTU (in)/(hr) (ft 2) ($^{\circ}$ F)	520	105	460
Electrical Resistivity (microhm-cm)	6.8	72	9.71
Melting Point ($^{\circ}$ C)	1455		1535

A low coefficient of thermal expansion is required to maintain contact through the tremendous temperature increase. Since the electrolyte is separated from the heat source by the collector, the highest thermal conductivity is desirable with a low electrical resistivity property. Nickel has the optimum values for these characteristics but during single cell tests, very little difference was noted between the type of metal used for the collectors.

Insulation

Since insulation is the largest contributing factor to a thermal battery's volume, this is a major component to be considered in achieving a 15 ampere hour battery with 140 in³ maximum volume. The amount of insulation required to maintain the operating temperature of a thermal battery is quite large (50% of the total battery volume) even when utilizing the best insulation available. The best insulation being used in long life thermal batteries today is min-K.

In searching for an insulator for thermal batteries, the following requirements must be met:

1. Withstand temperatures from -65°F to +200°F indefinitely and up to 1400°F for 30 minutes minimum.
2. Be nonhygroscopic and preferably contain no chemical water.
3. Be nonconductive electrically.
4. Have a very low thermal conductivity (less than that of min-K).
5. Meet dielectric strength requirements.
6. Meet insulation resistance requirements.
7. Be chemically stable over the temperature range from -65°F to +1400°F.
8. Meet limitation requirements for compression.
9. Have low creep properties.
10. Be shock and vibration resistant.

Contact has been made with suppliers of insulation, but no better alternatives have been found. The few insulators which may develop into super insulation for thermal batteries are microtherm, evacuated foil and high density ceramics.

Studies are currently being conducted on the materials with a side study involving nodal analyses to arrive at an optimum configuration for various insulators.

Summary

A thermal cell utilizing LiAl/KCl/LiCl Kaolin/CaCrO₄ has been developed with approximately 45% utilization of both the anode and cathode which delivers .4 amperes per square inch for 65 minutes. (This utilization was based on running the cell from a peak of 2.1 volts down to 1.0 volts.) Using 20% of peak voltage for an end voltage baseline, this cell has demonstrated a 30 minute life at .4 amperes per square inch (.062 A/cm²). This cell has been achieved with a higher percentage of binder (40%) than is normally used with the Ca/KCl LiCl/CaCrO₄ system so that it should be more resistant to severe environments. This cell is cathode limited as opposed to the Ca/KCl LiCl/CaCrO₄ which is anode limited. This cathode limitation does not change even when the amount of cathodic material is doubled. However, in using FeS₂ as the cathode, the cell becomes anode limited when the amount of cathodic material is increased to approximately twice the amount of anode material.

Developed during this program has been the use of powdered calcium versus the normal sheet calcium anode. Although no significant increase in capacity over the sheet calcium has resulted, the use of powdered calcium allows the blending of materials into it so that a possible avenue of overcoming the calcium oxide layering effect may result in a Ca/LiCl KCl/CaCrO₄ cell which is not anode limited.

In evaluating binders necessary for restraining the electrolyte during operation, yttrium oxide appears better than kaolinite. The use of the

Y_2O_3 results in a 20% increase in life with very little electrolyte leakage. The effectiveness of yttrium oxide as a binder is dependent upon the method in which it is used. Best results are obtained by grinding the Y_2O_3 and then blending with the eutectic as opposed to impregnation of the Y_2O_3 with eutectic.

A possible alternate for min-K insulation produced by Johns-Manville has been revealed through the literature search. This material, microtherm produced by Mircopore International Ltd., has a thermal conductivity similar to min-K but is about one fifth the price of min-K. The microtherm insulation is comprised of ceramic materials including silica, titania and alumina silicate. The physical properties of this material are very similar to those of min-K.

Typical Discharge Curve of Powdered Calcium/CaCrO₄ Cell

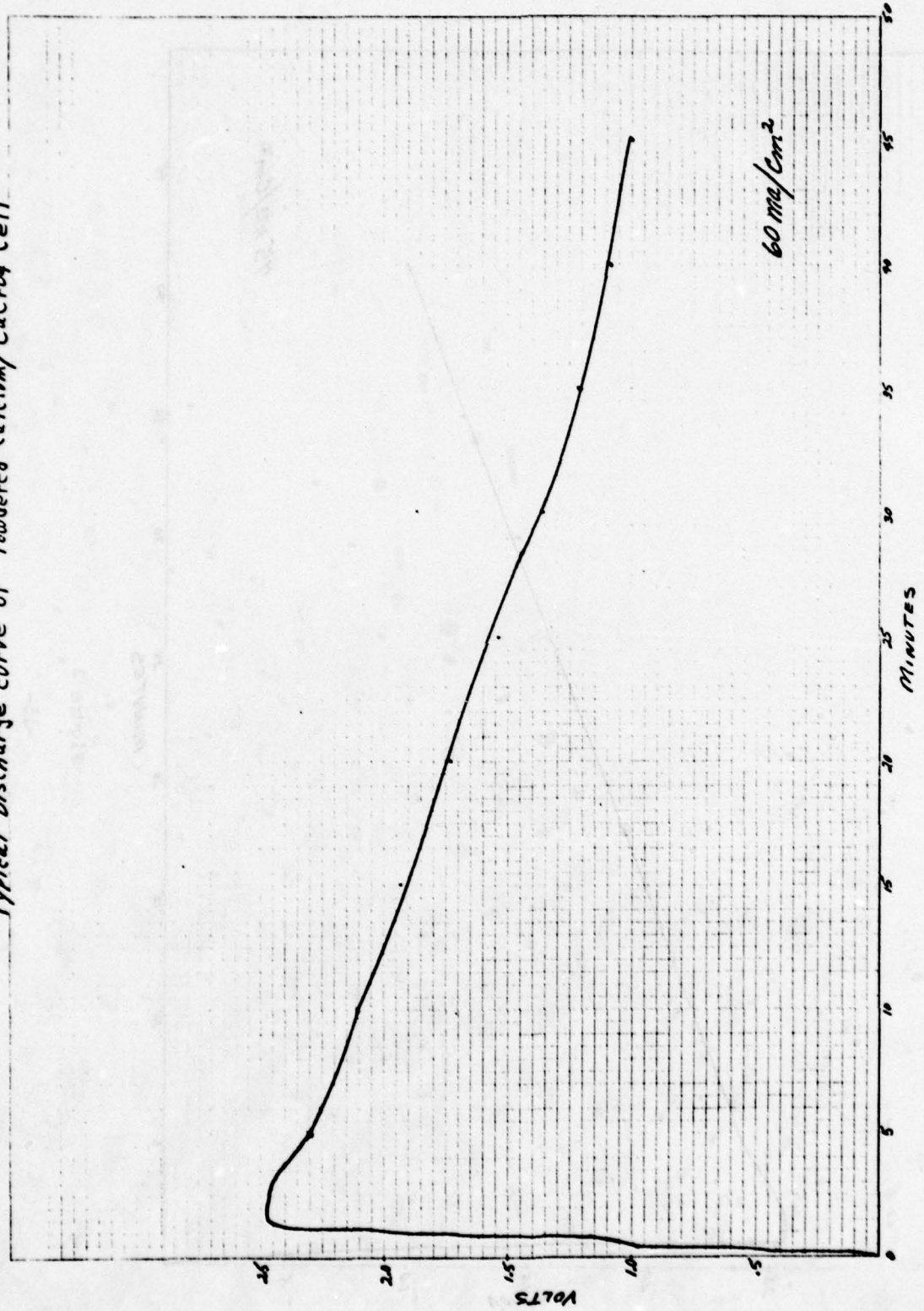


Figure 1

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-45-

TYPICAL DISCHARGE CURVE OF .020" SHEET CALCIUM/Ca-CrO₄ CELL

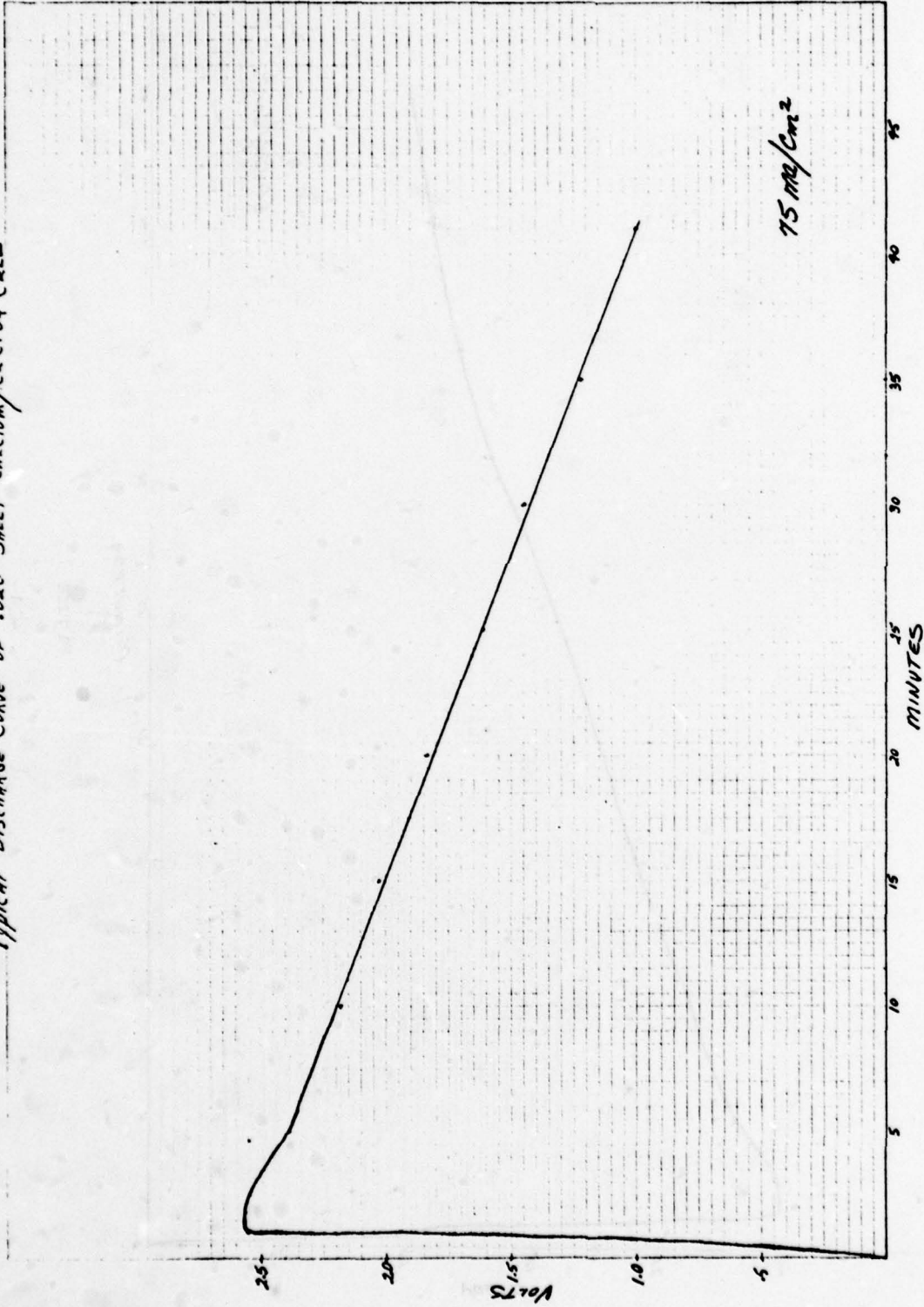


Figure 2

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TYPICAL DISCHARGE CURVE OF LiAl/C₂CrO₄ CELL

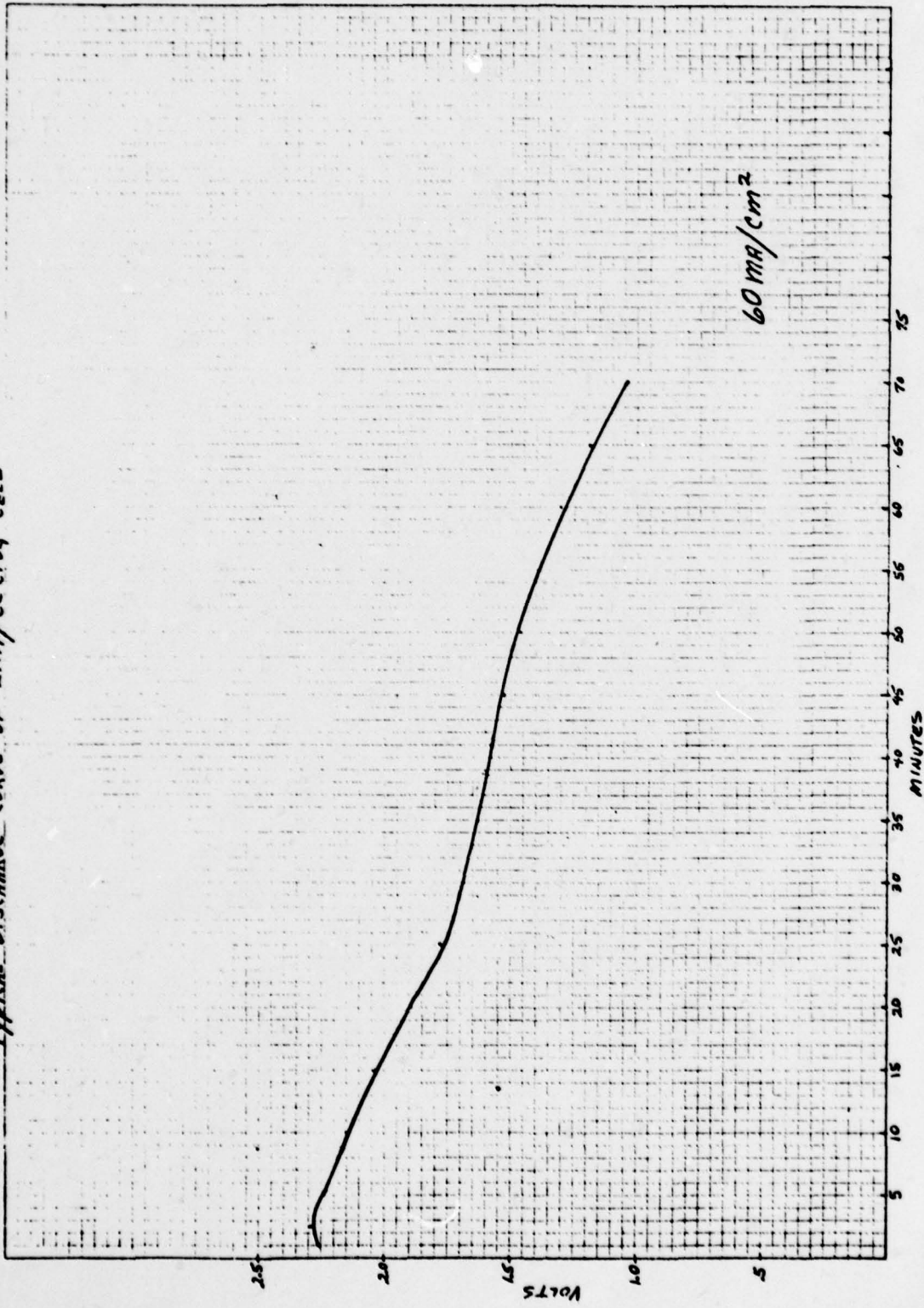


Figure 3

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APPENDIX B

INTERIM TECHNICAL REPORT
IMPROVED THERMAL BATTERY PERFORMANCE
1 MAY 1977 THROUGH 1 MAY 1978

USAF CONTRACT NO. F33615-76-C-2074

PREPARED FOR
UNITED STATES AIR FORCE
AIR FORCE SYSTEMS COMMAND
AERONAUTICAL SYSTEMS DIVISION
WRIGHT-PATTERSON AFB, OHIO 45433

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INTERIM TECHNICAL REPORT
IMPROVED THERMAL BATTERY PERFORMANCE
1 MAY 1977 THROUGH 1 MAY 1978

USAF CONTRACT NO. F33615-76-C-2074

APPROVAL PAGE

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ABSTRACT

This report describes the work achieved from May 1, 1977 through May 1, 1978 on the Improved Thermal Program funded by Wright-Patterson Air Force Base. The main effort has been expended on developing a 15-ampere/hour thermal battery using the Ca/LiClKCl/CaCrO₄ and LiAl/LiClKCl/FeS₂ systems. A number of other systems have been subjected to single cell testing to determine warranting of further investigation. These systems have included:

LiAl/CaCrO ₄	Ca/PbCrO ₄
LiAl/CuCl ₂	Ca/V ₂ O ₅
LiAl/FeCl ₃	Ca/NaCuCrO ₄
LiAl/V ₂ O ₅	Ca/FeS ₂
LiAl/TiS ₂	Li/FeS ₂
LiAl/AgCl	Mg/FeS ₂

All of the systems above have utilized the LiCl-KCl electrolyte. NaAlCl₄ electrolyte was also used with the LiAl/CuCl₂ and LiAl/FeCl₃ systems. Comparable results to those of Seiler Labs were achieved.

Some of the items accomplished have been:

1. Demonstration of a LiAl/FeS₂ cell which meets the contract design goals with an external heat source.
2. Development of a LiAl/FeS₂ battery which has demonstrated a 25-minute life under simulated battery conditions at 155 mA/cm². This life is measured to 80% of peak voltage, but the battery's volume exceeds the contract goal by approximately 40%.
3. Development of a new calcium anode (sintered powder) which should extend the Ca/CaCrO₄ system's capabilities.
4. Development of a CuCl₂/LiCl cathode which when used with the LiAl anode has demonstrated a very usable voltage under severe loading (1.35 volts at 2.48 A/cm² - 16A/in²).

1.0 INTRODUCTION

The "Improved Thermal Program" has been aimed at developing a thermal battery with the following characteristics:

- A. Voltage - 28 volts \pm 2
- B. Capacity - 15-ampere/hours at a 30-ampere discharge rate
- C. Weight - 17 pounds
- D. Volume - 140 cubic inches
- E. Activation Time - 1 second

The goal of a thermal battery with a half hour operating life while maintaining a current density of at least 1 ampere per square inch (155 mA/cm^2) is approximately five times beyond the state-of-the-art.

The program was initially directed toward the Ca/CaCrO₄ system with 25% of the effort to be expended in investigation of other electrochemical systems. However, since the LiAl alloy anode showed such promise, the program was redirected to an investigation of the calcium anode and the lithium aluminum anode on an equal basis.

The investigative process consisted of three test vehicles:

- A. Single-cell tests
- B. Simulated battery tests
- C. Actual battery tests

The majority of tests were conducted on the single-cell test level due to its comparative quickness, easiness and cost effectiveness of this test method. The final test mode (actual battery tests) will be employed during the final phase of the program.

Thus, presented herein are the studies completed the past year showing the advances made with various electrochemical systems with emphasis on Ca/CaCrO₄ and LiAl/FeS₂.

2.0 DISCUSSION

2.1 Ca/CaCrO₄

As reported in the first interim report, the C /CaCrO₄ system is anode limited with two main problems being the formation of a reaction layer which inhibits operating life and the formation of a calcium-lithium alloy which causes shorting during operational life. Since a high current density (which is demanded by the goals of this program) reduces the ill effects of calcium-lithium alloying, the program effort has concentrated on extending the life by prolonging the time required for the reaction layer to " suffocate" the negative. Figure 1 shows a typical calcium-calcium chromate cell with its operating life being abruptly ended by polarization of the anode.

Initially, attempts at improving the negative were made by using honeycomb, expanded metal, foam metal and various irregular collector structures as the substrate for vacuum deposited calcium. It was hoped that the porous or three-dimensional anode would provide an increase in active surface area without an increase to volume. The increased surface area would result in a lower current density and prolong the time required for the inhibiting reaction layer to choke off the negative. However, problems were encountered in getting a uniform deposit of calcium by vacuum deposition. The outermost surface received the majority of the calcium with very little calcium being deposited within the structure. Thus, the objective was defeated by the method of applying the reactive material to the collector. Chemical deposition (chemical vapor plating) is a method which would probably accomplish the necessary uniform coating. However, due to the cost, this method could not be investigated. Thus, the irregular substrate theory was abandoned and powdered calcium anodes were studied.

Various mixtures of powdered calcium and eutectic were investigated

SHEET Ca/CaCrO₄ - 155 mA/cm² - 500°C

KNEE OF
ANODE
POLARIZATION

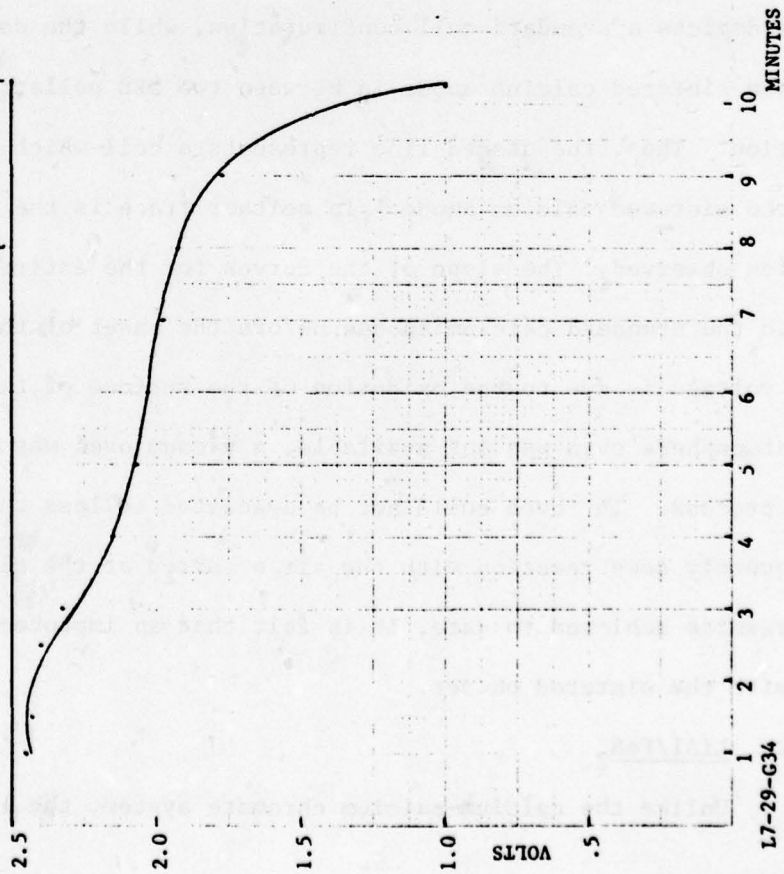


Figure 1

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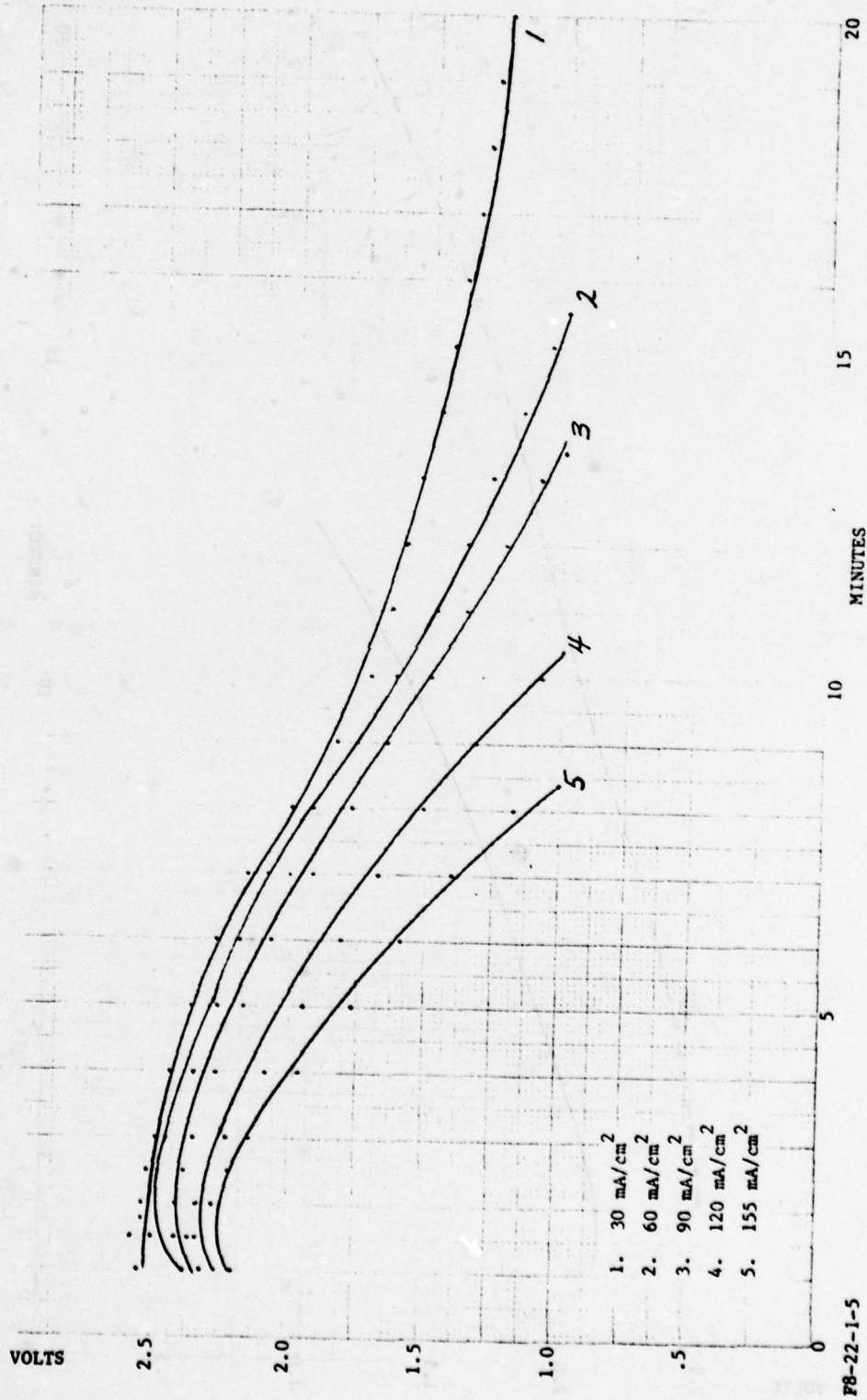
in trying to obtain a longer life above 80% of peak voltage. As the percentage of eutectic was increased, the life increased. This was true up to the point where the amount of eutectic in the anode started to leak and short the cell. Although the coarser calcium particles performed better than the fine particles, no improvements over the sheet calcium anode were noted as shown in the current density graph (Figure 2). The powdered calcium resulted in slightly lower peak voltages which was probably due to the material oxidizing.

By subjecting the calcium powder to a "metal powder sintering" process, an electrically and structurally bonded matrix has been formed. This type of structure can offer an effective surface area over 1,000 times greater than its apparent surface area. Although only limited success has been achieved to date, this is due primarily to the type of processing equipment available. Figure 3 shows the discharge characteristics of a sintered calcium anode. The solid line depicts a standard cell configuration, while the dashed line represents a sintered calcium anode in between two DEB pellets in a cup cell configuration. Thus, the dashed line represents a cell which is utilizing both sides of the sintered calcium anode. In neither trace is the "knee" of anode polarization observed. The slope of the curves for the entire discharge time is equal to the standard calcium anodes before the onset of the polarization. The lower voltage is due to the oxidation of the surface of the anode. Since an inert atmosphere oven was not available, a vacuum oven was used for the sintering process. The oven could not be evacuated to less than 10 microns and consequently some reaction with the air occurred at the elevated temperatures. With the results achieved to date, it is felt that an improved anode will be achieved with the sintered powder.

2.2 LiAl/FeS₂

Unlike the calcium-calcium chromate system, the lithium aluminum-iron

Powdered Ca/CaCrO_4 - 500°C



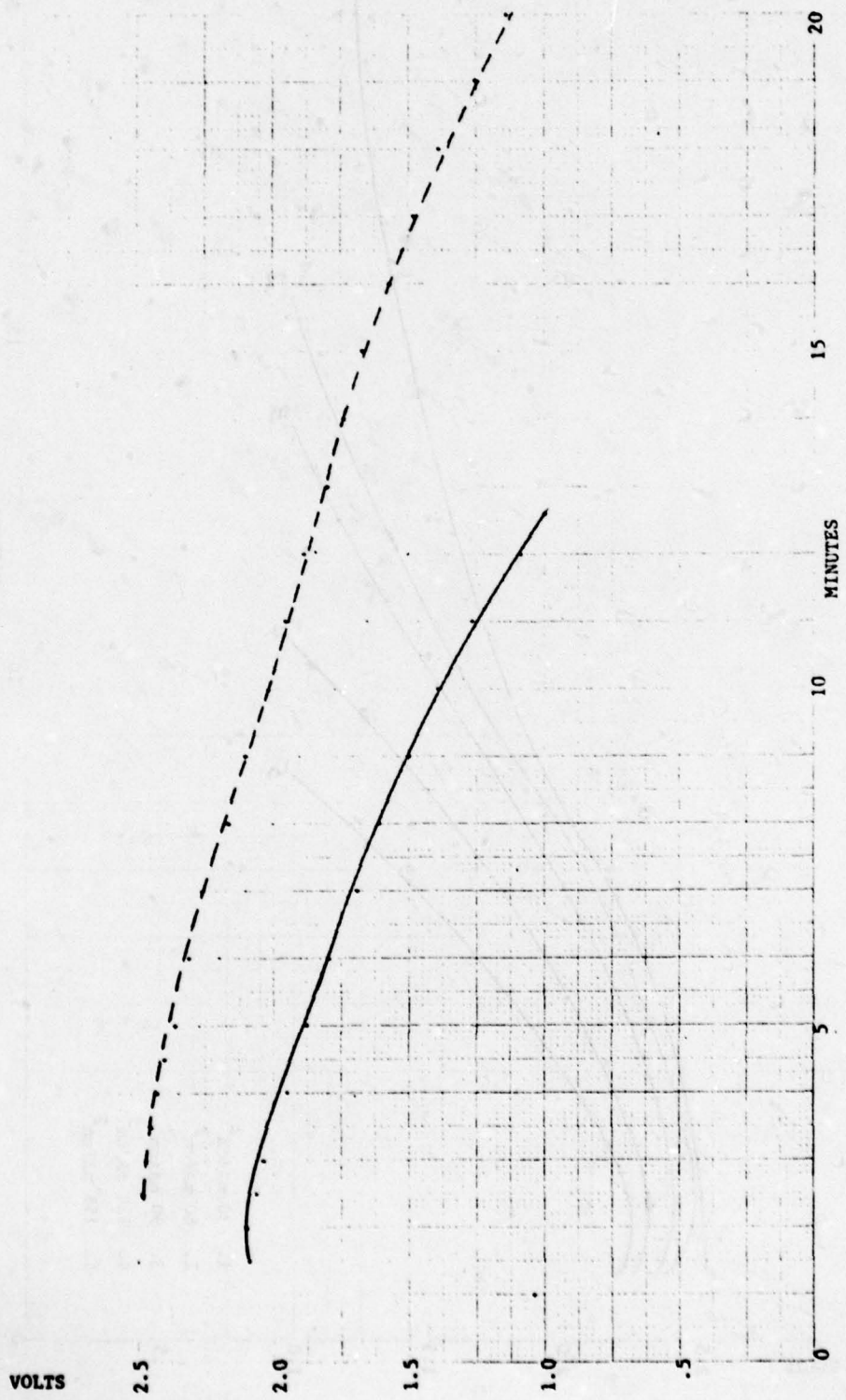
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Figure 2

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Sintered Ca/CaCrO₄ Cell - 155 mA/cm² - 500°C



A8-18-2

Figure 3

-7-

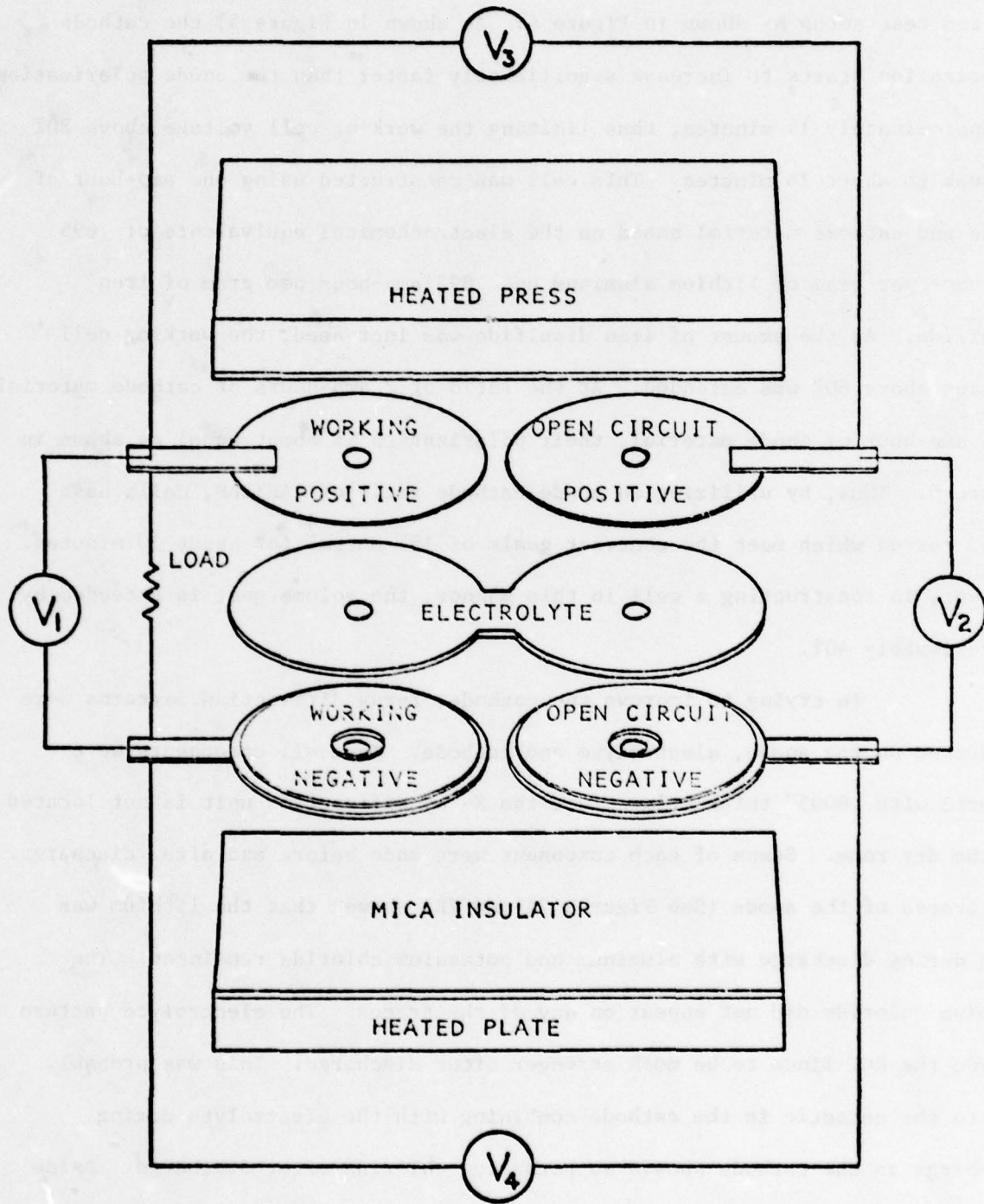
-58-

disulfide system is cathode limited. This has been demonstrated on the single-cell tester for both systems by utilizing a positive limited versus negative limited test setup as shown in Figure 4. As shown in Figure 5, the cathode polarization starts to increase significantly faster than the anode polarization at approximately 15 minutes, thus limiting the working cell voltage above 80% of peak to about 18 minutes. This cell was constructed using one amp-hour of anode and cathode material based on the electrochemical equivalents of .695 amp-hour per gram of lithium aluminum and .893 amp-hour per gram of iron disulfide. As the amount of iron disulfide was increased, the working cell voltage above 80% was extended. At the ratio of 2 amp-hours of cathode material to 1 amp-hour of anode material, their polarization is about equal as shown in Figure 6. Thus, by utilizing an anode-cathode ratio of 1AH:2AH, cells have been tested which meet the contract goals of 155 mA/cm^2 for about 30 minutes. However, in constructing a cell in this manner, the volume goal is exceeded by approximately 40%.

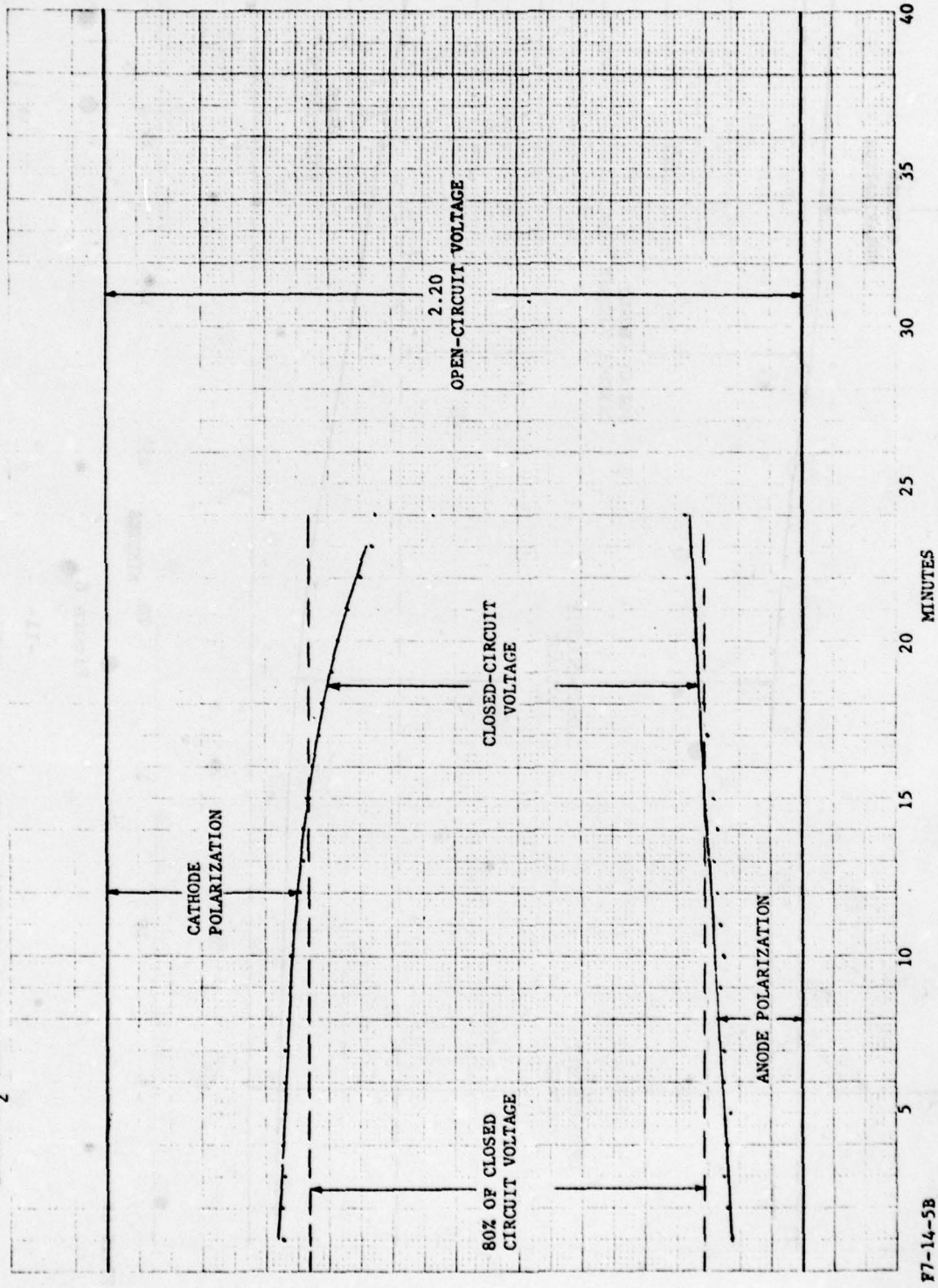
In trying to improve the cathode, X-ray diffraction patterns were conducted on the anode, electrolyte and cathode. The cell components were covered with .0005" thick mylar since the X-ray diffraction unit is not located in the dry room. Scans of each component were made before and after discharge. The traces of the anode (See Figures 7A and 7B) showed that the lithium was used during discharge with aluminum and potassium chloride remaining. The lithium chloride did not appear on any of the traces. The electrolyte pattern showed the KCl lines to be much stronger after discharge. This was probably due to the eutectic in the cathode combining with the electrolyte during discharge as the cathode showed no potassium chloride after discharge. Aside from the depletion of KCl in the cathode, no other conclusions were drawn from

FIGURE 4

POSITIVE LIMITED VS NEGATIVE LIMITED TEST



LiAl/FeS₂ (1Ah:1Ah) - 155 mA/cm² - 500°C



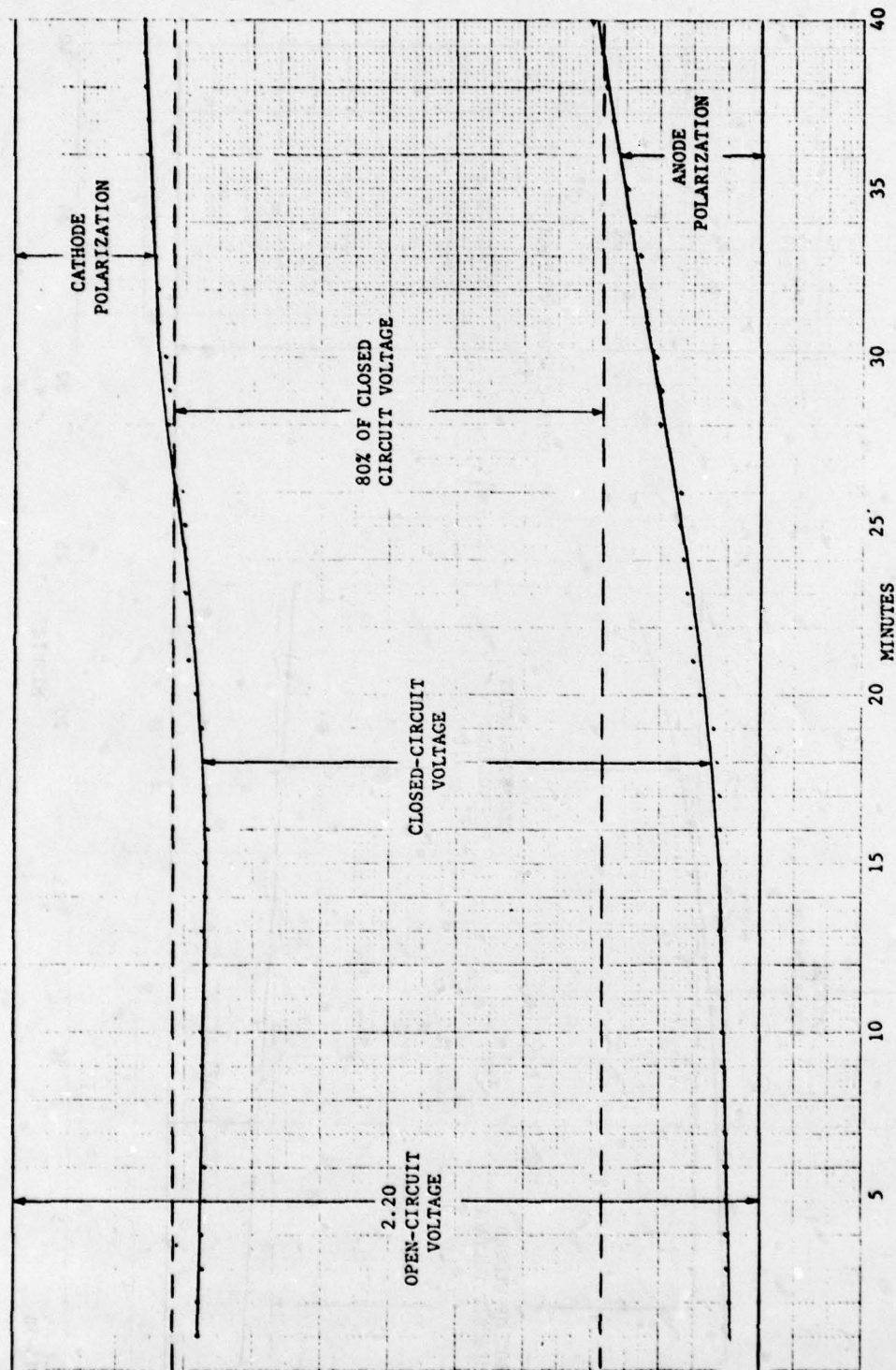
F7-14-5B

Figure 5

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-61-

LiAl/FeS₂ (1AH:2AH) - 155 mA/cm² - 500°C



77-15-68

Figure 6

-11-

-62-

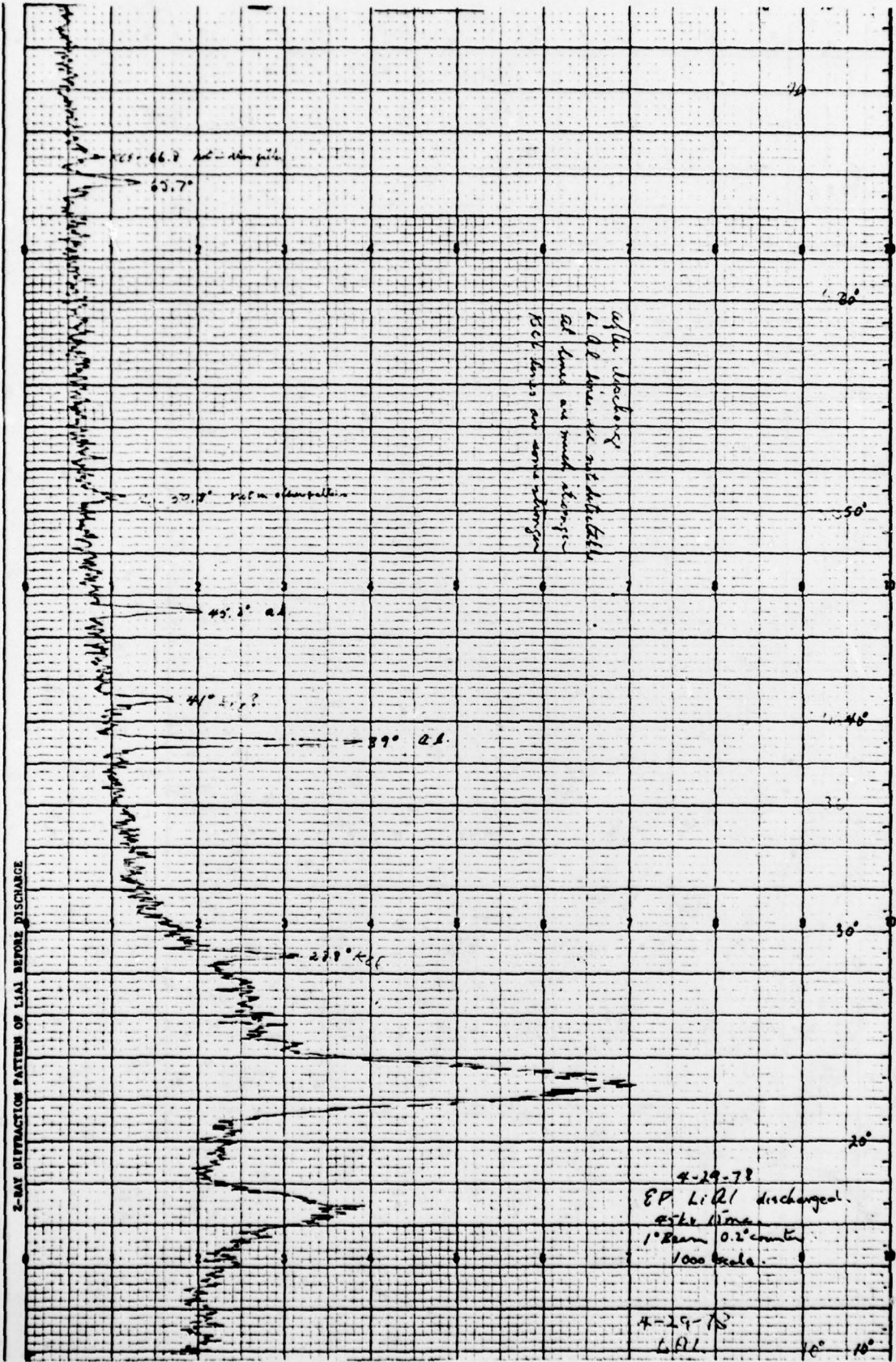


Figure 7A

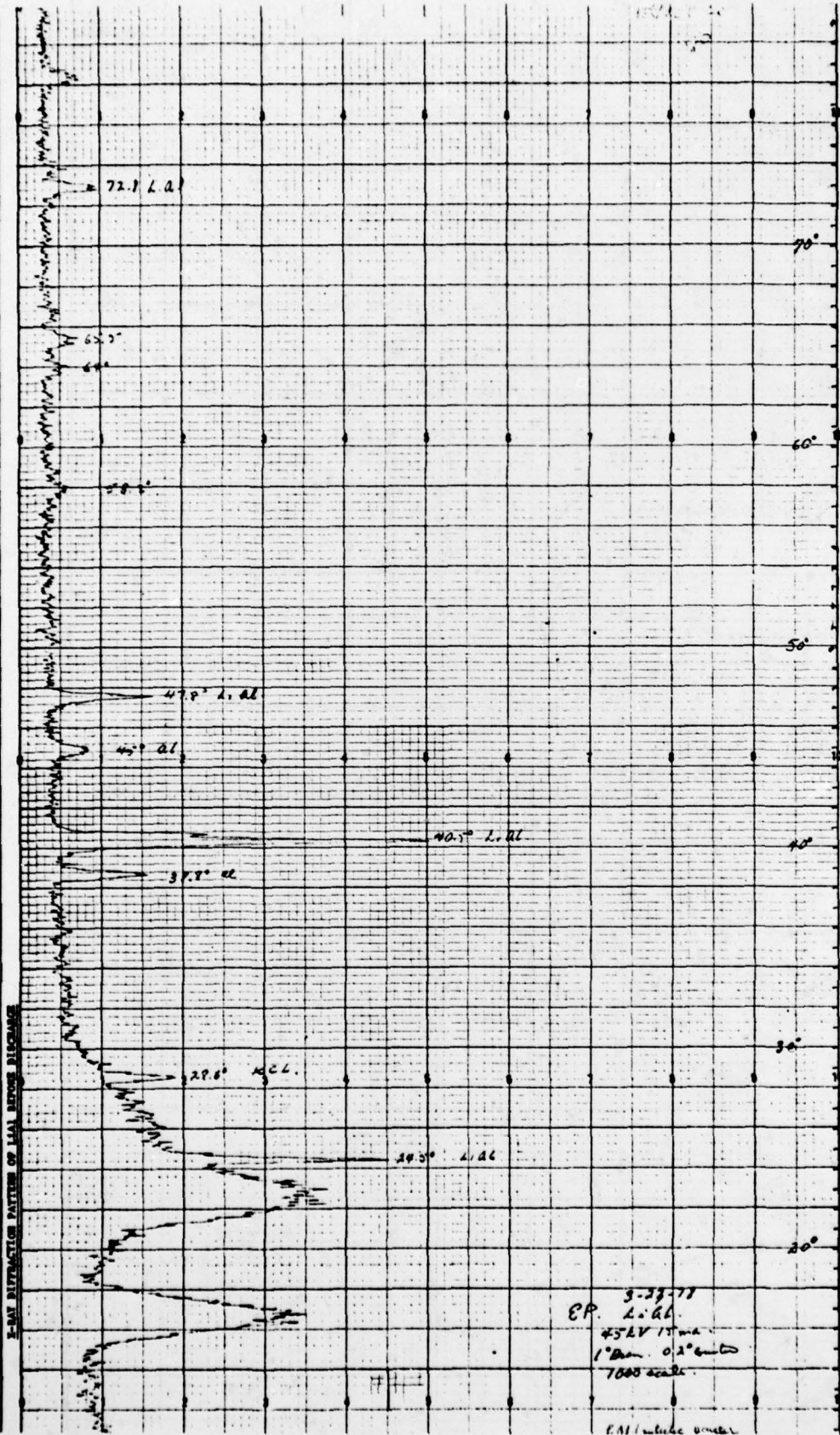


Figure 7B

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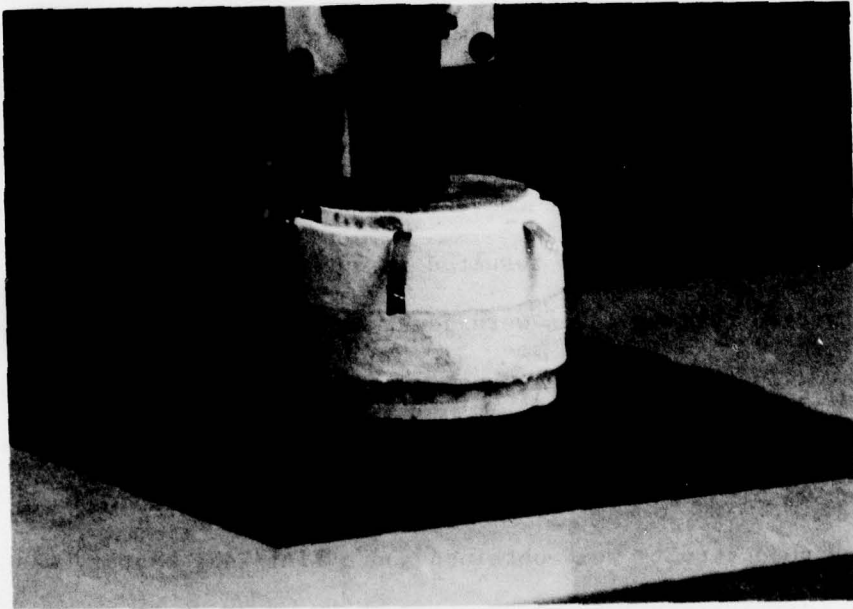
-64-

the cathode analysis. Evidently some rather complex sulfide compounds are formed and the time and work level required is beyond the scope of work for this program.

Since the LiAl/FeS_2 single-cell tests demonstrated this system's capability to meet the program electrical performance requirements, tests were moved to the next test level. That is, a number of cells were assembled in a conventional cell stack complete with heat pellets. These cells were placed in an aluminum fixture which maintained the stack pressure via means of a mechanical clamp (See Figure 8). The fixture and cells were placed into an oven preheated to 500°C where the iron heat pellets were allowed to auto-ignite. With this type of testing it was hoped that the best operating life with optimum thermal conditions would be determined. Many tests were conducted with thermocouples to determine the correct weight of heat pellets. About half of the required heat pellet weight resulted in optimum temperature curve. However, the expected optimum lives were never achieved. Only about 50% of the lives demonstrated on the single-cell tests were achieved.

Since Sandia had indicated good test results with a simulated battery confined within a block of min-K insulation, this method of tests was initiated. Very good results were obtained and a LiAl/FeS_2 battery was built and tested with with a life of 25 minutes to 80% of peak voltage. Five cells with a dummy cell on each end were stacked into a block of min-K insulation. The cell diameter was 1-7/16 inches with approximately one inch of insulation around the cells. A thickness of .5 inch of min-K was used on top and bottom of the cell stack. The same fixture used in the oven tests was used to apply cell stack pressure. The battery ignited under no-load condition and reached a peak voltage of 10.5 volts. At 30 seconds a 155 mA/cm^2 load was applied with the voltage dropping to 5.05 volts. The voltage climbed slowly to 6.8

FIGURE 8



ALUMINUM TEST FIGURE

volts at 3.5 minutes and then started to decline. Assuming that inadequate pressure was being exerted on the cell stack, the pressure was increased at 5 minutes. The voltage immediately jumped to over 7 volts and remained very constant with a discharge time to 80% of peak voltage at slightly less than 25 minutes. Figure 9 shows the discharge curve. This test showed that a LiAl/FeS₂ battery is capable of maintaining a proper internal temperature for the required operating life. Subsequent tests were conducted with the min-K thickness reduced progressively until the minimum amount necessary to provide a 30-minute life was determined.

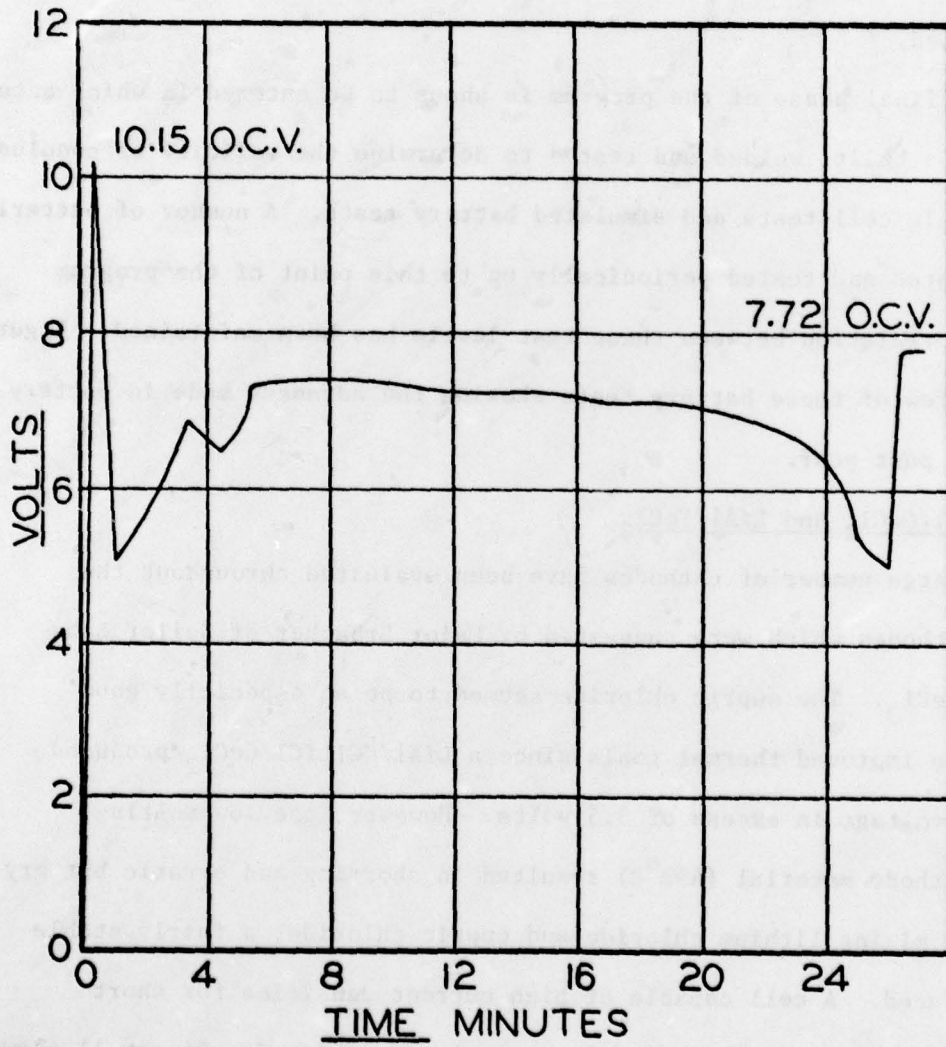
The final phase of the program is about to be entered in which actual batteries will be built, welded and tested to determine the validity of conclusions reached from single cell tests and simulated battery tests. A number of batteries have been fabricated and tested periodically up to this point of the program and a positive correlation between these test levels has been maintained. Figure 10 represents a few of these battery tests showing the advances made in battery performance this past year.

2.3 LiAl/CuCl₂ and LiAl/FeCl₃

A large number of cathodes have been evaluated throughout the program. Two cathodes which were suggested by Major Erbacher of Seiler Labs were CuCl₂ and FeCl₃. The cupric chloride seemed to be an especially good candidate for the improved thermal goals since a LiAl/KClLiCl/CuCl₂ produced an open circuit voltage in excess of 3.5 volts. However, the low melting point of this cathode material (498°C) resulted in shorting and erratic battery performance. By mixing lithium chloride and cupric chloride, a fairly stable cathode was produced. A cell capable of high current densities for short periods of time (similar to the Ca/CaCrO₄ system) was achieved. Figure 11 shows

FIGURE 9

SIMULATED BATTERY DISCHARGED AT 155 MA/CM²



LiAl/FeS₂ Battery Performance - Room Temp. - 155 mA/cm²

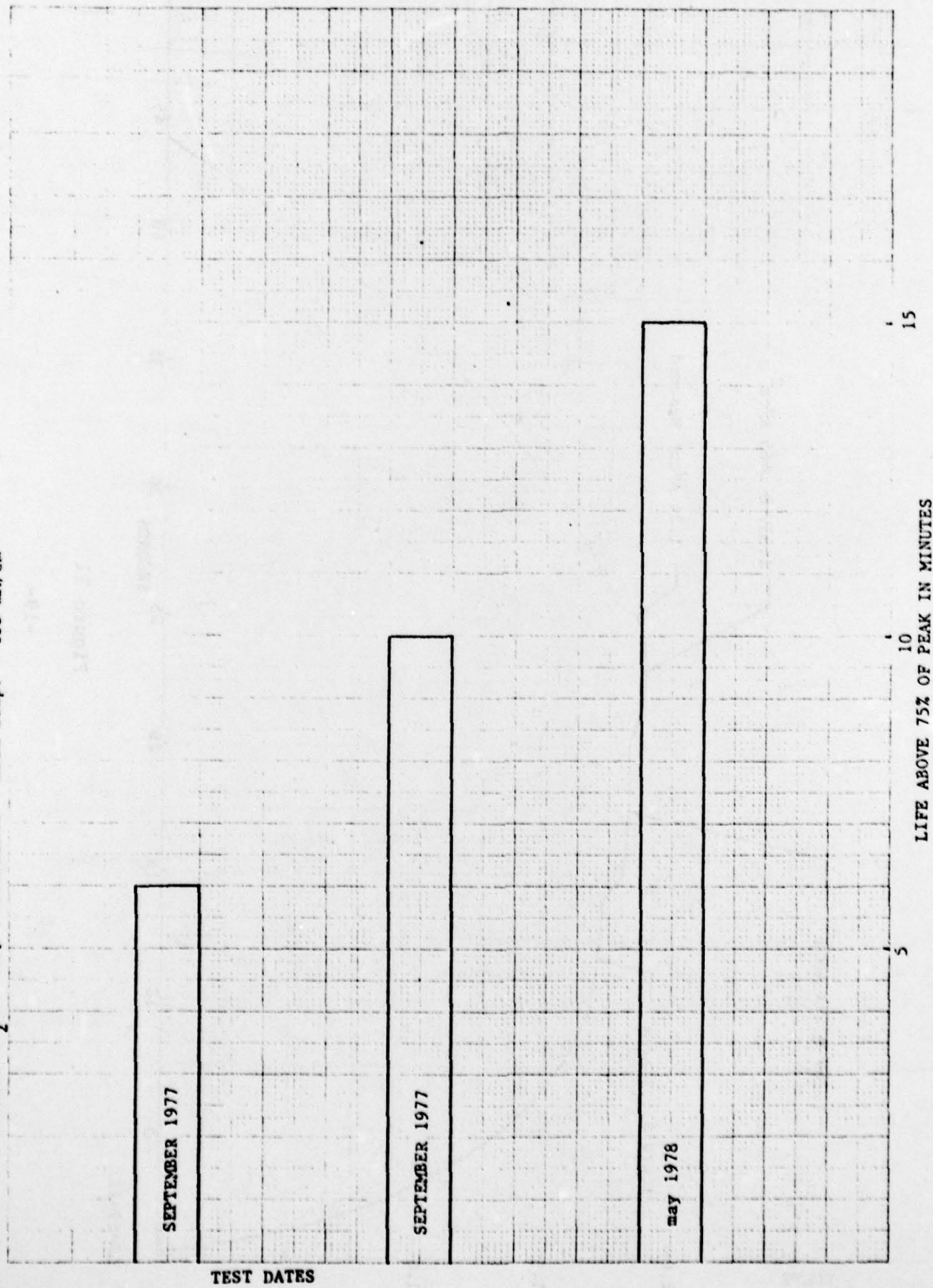


Figure 10

LiAl/CuCl₂ - LiCl 500°C

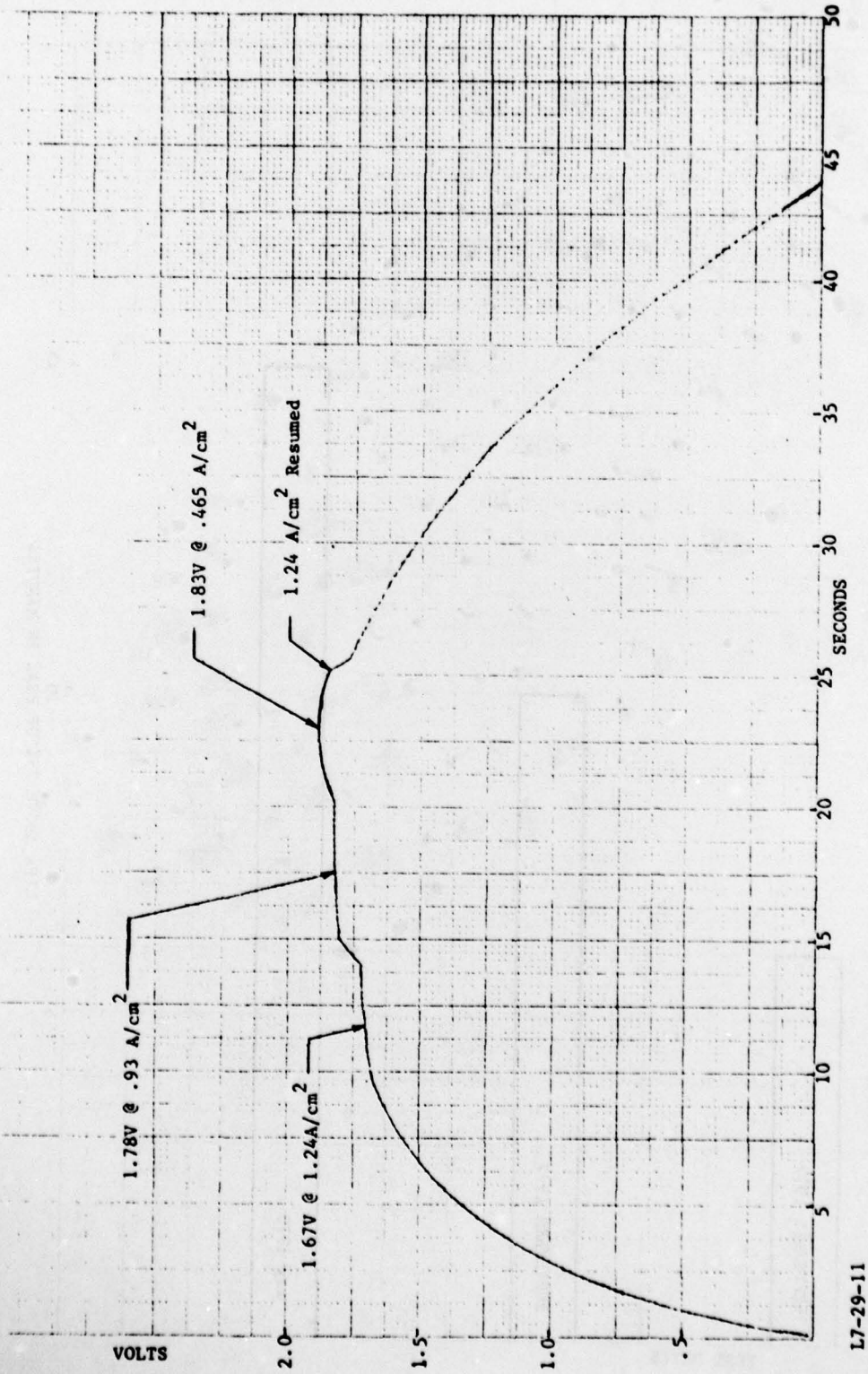


Figure 11

-19-

-70-

the voltage levels under the various loading. As can be seen from the graph, this cell is not capable of achieving the goals of this program; but it certainly warrants further investigation for other applications.

The iron trichloride cathode did not produce any significant test results. Its extremely hygroscopic nature made it rather difficult material to handle in the dry room.

2.4 Electrolytes

The electrolyte studies were divided primarily between the standard potassium chloride and lithium chloride electrolyte and the low melting sodium tetrachloroaluminate electrolyte.

The KCl-LiCl electrolyte was subjected to a number of experiments.

Since density of electrolyte-depolarizer pellets plays an important role in the performance of thermal batteries, a density study was conducted with three anodes. To eliminate as many variables as possible, a LiClKCl/CaCrO₄ two-layer pellet was used throughout this matrix. Thus, the only variables were the type of anode and density as shown in Figure 12. Here life in minutes versus density in grams per cubic centimeter were plotted. Each point represents the average life of two or more single-cell tests. The 2.25 gms/cc was the upper limit attainable on our press while any pellets below 1.50 gms/cc would not hold together when handled. The sheet calcium showed best lives with a density of 2 gms/cc while the powdered calcium displayed its best performance at 1.75 gms/cc. The lithium aluminum anode acted very differently than the calcium anodes with its performance increasing with every decrease in density. In another study, the performance was determined to be dependent on the electrolyte density and not the depolarizer density.

A number of parameters in the electrolyte processing were investigated including off-eutectics, particle size and distributions, additives and binders.

2-LAYER PELLETT DENISTY STUDY

155 mA/cm² - 500°C

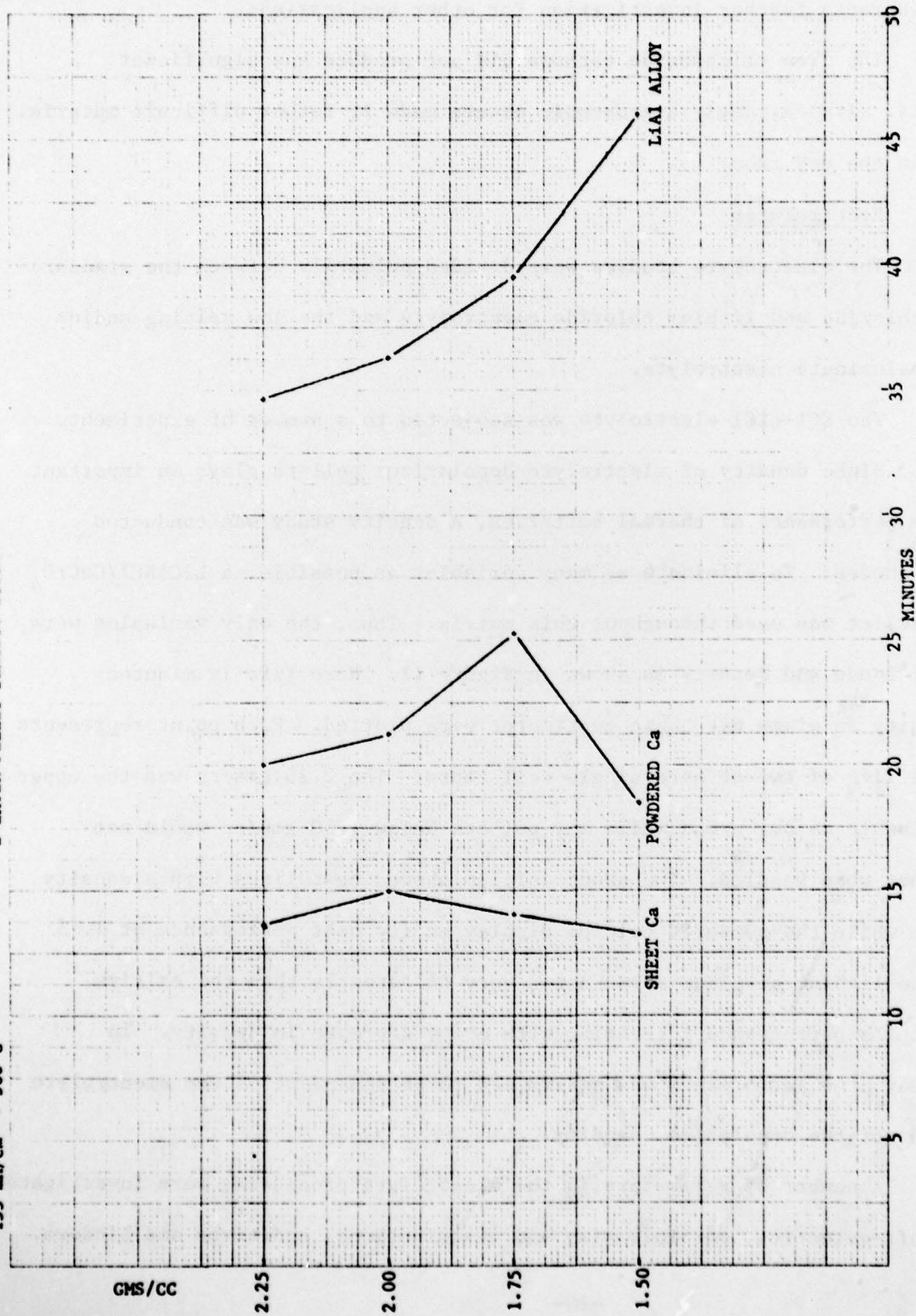


Figure 12

-21-

-72-

The percentage of binder varied not only with the type of binder but also with the type of cathode used. The amount of electrolyte leakage was found to be dependent upon the ratio of the binder in the electrolyte to the binder in the depolarizer. Figure 13 shows a typical graph of the percentage of binder versus operating life. As the percentage of binder increased, not only was a greater impedance generated but also pelletizing was more difficult. On the other end of the binder percentage, excessive electrolyte leakage caused cell shorting and short lives.

3.0 CONCLUSION

A number of systems have been studied and the Ca/CaCrO_4 and LiAl/FeS_2 appear to be the best systems for achieving the long-life goals. Figure 14 shows our projection of the LiAl/FeS_2 battery exceeding the goals with the Ca/CaCrO_4 battery very nearly achieving fifty percent (50%) of the goals.

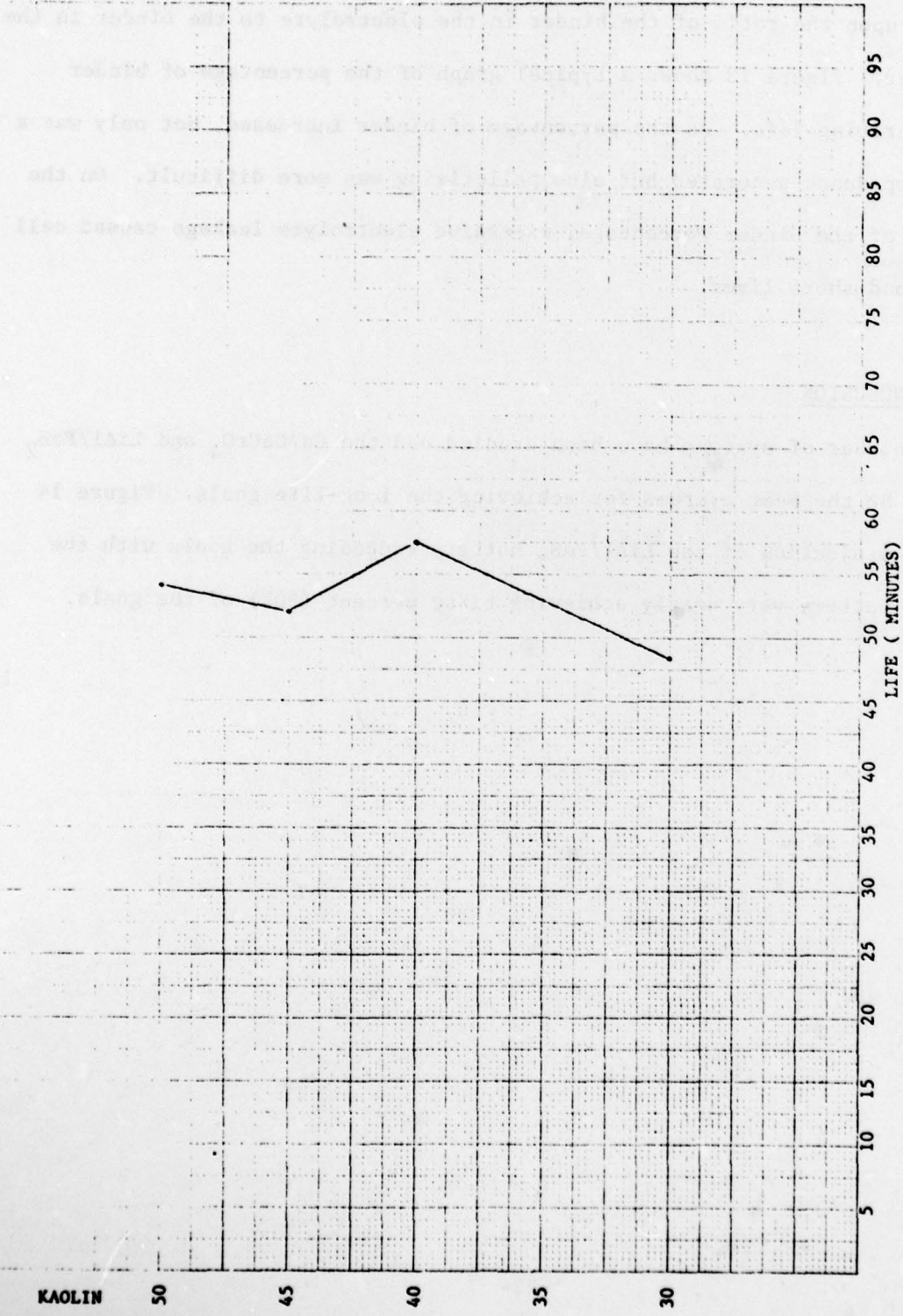


Figure 13

-23-

-74-

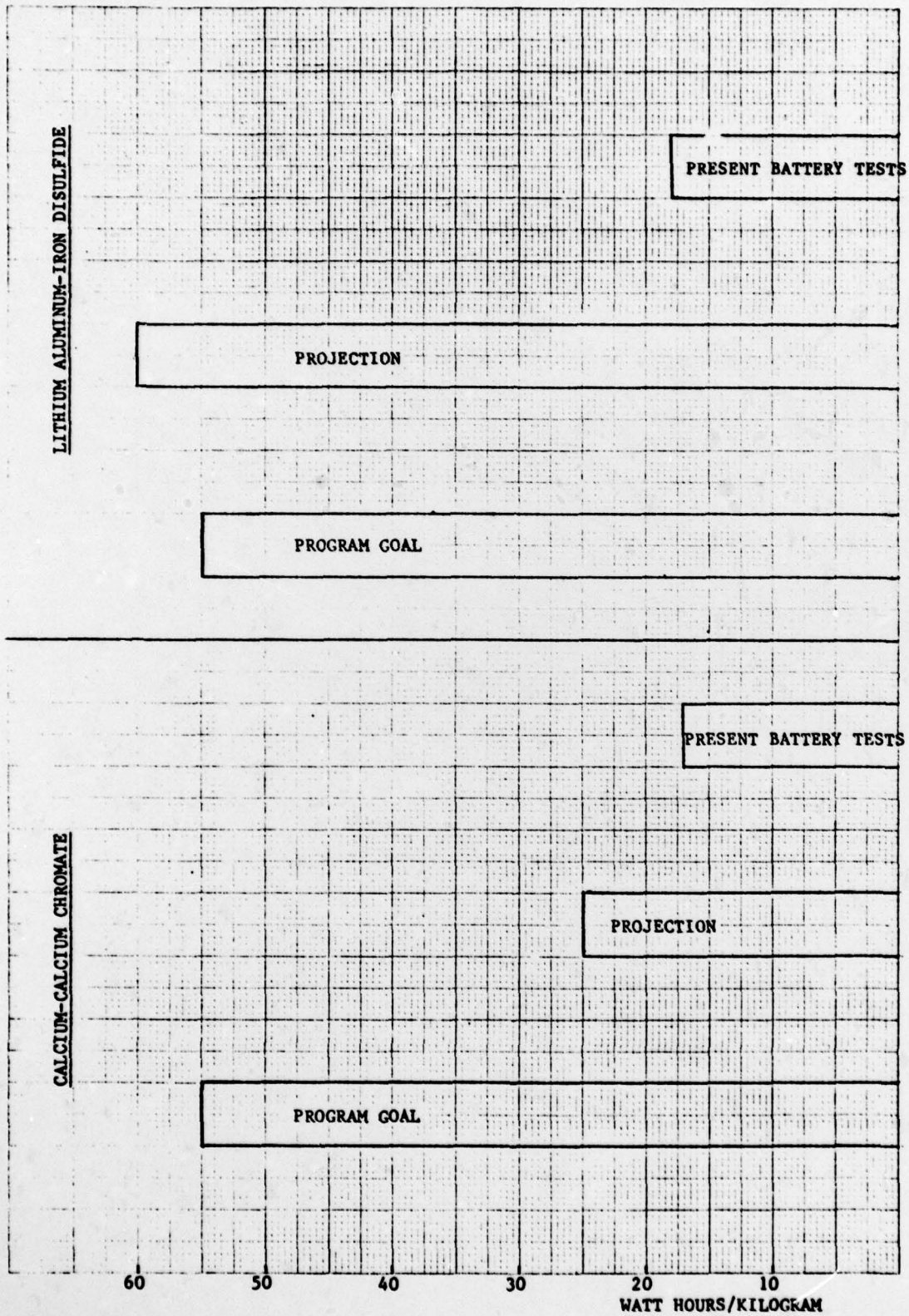


Figure 14.

-24-

-75-