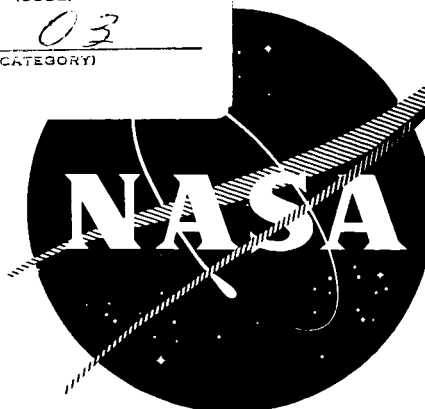


N66-15342
(ACCESSION NUMBER)
30
(PAGES)
(NASA CR OR TMX OR AD NUMBER)
(THRU)
1
(CODE)
03
(CATEGORY)

N66-15342
NASA CR-54859



GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) *200*

Microfiche (MF) *50*

ff 653 July 65

FIRST QUARTERLY REPORT

DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES

by

S. G. Abens, T. X. Mahy, and W. C. Merz

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-7632



LIVINGSTON ELECTRONIC CORPORATION
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FIRST QUARTERLY REPORT

22 June 1965 to 21 October 1965

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December 28, 1965

CONTRACT NAS 3-7632

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ABSTRACT

Electrolyte and electrode studies for the development of high energy lithium-copper fluoride cells were conducted. Vacuum distillation of propylene carbonate and butyrolactone reduced the water content significantly. Solubility of CuF_2 in butyrolactone was enhanced by the presence of water and by dissolved LiClO_4 . Studies of CuF_2 purity were undertaken. Electrochemical efficiency of prismatic CuF_2 electrodes of various thicknesses was determined.

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1. SUMMARY

Studies of electrolytes, electrode materials, and electrode and cell construction were conducted toward the development of high energy density CuF_2 -Li primary cells.

Electrolyte Systems Studies. The solubility of CuF_2 in butyrolactone (BL) and solutions of LiClO_4 in BL was studied. The copper salt was contacted for periods of 500 to 2500 hours with the test liquid, and the extract was titrated with the Karl Fischer reagent. These preliminary tests showed that CuF_2 solubility is enhanced by both water contamination and by LiClO_4 in solution.

Vacuum distillation of propylene carbonate and butyrolactone was performed. After a single batch distillation, water content was reduced from 580 to 120 ppm in propylene carbonate, and from 510 to 140 ppm in butyrolactone. Further study of solvent purification by distillation is in progress.

Positive Electrode Studies. The purity of CuF_2 received from several suppliers was studied by the X-ray diffraction method. Contamination of the various samples with $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ ranged from 0.8 to 22.0 percent (0.2 - 5.8 percent water). Methods for the removal of the water contamination by various methods was under study.

The effect of thickness of filter-mat CuF_2 electrodes was studied over the thickness range of 0.05 to 0.15 inches by discharging test cells in methyl formate and propylene carbonate electrolyte at 2 mA/cm^2 and 1 mA/cm^2 , respectively. The electrochemical efficiency of the CuF_2 electrodes was generally found to be independent of electrode thickness. The significance of this test series was reduced by generally poor cell performance as compared with other recent cell tests with equivalent construction and under similar test conditions.

Cell Systems Studies. Three-plate CuF_2 -Li cells were tested for ability to discharge at relatively high drain rates (1-20 hour discharge range). The CuF_2 electrodes had the filter-mat construction developed on the previous contract, and cell construction was similar to that of the prototype cells. With discharge loads of 2.5 to 20 ohms, poor voltage regulation resulted with both LiClO_4 -MF and LiClO_4 -PC electrolytes. Only cells with methyl formate electrolyte and 20-ohm loads showed discharge plateaus above a cell potential of 2.0 volts.

2. INTRODUCTION

The purpose of this program is the development of high energy primary battery systems suitable for space flight applications. Two types of batteries, differing in the rate of energy delivery, are being sought; these being (1) batteries operating at the 100-1000 hour discharge rate and capable of delivering 200 watt hours per pound, and (2) batteries operating at the 1-10 hour discharge rate and capable of delivering 50 watt hours per pound at the 1-hour discharge rate. The present report describes the progress of the program during the first quarterly reporting period, 22 June to 21 September 1965.

The work described in the present report is a direct continuation of the previous program conducted under contract number NAS 3-6004. During this period, studies of materials and electrode construction methods toward the development of high energy primary batteries were conducted. Lithium was chosen as the most desirable negative electrode material, and several electrolyte solvents, which were relatively stable in presence of lithium and formed adequately conductive electrolyte solutions, were identified. Positive electrode construction methods for high degree of active material utilization were developed, most of the work being performed with CuF_2 as the active material. At the end of the yearly contract period, prototype cells were constructed and discharged. Energy-to-weight ratios of over 500 watt hours per pound of active material weight and 200 watt hours per pound of cell weight were obtained with the system $\text{CuF}_2/1.4\text{M LiClO}_4$ in propylene carbonate/Li at a current density of ca. 0.5 mA/cm^2 , equivalent to the ca. 250-hour rate.

Although high energy-to-weight ratios for the Li-CuF_2 system have been demonstrated, several conditions must be resolved before practical batteries can be built and operated. These problems do not apply equally to the 100-1000 hour and 1-10 hour batteries because of the different discharge rates involved and the possibility of employing reserve activation for the 1-10 hour battery. In general, the following applies to the system in its present state of development:

1. The shelf life characteristics of Li-CuF_2 cells are poor. With propylene carbonate electrolyte, shelf life appears to be limited by the dissolution of the CuF_2 electrode. With methyl formate electrolyte, shelf life appears to be limited by the chemical action of the electrolyte on the lithium electrode.

2. Presence of water in the cell is detrimental to the shelf life capability of the cells. Water appears to accelerate the dissolution of CuF_2 in addition to increasing the rate of chemical attack on the lithium metal.

During the past quarter, the contractual effort was aimed mainly at the resolution of the above problems. Efforts were expended toward the purification and analysis of the electrolytes and the positive active material (CuF_2). Both distillation and chemical treatment were employed for the solvents (propylene carbonate and butyrolactone). The main objectives of this work were the removal of water from the materials and study of the effects on cell performance. In addition, work was initiated for the development of thin positive electrodes needed for the construction of the 1-10 hour battery.

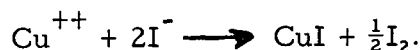
3. DESCRIPTION OF EXPERIMENTAL WORK

3.1. ELECTROLYTE SYSTEMS STUDIES

3.1.1. Study of Solubility of CuF_2 in Butyrolactone

The rate of dissolution of CuF_2 in butyrolactone and in solutions of LiClO_4 in BL (15 grams LiClO_4 /100 ml BL) was studied. The initial materials were analyzed for water content by X-ray diffraction (CuF_2) and by the Karl Fischer analysis (BL and LiClO_4). The copper fluoride samples were agitated with 50 ml of the solutions and were analyzed at various time intervals by titrating small aliquots with the Karl Fischer reagent.

In the presence of Cu^{++} (as indicated by the green-blue color of the solution), addition of Karl Fischer reagent to the sample produces a brown precipitate which eventually disappears upon further titration. Assuming that the initial precipitate to be Cu_2I_2 which dissolves upon further addition of Karl Fischer reagent as CuI_2^- , the water titer must be corrected by one-half of the titer needed to the clear copper end point, since Cu^{++} regenerates the iodine reduced by water according to the reaction



However, because of the presence of the copper ion, the Karl Fischer titers must be taken only as a relative measure of the water content in the various solutions.

Results of the dissolution tests with butyrolactone are presented in Table I, while those with BL- LiClO_4 electrolyte are shown in Table II. The data indicate that CuF_2 is more soluble in presence of water, probably by the formation of $\text{Cu} \cdot 3\text{H}_2\text{O}^{++}$ as indicated by the figures in the last column in Table II. In presence of LiClO_4 , the solubility is greatly enhanced, probably by a metathesis reaction yielding LiF and hydrated $\text{Cu}(\text{ClO}_4)_2$. In absence of the solute transfer of copper to the solution appeared to be very slow, as indicated by the lack of color in the solution.

TABLE I
SOLUBILITY OF CuF_2 IN BUTYROLACTONE

Sample No. 1

Butyrolactone: 50 ml, 41 $\mu\text{mols H}_2\text{O/ml}$
 CuF_2 : 3.0g, 3.9% H_2O , 130 $\mu\text{mols H}_2\text{O/ml}$

<u>Hours of Agitation</u>	<u>Water in Solution, $\mu\text{mols/ml}$</u>	<u>Specific Conductance, $\text{ohm}^{-1} \text{cm}^{-1}$</u>	<u>Color of Solution</u>
0	41	8×10^{-7}	Colorless
300	60	---	Yellow
500	61	---	Dark Yellow
2500	66	6×10^{-5}	Dark Tan

Sample No. 2

Butyrolactone: 50 ml, 41 $\mu\text{mols H}_2\text{O/ml}$
 CuF_2 : 0.01g, Initial Water: 3.9%, Vacuum dried at 110°C

0	41	8×10^{-7}	Colorless
300	41	---	Pale Yellow
500	41	---	Pale Yellow
2500	41	2×10^{-6}	Pale Yellow

Note: In both tests, undissolved CuF_2 was present at 2500 hours.

TABLE II
SOLUBILITY OF CuF_2 IN BUTYROLACTONE - LiClO_4 SOLUTIONS

Sample No. 1

Electrolyte Solution: 50 ml of 15g LiClO_4 /100 ml BL
 43 μmols H_2O /ml solution (615 ppm H_2O)
 CuF_2 : 4.06g, 3.9 weight percent H_2O (X-ray analysis)

Total water in the system is equivalent to 218 μmols /ml solution
 1.000 ml samples removed at various times for assaying

	Hours of Agitation			
	<u>0</u>	<u>100</u>	<u>300</u>	<u>500</u>
μmols I_2 added to Cu end point	--	--	52	62
μmols I_2 added to H_2O end point	43	131	192	188
μmols Cu per ml solution (calculated)	--	--	52	62
μmols H_2O per ml solution (calculated)	43	131	218	219
<u>μmols H_2O per ml</u>	--	--	4.2	3.5
μmols Cu per ml				
Solution Color	Clear	Blue Green	Green	Green

Sample No. 2

Electrolyte Solution: 50 ml of 15g LiClO_4 /100 ml BL
 43 μmols H_2O /ml solution
 CuF_2 : 5.25g, sample vacuum dried at 110°C, weight percent
 H_2O not known

Total water in the system is approximately equivalent to 43 μmols /ml solution
 1.000 ml samples removed at various times for assaying

	Hours of Agitation			
	<u>0</u>	<u>100</u>	<u>300</u>	<u>500</u>
μmols I_2 added to Cu end point	--	--	<1	<1
μmols I_2 added to H_2O end point	43	43	42	41
μmols Cu per ml solution (calculated)	--	--	<1	<1
μmols H_2O per ml solution (calculated)	43	43	42	41
<u>μmols H_2O per ml</u>	--	--	>42	>41
μmols Cu per ml				
Solution Color	Clear	Pale Green	Green	Green

TABLE II (Continued)

SOLUBILITY OF CuF_2 IN BUTYROLACTONE - LiClO_4 SOLUTIONSSample No. 3Electrolyte Solution: 50 ml of 15g LiClO_4 /100 ml BL38 μmols H_2O /ml solution (550 ppm H_2O) CuF_2 : 4.86g, 1.04 weight percent H_2O (X-ray analysis)Total water in the system is equivalent to 94 μm /ml solution

1.000 ml samples removed at various times for assaying

	Hours of Agitation			
	<u>0</u>	<u>100</u>	<u>300</u>	<u>500</u>
μmols I_2 added to Cu end point	--	--	22	26
μmols I_2 added to H_2O end point	38	--	81	79
μmols Cu per ml solution (calculated)	--	--	22	26
μmols H_2O per ml solution (calculated)	38	--	92	92
<u>μm H_2O per ml</u>	--	--	4.2	3.5
<u>μm Cu per ml</u>	--	--		
Solution Color	Clear	Green	Dark Green	Dark Green

Sample No. 4Electrolyte Solution: 50 ml of 15g LiClO_4 /100 ml BL38 μmols H_2O /ml solution CuF_2 : 1.46g, 5.70 weight percent H_2O (X-ray analysis)Total water in the system is equivalent to 131 μm /ml solution

1.000 ml samples removed at various times for assaying

	Hours of Agitation			
	<u>0</u>	<u>100</u>	<u>300</u>	<u>500</u>
μmols I_2 added to Cu end point	--	--	30	36
μmols I_2 added to H_2O end point	38	109	115	112
μmols Cu per ml solution (calculated)	--	--	30	36
μmols H_2O per ml solution (calculated)	38	109	130	130
<u>μmols H_2O per ml</u>	--	--	4.3	3.6
<u>μmols Cu per ml</u>	--	--		
Solution Color	Clear	Green	Dark Green	Dark Green

3.1.2. Vacuum Distillation of Propylene Carbonate and Butyrolactone

Vacuum distillation of the solvents was undertaken with the hope of producing materials having more desirable properties as the electrolyte solvents in Li-CuF₂ cells. This procedure is of interest not only for the removal of water and other possible impurities in the solvents as supplied by the manufacturer, but also as a means for removing some products resulting from chemical treatment (e.g., Li compounds after treatment with Li powder).

Results of vacuum distillation of butyrolactone at 17 mm Hg are presented in Table III.

TABLE III
VACUUM DISTILLATION OF BUTYROLACTONE

Source: Matheson, Coleman & Bell
Pressure: 17 mm Hg

	<u>Initial</u>	<u>Fractions</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Volume, cc	250	99	103	43	5
Boiling Range	---	89	89-90	90-92	92+
Color	White	White	White	White	Brown
Refractive Index	1.433	1.434	1.434	1.434	---
Water, ppm	510	180	140	390	---

The distillate was stored in polyethylene bottles and all fractions assumed a yellowish color after a stand period of three days. The yellowing does not occur readily in properly stoppered serum bottles and must, therefore, be caused by the contact between butyrolactone and the atmosphere. Further, yellow color indicates presence of water in excess of 1500 ppm as observed from various Karl Fischer analyses of this material, while the white samples tested have always contained less than 900 ppm water. It must be concluded that butyrolactone is strongly hygroscopic, and that yellow color is indicative of presence of water. (Storage of the solvent in serum bottles has not resulted in discoloration.)

With the present level of sensitivity of the equipment and measuring instruments, the physical properties of the solvent could not be correlated with the water content. The water contamination, however, was reduced considerably by vacuum distillation. The total amount of water collected in the distillate added up to less than that present in the original material indicating that some water was removed thru the vacuum system.

Propylene carbonate was distilled at 10 mm Hg, and the fractions were analyzed. Results of three distillation runs are given in Table IV.

TABLE IV
VACUUM DISTILLATION OF PROPYLENE CARBONATE

Source: Matheson, Coleman & Bell
Pressure: 10 mm Hg

<u>Run No. 1</u>					
	<u>Initial</u>	<u>Fractions</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Volume, cc	250	100	110	35	5
Boiling Range, °C	---	95-108	107	106	---
Color	White	White	White	White	Brown
Refractive Index	1.420	1.420	1.422	1.422	---
Water, ppm	580	120	140	180	---
<u>Run No. 2</u>					
Volume, cc	230	25	200	5	---
Boiling Range, °C	---	107	107	---	---
Color	White	White	White	Reddish Yellow	---
Refractive Index	1.420	1.420	1.422	---	---
Water, ppm	580	380	120	---	---

3.2. POSITIVE ELECTRODE STUDIES

3.2.1. Copper Fluoride Purity Study

Copper fluoride (CuF_2) continues to be the most effective positive active material which has been used on this program to date. Reduction of up to 80 percent of theoretical (2 electron change/mol) has been demonstrated in previous work, and the theoretical energy density of the Li- CuF_2 couple is acceptably high (720 watt hours/lb). However, even after considerable experience in the contractor's laboratory, certain difficulties in the application of the material persist. As was shown in the previous section of this report, the presence of water in the system tends to solubilize the CuF_2 , probably in the form of a trihydrate ion, $\text{Cu} \cdot 3\text{H}_2\text{O}^{++}$. In the prototype cells of the previous contract, the water content of the CuF_2 was about 1.0 percent compared to about 0.05 percent water in the electrolyte solution. Since the electrolyte solution and the positive active material in these cells contributed about equally to the weight of the cell, the CuF_2 can be seen to contribute most of the water of the system.

The water content in CuF_2 has been estimated by X-ray diffraction method, by titration with the Karl Fischer reagent, and by weight loss upon heating under vacuum. The weight loss method assumes a stoichiometric decomposition of the dihydrate according to the reaction



The manufacturer's analyses of the material are available also on request, but this method, based on fluorine analysis, does not differentiate between $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and CuO , and includes any residual HF present in the sample. Results of recent analyses of CuF_2 from two suppliers by X-ray, Karl Fischer, and weight loss methods are given in Table V.

TABLE V
RESULTS OF CuF_2 ANALYSES

Lot No.	Lot Size, kg	Supplier*	Water Content, Percent		
			X-ray	Karl Fischer	Weight Loss
1	1.0	ADM	---	---	---
2	2.0	ADM	3.9	3.5	3.3
3	1.0	ADM	1.0	1.0	0.8
4	1.0	ADM	5.8	5.4	3.6
5	0.2	OM	0.2	---	0.4
6	2.5	ADM	2.8	---	2.6
7	2.5	OM	2.5	---	---

*ADM - A. D. MacKay, Inc.

OM - Ozark Mahoning Company

Apparently the manufacturers are continuing to experience difficulty in controlling the level of residual water in the product. However, a product having a low water content must be obtainable by the process employed since individual 100g bottles of the material assayed by X-ray method have shown water content below 0.2 percent. Water is also removed by decomposition of the $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ under vacuum, but the results in this contractor's laboratory have been variable. Strong discoloration of the product has been observed on several occasions upon drying at 70-110°C and a vacuum of 50-200 μ , the cause of which has, at the present, not been determined. The subject of CuF_2 manufacture and purification will have to be given further consideration, since material having less than 0.1 percent and possibly less than 0.01 percent water may be necessary for construction of cells having the desired shelf life properties.

3.2.2. Filter-Mat Electrode Studies

The study of the filter-mat electrode construction described in previous reports was continued during the quarter. The effect of filter mat thickness on electrode performance in methyl formate electrolyte at 2 mA/cm², and in propylene carbonate electrolyte at 1 mA/cm² was studied. The thickness of the filter-mat was controlled by varying the amount of material used in the filter press, in this manner, electrodes with a theoretical capacity over the range 0.6-5.0 ampere hours and a corresponding variation in thickness were produced. The composition of the filter mat was in the ratio

CuF_2	100 parts	(by weight)
Graphite	14 parts	
Paper fiber	7 parts	

and was held constant for the test. A summary of the construction and discharge data for these tests is presented in Tables VI and VII.

TABLE VI

CHARACTERISTICS OF CuF_2 -Li CELLS IN METHYL FORMATE

Electrolyte: 50g LiClO_4 /100 ml MF
 Discharge Rate: 60 mA (2 mA/cm²)
 Temperature: -15°C

Cell No.	Theo. CuF_2 Cap., AH	Approx. Thickness, in.	Initial load Voltage	Time to 2VF, hrs.	Percent CuF_2 Efficiency
2-1	5.15	5/32	2.90	5.0	6
2-2	4.27	5/32	2.90	11.3	16
2-3	2.10	3/32	2.90	19.0	54
2-4	2.14	3/32	3.05	20.7	58

TABLE VI (Continued)

CHARACTERISTICS OF CuF_2 -Li CELLS IN METHYL FORMATE

Electrolyte: 50g LiClO_4 /100 ml MF
 Discharge Rate: 60 mA (2 mA/cm^2)
 Temperature: -15°C

<u>Cell No.</u>	<u>Theo. CuF_2 Cap., AH</u>	<u>Approx. Thickness, in.</u>	<u>Initial load Voltage</u>	<u>Time to 2VF, hrs.</u>	<u>Percent CuF_2 Efficiency</u>
2-5	1.16	1/16	3.05	12.0	62
2-6	1.28	1/16	3.05	13.5	63
2-7	0.68	3/64	3.14	5.7	52
2-8	0.64	3/64	3.09	4.5	42

TABLE VII

CHARACTERISTICS OF CuF_2 -Li CELLS IN PROPYLENE CARBONATE

Electrolyte: 15g LiClO_4 /100 ml PC
 Discharge Rate: 30 mA (1 mA/cm^2)
 Temperature: $+35^\circ\text{C}$

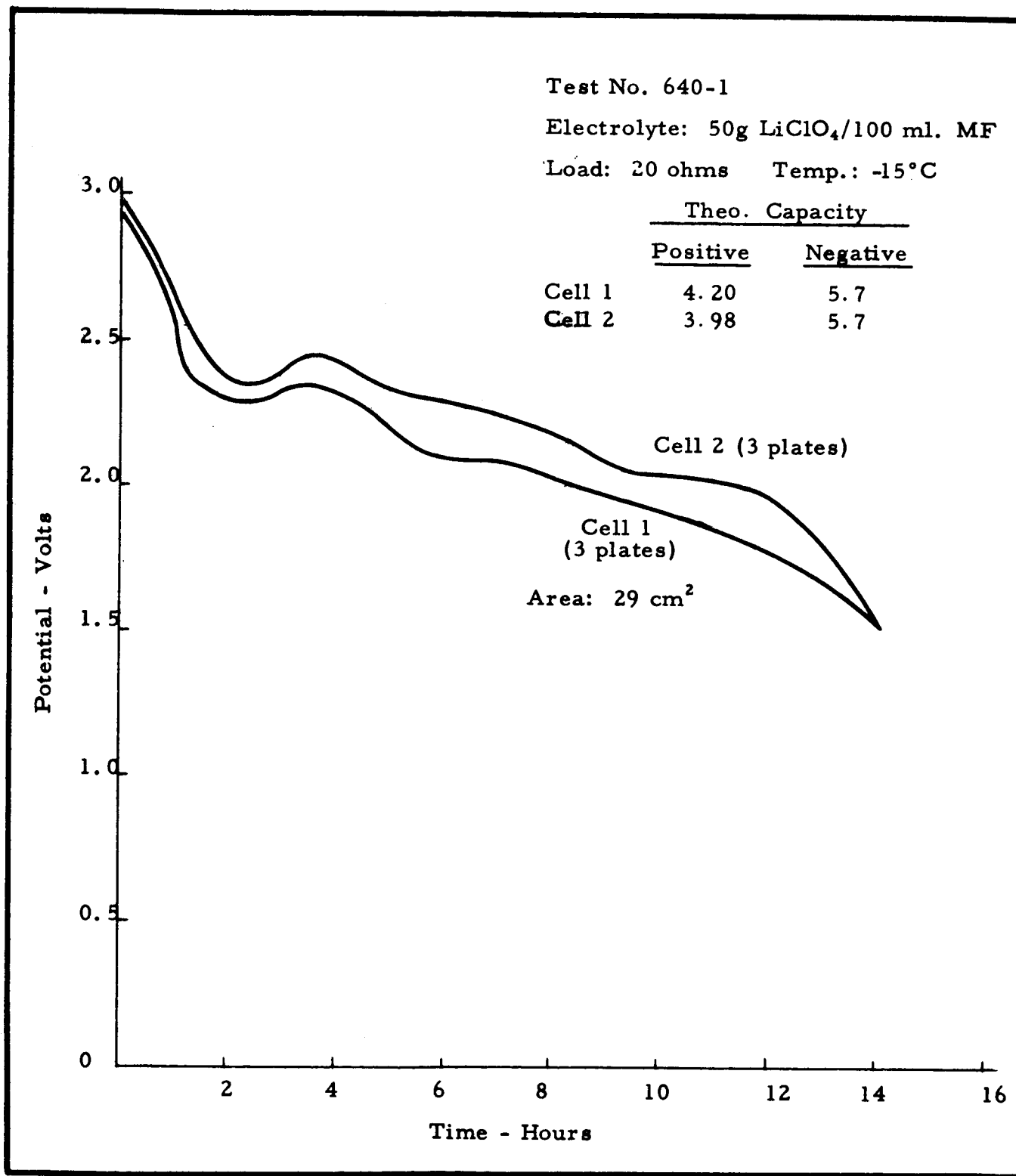
<u>Cell No.</u>	<u>Theo. CuF_2 Cap., AH</u>	<u>Approx. Thickness, in.</u>	<u>Initial load Voltage</u>	<u>Time to 2VF, hrs.</u>	<u>Percent CuF_2 Efficiency</u>
2A- 1	4.63	5/32	3.00	29.3	19
2	4.38	5/32	3.00	29.3	20
3	2.50	3/32	3.00	26.0	31
4	2.56	3/32	3.00	21.0	35
5	1.46	1/16	2.93	17.5	36
6	1.44	1/16	2.93	14.5	30
7	0.83	3/64	2.95	9.7	35
8	0.82	3/64	2.93	7.5	27

With the exception of the two cells having the thickest CuF_2 electrodes, performance in both electrolytes was nearly independent of electrode thickness. In methyl formate cell, the initial discharge voltage tended to increase with decreasing electrode thickness, while the converse trend was observed in cells having propylene carbonate electrolyte. The discharge characteristics of the cells in this series were generally poorer than those obtained in other recent test series (e.g., prototype cells of the last contract). The variability in the quality of the CuF_2 used in different tests may be contributing considerably to the present lack of reproducibility between individual test series.

3.3. CELL SYSTEMS STUDIES

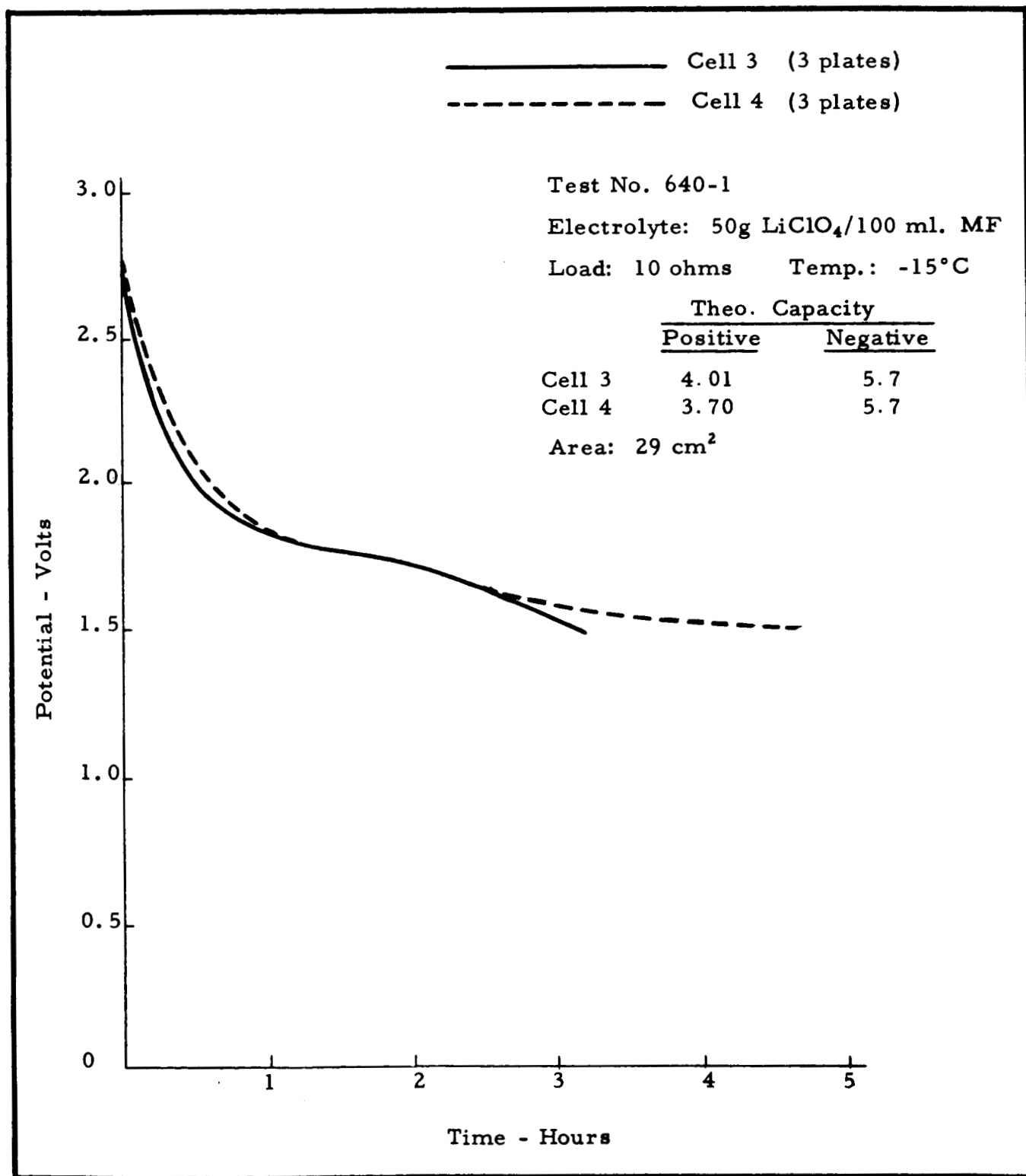
Twelve CuF_2 -Li cells were constructed and tested (at the request of NASA Project Manager) in order to evaluate the discharge rate capabilities of the present design. Construction of the cells was the same as that of the prototype cells built under the previous contract, except Cells 11 and 12 had two positive and three negative plates, the positives being one-half as thick as those in the three-plate cells to give twice the electrode area (58 cm^2) with the same theoretical positive electrode capacity (4-5 ampere hours). The cells were discharged through various resistive loads projected to give 1-20 hour rate discharges.

As can be seen from the discharge data presented in Figures 1 to 6, the loads were too high for the cells to form voltage plateaus at potentials higher than 2 volts. In the case of the methyl formate cells, increasing of the discharge temperature improved the discharge properties, as can be seen from comparing Cells 5 and 6 with Cells 11 and 12. The vapor pressure developed by Cells 11 and 12 during the discharge was about 10 psig (cells discharged at -15°C were open to the atmosphere). Results of these discharge tests show that modifications to the cathode matrix and larger discharge area (thin plates) are needed in order to utilize the present system at the 1-20 hour rates.



FORM FM-100

FIGURE 1
Discharge Characteristics of CuF₂-Li Cells



FORM FM-100

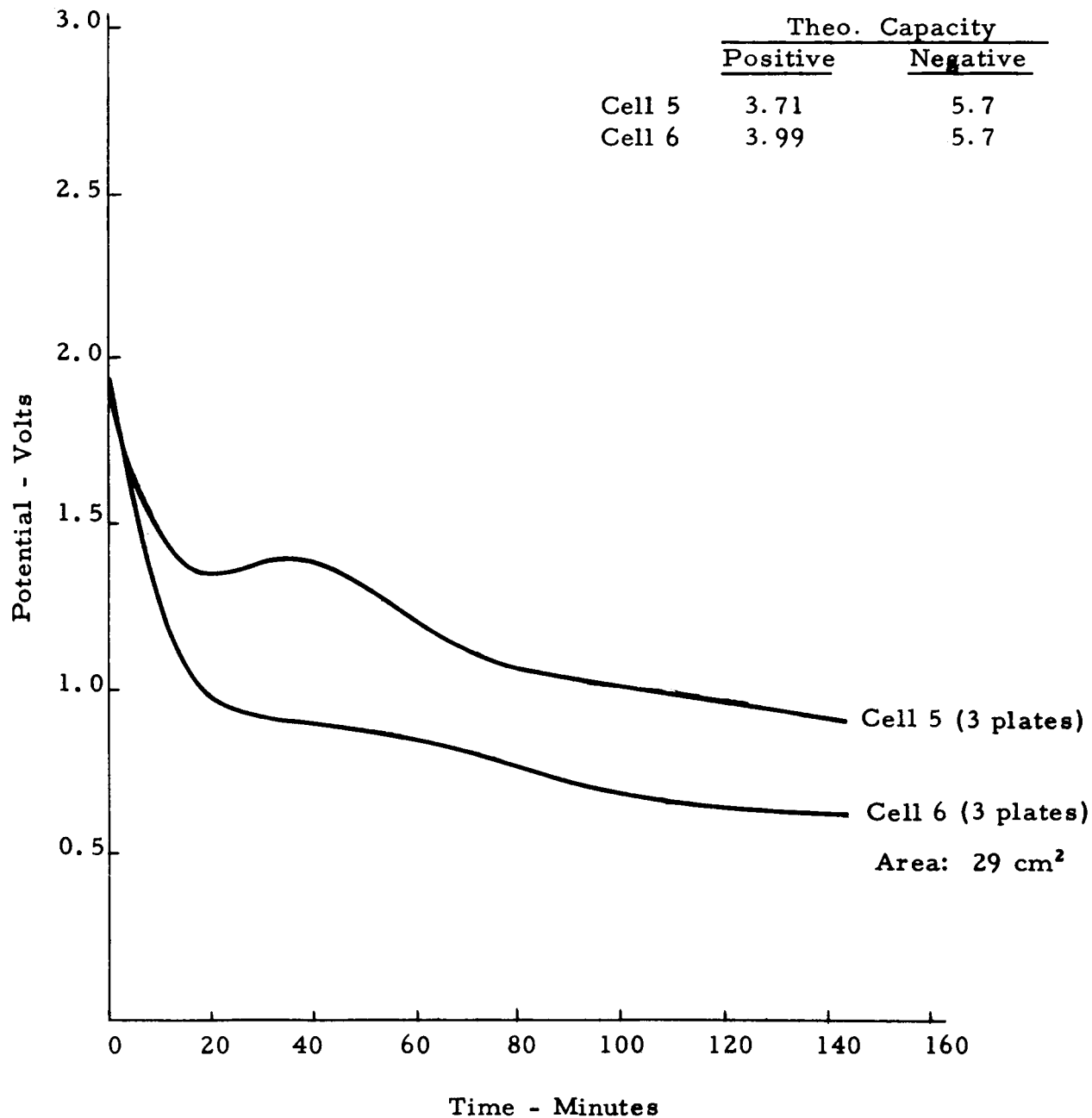
FIGURE 2

Discharge Characteristics of CuF₂-Li Cells

Test No. 640-1

Electrolyte: 50g LiClO_4 /100 ml. MF

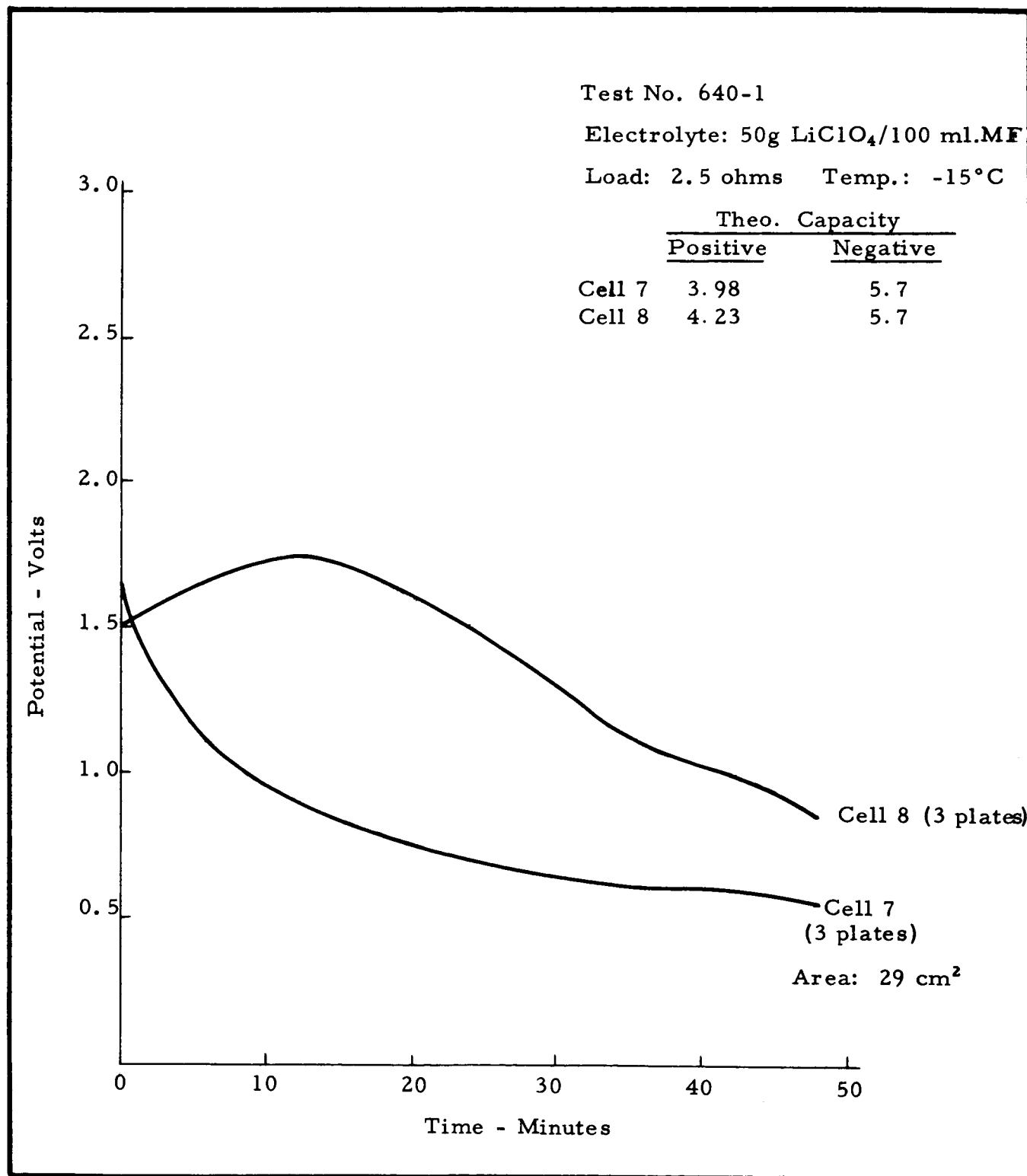
Load: 5 ohms Temp.: -15°C



FORM FM-100

FIGURE 3

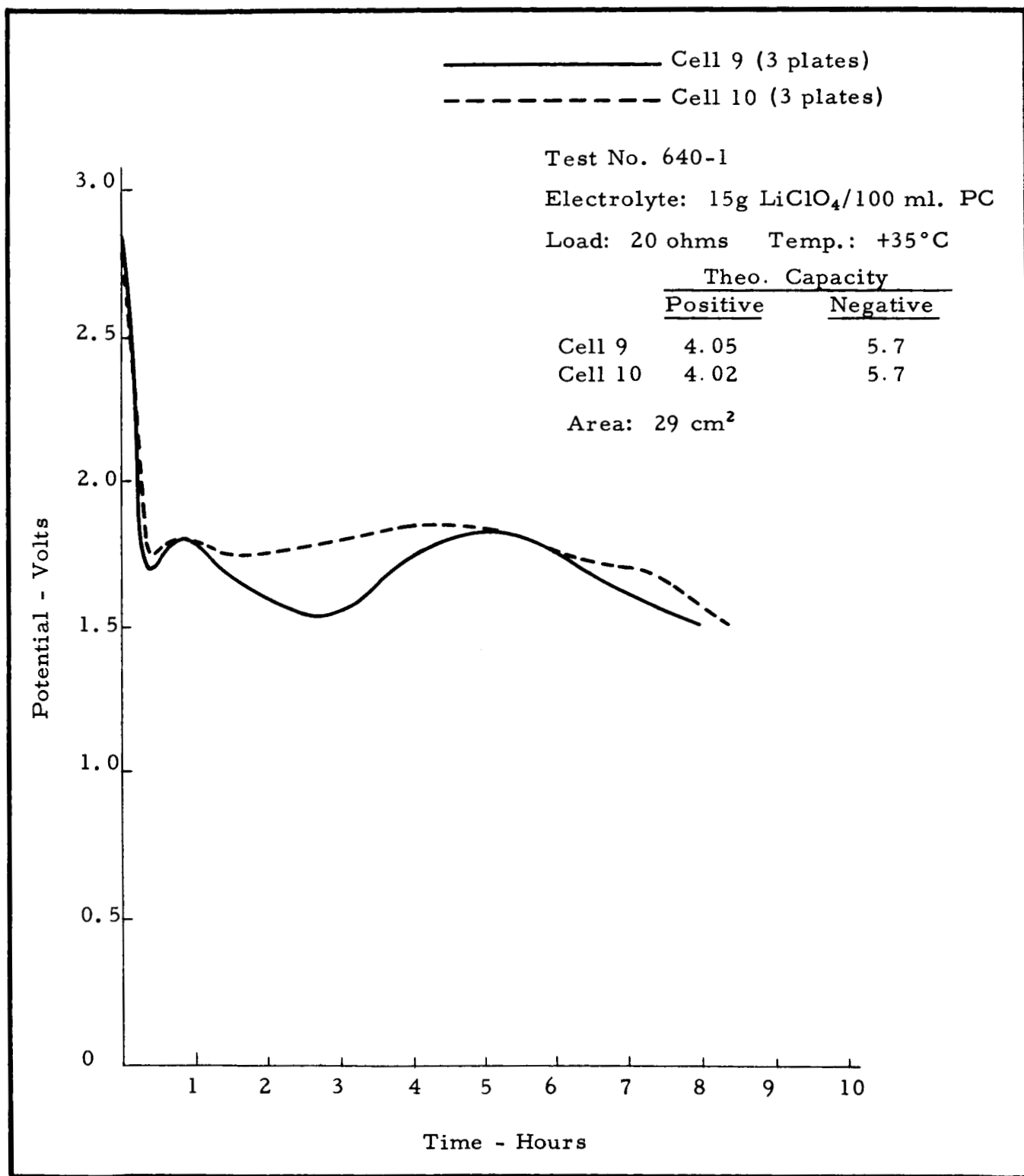
Discharge Characteristics of CuF_2 -Li Cells



FORM FM-100

FIGURE 4

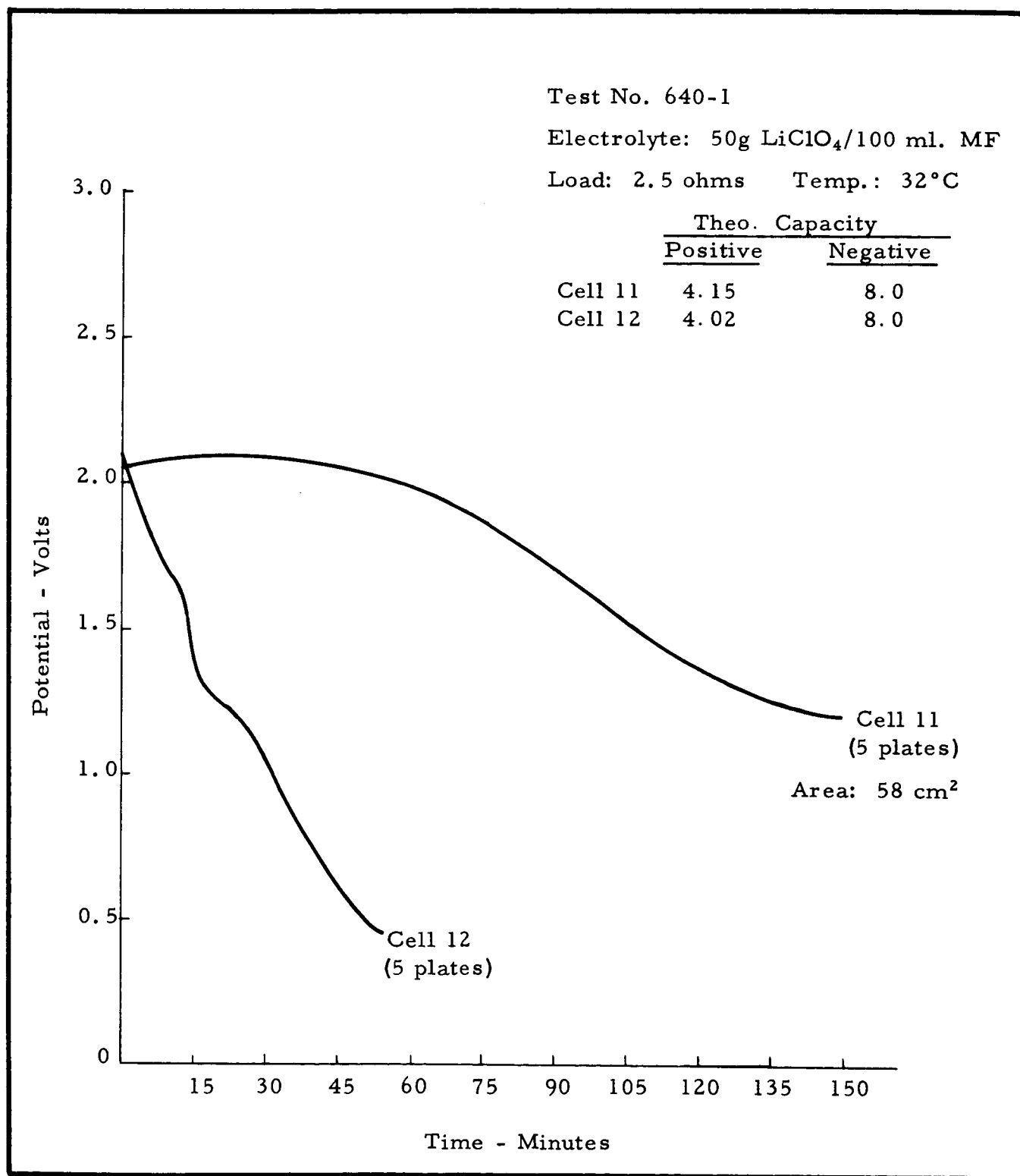
Discharge Characteristics of CuF_2 -Li Cells



FORM FM-100

FIGURE 5

Discharge Characteristics of CuF₂-Li Cells



FORM FM-100

FIGURE 6

Discharge Characteristics of CuF₂-Li Cells

4. ACTIVITY PLANNED FOR THE SECOND QUARTER

Since the solubility of CuF_2 in the electrolyte solutions continues to constitute the major problem in the low rate Li- CuF_2 cells, and since water appears to have a major effect on the extent of this solubility, development of purification methods and evaluation of the treated materials in cell tests will be continued. The chemical treatment and distillation of electrolyte solvents will be continued for the removal of water and possibly other detrimental impurities. The effect of these procedures on the electrolytes will be evaluated by the Karl Fischer analysis for water, specific conductance, and other tests. The treated electrolytes will also be used in comparative cell tests to determine whether improvement in shelf life and other characteristics have been obtained. These tests will be conducted with Li- CuF_2 and Li- Ag_2O_2 cells, the latter system being chosen with the hope of eliminating the effect of dissolved copper ion on the shelf life characteristics.

The effect of water on the solubility of CuF_2 , both in the form of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and as an impurity in the electrolyte solution, will be studied extensively. It will be attempted to evaluate this factor over the range of 60-6000 ppm of water in the system. Both propylene carbonate and butyrolactone will be employed in these tests.

Study of the construction of thin CuF_2 electrodes will continue. Modification in paste formulation will be studied in order to determine the optimum concentrations of conductor (graphite) and binder (cellulose acetate).

The extent of polarization of the lithium electrode in various electrolyte solutions will be studied. Electrolytic cells with anode and cathode reference electrodes will be employed in order to determine the optimum electrolyte concentrations for both the high rate (methyl formate) and low rate (propylene carbonate, butyrolactone) electrolytes.