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DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES 200 WATT HOURS PER POUND TOTAL BATTERY WEIGHT MINIMUM

THIRD QUARTERLY REPORT

William F. Meyers (Principal Investigator)
Sandors G. Abens (Author)

10 December 1964 to 9 March 1965

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6004

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ABSTRACT

Electrolyte and electrode studies for the development of high energy lithium-anode primary cells were conducted. The stability of lithium in the lower esters with and without $LiClO_4$ solute was determined. Methyl formate was less reactive than ethyl formate, but produced 117 psig of pressure. The specific conductance of various organic electrolyte solutions was not strongly affected by atmospheres of NH_3, SO_2, or CO_2. Powdered lithium metal was an effective water removing agent for organic solvents. In experimental CuF_2-Li cells, 79 percent cathode efficiency was recorded in methyl formate-$LiClO_4$ at 1 mA/cm^2, and 50-70 percent in propylene carbonate-$LiClO_4$ electrolyte at 0.5 mA/cm^2.

SUMMARY

Studies of materials and methods of construction for the development of high energy primary batteries were conducted.

The stability of metallic lithium in the lower esters, and in solutions of $LiClO_4$ in the esters was studied. At room temperature, methyl formate showed a lower rate of attack on lithium than did ethyl formate. Addition of diethyl ether to ethyl formate reduced the rate of lithium decomposition. Presence of lithium perchlorate accelerated the rate of lithium decomposition in all of the systems studied.

A number of solvents were electrolyzed between smooth platinum electrodes in presence of a gaseous atmosphere, using $LiClO_4$ and other salts as the supporting electrolyte. Sulfur dioxide and ammonia were strongly soluble in methyl formate and dimethyl formamide, but carbon dioxide was only slightly soluble in these solvents. Presence of SO_2 in the solution increased the solvent decomposition current appreciably. The specific conductance of the solutions was only moderately affected by the presence of the gaseous atmosphere. The maximum conductivity of LiBr solutions in methyl and ethyl formates was only about 20 percent of $LiClO_4$ solutions.

Compatibility tests of thirteen possible cathode materials with methyl formate and propylene carbonate electrolytes eliminated CrO_3 because of solubility, and KO_2 because of pyrophonic characteristics (the remaining materials were retained for cell tests).

Methods for removing trace water from several solvents were studied. Powdered lithium metal was the most effective water removing agent for acetic anhydride, butyrolactone, propylene carbonate, and dimethyl sulfoxide. Water concentration below 15 ppm were obtainable by this method.

Experimental cell tests with the CuF_2-Li couple were conducted using methyl formate and propylene carbonate as the electrolyte solvents, and $LiClO_4$ as the solute. Efficiency of the CuF_2 electrode was studied in positive limiting cells. Employing a filter mat electrode construction containing up to 82 percent by weight of CuF_2, electrochemical efficiencies as high as 79 percent were recorded with methyl formate as the electrolyte solvent at current densities of about 1 mA/cm^2. Efficiencies in propylene carbonate were somewhat lower, being generally in the range 50-70 percent at a current density of about 0.5 mA/cm^2.

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1. INTRODUCTION

The purpose of this program is to develop a primary battery system capable of an energy-to-weight ratio of over 200 watt hours per pound of total battery weight. The present report describes the activity and results obtained during the third quarter of the current contract period.

During the present contract, experimental tests have been designed for the development of a primary cell utilizing lithium as the negative active material; this required identification and study of electrolyte systems which are compatible with metallic lithium. Based on the results of the experimental program, five suitable solvents were identified, these being propylene carbonate, butyrolactone, dimethyl sulfoxide, acetic anhydride, and methyl formate. Comparative cell discharge tests with the five solvents were performed employing CuF_2-Li as the test couple and $LiClO_4$ as the electrolyte. At the conclusion of the cell tests, propylene carbonate and methyl formate were chosen for further use in cell tests, while the other solvents were retained in the program for studies of purifivation and water removal methods.

The major portion of the electrolyte tests was performed using $LiClO_4$ as the solute; this material was chosen because it forms relatively conductive solutions with many of the organic solvents and appears to be stable in presence of the electrode materials.

In the course of this program, several materials were evaluated as positive electrode reactants. Copper fluoride demonstrated the most desirable properties in terms of electrochemical efficiency and stability of discharge potential;

therefore, the major portion of positive electrode studies was performed with CuF_2 as the active material (the theoretical energy capability of the CuF_2-Li couple is [211 ampere hours per pound] [3.4 volts], or 720 watt hours per pound).

An appropriate construction for the positive electrode was recognized as a basic development task required for the evolution of an efficient CuF_2-Li cell. The electrode construction method which was most extensively studied was that of a filter press mat produced with a non-aqueous solvent vehicle, and paper fiber and carbon added for strength and conductivity, respectively.

During the past quarter, studies of lithium stability in the lower esters and diethyl ether were performed; these tests were performed for the purpose of elucidating the reaction mechanisms, and possibly finding means of reducing the rate of lithium decomposition. Other electrolyte studies were carried out, including evaluation of methods of water removal from the systems in preparation of evaluation of the effect of water contamination on cell performance. Studies of the CuF_2 electrode construction methods were continued in addition to the evaluation of several other materials as possible cathode reactants. The filter press construction method was more extensively evaluated and, at the present, appears to be suitable for constructing electrodes having a high electrochemical efficiency.

2. DESCRIPTION OF EXPERIMENTAL WORK

2.1. ELECTROLYTE STUDIES

2.1.1. Lithium Compatibility Tests

In order to further investigate the possibility of using the lower esters and, in particular, methyl formate as the electrolyte solvents in lithium-anode cells, reactions between lithium and some esters were observed. The test apparatus consisted of a glass tube equipped with a stainless steel coupler for connection of a 0 - 300 pound per square inch pressure gauge. Five milliliters of the test solution and a freshly cut and cleaned piece of lithium ribbon were introduced into the tube, and the system sealed. The free volume above the sample was about 4 cm^3. The system was allowed to stand at room temperature or in an alcohol bath at -40° C, and the changes in appearance of the lithium ribbon and of the solution, as well as the pressure of the system, were periodically recorded. A total of 16 compatibility tests were performed using methyl formate, ethyl formate, and diethyl ether as the solvents, and lithium perchlorate and lithium bromide as the solutes.

The test series described in Table I, page 5, was performed using materials as received from the suppliers. The esters used were "Spectroquality" grade (less than 500 ppm [parts per million] H_2O), while the diethyl ether was "anhydrous" grade (less than 100 ppm H_2O, less than 100 ppm C_2H_5OH). The anhydrous lithium perchlorate carried a manufacturer's specification of 0.3 percent H_2O or less; however, later analyses by the Karl Fischer method have shown that the water content of $LiClO_4$ increased during storage of the salt and may have been as high as 3 percent by weight in some of the tests.

With all of the solvents studied, presence of lithium perchlorate in the solution accelerated the attack on the lithium sample; this effect was more pronounced at room temperature than at -40° C. When lithium bromide was substituted for $LiClO_4$ as the solute at the same molal concentration, a significant reduction of the decomposition rate of lithium in metyl formate was observed.

Addition of diethyl ether to ethyl formate significantly reduced the rate of lithium decomposition (compare Trials No. 3 and No. 7). In the presence of lithium perchlorate, decomposition of lithium was rapid in both systems.

At room temperature, methyl formate showed a lower rate of attack on lithium than did ethyl formate. At -40° C, no attack on lithium by methyl formate was evident after one month, and only a slight amount of attack was observed in ethyl formate.

The addition of ether to the ester electrolytes appears to be a possible method of improving the stability of the lithium. From the present results, methyl formate appears more suitable for Li-anode cells than ethyl formate. Diethyl ether shows good stability in the presence of metallic lithium, but the conductivity of its solutions are too low to be considered for use as the electrolyte.

TABLE I

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 1 — Methyl Formate (Matheson Coleman & Bell Spectroquality) Room temperature (77°F)

Time	Remarks
0	Immersed sample and sealed system.
3 hours	No visible change.
4 hours	White deposit on Li surface; gassing from deposit.
5 hours	White deposit accumulated on bottom of tube; gas emanating from deposit.
24 hours	Yellow, semi-translucent film on Li surface; gassing rate diminished. Gauge pressure: 55 pounds per square inch
48 hours	Same as at 24 hours. System moved to 22°F environment.
50 hours	Gauge pressure: 2 pounds per square inch System moved to room temperature (77°F) environment.
74 hours	Gauge pressure: 8 pounds per square inch Liquid clear yellow. Fresh piece of Li placed in tube.
1 month	No change in appearance of Li sample or solution.

Trial No. 2 — Methyl Formate (Matheson, Coleman & Bell Spectroquality) Temperature: -40°C

Time	Remarks
0	Immersed sample and sealed system.
24 hours	Small amount of white precipitate accumulated on bottom of test tube.
1 month	No visible changes in appearance of lithium or solution.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 3	33 mol percent diethyl ether in ethyl formate. Room temperature.	
	Time	Results
	0	Immersed Li sample and sealed system.
	1 month	No change in appearance of solution; yellow film formed over areas of sample which were slightly discolored at the beginning of the test.
Trial No. 4	33 mol percent diethyl ether in ethyl formate. Temperature: -40°C.	
	Time	Results
	0	Immersed sample and sealed system.
	1 month	No visible change in appearance of lithium sample or solution.
Trial No. 5	Diethyl Ether. Room temperature.	
	Time	Results
	0	Immersed sample and sealed system.
	1 month	No visible change in appearance of sample or solution.
Trial No. 6	Diethyl Ether. Temperature: -40°C.	
	Time	Results
	0	Immersed sample and sealed system.
	1 month	No visible change in appearance of sample or of solution.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 7 Ethyl Formate. Room temperature (76°F)

Time	Results
0	Immersed sample and sealed system.
1 hour	Yellow deposit on Li surface; white precipitate collecting on bottom of tube.
2 hours	Gas bubbles emanating from precipitate and from lithium surface.
100 hours	Liquid brownish, heavy yellow-red precipitate on bottom of tube. Liquid level decreased by about 20 percent. Gauge pressure: 275 pounds per square inch
	System moved to 22°F environment.
101 hours	Gauge pressure: 6 pounds per square inch System moved to room temperature.
125 hours	Material completely solidified. Gauge pressure: 195 pounds per square inch

Trial No. 8 Ethyl Formate. Temperature: -40°C.

Time	Results
0	Immersed sample and sealed system.
24 hours	White precipitate suspended in solution.
1 month	Small amount of white precipitate on bottom of tube; no additional changes in appearance of lithium sample or of solution.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 9 — Methyl Formate (Matheson Coleman & Bell Spectroquality); Lithium Perchlorate, anhydrous (Foote Mineral Company); 250 grams solute/liter solvent; room temperature (77°F)

Time	Remarks
0	Immersed sample and sealed system.
1 hour	Rapid gassing, very small bubbles; 5 pounds per square inch gauge.
2 hours	Solution hazy, especially near the Li surface; 10 pounds per square inch gauge.
5 hours	White substance in bottom of tube; pale yellow substance on Li surface; 13 pounds per square inch gauge.
16 hours	Solution yellow; Li not gassing; Li under the solution surface completely covered by a yellow material; Li above the solution surface unaffected.
150 hours	117 pounds per square inch gauge.
225 hours	117 pounds per square inch gauge. System moved to 25°F environment.
235 hours	0 pounds per square inch gauge. System moved to 77°F environment.
236 hours	9 pounds per square inch gauge.
250 hours	16 pounds per square inch gauge.
260 hours	16 pounds per square inch gauge; solution dark yellow; much less solid material than in Trial No. 1; liquid level unchanged.

L_s (original solution) = 2.0×10^{-2} mhos/cm

L_s (final solution) = 1.4×10^{-2} mhos/cm

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 9 Continued

Methyl Formate (Matheson Coleman & Bell Spectroquality)
Lithium Perchlorate, anhydrous (Foote Mineral Compahy)
250 grams solute/liter solvent; room temperature (77°F)

Time	Remarks
261 hours	Added a new piece of Li.
285 hours	No apparent Li attack; no pressure rise; liquid a lighter yellow.
309 hours	All Li surfaces covered with a yellow, coherent, clinging, film-like material; no pressure rise.
333 hours	No additional changes; test terminated.

Trial No. 10

Methyl Formate (Matheson, Coleman & Bell Spectroquality)
Lithium Perchlorate, anhydrous, (Foote Mineral Company)
250 grams solute/liter solvent; temperature: -40°F

Time	Remarks
0	Immersed sample and sealed tube.
24 hours	No evidence of any reactions.
48 hours	Gray film covering about two-thirds of the Li surface under the solution; Li above the solution not affected.
140 hours	Gray film covering all of the Li under the solution surface; some gas bubbles clinging to the Li.
210 hours	Same as at 140 hours.
360 hours	Gray film has thickened; solution cloudy.
675 hours	The weight of the reaction products has apparently caused the Li to sink further into the solution, thus exposing uncorroded Li to the solution; this new Li is not being attacked.
675 hours + 1 month	No attack on the "new" Li surface exposed.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 11

Ethyl Formate (Matheson Coleman & Bell Spectroquality)
Ethyl Ether, anhydrous (Fisher Reagent Grade)
Lithium Perchlorate, anhydrous (Foote Mineral Company)
250 grams solute/liter of 33 mole percent ethyl ether in ethyl formate; Room temperature (77°F)

Time	Remarks
0	Immersed sample and sealed system; immediate gassing with concomitant removal of any foreign material present on the Li—shiniest Li ever seen here; red, soluble substance being formed at the Li surface; considerable heat being generated.
1 hour	Reaction has gone to completion; no evidence of Li in the mixture.

Trial No. 12

Ethyl Formate (Matheson Coleman & Bell Spectroquality)
Ethyl Ether, anhydrous (Fisher Reagent Grade)
Lithium Perchlorate, anhydrous (Foote Mineral Company)
250 grams solute/liter of 33 mole percent ethyl ether in ethyl formate; Temperature: -40°F

Time	Remarks
0	Immersed sample and sealed system.
24 hours	No evidence of any reactions.
48 hours	Brown film covering about one-sixth of the Li surface.
1.5 months	No further changes.

Trial No. 13

Ethyl Ether, anhydrous (Fisher Reagent Grade)
Lithium Perchlorate, anhydrous (Foote Mineral Company)
263 grams solute/liter solvent; Room temperature (77°F)

Time	Remarks
	Solution pale yellow: $L_s = 5.0 \times 10^{-4}$ mhos/cm
0	Immersed sample and sealed system; immediate, vigorous gassing; no heat development detectable; gray film rapidly covering Li surface.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 13 Continued

Ethyl Ether, anhydrous (Fisher Reagent Grade)
Lithium Perchlorate, anhydrous (Foote Mineral Company)
263 grams solute/liter solvent; room temperature (77°F)

Time	Remarks
1 hour	Li almost completely covered by the gray film; gassing rate reduced considerably.
3 hours	No shiny Li visible; gassing almost stopped; no appreciable pressure rise.
20 hours	Gray, white, and yellow materials completely covering the Li; no pressure.
	Test terminated

Trial No. 14

Ethyl Ether, anhydrous (Fisher Reagent Grade)
Lithium Perchlorate, anhydrous (Foote Mineral Company)
263 grams solute/liter solvent; temperature: -40°F

Time	Remarks
0	Immersed sample and sealed system.
24 hours	No visible reactions
48 hours	No visible reactions
1.5 months	No visible reactions

Trial No. 15

Methyl Formate (Matheson, Coleman & Bell Spectroquality)
Lithium Bromide, anhydrous (Bios Laboratories, Inc.)
200 grams solute/liter solvent; room temperature (77°F)

Time	Remarks
0	Immersed sample and sealed system; immediate gassing.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 15 Continued

Methyl Formate (Matheson Coleman & Bell Spectroquality)
Lithium Bromide, anhydrous (Bios Laboratories, Inc.)
200 grams solute/liter solvent; Room temperature (77°F)

Time	Remarks
1 hour	Li under the solution surface completely covered by a gray smooth material; moderate gassing; solution pale yellow; 5 pounds per square inch gauge.
2 hours	Solution in the immediate vicinity of the Li is dark yellow, remainder pale yellow; moderate gassing; 7 pounds per square inch gauge.
18 hours	All shiny Li under the solution covered by a white film; solution brownish yellow; gray material in bottom of tube; 15 pounds per square inch gauge.
42 hours	22 pounds per square inch gauge; no further changes visible.
48 hours	22 pounds per square inch gauge; released pressure-immediate, vigorous gassing of material in bottom; then vigorous gassing of the white material on the Li surface; resealed system.
68 hours	0 pounds per square inch gauge; added new piece of Li to solution—solids had been removed.
75 hours	0 pounds per square inch gauge; no visible gassing.
90 hours	4 pounds per square inch gauge; no visible gassing or Li attack; white material in bottom of tube.
170 hours	9 pounds per square inch gauge; yellow-gray film covering about 80 percent of the Li; solution amber-tan; white material in bottom increased considerably.
380 hours	35 pounds per square inch gauge; released pressure immediate gassing by white material in bottom; mixture does not smell like methyl formate—almost no odor at all; white material freely and exothermically soluble in water.

TABLE I Continued

RESULTS OF LITHIUM COMPATIBILITY TESTS

Trial No. 16

Methyl Formate (Matheson Coleman & Bell Spectroquality)
Lithium Bromide, anhydrous (Bios Laboratories, Inc.)
200 grams solute/liter solvent; Temperature: -40°F

Time	Remarks
0	Immersed sample and sealed system.
5 hours	No visible Li attack; solution very cloudy.
24 hours	Solution now clear; no visible Li attack; suspensoid-like white particles clinging to sides of tube.
53 hours	No further changes.
100 hours	No further changes.
180 hours	Gray film material covering about 60 percent of Li surface.
390 hours	No additional changes.

2.1.2 Decomposition Potential Studies

The decomposition potential of a candidate electrolyte solvent has been used in the previous and present work as an indication of its ability to withstand the oxidizing and reducing action of the electrode materials. During the Third Quarter, twelve decomposition potential tests were conducted both with and without an applied gaseous atmosphere. The solvents were electrolyzed between smooth platinum electrodes using lithium perchlorate and other salts as the supporting electrolyte. The equipment and methods were as described in earlier reports (NASA CR-54307, page 10). Silver coated with silver chloride, and lead coated with lead sulfate were used as reference electrode materials. The reference electrodes were contacted with the solution by immersing them in the liquid above the working electrodes. The cells were sealed in a steel chamber, allowing introduction of gases at various pressures above the solution.

The specific conductance of the solution was measured before the electrolysis was performed. The gas was admitted into the chamber, and the pressure and specific conductance were monitored. The variation of specific conductance with the amount of gas absorbed by the solution is presented in Table III, page 20. Sulfur dioxide and ammonia exhibited considerable solubility in metyl formate and dimethyl formamide, respectively. Only a small reduction in specific resistance of the solutions was observed, which is not surprising considering that the solutions become more dilute as the gas dissolves. Carbon dioxide was relatively insoluble in both propylene carbonate and in butyrolactone.

At the end of the gas absorption test, the solutions were electrolyzed at essentially potentiostatic conditions. The potential was applied in about 1.4 volt steps, and the cell current and the various potentials were recorded as soon as steady state conditions were indicated (usually about 30 minutes). Time, current density, and potential (cell, anode, and cathode) are presented in Table II, page 16. Addition of SO_2 to methyl formate and dimethyl sulfoxide solutions increased the decomposition current appreciably. Presence of CO_2 did not affect the decomposition current of propylene carbonate solutions.

After investigation of 27 electrolyte systems as part of the present contract scope, no significant increase in specific conductance of difficultly soluble salt solutions or reduction of decomposition current has been observed from addition of NH_3, SO_2, and CO_2 to the electrolyte systems.

TABLE II

SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL
OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
Run #16 - N, N-Dimethyl Formamide (CaO dried) - 1.0M $LiClO_4$ - NH_3 - 96 psia					
Reference Electrode: $Pb/PbSO_4$					
ρ = 26.5Ω cm					
.58	27.2	.90	.09	- .82	Black deposit on cathode at
2.16	46.1	2.22	.13	-2.10	end of run
2.91	262	3.44	.24	-3.18	
3.58	314	4.80	.25	-4.51	
4.16	398	6.10	.33	-5.80	
Run #17 - Methyl Formate - No Solute - Argon					
Reference Electrode: Ag/AgCl					
ρ = 1.05M Ω cm					
.50	1.74	.30	.12	- .18	
2.58	3.04	1.11	.70	- .45	
4.00	3.25	1.06	.69	- .37	
5.08	29.4	3.78	1.75	-1.93	
5.58	48.3	5.08	2.38	-2.70	
7.26	77.6	6.40	2.82	-3.61	
Run #18 - Methyl Formate - 1.5M $LiClO_4$ - Argon					
Reference Electrode: Ag/AgCl					
ρ = 50.5Ω cm					
.68	3.66	1.02	.53	- .48	
1.36	18.0	2.28	1.49	- .80	
1.86	58.6	3.59	2.00	-1.58	
2.36	272	4.75	2.33	-2.40	
2.86	5660	5.35	2.56	-2.86	

TABLE II Continued

SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL
OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
		Run #19 - Methyl Formate - 1.5M $LiClO_4$ - SO_2 - 30 psia			
		Reference Electrode: Ag/AgCl			
		ρ = 52.6Ω cm			
.93	3.06	.12	.01	- .11	Black deposit on cathode at end
1.35	77.5	.94	.42	- .50	of run; solution was dark brown
1.85	120	2.22	.50	-1 72	
2.19	252	3.56	.58	-2.97	
2.78	922	4.80	1.60	-3.18	
3.37	4190	5.51	2.34	-3.17	
3.71	9230	5.75	2.50	-3.25	
3.88	36700	6.12	2.78	-3.34	
		Run #20 - Propylene Carbonate - No Solute - Argon			
		Reference Electrode: Ag/AgCl			
		ρ = 366 KΩ cm			
1.25	1.21	1.05	0.61	- .55	
1.83	2.20	2.33	1.33	-1.04	
2.33	4.82	3.66	1.85	-1.70	
2.83	7.13	4.98	2.30	-2.58	
3.33	35.6	6.21	3.11	-3.12	
		Run #21 - Propylene Carbonate - 1.5M $LiClO_4$ - CO_2 - 91.5 psia			
		Reference Electrode: Ag/AgCl			
		ρ = 226Ω cm			
.50	2.20	1.06	.22	- .83	Black deposit on cathode at end
1.67	4.18	2.35	.59	-1.75	of run; solution was orange-brown
2.34	7.32	3.70	1.11	-2.59	
3.01	39.7	4.94	2.18	-2.74	
3.68	2095	5.89	2.89	-3.00	
4.18	6070	6.66	3.33	-3.33	
4.68	10500	6.99	3.49	-3.50	

TABLE II Continued

SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL
OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
		Run #22 - Propylene Carbonate - LiF (saturated) - Argon			
		Reference Electrode: Ag/AgCl			
		ρ = 620 KΩ cm			
.42	.09	.78	.48	- .30	
1.26	.57	1.12	.69	- .55	
1.76	3.67	2.35	1.36	- .99	
2.76	8.17	3.69	1.93	-1.65	
3.26	15.5	5.00	2.51	-2.40	
3.68	21.0	6.30	3.14	-3.17	
		Run #23 - Propylene Carbonate - LiF (saturated) - CO_2 - 163 psia			
		Reference Electrode: Ag/AgCl			
		ρ = 164 KΩ cm			
.68	.36	1.07	1.20	+ .14	
1.76	1.68	2.31	2.45	+ .12	
2.52	6.70	3.61	3.72	+ .11	
3.02	12.2	4.97	5.05	+ .08	
3.70	16.9	6.20	6.21	+ .06	
		Run #24 - Butyrolactone (CaO dried) - $Al_2(SO_4)_3$ (saturated) - Argon			
		Reference Electrode: Ag/AgCl			
		ρ = 339 KΩ cm			
.85	11.1	1.00	.16	- .84	
1.53	45.0	2.25	.49	-1.75	
2.53	71.3	3.52	.96	-2.56	
4.03	92.1	4.85	1.60	-3.25	
4.71	105	6.10	2.20	-3.90	

TABLE II Continued

SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL
OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
Run #25 - Butyrolactone (CaO dried) - $Al_2(SO_4)_3$ (saturated) + CO_2 - 96 psia					
		Reference Electrode: Ag/AgCl			
		ρ = 151 KΩ cm			
.68	.84	.62	.36	- .26	
1.53	2.30	1.09	.66	-.43	
2.29	9.43	2.34	1.26	-1.08	
3.71	21.0	3.66	2.03	-1.53	
4.30	37.7	4.92	2.95	-1.98	
4.80	54.5	6.20	3.66	-2.54	
Run #26 - N, N-Dimethyl Formamide - KBr (saturated) - NH_3 - 73 psia					
		Reference Electrode: Ag/AgCl			
		ρ = 189Ω cm			
2.34	142	.93	.06	- .88	Deposit on both electrodes at
3.92	2310	1.93	.54	-1.40	end of run; discoloration on
5.17	4610	2.78	.94	-1.84	reference electrode
5.84	8390	3.22	1.15	-2.07	
6.84	24100	3.70	1.60	-2.10	
7.42	33500	4.47	2.07	-2.40	
8.09	49300	5.53	2.70	-2.83	
Run #27 - Propylene Carbonate - $MgBr_2$ (saturated) - CO_2 - 91 psia					
		Reference Electrode: Ag/AgCl			
		ρ = 3.82 KΩ cm			
.33	.63	.62	.58	- .04	Film on reference electrode at
1.00	54.5	.95	.78	- .17	end of run; light gray deposit on
1.83	21.0	2.20	.70	-1.50	platinum electrode
2.50	56.5	3.54	.78	-2.75	
4.00	21.0	4.95	.76	-4.17	
5.17	15.3	6.10	.74	-5.40	

NOTE: Saturated solutions were made by adding excess solute to the solvent, agitating the solution, and letting it sit for at least eight days.

TABLE III

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #19 - Methyl Formate/1.5 M $LiClO_4/SO_2$

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in^2	Specific Resistance Ω cm	Moles SO_2 per Mole MF
	79	0 (Argon)	49.6	
	SO_2 introduced into chamber			
0	79	35	42.4	
.25	78	17	42.4	.06
	SO_2 introduced into chamber			
.42	79	35	42.4	
2.00	77	15	42.9	.13
	SO_2 introduced into chamber			
2.08	77	37	42.9	
3.00	79	20	43.1	.19
	SO_2 introduced into chamber			
3.08	79	35	43.1	
3.42	78	21	43.3	
4.76	79	20	43.6	.24
	SO_2 introduced into chamber			
4.84	79	39	43.6	
5.26	79	21	44.0	
5.60	78	20	44.0	.31
	SO_2 introduced into chamber			
5.68	78	40	44.0	
21.25	78	23	44.7	.37
	SO_2 introduced into chamber			
21.33	78	38	44.7	
22.50	70	25	45.4	.41
	SO_2 introduced into chamber			
22.58	70	35	45.4	
23.66	80	25	45.9	.45
	SO_2 introduced into chamber			
23.74	80	40	45.9	
24.42	79	30	47.3	
25.67	79	29	47.3	.49
	SO_2 introduced into chamber			
25.75	79	40	47.3	
26.92	80	30	48.0	.52
	SO_2 introduced into chamber			
27.26	80	40	48.0	
28.68	79	29	49.0	.56

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #19 - Methyl Formate/1.5M $LiClO_4/SO_2$ Continued

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in^2	Specific Resistance Ω cm	Moles SO_2 per Mole MF
		SO_2 introduced into chamber		
28.76	79	41	49.0	
29.01	76	30	50.3	.60
		SO_2 introduced into chamber		
29.09	76	40	50.3	
45.33	76	30	51.6	.64
		SO_2 introduced into chamber		
45.50	76	40	51.6	
50.00	75	30	52.6	.68
50.17	Start of decomposition potential test*			

*See page 17, Run #19

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #21 - Propylene Carbonate/1.5M $LiClO_4/CO_2$

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in²	Specific Resistance Ω cm	Moles CO_2 per Mole PC
	80	0 (Argon)	222	
		CO_2 introduced into chamber		
0	80	100	221	
17.34	79	96	217	
22.26	79	94	221	
41.76	74	91.5	232	
43.26	74	91.5	226	.03
43.34	Start of decomposition potential test*			

*See page 17, Run #21

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #23 - Propylene Carbonate/LiF (saturated)/CO_2

Elapsed Time Hours	Temp. ° F	Gauge Pressure lbs/in.^{2}	Specific Resistance KΩ cm	Moles CO_2 per Mole PC
	78	0 (Argon)	530	
		CO_2 introduced into chamber		
0	78	100	530	
.08	78	95	286	
16.25	78	90	202	
23.17	77	89	194	
40.33	77	87	184	.06
		CO_2 introduced into chamber		
40.41	77	181	184	
44.99	77	177	180	
64.49	78	165	168	
88.32	77	163	164	.15
88.66	Start of decomposition potential test*			

*See page 18, Run #23

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #25 - Butyrolactone/$Al_2(SO_4)_3$ (saturated)/CO_2

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in.^{2}	Specific Resistance KΩ cm	Moles CO_2 per Mole BL
	74	0 (Argon)	228	
		CO_2 introduced into chamber		
0	74	100	228	
3.58	78	96	212	
7.66	78	95	196	
24.58	78	91	175	.05
		CO_2 introduced into chamber		
24.66	78	100	175	
31.34	78	96	167	
47.08	78	96	155	
53.92	77	95	158	
71.17	77	94	154	.07
		CO_2 introduced into chamber		
71.42	78	100	154	
75.92	77	100	152	
95.42	78	96	151	.09
95.92		Start of decomposition potential test*		
100.77		End of decomposition potential test		
102.42	78	96	149	

*See page 19, Run #25

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #26 - N, N-Dimethyl Formamide/KBr (saturated)/NH_3

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in.^{2}	Specific Resistance Ω cm	Moles NH_3 per Mole DMF
0	77	0 (Argon)	265	
	NH_3 introduced into chamber			
.08	77	100	256	
4.33	76	66	238	
6.16	76	62	229	.17
	NH_3 introduced into chamber			
6.24	76	100	229	
21.57	78	63.5	200	.42
	NH_3 introduced into chamber			
21.99	76	100	200	
26.82	78	89.5	192	
29.65	76	85.0	188	.58
	NH_3 introduced into chamber			
29.84	76	98	188	
93.34	76	68.5	192	.87
	NH_3 introduced into chamber			
93.67	76	100	192	
93.75	76	97	192	
117.83	75	73	189	1.00
118.17	Start of decomposition potential test*			

*See page 19, Run #26

TABLE III Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Run #27 - Propylene Carbonate/$MgBr_2$ (saturated/CO_2

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in.^{2}	Specific Resistance KΩ cm	Moles CO_2 per Mole PC
	78	0 (Argon)	4.97	
	CO_2 introduced into chamber			
0	78	150	4.97	
4.25	78	144	5.00	
5.17	76	142	5.13	
6.75	76	142	5.13	
22.42	78	138	4.80	
27.67	78	137	4.73	
30.25	76	135	4.73	
94.09	76	130	3.84	
118.26	75	127	3.59	
118.67	74	126	3.44	.11
	CO_2 introduced into chamber			
118.84	74	134	3.44	
192.92	74	130	3.12	
334.17	76	132	3.35	
358.42	76	130	3.51	
406.09	71	132	3.82	.12
406.59	Start of decomposition potential test*			

*See page 19, Run #27

2.1.3. Specific Conductance Measurements

Although lithium perchlorate forms relatively conductive solutions in methyl formate and in the other solvents studied in this program, it appears to contribute toward the decomposition of lithium metal in contact with the liquid. This effect is particularly pronounced in the esters. Since lithium bromide, when substituted for the perchlorate, produced less pronounced attack on the metal samples, the conductivity of its solutions in the lower esters was studied, and the results are presented in Tables IV and V, page 28 ($LiClO_4$ data is included in Table V, page 28 for comparison). In methyl formate, the maximum conductance was found to be $6.35 \times 10^{-3} ohm^{-1} cm^{-1}$ at 35 grams solute per 100 ml of solvent. This is considerably less than the maximum conductance of $26 \times 10^{-3} ohm^{-1} cm^{-1}$ obtained with $LiClO_4$. A similar relationship was found in ethyl formate, where $LiClO_4$ again produced more conductive solutions than LiBr ($12.6 \times 10^{-3} ohm^{-1} cm^{-1}$ at 2.5 M vs $2.6 \times 10^{-3} ohm^{-1} cm^{-1}$ at 3.5 M).

TABLE IV

CONDUCTIVITY OF SOLUTIONS OF LiBr
IN METHYL FORMATE AT ROOM TEMPERATURE (76°F)

Concentration Grams LiBr/100 ml of Solvent	Specific Conductance, $ohm^{-1}\ cm^{-1}$
1.0	0.22×10^{-3}
2.0	0.47
5.0	1.36
10.0	2.75
15.0	4.59
20.0	5.65
25.0	6.00
31.1	6.33
35.0	6.35
41.6 (sat'd)	6.00

TABLE V

CONDUCTIVITY OF SOLUTIONS OF LiBr AND $LiClO_4$
IN ETHYL FORMATE AT ROOM TEMPERATURE (76°F)

Concentration mols solute/liter of solvent	Specific Conductance $ohm^{-1}cm^{-1}$	
	LiBr	$LiClO_4$
0.1	6.32×10^{-6}	2.02×10^{-4}
0.2	1.26×10^{-5}	3.67×10^{-4}
0.5	5.70×10^{-5}	2.15×10^{-3}
1.0	2.40×10^{-4}	6.30×10^{-3}
1.5	5.34×10^{-4}	9.80×10^{-3}
2.0	9.26×10^{-4}	1.19×10^{-2}
2.5	1.61×10^{-3}	1.26×10^{-2}
3.0	1.88×10^{-3}	1.26×10^{-2}
3.5	2.66×10^{-3}	1.19×10^{-2}
4.0	2.17×10^{-3}	1.06×10^{-2}
4.5	2.16×10^{-3}	

2.1.4. Studies of Water Removal Methods

In order to effect control on the level of water contamination of the cells, several methods for removal of water from the solvents and electrolyte solutions were studied. Dolomitic lime (about 50 percent MgO, rest CaO), LiCl, and powdered lithium were used as the drying agents. The solvents studied were propylene carbonate, dimethyl sulfoxide, butyrolactone, acetic anhydride, and methyl formate; $LiClO_4$ was the solute used in all tests.

Fifty milliliters of the liquid to be dried were placed in a closed bottle with 2 grams of the drying agent, and the mixture was agitated vigorously eight hours per day for five days. The water concentration before and after treatment was determined by the Karl Fischer analysis.[1] The specific conductance of the solutions before and after the drying treatment was also determined, and any visible changes in the appearance of the solutions were noted.

The present method for storing electrolyte solutions (serum bottles with rubber stoppers) appears to be satisfactory, since a sample of butyrolactone (which appears to be at least as hygroscopic as the other solvents in the program) was found to have a water concentration of 46 ppm after nine months of storage at room temperature and humidity. Previous to the stand period, the solvent had been dried by contacting it with high calcium lime (initial Karl Fischer analysis was not available).

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[1] Mitchell, J., Jr., and Smith, D. M. "AQUAMETRY" Interscience Publishers, Inc., New York (1948)

TABLE VI

RESULTS OF WATER

Solution	Initial			CaO · MgO		
	ppm H_2O	L_s	Remarks	ppm H_2O	L_s	Remarks
ACAN (Fisher)	180	3.7×10^{-6}		<15	6.1×10^{-6}	2 distinct solid phases
BL (Antara)	890	3.1×10^{-6}	solvent pale yellow			
BL (Aldrich)	3,230	1.6×10^{-6}				
BL (MC & B)	150	8.3×10^{-7}		105	2.5×10^{-6}	
DMSO (C. Z.)	75	2.5×10^{-6}				
DMSO (Fisher)	150	1.7×10^{-6}		<15	1.4×10^{-6}	
MF (MC & B) (7 months old)	880	2.5×10^{-7}		75	1.2×10^{-6}	solvent pale pink
MF (MC & B) (new shipment)	350	1.1×10^{-7}				
MF: 2.4M $LiClO_4$ (2)	5,860	2.3×10^{-2}				NT (4)
MF: 2.4M $LiClO_4$ (3)	630	2.6×10^{-2}				NT
PC (Eastman)	3,550	1.3×10^{-6}				
PC (Jefferson)	450	1.8×10^{-6}				
PC (MC & B)	240	6.0×10^{-7}		170	1.6×10^{-6}	
PC: 1.4M $LiClO_4$ (2)	3,500	4.5×10^{-3}				NT
PC: 1.4M $LiClO_4$ (3)	400	3.3×10^{-3}				NT

(1) LiCl heated at 110°C and hard vacuum for 15 hours; H_2O <0.002 wt. %

(2) $LiClO_4$ as received in Foote's unopened bottle after 9 months at LEC; H_2O = 2.73 wt. %

(3) $LiClO_4$ same conditions as (2), subjected to 15 hours of vacuum at 155°C; product slightly discolored; H_2O = 0.09 wt. %

(4) No Test

REMOVAL STUDIES

LiCl[1]			Li Powder			Density gm/ml at 25°C
ppm H_2O	L_s	Remarks	ppm H_2O	L_s	Remarks	
<15	2.3×10^{-4}		<15	1.3×10^{-5}	solution pale green	1.08
LiCl soluble			25	2.5×10^{-5}		1.12
LiCl very soluble			<15	2.2×10^{-6}	solution yellow	1.10
690	7.7×10^{-5}		<15	1.4×10^{-5}	solution yellow ppt. gray	0.98
			<15	1.0×10^{-5}	solution clear ppt. gray treated at -15°C	
		NT		1.3×10^{-2}	solvent dark red	1.10 initially
		NT	<15	1.6×10^{-2}	solvent yellow-brown	1.10 initially
200	3.4×10^{-4}		50	2.2×10^{-5}		1.19
		NT	430	4.8×10^{-3}		1.34 init.
		NT	200	4.0×10^{-3}		and finally

TABLE VII

DESCRIPTION OF MATERIALS USED IN THE WATER REMOVAL STUDIES

SOLVENT	SOURCE	CAT. NO.	REMARKS
Acetic Anhydride (ACAN)	Fisher Scientific Company	A-10	certified reagent
Butyrolactone (BL)	General Aniline & Film Corp. (Antara)		special sample for LEC
Butyrolactone (BL)	Aldrich Chemical Company, Inc.		special sample for LEC
Butyrolactone (BL)	Matheson Coleman & Bell	BX2185	special sample for LEC
Propylene Carbonate (PC)	Eastman Organic Chemicals		practical grade
Propylene Carbonate (PC)	Jefferson Chemical Co., Inc.		special sample for LEC
Propylene Carbonate (PC)	Matheson Coleman & Bell	PX1705	special sample for LEC
Dimethyl Sulfoxide (DMSO)	Crown Zellerbach		sample
Dimethyl Sulfoxide (DMSO)	Fisher Scientific Company	D-128	certified reagent
Methyl Formate (MF)	Matheson Coleman & Bell	MX1040	spectroquality reagent

OTHER	SOURCE		REMARKS
$LiClO_4$ (anhydrous)	Foote Mineral Company		special for LEC
Li dispersion in hexane	Foote Mineral Company	lot #410-11	partical size $\leq$100 microns
LiCl	Fisher Scientific Company	cat. #121	certified reagent
CaO (high Ca)	G. & W.H. Corson, Inc.		special for LEC
CaO · MgO	G. & W.H. Corson, Inc.		

2.2. POSITIVE ACTIVE MATERIAL STUDIES

In preparation for cell tests of various possible cathode reactants, the chemical stability of the materials in propylene carbonate and methyl formate electrolyte solutions was tested. The thirteen materials, together with the source and manufacturer's grade designation, are listed in Table VIII.

TABLE VIII

MATERIALS USED IN COMPATIBILITY TESTS

Material		
NiF_2	Varlacoid Chem. Co., 116 Broad St., N. Y.	Anhyd.
AgF_2	City Chemical Corp., New York, N. Y.	Tech.
MnF_3	Harshaw Chemical Co., Cleveland, Ohio	Tech.
V_2O_5	Fisher Scientific Co., Fair Lawn, N. J.	Reagent
I_2O_5	K & K Laboratories, Plainview, N. Y.	---
Ag_2O_2	City Chemical Corp., New York, N. Y.	Purified
Li_2O_2	Foote Mineral Company, Exton, Pa.	---
NaO_2	MSA Research Corp., Callery, Pa.	---
CrO_3	Merck & Company, Inc., Rahway, N. J.	N. F. X.
KO_2	MSA Research Corp., Callery, Pa.	---
TICA*	FMC Corp., New York, N. Y.	100%
KDIC**	FMC Corp., New York, N. Y.	100%
AgCl	Fisher Scientific Co., Fair Lawn, N. J.	Reagent

* Trichloroisocyanuric acid
** Potassium dichloroisocyanurate

Only initial, short contact period stability tests were considered necessary to eliminate potentially hazardous combinations from cell tests. The tests were performed in stoppered test tubes under argon atmosphere. About 100 milligrams of the material was placed in the test tube, and 4 milliliters of the solvent were added.

After observing the test samples for 24 hours, lithium perchlorate was added to the test tubes to give a solute concentration of about 1.5 moles per liter. The samples were manually agitated, and visual observation of the systems was continued for another 24 hour period.

Results of the compatibility tests are presented in Table IX, page 35. Of the thirteen materials tested, two were eliminated from further consideration. Chromium trioxide was found to be strongly soluble in both solvents and the potassium superoxide-methyl formate mixture was pyrophoric. Except for AgF_2, which changed from brown to yellow in methyl formate, the remaining material appeared to be compatible with the electrolyte solution.

Electrodes were constructed from all the materials which were adjudged compatible with the electrolyte solvents. The standard electrode construction method was modified because of the instability of some of the test materials. Perchloroethylene was substituted for heptane as the mixing solvent, and asbestos filter fiber was substituted for polyethylene-coated cellulose. Mixes having the composition

active material	3 grams
Dixon graphite	1.5 grams
Perchloroethylene	25 ml

were blended in a micropulverizer (Hi-Speed) for 10 seconds. The resulting slurry was thinned with additional perchloroethylene and 0.5 grams of acid-washed asbestos fibers (powminco) were added. The mixture was suction-filtered on a 55mm I. D. Buchner funnel, pressed at 10 psi, and vacuum dried.

TABLE IX

COMPATIBILITY OF POSSIBLE CATHODE ACTIVE MATERIALS IN PROPYLENE CARBONATE AND METHYL FORMATE ELECTROLYTES

		No Solute		1.5M $LiClO_4$	
		MF	PC	MF	PC
1.	CuF_2	N.R.	N.R.	N.R.	N.R.
2.	NiF_2	N.R.	N.R.	N.R.	N.R.
3.	AgF_2	R.	N.R.	---	N.R.
4.	MnF_3	N.R.	N.R.	N.R.	N.R.
5.	V_2O_5	N.R.	N.R.	N.R.	N.R.
6.	I_2O_5	N.R.	N.R.	N.R.	N.R.
7.	Ag_2O_2	N.R.	N.R.	N.R.	N.R.
8.	Li_2O_2	N.R.	N.R.	N.R.	N.R.
9.	NaO_2	N.R.	N.R.	N.R.	N.R.
10.	KO_2	Pyr.	N.R.	---	N.R.
11.	CrO_3	Sol.	Sol.	---	---
12.	TICA*	Sol.	N.R.	---	N.R.
13.	KDIC**	N.R.	N.R.	N.R.	N.R.

*Trichloroisocyanuric acid
**Potassium dichloroisocyanurate

CODE

N.R. - no reaction
Sol. - soluble
R. - reactive
Pyr. - pyrophoric

In general, the resulting filter mats had poor strength and coherence, and some electrodes had to be discarded (two mats had been prepared for each material). The remaining mats were assembled in two-plate cells with a lithium anode and 0.04 inch MPR separation. Expanded silver was used as the connector for both anode and cathode, and heat-sealed polypropylene envelopes were used for the external case. The cross-sectional area of the electrodes was 30 cm^2.

Cells with methyl formate electrolyte (25 grams $LiClO_4$/100 ml MF) were tested at a discharge current of 22 mA and a temperature of -15°C. Results of the discharge are presented in Table X.

TABLE X

DISCHARGE CHARACTERISTICS OF VARIOUS CATHODE MATERIALS AGAINST LITHIUM IN METHYL FORMATE ELECTROLYTE

Cell Potential, Volts

Time, hrs.	CuF_2	NiF_2	I_2O_5	MnF_3	Ag_2O_2	Li_2O_2
open-circuit	3.56	3.27	3.66	3.63	3.66	2.94
0	1.95	1.75	1.25	1.15	2.75	1.25
3	1.75	1.25	0.90	0.80	2.80	1.05
6	1.80	1.05	0.80	0.65	2.75	1.00
9	1.50	1.05	0.75	0.40	2.70	0.95
12	2.10	1.05	0.70	---	2.72	0.85
15	2.00	1.05	0.45	---	2.70	0.80
18	2.00	1.05	---	---	2.67	0.70
21	1.85	1.00	---	---	2.60	0.55
24	1.70	1.00	---	---	1.90	---
27	1.55	1.00	---	---	1.55	---
30	1.45	1.00	---	---	1.35	---

The characteristics of the CuF_2 control cell are poor compared with other cell tests at equivalent discharge conditions. This indicates that an optimum electrode and cell construction had not been obtained, and, therefore, the cell discharge data for the other materials probably is not representative. It should also be noted that a secondary cathode reaction sets in at about -1.5 volts S.H.E. at the current densities employed (probably caused by solvent reduction), which makes any discharge data for cells having lithium anodes of questionable value below a cell potential of about 1.5 volts. In this group of cells, silver II oxide showed the best characteristics, and its reduction efficiency to 1.90 volts was about 41 percent.

Cells activated with propylene carbonate electrolyte (15 grams $LiClO_4$/100 ml PC) were discharged at room temperature and 17 mA (except for the KO_2 cell, which ignited upon addition of the electrolyte solution). With the exception of TICA, all of the cells polarized severely under this load, and the discharge was terminated after 1.5 hours. After a recovery period of 3.25 hours, the open-circuit potentials of the cells were recorded, and discharge was continued at 11 mA. The open-circuit potential and discharge characteristics for the cells having PC electrolyte are listed in Table XI.

TABLE XI

DISCHARGE CHARACTERISTICS OF VARIOUS CATHODE MATERIALS AGAINST LITHIUM IN PROPYLENE CARBONATE ELECTROLYTE

Discharge Current: 17 mA

	CuF_2	NiF_2	MnF_3	Ag_2O_2	I_2O_5	TICA
Initial o.c. Potential	3.60	3.32	3.61	3.64	3.61	3.84
Load Potential after 1.5 hrs. at 17 mA	2.45	1.85	0.75	2.55	0.95	3.45
o.c. Potential after 3.25 hrs. of recovery	3.31	2.76	2.50	3.31	1.78	3.70*

* Immediately after termination of discharge, o.c. potential decreased to 3.5 volts after 3.25 hours of recovery.

TABLE XI (Continued)

DISCHARGE CHARACTERISTICS OF VARIOUS CATHODE MATERIALS AGAINST LITHIUM IN PROPYLENE CARBONATE ELECTROLYTE

Cell Potential, Volts
Discharge Current at 11 mA

Time, hrs.	CuF_2	NiF_2	MnF_3	Ag_2O_2	I_2O_5	TICA
0	2.50	2.00	1.00	2.70	1.30	1.80
3	2.40	1.75	0.65	2.45	0.70	1.70
6	2.35	1.50	0.60	2.35	0.70	1.50
9	2.30	1.25	0.60	2.30	0.70	1.30
12	2.25	1.30	0.60	2.20	0.70	0.80
18	2.20	1.25	---	2.10	---	---
30	2.10	1.30	---	2.10	---	---
38	2.05	1.25	---	2.05	---	---
50	1.85	1.10	---	1.95	---	---
62	1.80	0.90	---	1.25	---	---
68	1.75	0.75	---	0.60	---	---
80	1.65	0.55	---	---	---	---

As was observed with methyl formate electrolyte, the discharge potential of the control cell (CuF_2) was abnormally low at the current density employed, making the discharge data for the other cells of questionable significance. However, some tentative conclusions may be made from the data obtained for the two electrolyte systems:

1. The superoxides are pyrophoric with both electrolytes tested.

2. Iodine pentoxide, lithium peroxide and manganese trifluoride show little activity as cathodes.

3. Silver II oxide shows strong cathodic activity.

4. Trichloroisocyanuric acid shows a high open-circuit potential and good initial discharge characteristics, but is too soluble for prolonged discharge.

5. The open-circuit potential of the cells is masked by the presence of graphite in the cathode mix. This is particularly true if the material being tested has poor cathodic activity.

A new set of electrodes was being manufactured at the end of the quarter for the continuation of positive active material studies.

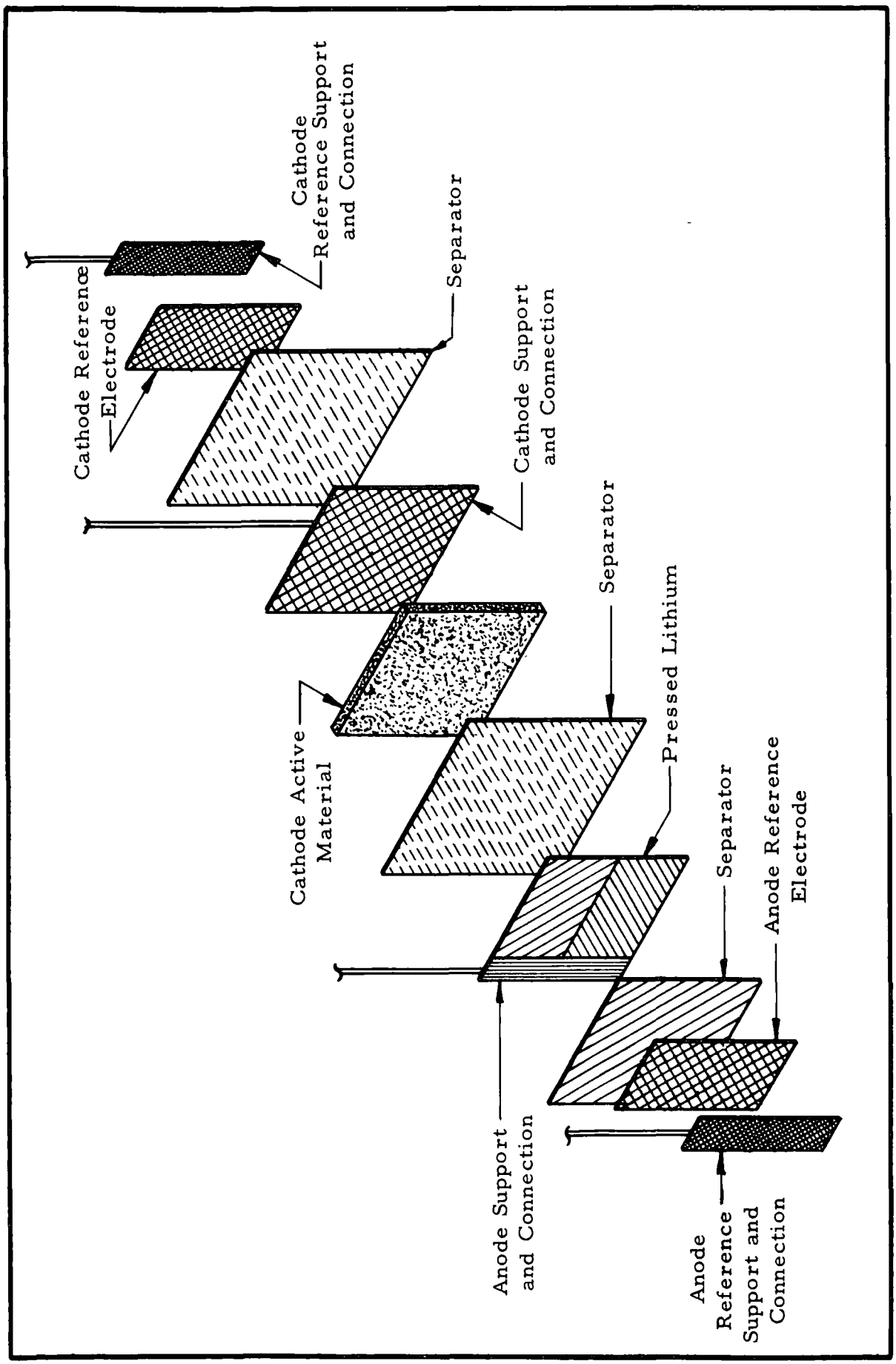
2.3. "RESEARCH CELL" TESTS

The $Li/PC:LiClO_4/CuF_2$ system was studied by discharging cells built with two working and two reference electrodes as shown in Figure 1, page 42, which were assembled in polyethylene envelope. The components of the cell were assembled in a polyethylene envelope, which was placed between rigid blocks for latteral support. The cells were tested on the "Research Recorder" apparatus described in earlier reports. The reference electrodes in the cells were identical in composition to the working electrodes, (Reference: Final Report NASA CR-54083) i.e., Li at the negative electrode and CuF_2 at the positive electrode of the working cell. The electrodes were separated by 1.1 mm thick microporous rubber sheet having a cross-sectional area of about 15 cm^2. The positive working electrode, which was prepared by the filter mat method described in Section 2.4, page 47, had a capacity of approximately one ampere hour.

The cells were discharged at an average current of 8 mA (16 mA, 1 mA per cm^2, for 11 seconds, open-circuit for 11 seconds). The potentials of the electrodes during the discharge are plotted versus the negative reference electrode in Figures 2 and 3, pages 43 and 44.

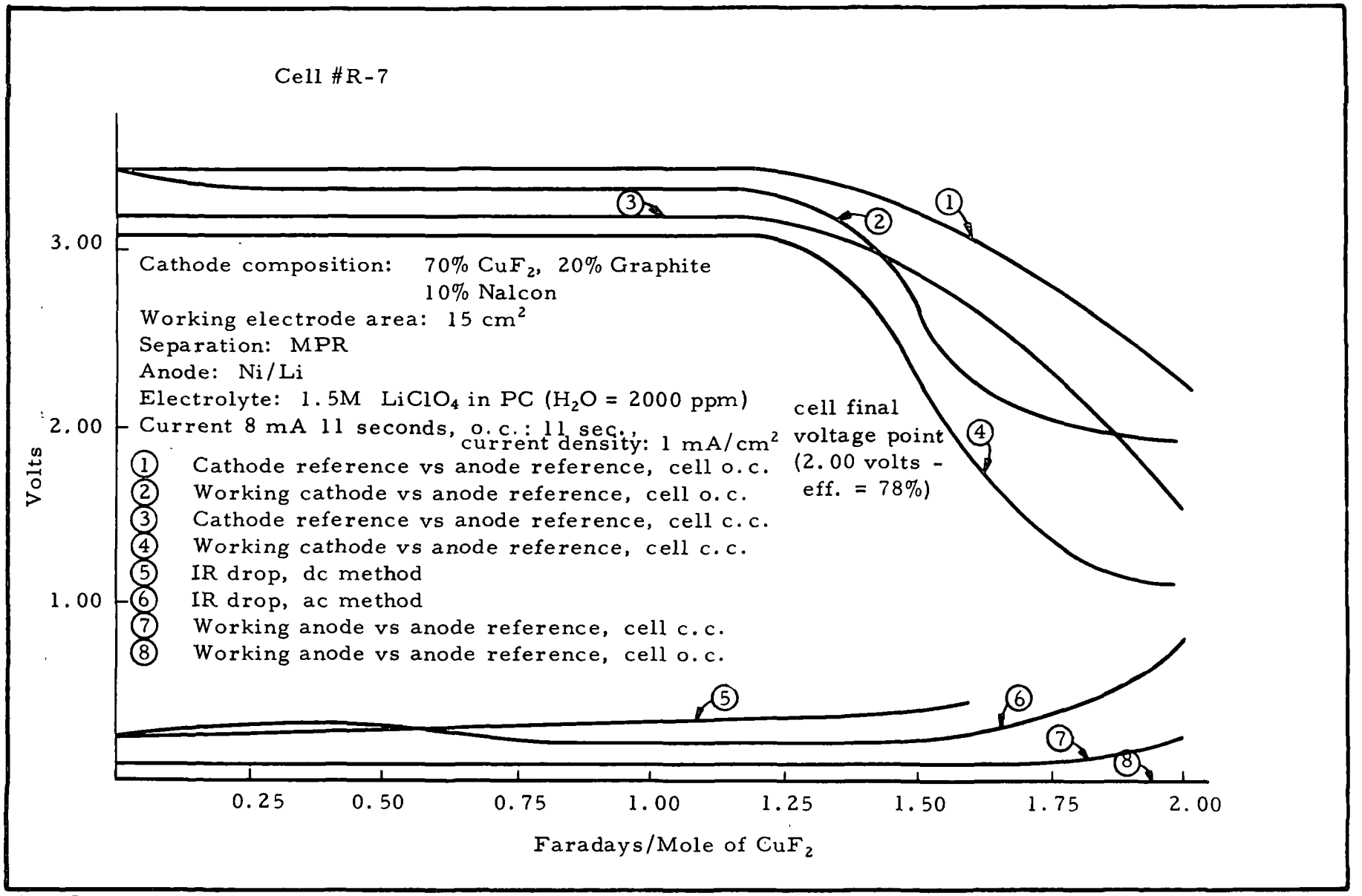
At various points during the discharge, the voltage-current relationship between the working electrodes was determined. Results of these tests are presented in Figures 4 and 5, pages 45 and 46. The change in the apparent cell resistance could be estimated from the slope of the cell polarization-current curves.

The potential-time curves for the two cells indicated that the positive electrodes limitated the cell capacity. The electrochemical efficiency of the CuF_2 electrodes to a polarization of about 1.0 volts was 78 and 85 percent for Cells R-7 and R-8, respectively. This compares favorably with results obtained previously (61 percent efficiency) on positive efficiency tests in R-cells.



EXPLODED VIEW OF R-CELL CONSTRUCTION

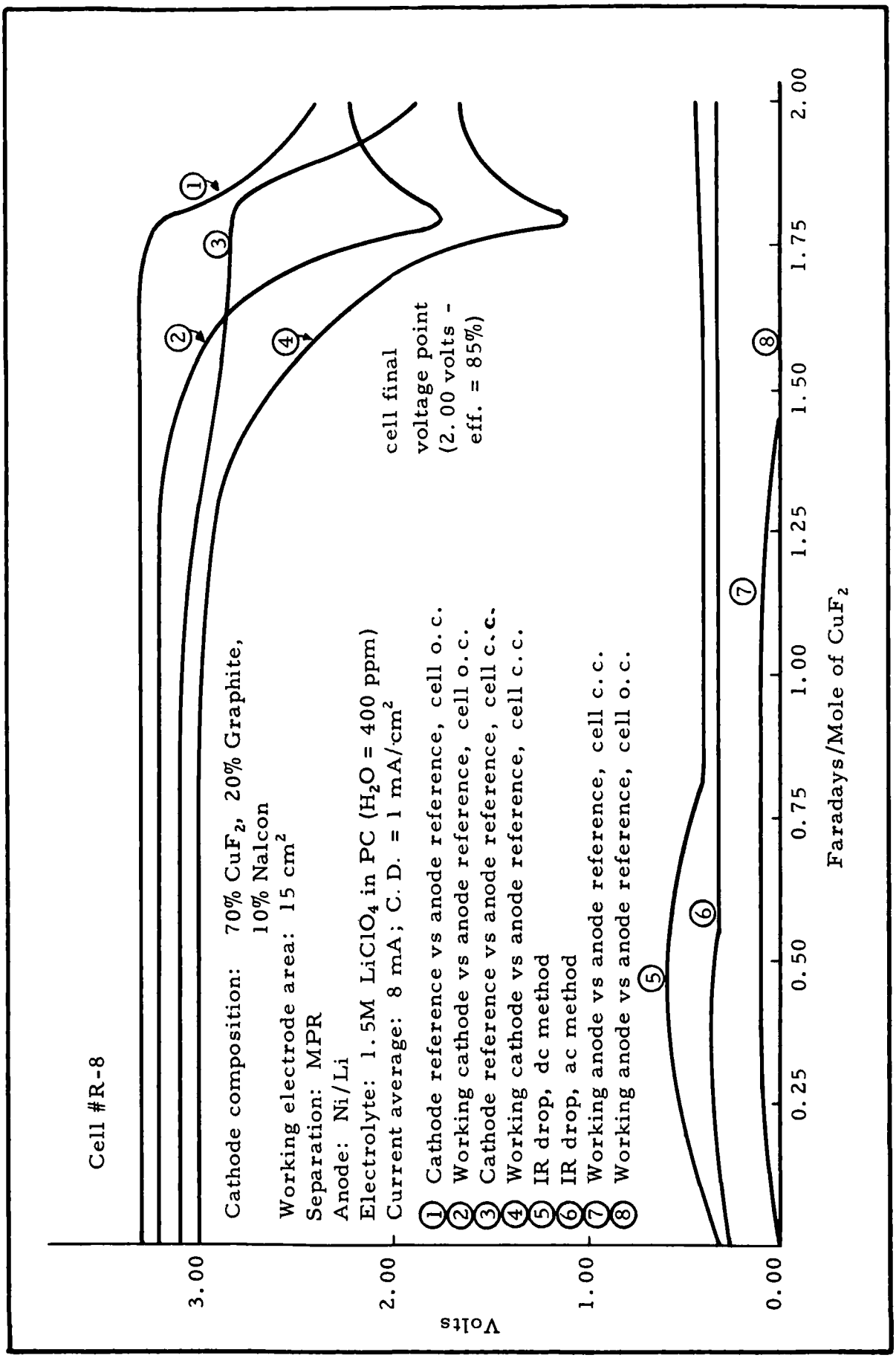
FIGURE 1



FORM FM-101

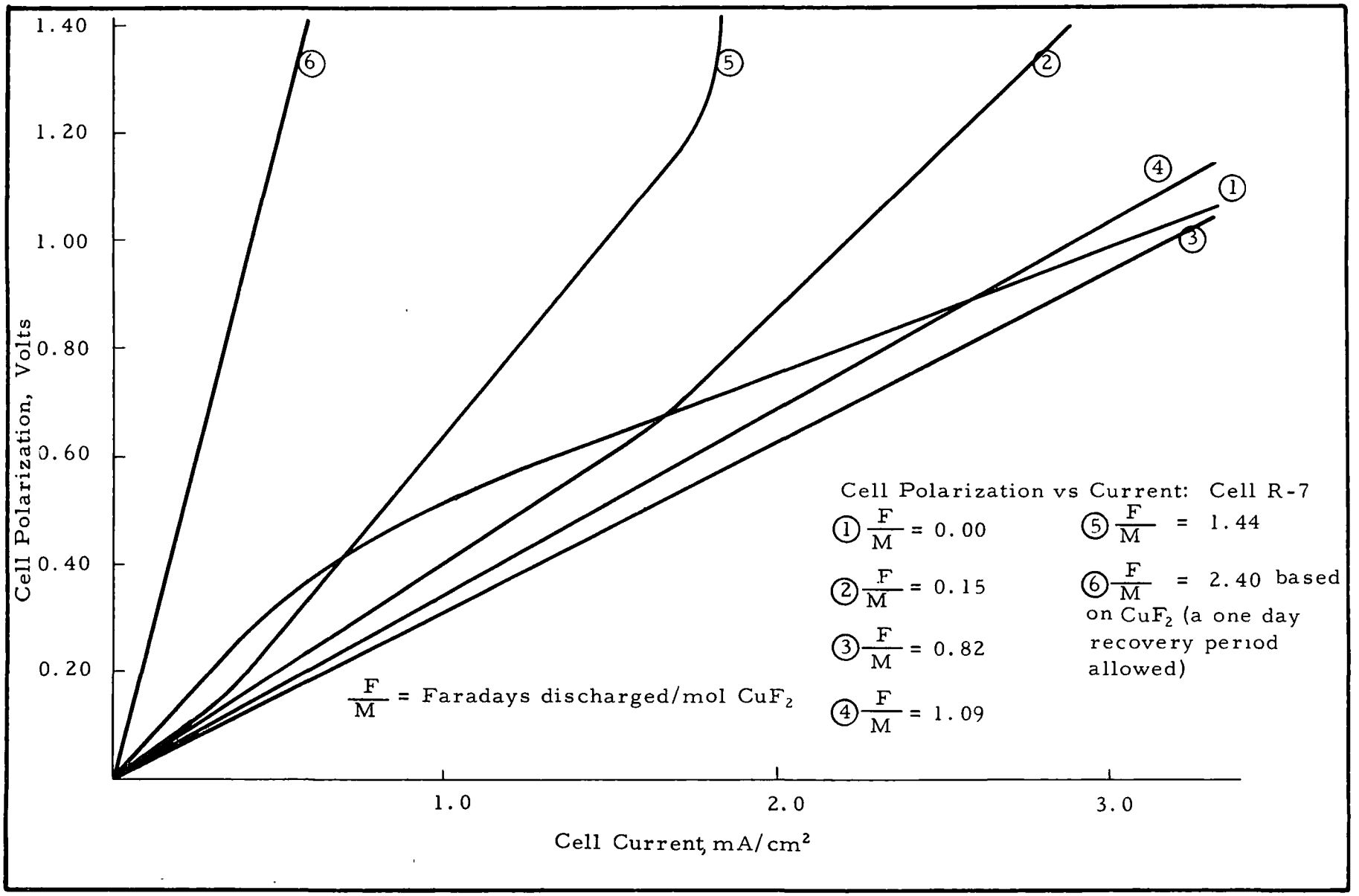
DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL WITH PROPYLENE CARBONATE SOLVENT

FIGURE 2



DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL WITH PROPYLENE CARBONATE SOLVENT

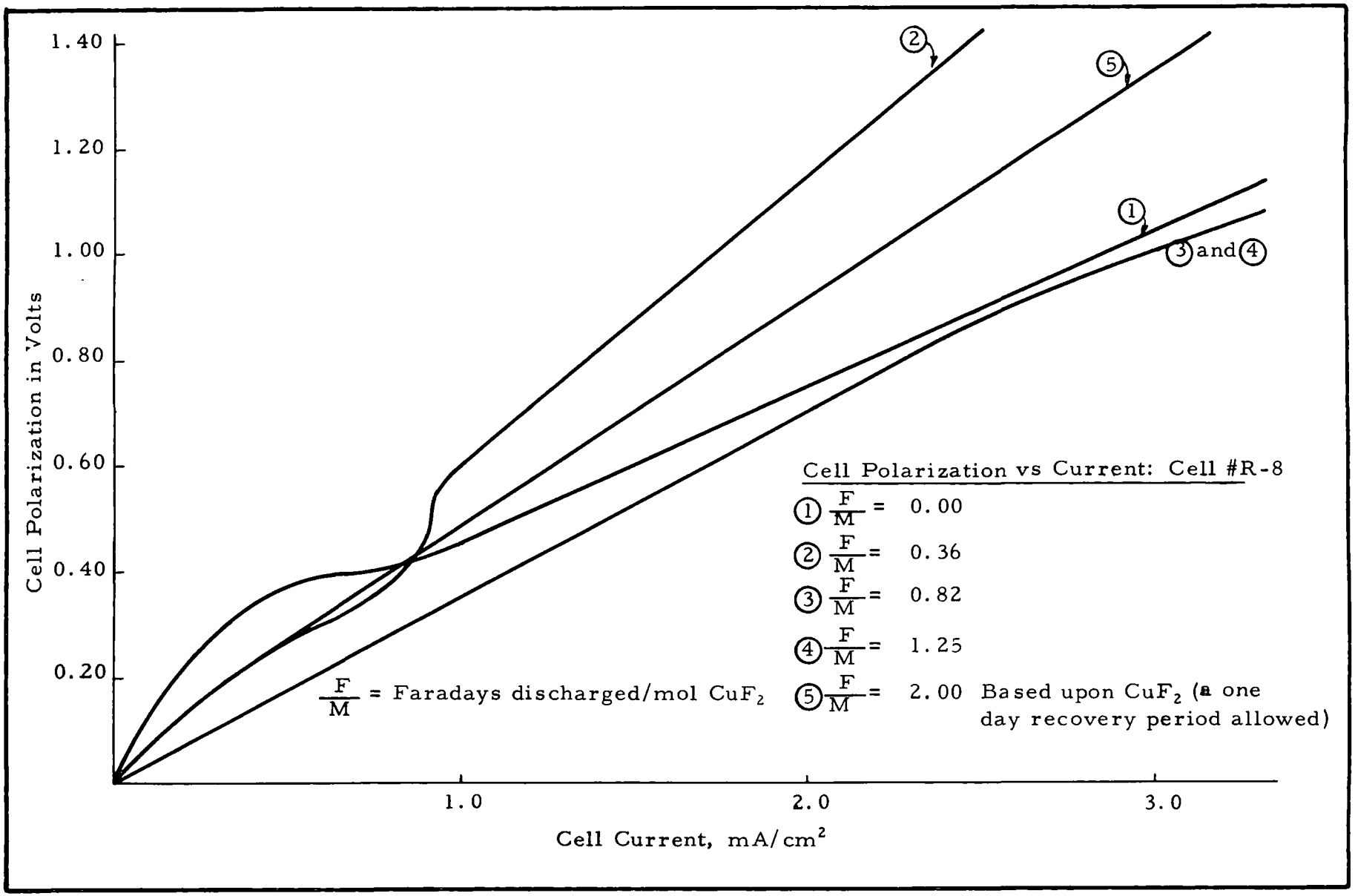
FIGURE 3



FORM FM-101

CELL POLARIZATION VERSUS CURRENT AT VARIOUS DEPTHS OF DISCHARGE

FIGURE 4



FORM FM-101

CELL POLARIZATION VERSUS CURRENT AT VARIOUS DEPTHS OF DISCHARGE

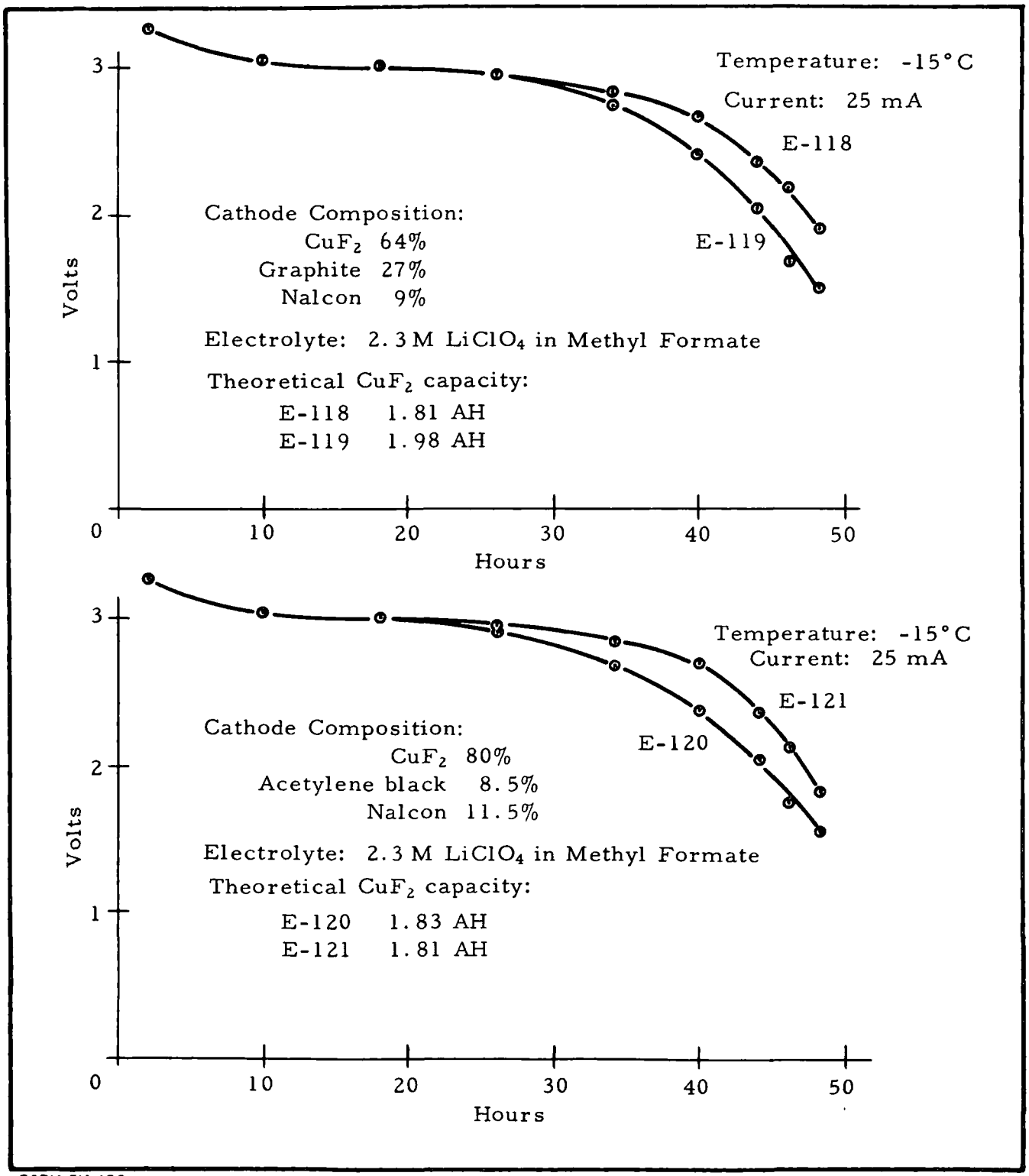
FIGURE 5

2.4. "EXPERIMENTAL CELL" TESTS

During the third quarter, study of the filter mat CuF_2 electrode construction was continued, and results of 76 cell discharge tests are reported in this section. The objective of these tests was to develop an electrode structure having a high ratio of active-to-inactive material weights and permitting a high level of active material utilization.

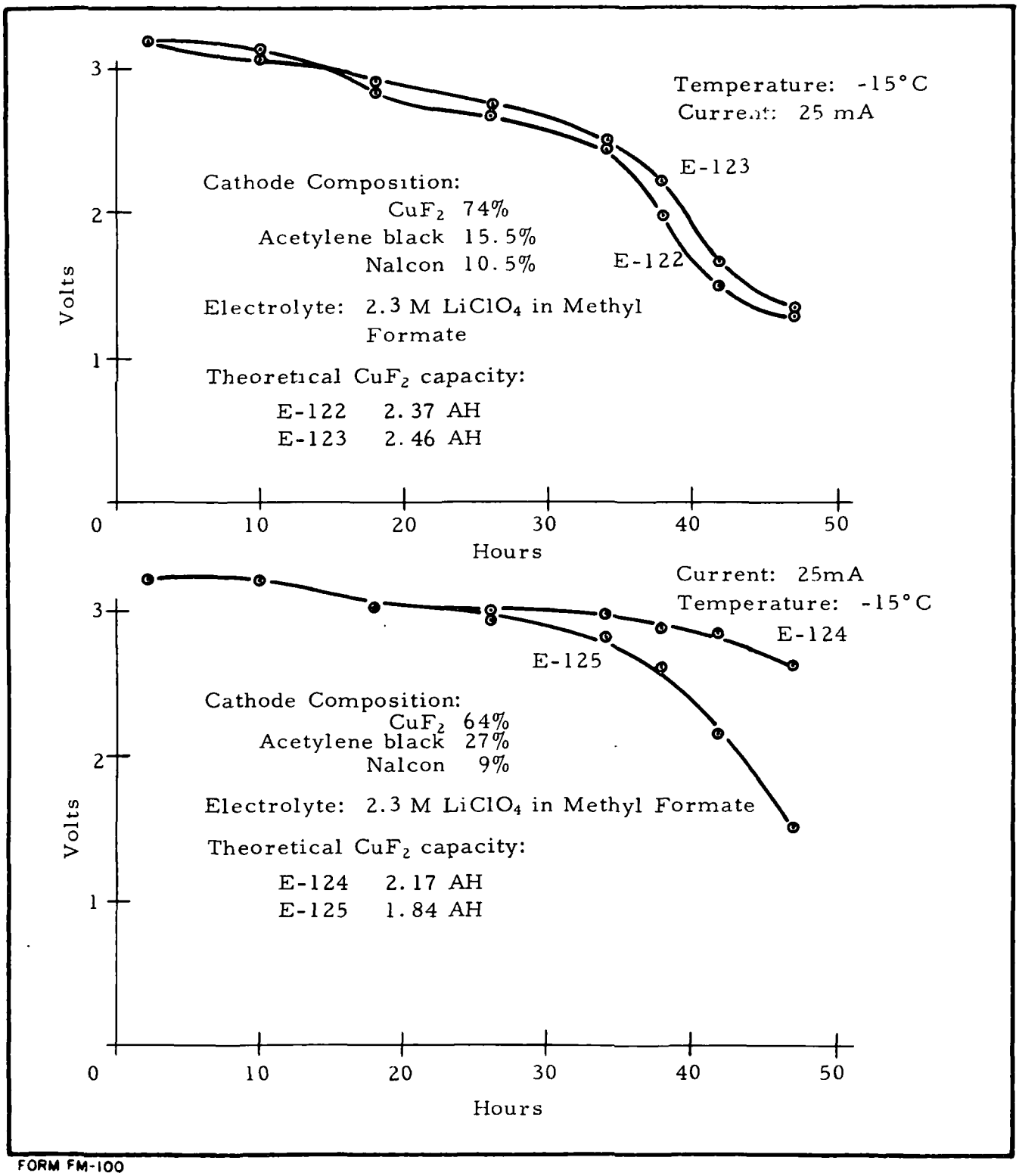
The CuF_2 was jar-milled under heptane for 16 to 20 hours, blended with the additives on the "Osterizer" blender for one minute, and filtered in a paper sheet mold. The filter mat was then pressed at 60 psig between flat plates. Electrodes having dimensions of 1.5 x 1.5 inches were cut from the sheet, and the heptane was removed by vacuum drying. The electrodes were tested by constructing three-plate cells with outside lithium negatives. The theoretical capacity of the CuF_2 electrode was about 2 ampere hours, while the combined capacity of the lithium electrodes was about 6 ampere hours. The materials which were studied as the component of the filter mat included graphite, acetylene black, and nickel flake (battery type) as conductors, and Nalcon and asbestos fibers as binders.

Results of the comparative cell discharge tests are presented in Table XII and XIII, pages 55 and 57. The discharge characteristics of some typical cells are presented in Figures 6 to 10, pages 48 to 52. Although the agreement between replicate cells in the above test series was fairly good, no direct correlation emerges between the concentrations of the various additives and the cell performance. The efficiency figures indicate that 80 percent and higher fractions of the filter mat can be CuF_2 without adversely affecting the performance of the electrode. Also, doubling the concentration of $LiClO_4$ in methyl formate from 25 grams per 100 ml of solvent to 50 grams per 100 ml of solvent appeared to improve cell characteristics.



CHARACTERISTICS OF Li-CuF_2 CELLS

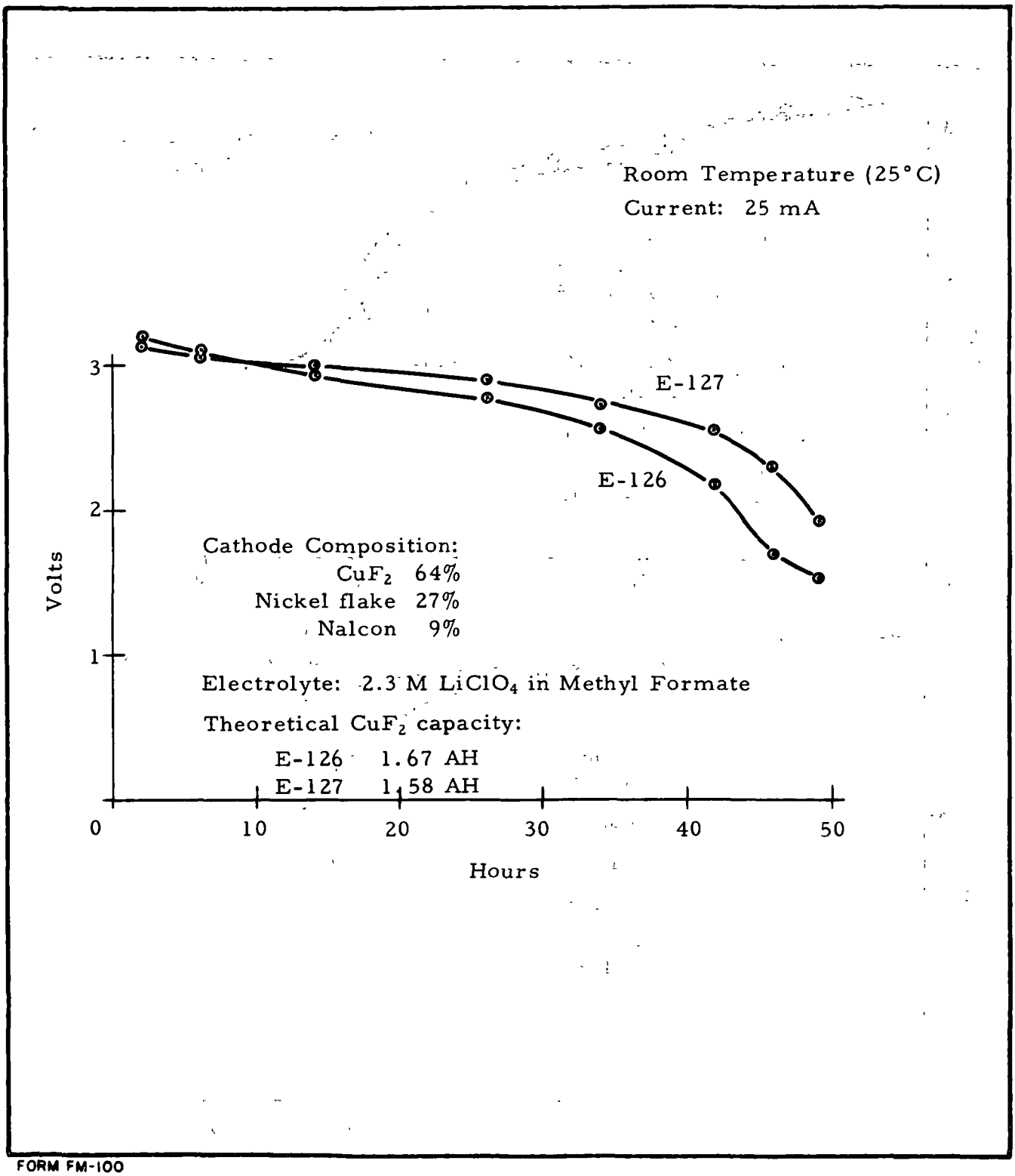
FIGURE 6



FORM FM-100

CHARACTERISTICS OF Li-CuF_2 CELLS

FIGURE 7



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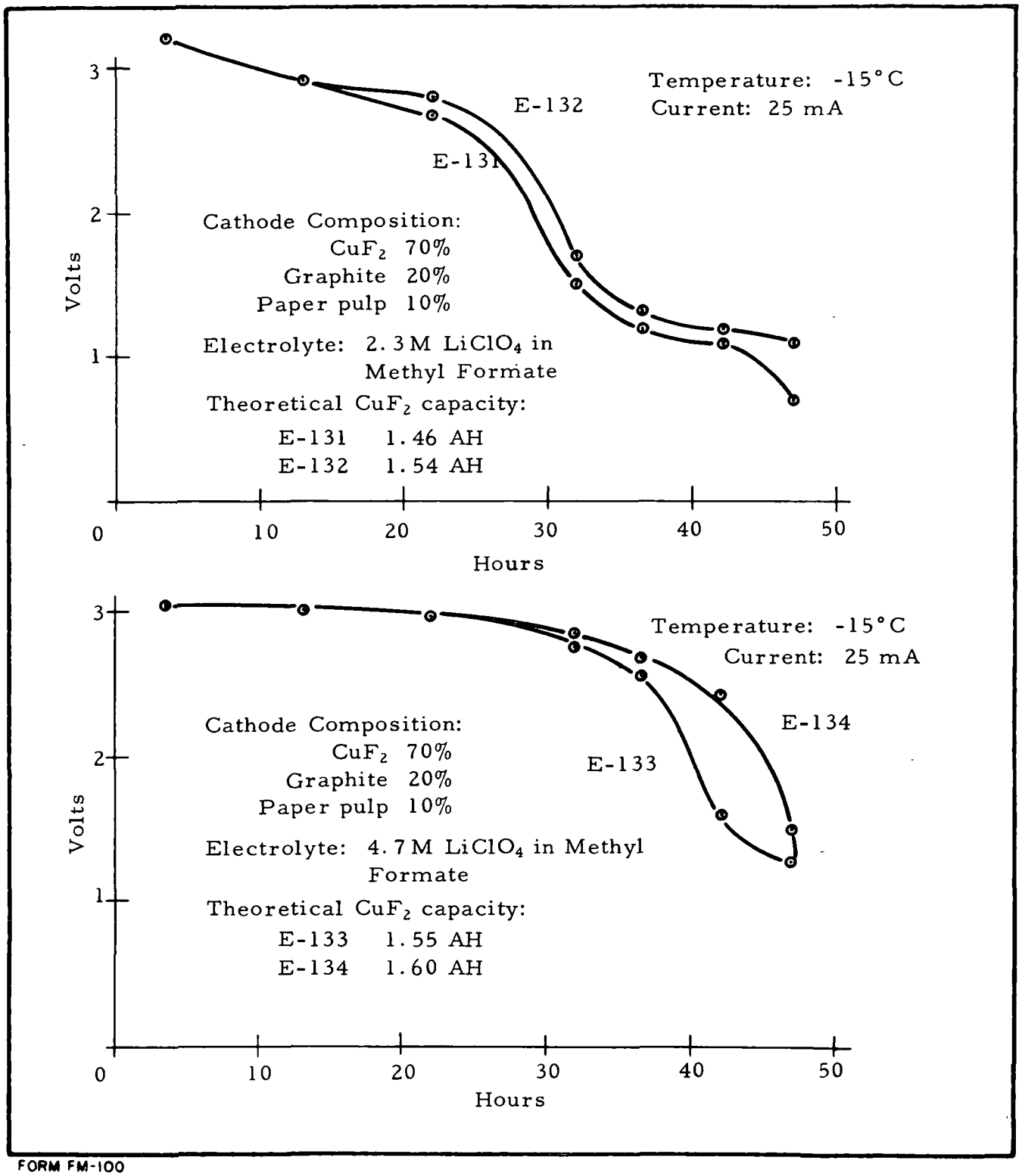
CHARACTERISTICS OF Li-CuF_2 CELLS

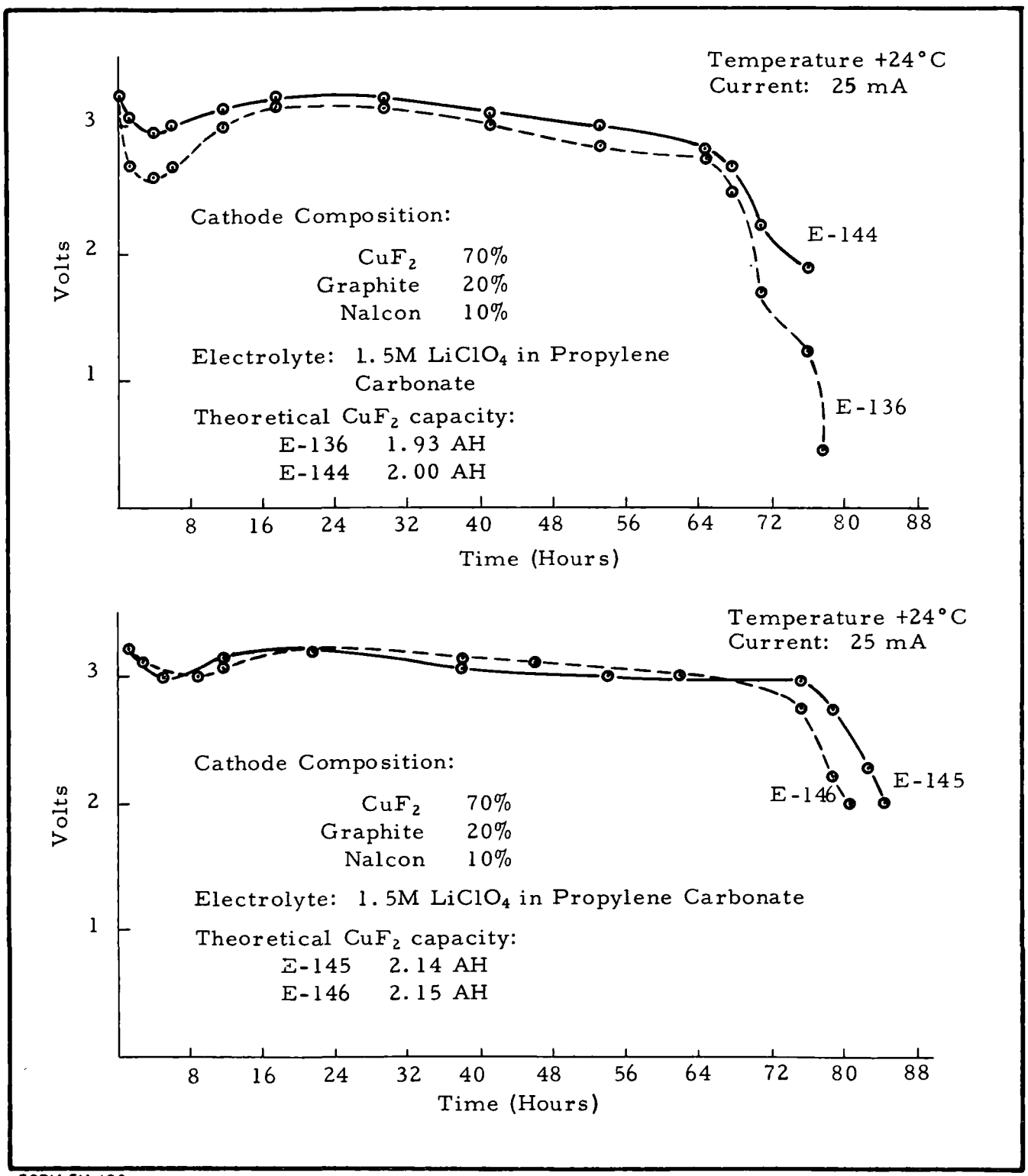
FIGURE 8



FORM FM-100

CHARACTERISTICS OF Li-CuF_2 CELLS

FIGURE 9



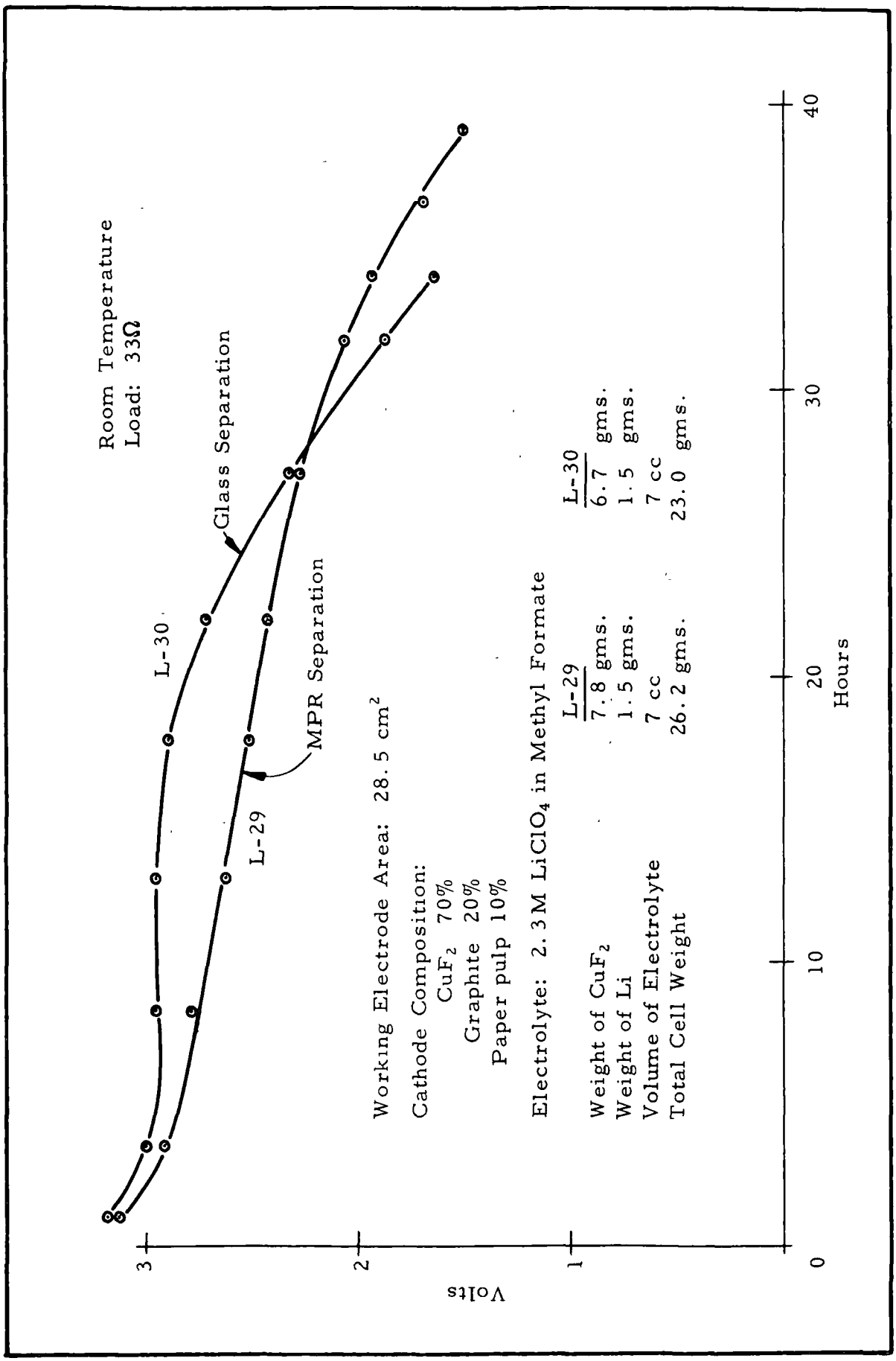
FORM FM-100

CHARACTERISTICS OF Li-CuF_2 CELLS

FIGURE 10

At the present time, cell discharge studies are complicated by the presence of random variables which affect discharge characteristics. One of these variables is probably the presence of water as a contaminant in the materials of construction. Methods for the control of these variables still needs to be developed.

Six three-plate cells having a theoretical positive and negative electrode capacity of four and six ampere hours, respectively, were constructed and discharged to obtain an indication of the overall capability of the presently employed cell construction. The discharge curves for Cells L-29 and L-30 are presented in Figure 11, page 54. The weight of Cell L-30 was 23 grams including the weight of the polyethylene envelope. The energy-to-weight ratio of this cell was 156 watt hours per pound of total cell weight and 417 watt hours per pound of electrode reactants to a final voltage of 1.5 volts. These figures correspond, respectively, to about 21 and 58 percent of the theoretical energy capacity of the CuF_2-Li couple (720 watt hours per pound). This cell represents the best result in terms of energy-to-weight ratio obtained on this program.



CHARACTERISTICS OF Li-CuF_2 CELLS

FIGURE 11

TABLE XII

EFFECT OF ADDITIVES ON THE PERFORMANCE OF FILTER-MAT CuF_2 ELECTRODES IN METHYL FORMATE - TEMPERATURE: -15°C

Discharge Current: 25 mA (1 mA/cm^2)

	Composition, percent								
Cell No.	CuF_2	GR	AB	NF	NA	Theo. AH	AH/2VF	% eff.	AH/g filter mat
E-118	64	27	---	---	9	1.81	1.19	65.7	.220
E-119	64	27	---	---	9	1.98	1.08	54.5	.200
E-120	80	--	8.5	---	11.5	1.83	1.11	60.6	.255
E-121	80	--	8.5	---	11.5	1.81	1.18	65.2	.274
E-122	74	--	15.5	---	10.5	2.37	1.00	42.3	.164
E-123	74	--	15.5	---	10.5	2.46	0.93	37.8	.148
E-124	64	--	27.	---	9	2.18	1.50	68.8	.231
E-125	64	--	27	---	9	1.85	1.07	57.8	.195
E-126*	64	--	---	27	9	1.67	1.10	65.7	.222
E-127*	64	--	---	27	9	1.58	1.23	77.8	.262

Legend

GR - Graphite
AB - Acetylene Black
NF - Nickel flake
NA - Nalcon
A - Asbestos

*Room Temperature

TABLE XII Continued

EFFECT OF ADDITIVES ON THE PERFORMANCE OF FILTER-MAT CuF_2 ELECTRODES IN METHYL FORMATE - TEMPERATURE: -15°C

Discharge Current: 25 mA (1 mA/cm^2)

	Composition, percent									
Cell No.	CuF_2	GR	AB	NF	A	NA	Theo. AH	AH/2VF	% eff.	AH/g filter mat
E-155	70	20	---	---	---	10	1.68	1.06	63	.232
E-156	70	20	---	---	---	10	2.24	1.47	66	.242
E-157	70	20	---	---	10	--	2.13	1.30	61	.225
E-158	70	20	---	---	10	--	2.23	1.33	60	.220
E-159	70	20	---	---	---	10	2.19	1.66	76	.279
E-160	70	20	---	---	---	10	2.01	1.59	79	.292
E-161	78	11	---	---	---	11	2.32	1.19	51	.211
E-162	78	11	---	---	---	11	2.12	..665	31	.129
E-163	78	--	11	---	---	11	2.43	---	--	---
E-164	78	--	11	---	---	11	2.29	1.32	58	.237
E-165	82.5	--	5.9	---	---	11.6	2.92	1.66	57	.247
E-166	82.5	---	5.9	---	---	11.6	2.82	1.24	44	.191
E-167	78	--	5.5	5.5	---	11	1.94	1.19	61	.253
E-168	78	--	5.5	5.5	---	11	1.85	1.01	55	.225
E-169	82.5	--	3.4	2.5	---	11.6	2.45	1.59	65	.282
E-170	82.5	--	3.4	2.5	---	11.6	2.24	1.10	49	.214

TABLE XIII

EFFECT OF ADDITIVES ON THE PERFORMANCE OF FILTER MAT CuF_2 ELECTRODES IN PROPYLENE CARBONATE - ROOM TEMPERATURE

Discharge Current: 17 mA (.5 mA/cm²)

Cell No.	Composition, percent					Theo. AH	AH/2VF	% eff.	AH/g filter mat
	CuF_2	GR	AB	NF	NA				
E-135	70	20	--	--	10	2.11	1.18	56	.206
E-136	70	20	--	--	10	1.93	1.18	61	.226
E-137	78	11	--	--	11	2.45	1.32	54*	.221
E-138	78	11	--	--	11	2.38	1.08	45.5	.186
E-139	78	--	11	--	11	2.37	1.11	47	.192
E-140	78	--	11	--	11	2.53	1.05	41.5	.169
E-141	82.5	--	5.9	--	11.6	2.34	.620	26.5	.115
E-142	82.5	--	5.9	--	11.6	2.32	.660	28.5	.124
E-143	70	20	--	--	10	1.78	1.05	59	.216
E-144	70	20	--	--	10	2.00	1.21	60.5	.223
E-145	70	20	--	--	10	2.14	1.35	63	.232
E-146	70	20	--	--	10	2.15	1.29	60	.221
E-147	78	11	--	--	11	2.24	1.05	47	.193
E-148	78	11	--	--	11	1.91	.99	52	.213
E-149	78	--	11	--	11	2.63	1.25	48	.195
E-150	78	--	11	--	11	2.56	1.09	43	.175

*2.6 VF

TABLE XIII Continued

EFFECTS OF ADDITIVES ON THE PERFORMANCE OF FILTER MAT CuF_2 ELECTRODES IN PROPYLENE CARBONATE - ROOM TEMPERATURE

Discharge Current: 17 mA (.5 mA/cm²)

	Composition, percent									
Cell No.	CuF_2	GR	AB	A	NF	NA	Theo. AH	AH/2VF	% eff.	AH/g filter mat
E-151	82.5	---	5.9	--	--	11.6	2.48	.755	30	.133
E-152	82.5	---	5.9	--	--	11.6	2.21	.773	34	.152
E-153	78	---	5.5	--	5.5	11	1.97	.93	47	.194
E-154	78	---	5.5	--	5.5	11	1.81	.64	35	.145
E-171	70	20	--	10	--	---	1.85	0.98	53	.196
E-172	70	20	--	10	--	---	2.00	1.12	56	.207
E-173	70	20	--	--	--	10	1.87	1.12	60	.221
E-174	70	20	--	--	--	10	1.88	1.14	60.7	.224
E-175	80	13	--	7	--	---	2.07	1.07	51.6	.218
E-176	80	13	--	7	--	---	2.49	0.62	24.9	.105
E-177	70	20	--	10	--	---	2.19	1.00	45.7	.169
E-178	70	20	--	10	--	---	2.19	1.16	53	.196
E-179	70	20	--	--	--	10	1.99	1.24	62.4*	.230
E-180	70	20	--	--	--	10	2.20	1.43	65	.241
E-181	80	13	--	7	--	---	2.56	1.79	70	.293
E-182	80	13	--	7	--	---	2.38	.095	--	---

*2.15 VF

Legend

GR - Graphite
AB - Acetylene Black
A - Asbestos
NF - Nickel flake
NA - Nalcon

3. ACTIVITY PLANNED FOR THE FOURTH QUARTER

During the last quarter of the current contract period, the following tasks will be pursued:

1. Since water appears to be a singularly important contaminant in the organic cell systems, studies of water removal methods from the organic electrolytes will be continued. The effect of the water concentration on cell discharge characteristics will be evaluated.

2. The studies of candidate positive active materials started during the past quarter will be continued. The materials will be used to construct experimental cells using lithium anodes and methyl formate and propylene carbonate electrolyte solvents.

3. The development of filter-press mat CuF_2 electrodes will be continued. In addition, the feasibility of constructing and discharging cylindrical CuF_2-Li cells will be studied.

4. Prototype batteries will be constructed and tested according to the provisions of the contract.

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Attention: Dr. A. Langer