NASA CR-54803

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

FINAL REPORT

June 10, 1964 to June 9, 1965

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6004

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LIVINGSTON ELECTRONIC CORPORATION

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ABSTRACT

Studies of electrolyte solutions, electrode reactants and construction, cell manufacture, and discharge properties were conducted toward the development of high energy density, lithium-anode primary cells. Propylene carbonate showed least attack on metallic lithium among the solvents studied. Methyl formate formed the most conductive solution with $LiClO_4$ (2.6×10^{-2} ohm^{-1} cm^{-1} at 25 grams/100 ml). In cell tests, copper fluoride was the best cathode material; with propylene carbonate, active material utilization was in excess of 80 percent at 0.5 mA/cm^2.

Thirty CuF_2-Li prototype cells of ca. 4 AH capacity were built and discharged. A group of five cells having propylene carbonate-$LiClO_4$ electrolyte and discharging at 0.5 mA/cm^2 (ca. 250-hour rate) averaged in excess of 200 watt hours per pound of cell weight (including polyethylene cell case). The highest energy density for an individual cell was 522 watt hours per pound of active material weight and 223 watt hours per pound of total cell weight.

Author

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1. SUMMARY

Studies of electrode and electrolyte materials, and electrode and cell construction methods were conducted toward the development of primary batteries having an energy-to-weight ratio in excess of 200 watt hours per pound.

Studies of Lithium Stability

The compatibility of metallic lithium with solvents and electrolyte solutions was studied by observing changes on the surface of a lithium ribbon immersed in the test liquid. Propylene carbonate showed the the least amount of attack on the sample, whereas, butyrolactone, dimethyl sulfoxide, and acetic anhydride showed somewhat more pronounced attack. Presence of $LiClO_4$ accelerated the reaction in all systems. Methyl formate reacted with the metal more rapidly and generated pressures of over 100 psig at room temperature. The resultant solution (strongly discolored) produced little attack on a fresh piece of lithium, and less than 10 psig of pressure was generated.

Measurement of Decomposition Current

As part of the solvent evaluation program, decomposition potentials on smooth platinum electrodes were studied. The lower decomposition currents were observed in propylene carbonate (4.5μA/cm^2 at 3.95V vs Li/Li$^+$) when the anode potential was maintained below +4.0 volts with respect to a lithium reference electrode. Butyrolactone also produced low decomposition current (15 μA/cm^2 at 3.70V vs Li/Li$^+$), but N, N dimethyl formamide gave fairly high decomposition current (190 μA/cm^2 at 3.48V vs Li/Li$^+$), and appeared to react with the freshly deposited lithium at the cathode.

Solubility and Specific Conductance Measurement

The solubility and specific conductance of various salts in organic solvents were studied. Lithium perchlorate produced more conductive solutions than the other materials tested. In methyl formate, the highest specific conductance of 26 x 10^{-3}ohm^{-1}cm^{-1} was recorded at 25 grams salt/100 ml solvent. In propylene carbonate, the conductance was 4.6 x 10^{-3}ohm^{-1}cm^{-1} at 15 grams/100 ml of solvent, while at the same concentration, the specific conductance in butyrolactone was 10.6 x 10^{-3}ohm^{-1}cm^{-1}. The solubility of cathode materials in the organic solvents was also studied. Copper fluoride consistantly produced less conductive solutions than copper chloride. The smaller degree of solubility of the fluoride was further indicated by the less strongly colored solutions which resulted with this salt as compared to the $CuCl_2$ solutions.

Solvent Purification Studies

Since water was considered to be a detrimental impurity in a lithium anode cell, methods for reducing its concentration to low levels were studied. Powdered lithium was found to be the most effective drying agent (except for methyl formate-lithium perchlorate electrolytes where strong reaction occurred), producing water concentrations of less than 15 ppm (limit of sensitivity of the Karl Fischer titration).

Experimental Cell Tests

Experimental cells of various types were constructed and tested. Lithium pressed onto expanded metal screen was used as the anode material in all tests. Although several materials were studied for the construction of the cathode, copper fluoride was used most extensively in the cell tests. Electrochemical efficiency of over 80 percent was obtained from CuF_2 electrodes constructed by a filter-mat technique. In cells designed with excess negative capacity, discharges were found to be positive-limited when propylene carbonate and methyl formate solvents with $LiClO_4$ as the solute were employed as the electrolyte solution.

Prototype Cell Tests

A series of three-plate prototype cells having a theoretical capacity of about 5 ampere hours and employing heat-sealed polyethylene envelopes as the external container were constructed and discharged. The highest energy density was obtained from CuF_2-Li cells with propylene carbonate-lithium perchlorate electrolyte. At the 250-hour discharge rate (ca. 1/2 mA/cm^2) at 35° C, the best cell gave 522 watt hours per pound of active material and 223 watt hours per pound of cell weight (including polyethylene envelope). At the 100-hour rate (1 mA/cm^2), the respective figures were 387 and 154 watt hours per pound at 35° C. With methyl formate electrolyte, the highest corresponding figures obtained were 302 and 124 watt hours per pound at the 75-hour rate at -15° C (1 mA/cm^2).

2. INTRODUCTION

In order to develop batteries having high energy-to-weight ratios, cell couples having high potential and low combined equivalent weight must be employed. A search for suitable electrode and electrolyte materials for a battery system having an energy density in excess of 200 watt hours per pound was conducted during an initial one-year study (CR 54083). The present report describes the experimental work and results of the second yearly contract period (10 June 1964 to 9 June 1965) of the program.

On the basis of extensive work performed by this contractor and by other investigators, lithium emerged as the most probable negative electrode material for a high energy density system. Lithium can be oxidized at strongly negative potentials (approximately -3.0V vs S.H.E.), possesses a low equivalent weight (6.94 grams/equivalent), and can be handled more easily than other alkali metals. Lithium electrodes can be produced by shaping the malleable metal in molds, or by pressing it onto substrates of silver or nickel. As a result of these and other considerations, experimental work performed on the present contract was aimed toward the development of a primary cell system utilizing lithium as the negative active material.

Identification and study of electrolyte systems which are adequately compatible with metallic lithium became a major task of the present program. Based on the results of a series of stability tests, five solvents were selected for more intensive study, these being propylene carbonate, butyrolactone, dimethyl sulfoxide, acetic anhydride, and methyl formate.

The major portion of the electrolyte and cell tests on this program was performed using lithium perchlorate as the solute. This salt had been identified during the previous year's work as one which forms relatively conductive solutions in many of the organic solvents, and appears to be chemically stable with respect to the electrode materials of the cell.

Numerous materials had been studied on the previous program for their ability to undergo reduction in the organic electrolyte systems. In general, this work had been greatly impeded by the lack of an electrode construction technique applicable to a wide range of materials. The electrode construction method which was most extensively employed during these tests, and during the present contract period consisted of mixing the active material with small amounts of graphite and a fibrous binder. This mixture was then either pressed into a mold or a filter mat was produced using a non-aqueous solvent vehicle such as heptane.

From a large number of discharge tests performed with cells having lithium sheet anodes, experimental cathodes, appropriate electrolyte solutions, and electrode separation, anhydrous copper fluoride evolved as the most probable positive active material for the high energy system. The open-circuit potential of the CuF_2-Li couple in the organic electrolytes was observed to be approximately 3.4 volts; hence, the theoretical energy density of the couple computed from this potential and the equivalent weights of 7 for lithium and 51 for copper fluoride is 720 watt hours per pound of electrode active materials.

During the latter part of this program, efforts were expended toward improvement of the positive matrix construction in order to achieve a high degree of electrochemical utilization of the active material, and good cell voltage regulation. Since the reaction at the positive electrode probably is

$$CuF_2 + 2Li^+ + 2e^- \longrightarrow Cu^\circ + 2LiF,$$

appropriate electrode construction is needed to minimize the masking tendency of the lithium fluoride. Using the filter mat matrix construction, efficiencies of over 80 percent to a 20 percent drop in cell potential were demonstrated toward the end of the present contract period; thus, the copper fluoride-lithium couple appears to hold promise for development of a high energy density primary cell.

3. ELECTROLYTE SYSTEMS STUDIES

3.1. STUDIES OF LITHIUM METAL STABILITY IN SOLVENTS AND ELECTROLYTE SOLUTIONS

In order to be considered for use in Li-anode cells, an electrolyte solvent must posses acceptable chemical stability when placed in contact with lithium metal. For the purpose of identifying the more suitable materials for cell construction, qualitative tests of the stability of metallic lithium in various solvents and electrolyte solutions were performed. The test samples were cut from 1/2 x 1/16 inch lithium ribbon, and pressed onto expanded nickel or silver screen. The samples were submerged in glass tubes containing about 10 ml of the test solutions. The tubes were then stoppered, and changes in appearance of the Li metal and of the solution were observed and recorded at periodic intervals.

For systems in which pressure rises were produced during the test, glass tubes equipped with stainless steel couplers for connection of pressure gauges were employed. In these tests, the free volume in the tube was about equal to the volume of the test solution. A total of nineteen solvents, selected on the basis of results of previous studies and the chemical and physical nature of the materials, were used in the test series. The solvents were either "Spectroquality" grade (less than 500 ppm of water), or specially prepared for Livingston Electronic Corporation by the manufacturer; no additional treatment of materials was performed. Most of the compatibility tests were performed using either the pure solvent, or solutions of $LiClO_4$. The lithium samples used had bright metallic appearance after the protective petrolatum coating was removed by rinsing with hexane.

Results of the lithium compatibility tests are tabulated in Table I , page 6. With no solute present, several solvents showed little or no visible attack on the lithium sample as observed over a 10-day period. With $LiClO_4$ in solution, the rate of reaction was accelerated; this effect was more pronounced with some solvents (e.g., the esters) than with others. Propylene carbonate was the only solvent in the test series for which no increase in reaction rate with $LiClO_4$ was observed. Thus, on the basis of the lithium stability tests, propylene carbonate was adjudged as potentially the best solvent for low rate cells; dimethyl sulfoxide, acetic anhydride, and butyrolactone were selected as possible next choices.

Of the ester group, methyl formate showed the least amount of reactivity with lithium; however, the system with $LiClO_4$ present was metastable, and the reaction proceeded with pressure rises up to 120 psig at room temperature. It appears that this solvent will be useful only in reserve-type cells. It is likely, however, that the lithium compatibility of several of the solvents studied would be improved by redistillation or other purification procedures.

TABLE I

STABILITY OF LITHIUM METAL IN SOLVENTS AND ELECTROLYTE SOLUTIONS

Solvent	No Solute	CuF_2 (saturated)	$CuCl_2$ (saturated)	$LiClO_4$ $\left(\frac{15\text{ grams}}{100\text{ ml}}\right)$	Other Solute
Acetic Anhydride	A	D	D	C	
Acetone	F				
2-Butanone	E				
n-Butyl Formate	C			F	C-$AlCl_3$
γ-Butyrolactone	B	B	C	C	B-LiCl
Diethyl Ether at 25°C	A			F	
Diethyl Ether at -40°C	A			A	
Dimethyl Formamide	D				
Dimethyl Sulfoxide	A	A	E	B	A-LiCl
1, 2 Epoxypropane	A			D	
Ethyl Acetate	C			D	
Ethyl Acetoacetate	F				
Ethyl Formate at 25°C	E			E	
Ethyl Formate at -40°C	A			C	
67V% Ethyl Formate 33V% Diethyl Ether					
Test at 25°C	A			F	
Test at -40°C	A			B	
Methyl Acetate	D			E	
Methyl Chloroform	A				

TABLE I (Continued)

STABILITY OF LITHIUM METAL IN SOLVENTS AND ELECTROLYTE SOLUTIONS

Solvent	No Solute	CuF_2 (saturated)	$CuCl_2$ (saturated)	$LiClO_4$ $\frac{15\ \text{grams}}{100\ \text{ml}}$	Other Solute
Methyl Formate at 25°C	D			D	D-LiBr
Methyl Formate at -5°C	A			C	C-LiBr
Methyl Formate at -40°C	A			C	C-LiBr
Methyl Formate pretreated with Li powder	A			D	D-LiBr
67V% Methyl Formate 33V% Dimethyl Ether at -40°C Test at 25°C	D			D	
1-Methyl-2-Pyrrolidone	C				
Nitromethane	C	D	D	D	
Propylene Carbonate	A	B	D	A	
Pyridine	F				
Tetrahydrofuran	A	B	C	C	

Evaluation Coding:

A - no attack after 250 hours
B - moderate attack after 150 hours
C - moderate attack after 25 to 100 hours, heavy attack after 150 hours
D - moderate attack after 10 hours, heavy attack after 25 hours
E - heavy attack after 10 hours
F - heavy attack within 1 hour

3.2. MEASUREMENT OF DECOMPOSITION CURRENT ON SMOOTH PLATINUM ELECTRODES

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. The solvents were electrolyzed between smooth platinum electrodes using lithium perchlorate and other salts as the supporting electrolyte. The methods were as described in earlier reports (NASA CR-54083, pp. V-9 to V-19). Lithium metal, silver/silver chloride, and lead/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 resistance with the amount of gas absorbed by the solution is presented in Table II, page 10. Sulfur dioxide and ammonia exhibited considerable solubility in methyl formate and dimethyl formamide, respectively. Only a small reduction in specific resistance of the solutions was observed. 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 III, page 17.

At anode potentials up to +4.0 volts with respect to lithium, the lowest decomposition currents were exhibited by propylene carbonate (4.5 $\mu a/cm^2$ at 3.95 volts) and dimethyl sulfoxide (1.4 $\mu a/cm^2$ at 3.95 volts). At anode potentials of about +5 volts, dimethyl sulfoxide showed strong anodic decomposition (11,000 $\mu a/cm^2$ at 5.0 volts), while propylene carbonate remained more resistant to reduction at this anode potential (60 $\mu a/cm^2$ at 4.9 volts).

With all of the solvents studied, metallic lithium was deposited on the cathode of the cell during electrolysis; this reaction proceeded with little polarization (ca. 0.1 volt) at the current densities employed.

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

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Methyl Formate/1.5M $LiClO_4/SO_2$ - (See Run #19, Table III)

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in.^{2}	Specific Resistance Ω cm	Moles CO_2 per Mole PC
	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 II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Methyl Formate/1.5M $LiClO_4$ /SO_2 - (See Run #19, Table III) 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*			

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*See page 21 , Run #19

TABLE II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Propylene Carbonate/1.5M $LiClO_4/CO_2$ - (Run #21, Table III)

Elapsed Time Hours	Temp. °F	Gauge Pressure lbs/in.^{2}	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*			

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*See page 22, Run #21

TABLE II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Propylene Carbonate/LiF (saturated)/CO_2 (Run #23, Table III)

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*			

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*See page 23, Run #23

TABLE II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

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

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	

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*See page 23, Run #25

TABLE II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

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

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	1.00
117.83	75	73	189	
118.17	Start of decomposition potential test*			

*See page 24 , Run #26

TABLE II Continued

VARIATION OF SPECIFIC RESISTANCE WITH GAS PRESSURE

Propylene Carbonate/$MgBr_2$ (saturated)/CO_2 (Run #27, Table III)

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 24, Run #27

TABLE III

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Reference Electrode: Li/Li^+

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
		Run #1 - Acetic Anhydride + 1.5 M $LiClO_4$			
2.05	3.1	1.07	3.65	2.55	
4.42	18	2.30	4.65	2.33	
6.25	180	3.68	5.03	1.50	
6.42	180	4.90	5.03	0.10	Gassing on cathode
		Run #2 - Butyrolactone + 1.4 M $LiClO_4$			
1.06	1.6	1.34	3.05	1.68	Gassing on reference electrode
3.80	4.2	2.60	3.00	0.40	
4.80	43	3.90	4.00	0.14	Darkening on cathode
6.1	172	5.00	5.02	0.04	
6.4	>5000	5.90	5.50	-0.36	Solvent brown around anode
		Run #3 - Butyrolactone + 1.4 M $LiClO_4$			
.75	2.4	1.31	2.95	1.62	Gassing on reference electrode
2.82	11	2.50	3.11	0.58	
3.25	120	3.90	3.82	.10	
3.66	250	5.20	5.00	-.20	Darkening and gassing on cathode
3.75	590	5.95	5.44	-.46	
		Run #4 - Butyrolactone + 1.4 M $LiClO_4$			
1.42	7.5	1.11	3.55	2.40	Gassing on reference electrode
2.66	11	2.50	3.20	0.86	
4.83	15	3.80	3.70	0.06	
6.42	20	5.20	5.20	-.01	Darkening and gassing on cathode
6.58	21	5.80	5.70	-.13	Solvent brown around anode
7.16*	32	5.10	5.40	.28	
7.42	6.1	3.80	5.00	1.24	
7.5	20	2.40	3.45	1.09	

*Decreased applied potential

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Reference Electrode: Li/Li^+

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
		Run #5 - Dimethyl Sulfoxide + 1.78 M $LiClO_4$			
1.83	1.9	1.35	3.74	2.36	Gassing on reference electrode
3.66	3.40	2.75	4.40	1.65	
5.43	10	4.00	4.42	0.46	Darkening on cathode
5.83	4000	4.90	4.80	-.12	
6.08	5000	5.00	4.80	-.30	Heavy gassing on cathode
		Run #6 - Dimethyl Sulfoxide + 1.78 M $LiClO_4$			
1.75	.02	1.28	2.79	1.50	Gassing on reference electrode
2.25	.32	2.60	3.24	0.61	
2.75	1.4	4.00	3.95	-.05	
2.78	1800	5.00	4.54	-.44	Darkening on cathode
2.83	8000	5.60	4.70	-.90	
		Run #7 - Dimethyl Sulfoxide + 1.78 M $LiClO_4$			
1.42	12	1.08	3.05	1.90	Gassing on reference electrode
3.92	15	2.48	3.20	0.73	
5.25	48	3.72	4.20	0.44	Darkening on cathode
22.75*	32	2.55	4.00	1.50	
24.5	11	1.10	3.20	2.10	
		Run #8 - Dimethyl Sulfoxide + 1.78 M $LiClO_4$			
2.25	12	1.12	3.95	2.82	Gassing on reference electrode
3.75	110	2.45	4.40	1.92	
5.08	110	3.85	4.45	0.60	
5.83	6000	4.90	4.80	-.17	Gassing on cathode
6.00	11000	5.20	5.00	-.22	Darkening on cathode
6.38*	5000	4.92	4.82	-.06	
21.06	800	3.92	4.18	.22	
22.92	13	2.50	2.90	.38	
23.75	--	2.38	2.80	.41	

*Decreased applied potential

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Reference Electrode: Li/Li^+

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
Run #9 - Methyl Formate + 1.5 M $LiClO_4$					
1.25	2.6	1.04	3.59	2.50	Heavy gassing on reference electrode
2.75	32	2.20	3.92	1.75	
4.58	73	3.72	4.80	1.10	Heavy gassing on cathode
6.16	230	4.90	4.90	-.02	Pressure retards gassing
6.33	3200	5.50	5.40	-.10	
6.83*	180	5.00	5.00	.01	
7.5	54	3.74	4.60	.90	
8.00	25	2.45	3.22	.77	
Run #10 - N, N - Dimethyl Formamide (CaO dried) + 1.0 M $LiClO_4$					
3.50	0.86	1.09			
21.25	25.4	2.50			Replaced reference electrode
23.25	190	3.58			Gelatinous yellow-orange deposit on Li
23.75	1590	4.60			Darkening on cathode
24.25	700	6.10			Solution turned orange-brown
Run #11 - Propylene Carbonate + 1.5 M $LiClO_4$					
.25	3.8	1.06	2.90	1.80	Darkening & gassing on reference electrode
1.58	7.0	2.38	2.98	0.59	
4.00	13	3.78	3.92	.16	Darkening on cathode
5.33	120	5.02	5.10	.08	
6.25	1170	5.88	5.82	-.06	Cathode grey, gassing
6.75*	83	5.10	5.10	.00	
24.83	1100	3.10	5.60	2.52	
26.25	180	2.17	5.00	2.88	
27.50	18	.94	3.87	2.90	
Run #12 - Propylene Carbonate + 1.5 M $LiClO_4$					
1.66	.51	1.04	3.50	2.40	Darkening & gassing on reference electrode
2.83	.43	2.43	3.20	0.76	
4.50	4.5	3.80	3.95	0.16	Darkening on cathode
4.60	60	4.98	4.90	0.00	

*Decreased applied potential

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
Run #13 - N, N-Dimethyl Formamide (CaO dried) + 1.0 M $LiClO_4$ + Ammonia					
Reference Electrode: Not Employed					
1.33	2.64	1.06			
2.83	10.2	2.38			
3.20	101	3.65			
4.17	181	5.00			
4.92	286	6.25			
Run #14 - Dimethyl Sulfoxide + 1.0 M $LiClO_4$ + SO_2					
Reference Electrode: $Pb/PbSO_4$					
.58	334	0.77	0.71	-0.06	
1.42	1080	1.82	1.16	-0.70	
2.17	1080	3.20	1.20	-2.00	Potential-current fluctuations
2.92	2480	4.35	1.30	-3.05	
3.92	3670	5.39	1.49	-3.90	
Run #15 - Dimethyl Sulfoxide + 1.0 M $LiClO_4$ + SO_2					
Reference Electrode: $Pb/PbSO_4$					
1.25	413	0.70	0.74	-0.04	
2.50	955	1.90	0.76	-1.14	
4.42	1113	3.15	0.77	-2.35	
6.09	1845	4.25	1.21	-3.06	
7.26	5570	5.18	1.83	-3.35	
Run #16 - N, N-Dimethyl Formamide (CaO dried) - 1.0 M $LiClO_4$ - NH_3 - 96 psia					
Reference Electrode: $Pb/PbSO_4$					
$\rho = 26.5 \Omega$ cm					
.58	27.2	.90	.09	- .82	Black deposit on cathode at end of run
2.16	46.1	2.22	.13	-2.10	
2.91	262	3.44	.24	-3.18	
3.58	314	4.80	.25	-4.51	
4.16	398	6.10	.33	-5.80	

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. μa/cm^2	Potential, Volts			Remarks
		Cell	Anode	Cathode	
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 - 1.5 M $LiClO_4$ - Argon					
Reference Electrode: Ag/AgCl					
ρ = 50.5Ω cm					
.68	3.66	1.02	.53	- .48	
1.36	10.0	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	
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 of run; solution was dark brown
1.35	77.5	.94	.42	- .50	
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	

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
Run #20 - Propylene Carbonate - No Solute - Argon Reference Electrode: Ag/AgCl $\rho = 366\ K\Omega$ 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 - 1.5 M $LiClO_4$ - CO_2 - 91.5 psia Reference Electrode: Ag/AgCl $\rho = 226\Omega$ cm					
.50	2.20	1.06	.22	- .83	Black deposit on cathode at end of run; solution was orange-brown
1.67	4.18	2.35	.59	-1.75	
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	
Run #22 - Propylene Carbonate - LiF (saturated) - Argon Reference Electrode: Ag/AgCl $\rho = 620\ K\Omega$ 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	

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Run #23 - Propylene Carbonate - LiF (saturated) - CO_2 - 163 psia

Reference Electrode: Ag/AgCl

ρ = 164 KΩ cm

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
.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

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
.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	

Run #25 - Butyrolactone (CaO dried) - $Al_2(SO_4)_3$ (saturated) + CO_2 - 96 psia

Reference Electrode: Ag/AgCl

ρ = 151 KΩ cm

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts			Remarks
		Cell	Anode	Cathode	
.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	

TABLE III Continued

DECOMPOSITION CURRENT OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Time, hrs.	C. D. µa/cm^2	Potential, Volts			Remarks
		Cell	Anode	Cathode	
Run #26 - N, N-Dimethyl Formamide - KBr (saturated) - NH$_3$ - 73.0 psia					
Reference Electrode: Ag/AgCl					
$\rho = 189\ \Omega$ cm					
2.34	142	.93	.06	- .88	Deposit on both electrodes at end of run; discoloration on reference electrode
3.92	2310	1.93	.54	-1.40	
5.17	4610	2.78	.94	-1.84	
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$_2$ - 91.5 psia					
Reference Electrode: Ag/AgCl					
$\rho = 3.82\ K\Omega$ cm					
.33	.63	.62	.58	- .04	Film on reference electrode at end of run; light gray deposit on platinum electrode
1.00	54.5	.95	.78	- .17	
1.83	21.0	2.20	.70	-1.50	
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.

3. 3. SPECIFIC CONDUCTANCE AND SOLUBILITY STUDIES

The approximate solubility of a number of salts in several solvents (about 90 combinations), and the specific conductance of the solutions were determined in order to study the general feasibility of constructing cells having a cathodic discharge of the type

$$CuX_2 + 2Li^+ + 2e^- \longrightarrow Cu + 2LiX.$$

Copper and lithium chlorides and fluorides were included in the study, since they would represent the reactants and discharge products of the above described electrode reaction. It was anticipated that a relatively large solubility of the lithium salt is desirable, while the copper salts should have minimum solubility. Most of the solvents were selected for the study because of their potential usefulness in a lithium-anode cell, but some were also included in order to study the general behavior trends of the organic solutions. Solubility of $LiClO_4$ and $AlCl_3$ in the solvents was studied in order to evaluate their effectiveness as supporting electrolytes in the various solvents.

The specific conductance and solubility data obtained at room temperature are presented in Table IV, page 27 . Lithium chloride was found to be only moderately soluble in methyl formate (10. 8 grams/liter) and butyrolactone (33. 3 grams/liter), but was considerably more soluble in dimethyl sulfoxide (75 grams/liter); the specific conductance of this solution was about as high as that of the 1. 5M $LiClO_4$ solution in the same solvent.

In all of the solvents studied, more conductive solutions were formed with $LiClO_4$ than with $AlCl_3$; the solution of the latter salt was in all cases exothermic and a strongly colored solution resulted. With dimethyl sulfoxide, $AlCl_3$ formed a white suspensoid which did not settle out of the solution after a one month stand.

Several rather unexpected results were recorded during the above described investigation. Lithium fluoride was found to have considerable solubility in n-butyl formate (6. 5 grams/liter), and in nitromethane (5. 0 grams/liter). The specific conductance of these solutions did not, however, differ significantly from that of the pure solvents.

Copper fluoride consistently produced less conductive solutions then copper chloride, indicating a lower degree of solubility. The fluoride solutions were also less strongly colored then those obtained with the chloride at the saturation level. In combination with the lower equivalent weight, this appears to make copper fluoride the more desirable of the two salts as a battery cathode material. Thus, the CuF_2-Li couple with $LiClO_4$ as the electrolyte salt was the system studied most extensively on the present program.

TABLE IV

SPECIFIC CONDUCTANCE AND SOLUBILITY DATA

Solvent	Solute	Grams solute / Liter of solvent	Specific Conductance $(\text{ohm}^{-1}\text{cm}^{-1})$*	Remarks
Acetic Anhydride	None		3.7×10^{-6}	
	CuF_2	<0.500	4.3×10^{-6}	Yellow-green solution, blue-green salt
	LiF	$\overset{\circ}{=}5.00$	2.7×10^{-6}	Yellow solution, white salt
	$CuCl_2$	<0.500	3.1×10^{-5}	Green solution, brown salt
	LiCl	≥ 0.500	2.3×10^{-4}	Colorless solution
	$AlCl_3$	<66.8	2.7×10^{-4}	Exothermic, two solid phases
	$LiClO_4$	$\overset{\circ}{=}53$	5.9×10^{-3}	Exothermic, pale yellow solution
2-Butanone	None			
	CuF_2	<0.500	1.3×10^{-5}	Colorless solution, blue-green salt
	LiCl	<0.500	3.1×10^{-5}	Colorless solution, white salt
n-Butyl Formate	None			
	CuF_2	<0.500	3×10^{-8}	Colorless solution, gray salt
	LiF	$\overset{\circ}{=}6.50$	2×10^{-8}	Colorless solution
	$CuCl_2$	<0.500	1.0×10^{-6}	Pale yellow solution, brown salt
	LiCl	<0.500	3×10^{-8}	Solution clear, salt white
	$AlCl_3$	>66.8	6.3×10^{-4}	Exothermic, hot solution dark red, but after cooling dark purple
	$LiClO_4$	>300	4.6×10^{-3}	Somewhat exothermic, colorless solution
γ Butyrolactone	None		8.3×10^{-7}	
	CuF_2	<0.204	2.0×10^{-6}	Colorless solution, gray salt
	LiF	$0.208<S<0.312$	1.4×10^{-6}	Colorless solution, white salt
	$CuCl_2$	≥ 0.500	7.3×10^{-5}	Amber solution
	LiCl	≥ 33.3	8.3×10^{-5}	Colorless solution
	$AlCl_3$	>66.8	4.4×10^{-3}	Solution process exothermic, but slow; dark tan solution
	$LiClO_4$	>400	4.8×10^{-3}	Exothermic, colorless solution

TABLE IV Continued

SPECIFIC CONDUCTANCE AND SOLUBILITY DATA

Solvent	Solute	Grams solute / Liter of solvent	Specific Conductance $(ohm^{-1}cm^{-1})$*	Remarks
Diethyl Ether			$L_s < 10^{-8}$	
	$LiClO_4$	>270	5.0×10^{-4}	Exothermic, yellow; viscous solution
	LiBr	<< 200	$L_s < 10^{-8}$	Pale yellow solution, white salt
Dimethyl Formamide	CuF_2	<0.500	1.4×10^{-5}	Yellow solution, gray salt
	LiCl	$\geq$1.00	2.1×10^{-4}	Colorless solution
Dimethyl Sulfoxide			1.7×10^{-6}	
	CuF_2	< 0.500	1.4×10^{-5}	Colorless solution, gray salt
	LiF	< 0.500	3.5×10^{-6}	Colorless solution, white salt
	$CuCl_2$	$\geq$27.8	1.1×10^{-3}	Bilious green solution
	LiCl	$\geq$75.0	4.6×10^{-3}	Colorless solution
	$AlCl_3$	<66.8	3.7×10^{-4}	Viscous white stable suspension; exothermic
	$LiClO_4$	>250	5.2×10^{-3}	Exothermic, colorless solution
1, 2 Epoxypropane	$AlCl_3$			Pyrophoric
	$LiClO_4$	>400	1.3×10^{-2}	Exothermic, colorless solution
	LiBr	>160		Rapid exothermic solution followed by a slow, but exothermic reaction leading to a dark red solution and an orange, gelatinous solid after two days.

TABLE IV Continued

SPECIFIC CONDUCTANCE AND SOLUBILITY DATA

Solvent	Solute	Grams solute / Liter of solvent	Specific Conductance $(ohm^{-1}cm^{-1})$*	Remarks
Ethyl Acetate	LiCl	<2	$L_s < 10^{-5}$	
	$AlCl_3$	<2	$L_s < 10^{-5}$	
	$LiClO_4$	>400	5.0×10^{-3}	Exothermic, colorless solution
	KSCN	<2	$L_s < 10^{-5}$	
	KI	<2	$L_s < 10^{-5}$	
	LiI	<2	$L_s < 10^{-5}$	
	AlF_3	<2	$L_s < 10^{-5}$	
Ethyl Acetoacetate	$LiClO_4$	>350	3.3×10^{-3}	Exothermic, colorless solution
Ethyl Formate	CuF_2	<0.500	9×10^{-7}	Blue-green solution, blue-green salt
	LiCl	<0.500	2×10^{-6}	Colorless solution, white salt
	$LiClO_4$	>420	1.1×10^{-2}	Exothermic, pale yellow solution
	LiBr	>390	2.2×10^{-3}	Exothermic, pale yellow solution
Methyl Acetate	$LiClO_4$	>400	1.1×10^{-2}	Exothermic, pale yellow solution
Methyl Chloroform			$L_s < 10^{-8}$	
	CuF_2	< 0.500	$L_s < 10^{-8}$	Colorless solution; gray salt
	$AlCl_3$	<10	$L_s < 10^{-8}$	Tan solution, orange-brown salt
	$LiClO_4$	<10	$L_s < 10^{-8}$	Colorless solution, white salt

TABLE IV Continued

SPECIFIC CONDUCTANCE AND SOLUBILITY DATA

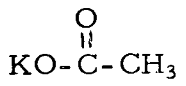
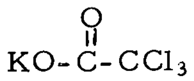
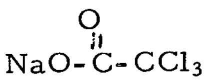
Solvent	Solute	Grams solute / Liter of solvent	Specific Conductance $(ohm^{-1}cm^{-1})$*	Remarks
Methyl Formate			1.1×10^{-7}	
	CuF_2	<0.204	2.7×10^{-6}	Pale yellow solution, pale yellow salt
	LiF	0.208<S<0.312	1.7×10^{-7}	Colorless solution, white salt
	$CuCl_2$	≥10.5	1.5×10^{-5}	Solution initially a heavy green; after 24 hours a green solid phase had appeared, and the solution was then merely green
	LiCl	≥10.8	7.7×10^{-5}	Pale yellow solution
	$AlCl_3$	≥5.0	1.4×10^{-5}	Required one week for complete solution; solution dark green
	$LiClO_4$	>800	1.6×10^{-2}	Exothermic, pale yellow solution
	LiBr	>420	6.0×10^{-3}	Exothermic, pale yellow solution
	KSCN	>5.0		Solution of heavy orange after 24 hours; large amount of yellow precipitate after one week
	 $KO\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$	<5.0	$L_s < 10^{-5}$	Colorless solution
	 $KO\text{-}\overset{\overset{O}{\|}}{C}\text{-}CCl_3$	<5.0	$L_s < 10^{-5}$	Colorless solution
	 $NaO\text{-}\overset{\overset{O}{\|}}{C}\text{-}CCl_3$	>5.0	$L_s < 10^{-5}$	5 grams/liter dissolved immediately, but a second solid phase was found after 24 hours
	KCl	<5.0	$L_s < 10^{-5}$	Solution yellow
	NaCl	<5.0	$L_s < 10^{-5}$	Solution yellow
	$NaBF_4$	<5.0	$L_s < 10^{-5}$	Solution yellow

TABLE IV Continued

SPECIFIC CONDUCTANCE AND SOLUBILITY DATA

Solvent	Solute	Grams solute / Liter of solvent	Specific Conductance $(\text{ohm}^{-1}\text{cm}^{-1})$*	Remarks
1-Methyl-2-Pyrrolidone	CuF_2	< 0.500	4×10^{-6}	Colorless solution, gray salt
	LiCl	≥ 1.0	1.6×10^{-4}	Colorless solution
	$LiClO_4$	>200	6.1×10^{-3}	Exothermic, colorless solution
Nitromethane	CuF_2	< 0.500	1.6×10^{-5}	Yellow-green solution, blue-green salt
	LiF	$\overset{\circ}{=} 5.0$	2.8×10^{-6}	Colorless solution, white salt
	$CuCl_2$	≥ 0.500	2.7×10^{-5}	Amber-green solution
	LiCl	<0.500	7.3×10^{-6}	Colorless solution, white salt
Propylene Carbonate			6.0×10^{-7}	
	CuF_2	< 0.204	2.3×10^{-5}	Colorless solution, gray salt
	LiF	$0.208 < S < 0.312$	1.1×10^{-6}	Colorless solution, white salt
	$CuCl_2$	≥ 5.00	1.8×10^{-4}	Amber-black solution
	LiCl	≥ 0.500	3.4×10^{-4}	Colorless solution
	$AlCl_3$	>66.8	4.4×10^{-3}	Exothermic, dark brown solution
	$LiClO_4$	>250	2.5×10^{-3}	Exothermic, colorless solution
Pyridine	CuF_2	<0.500	9×10^{-6}	Yellow-green solution, blue-green salt
	LiCl	≥ 2.50	9×10^{-5}	Yellow solution
Tetrahydrofuran			1.8×10^{-7}	
	CuF_2	<0.500		Solution colorless, salt gray
	$CuCl_2$	$\overset{\circ}{=} 0.500$		Solution brown yellow
	$LiClO_4$	>160	8.2×10^{-3}	Exothermic, pale yellow solution

$\overset{\circ}{=}$ small excess of solute; $<$ large excess of solute; $>$ dissolved rapidly; $\geq$ dissolved slowly.

*L_s for the saturated solution, or for the highest concentration listed.

3.4. SPECIFIC CONDUCTANCE-CONCENTRATION CHARACTERISTICS OF VARIOUS ORGANIC ELECTROLYTE SOLUTIONS

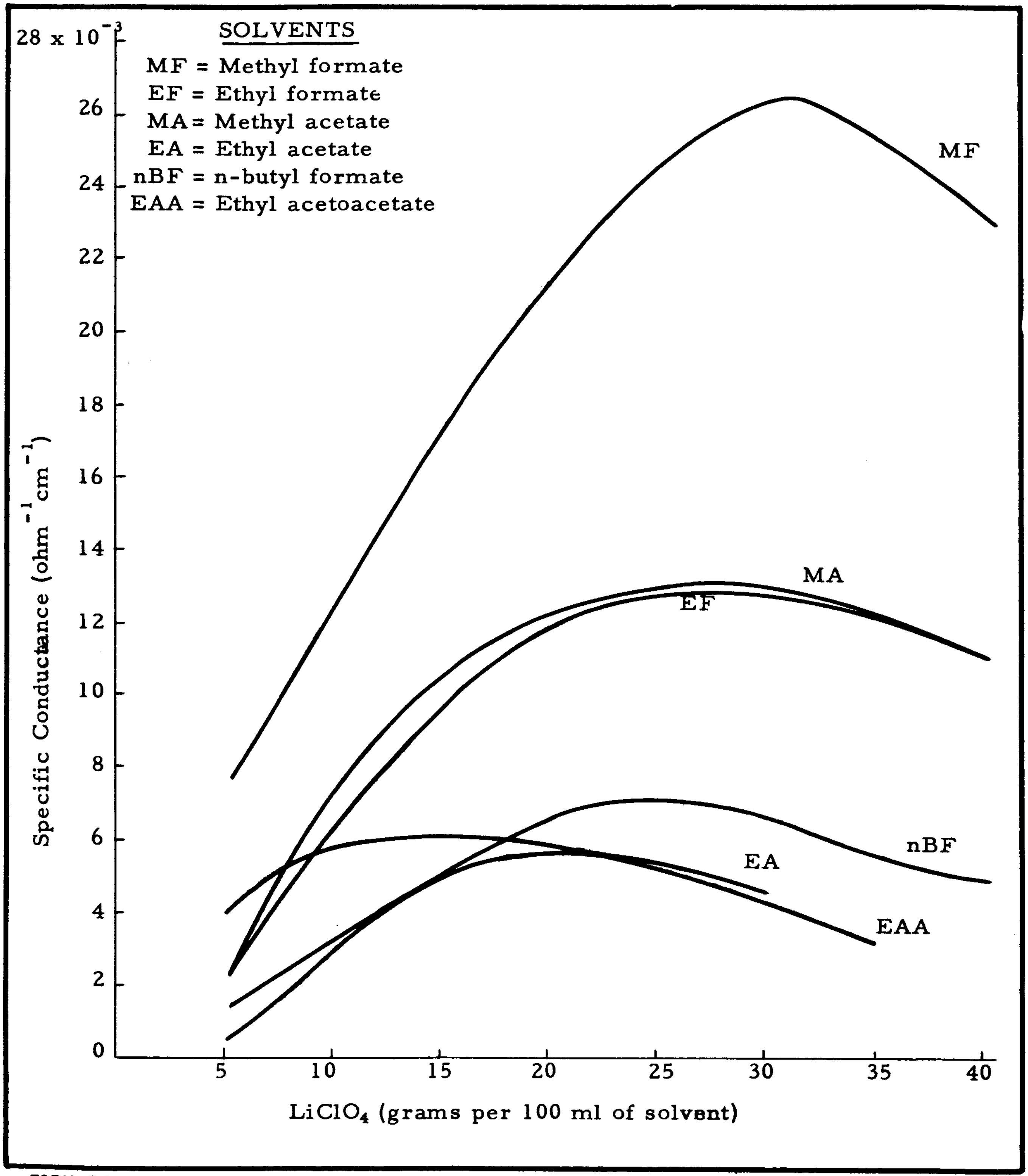
During the contract year, specific conductance-concentration data on several electrolyte systems were obtained. Since lithium perchlorate was found to produce the most conductive solutions in the organic solvents, and appeared to be acceptable as an electrolyte solute from stability consideration, it was the material most extensively used in these tests.

The solvents used in these conductivity studies could be divided into two groups: those that appeared moderately stable in presence of metallic lithium (propylene carbonate, butyrolactone), and those that definitely reacted with the metal (the esters). In the former group, butyrolactone formed the most conductive solutions with lithium perchlorate, the maximum specific conductance being 10.6×10^{-3} $ohm^{-1}cm^{-1}$ at 15 grams/100 ml of solvent (1, 2 epoxypropane had a specific conductance of 13.4×10^{-3} $ohm^{-1}cm^{-1}$ at 30 grams/100 ml of solvent, but this electrolyte was found to be unstable in presence of the CuF_2 electrode, and its use was temporarily discontinued from the program). Of the ester group, the methyl formate solution had a specific conductance of 26.6×10^{-3} $ohm^{-1}cm^{-1}$ at a concentration of 30 grams per 100 ml of solvent, while the maximum conductivity in the other esters was considerably less. The specific conductance-concentration data for the above electrolyte systems are given in Figure 1 and Figure 2, pages 33 and 34 .

The specific conductance-concentration behavior of butyrolactone-methyl formate mixtures was determined. No synergistic effects in this system were observed, as may be seen from the data presented in Figure 3, page 35.

The specific conductances of equimolar solutions of $LiClO_4$ and LiBr in methyl formate and ethyl formate were compared, and the data have been presented in Figure 4, page 36 . In both solvents, the perchlorate formed the more conductive solutions at equal concentrations indicating a higher conductivity for the perchlorate ion compared to the bromide ion.

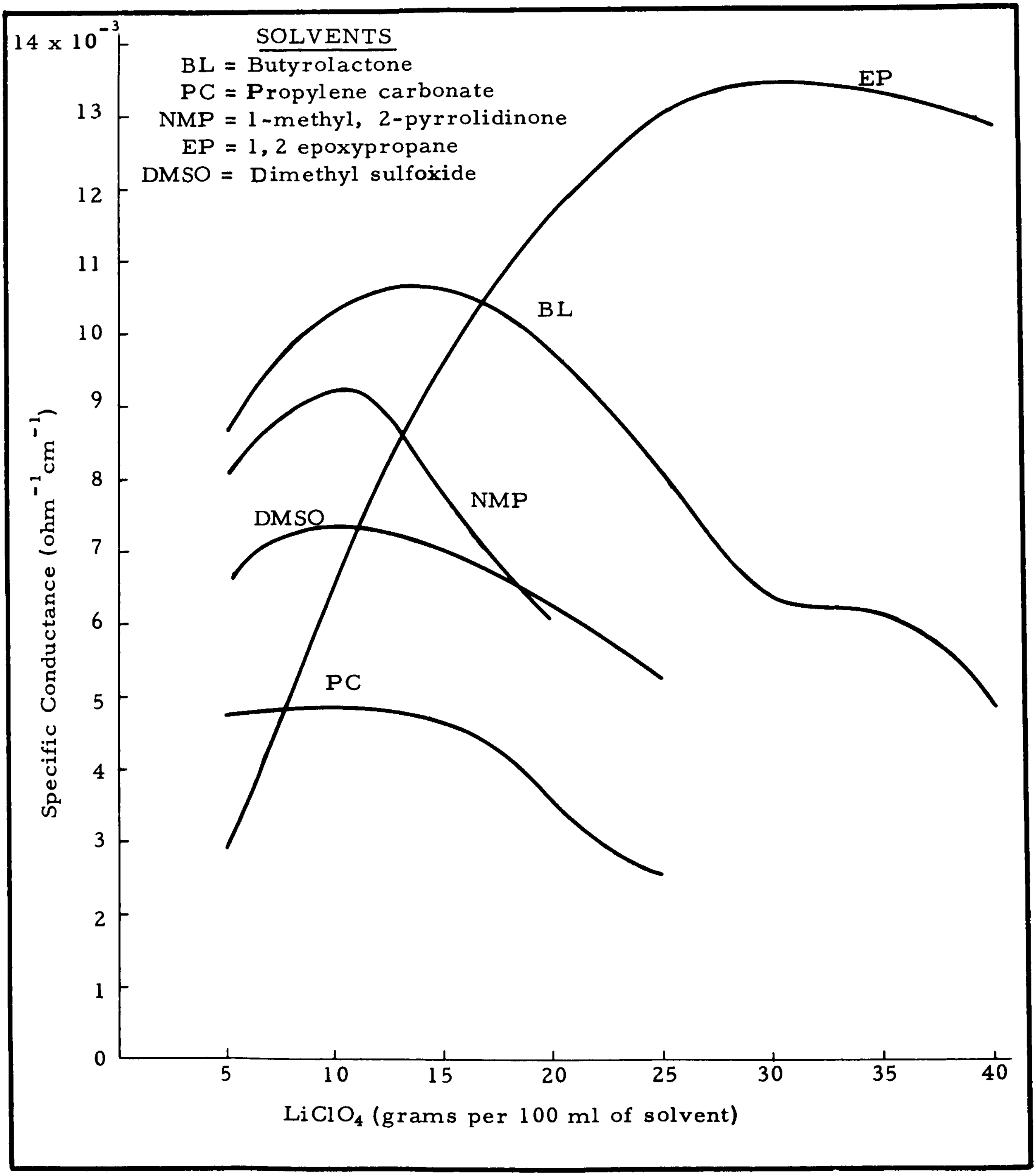
With the exception of methyl formate, the specific conductances obtained with the solvents studied were of the same order of magnitude. Therefore, selection of electrolyte systems for further development will have to be made on the basis of other physical and chemical properties.



FORM FM-100

SPECIFIC CONDUCTANCE OF $LiClO_4$ SOLUTIONS IN VARIOUS ESTERS AT ROOM TEMPERATURE

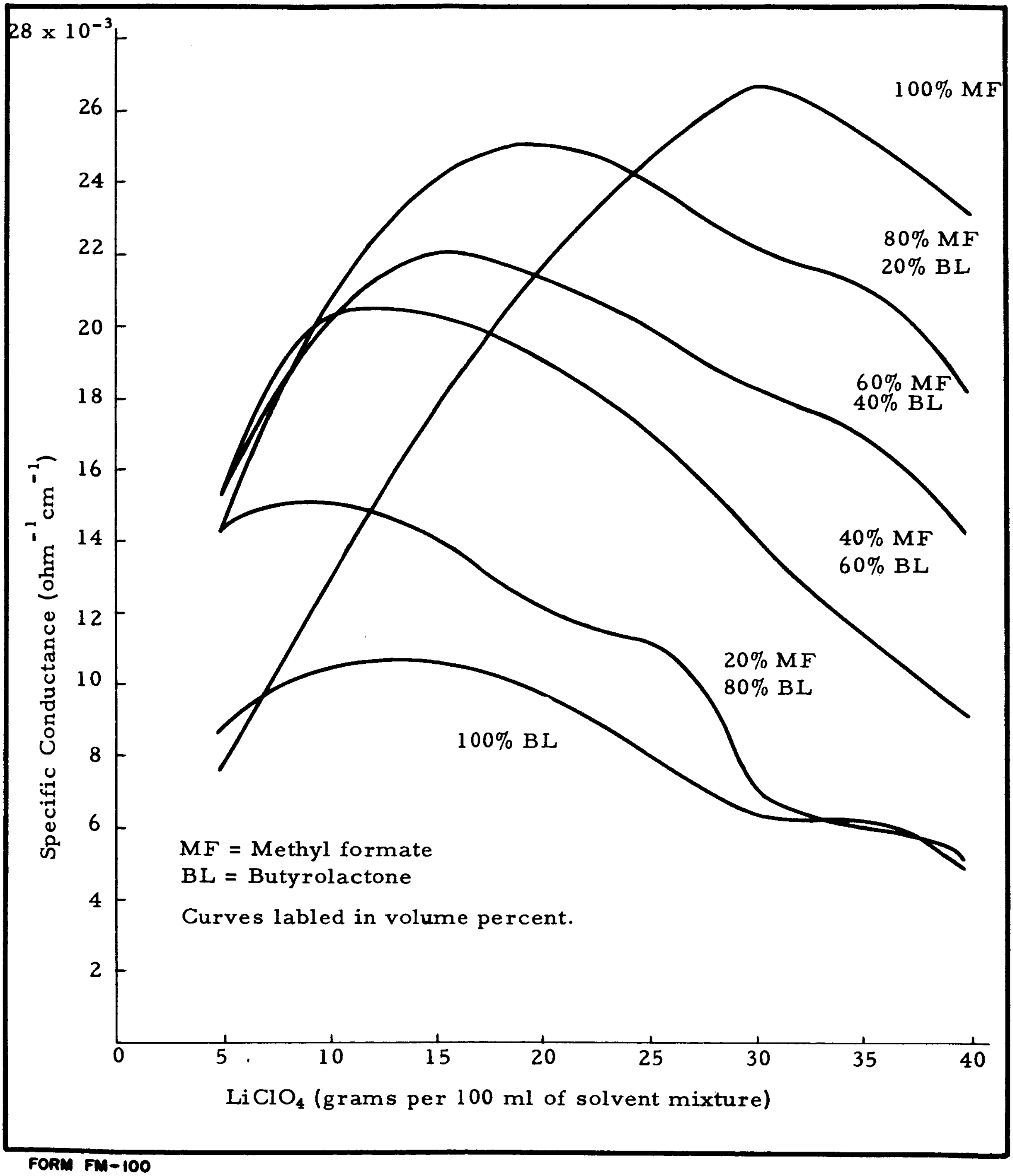
FIGURE 1



FORM FM-100

SPECIFIC CONDUCTANCE OF $LiClO_4$ SOLUTIONS IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

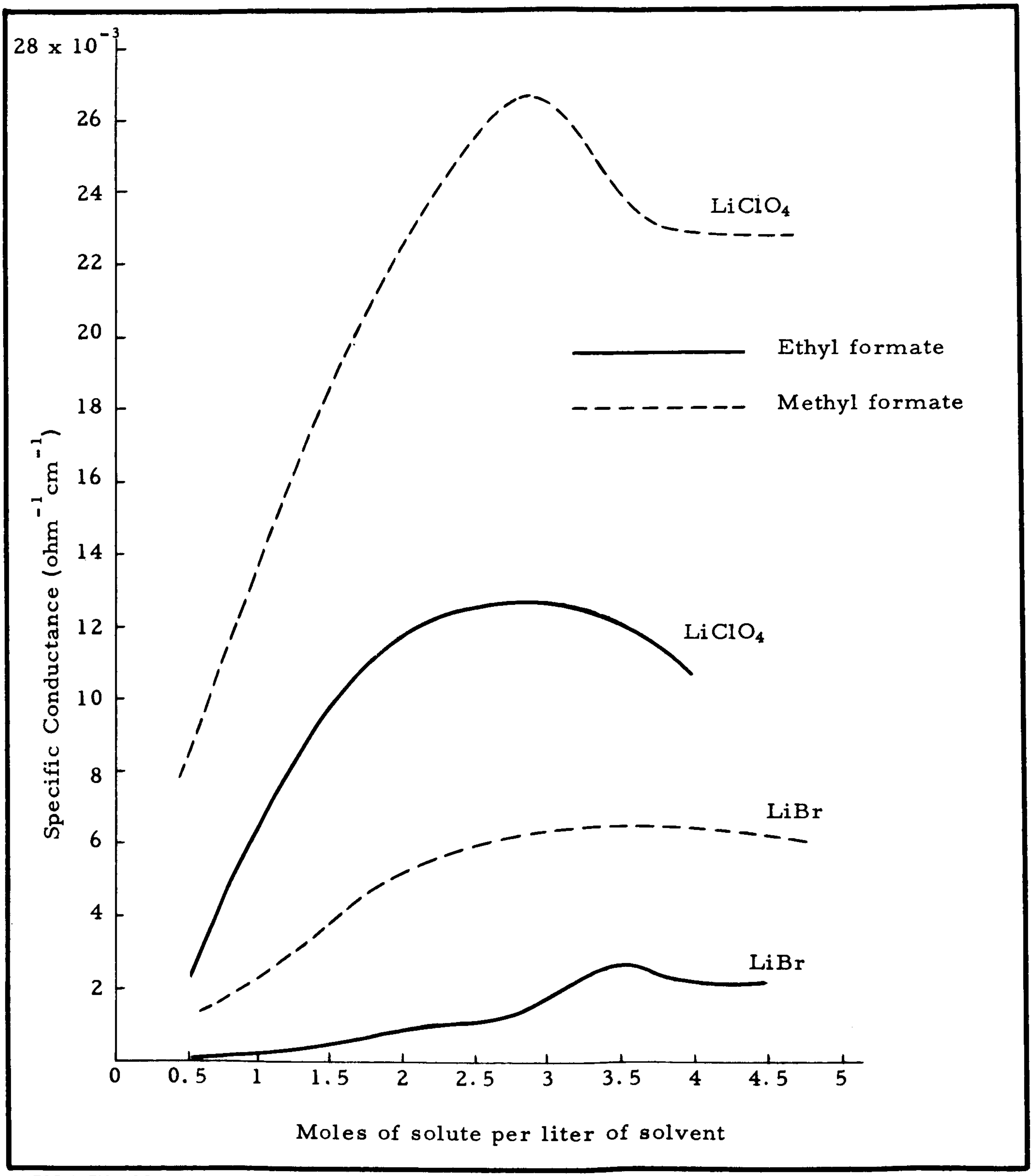
FIGURE 2



FORM FM-100

SPECIFIC CONDUCTANCE OF $LiClO_4$ SOLUTIONS
IN BUTYROLACTONE - METHYL FORMATE MIXTURES

FIGURE 3



CONDUCTIVITY OF $LiClO_4$ and LiBr SOLUTIONS IN METHYL FORMATE AND ETHYL FORMATE

FIGURE 4

3.5. STUDIES OF METHODS FOR REMOVAL OF WATER FROM ELECTROLYTE SOLUTIONS

In order to effect a degree of control on the amount of water contamination of the test cells, methods for the removal of water from the solvents and electrolyte solutions have to be developed. On this program, dolomitic lime (50% MgO, 50% CaO), lithium chloride, and lithium powder were studied as decontaminating agents. The solvents employed in this study were propylene carbonate, dimethyl sulfoxide, butyrolactone, acetic anhydride, and methyl formate. Lithium perchlorate was the only electrolyte salt employed in these 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 Karl Fischer analysis. 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. Results of these tests are presented in Table V, page 38.

In the solvents used for this study, metallic lithium was found to be the most effective water removing agent. As expected, the final water content of a solvent depended on the water level at the beginning of the 40-hour agitation period. In propylene carbonate, the water concentration decreased from 240 to 50 ppm and in butyrolactone, the decrease was from 150 to 25 ppm. The other solvents could be dried from an initial concentration of 150-300 to below the sensitivity of the Karl Fischer determination which was in the order of 15 ppm.

Water removal from the $LiClO_4$ solutions proceeded more slowly than with the solvents alone. A 2.4M solution in methyl formate was dried from 630 ppm to below 15 ppm, but 1.4M solutions in propylene carbonate were only reduced from 3,500 ppm to 430 ppm, and from 400 ppm to 200 ppm in the same drying period. It appears, however, that a prolonged agitation period could further reduce the water level in these solutions.

In addition to being effective in removing the water contamination, the lithium powder treatment probably decomposes any other contaminants which would otherwise be reduced at the lithium electrode in the cell. It appears, therefore, that this method of solvent purification, possibly combined with redistillation, would tend to improve the stability of the electrolyte systems.

TABLE V

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}				NT
MF:2.4M $LiClO_4$②	5, 860	2.3×10^{-2}				NT
MF:2.4M $LiClO_4$③	630	2.6×10^{-2}				NT
PC (Eastman)	3, 550	1.3×10^{-5}				
PC (Jefferson)	450	1.8×10^{-5}				
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 Could not assay because of strongly colored solution

REMOVAL STUDIES

LiCl①			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 dark brown	1.10
690	7.7×10^{-5}		<15	1.4×10^{-5}	solution yellow ppt. gray	0.98
		NT	<15	1.0×10^{-5}	solution clear ppt. gray treated at -15°C	0.98
			NT[4]	1.3×10^{-2}	solution dark red	1.10 init.
		NT	<15	1.6×10^{-2}	solution yellow-brown	1.10 init.
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

4. CELL DISCHARGE TESTS

4.1. DETERMINATION OF ELECTRODE POLARIZATION IN REFERENCE - ELECTRODE CELLS

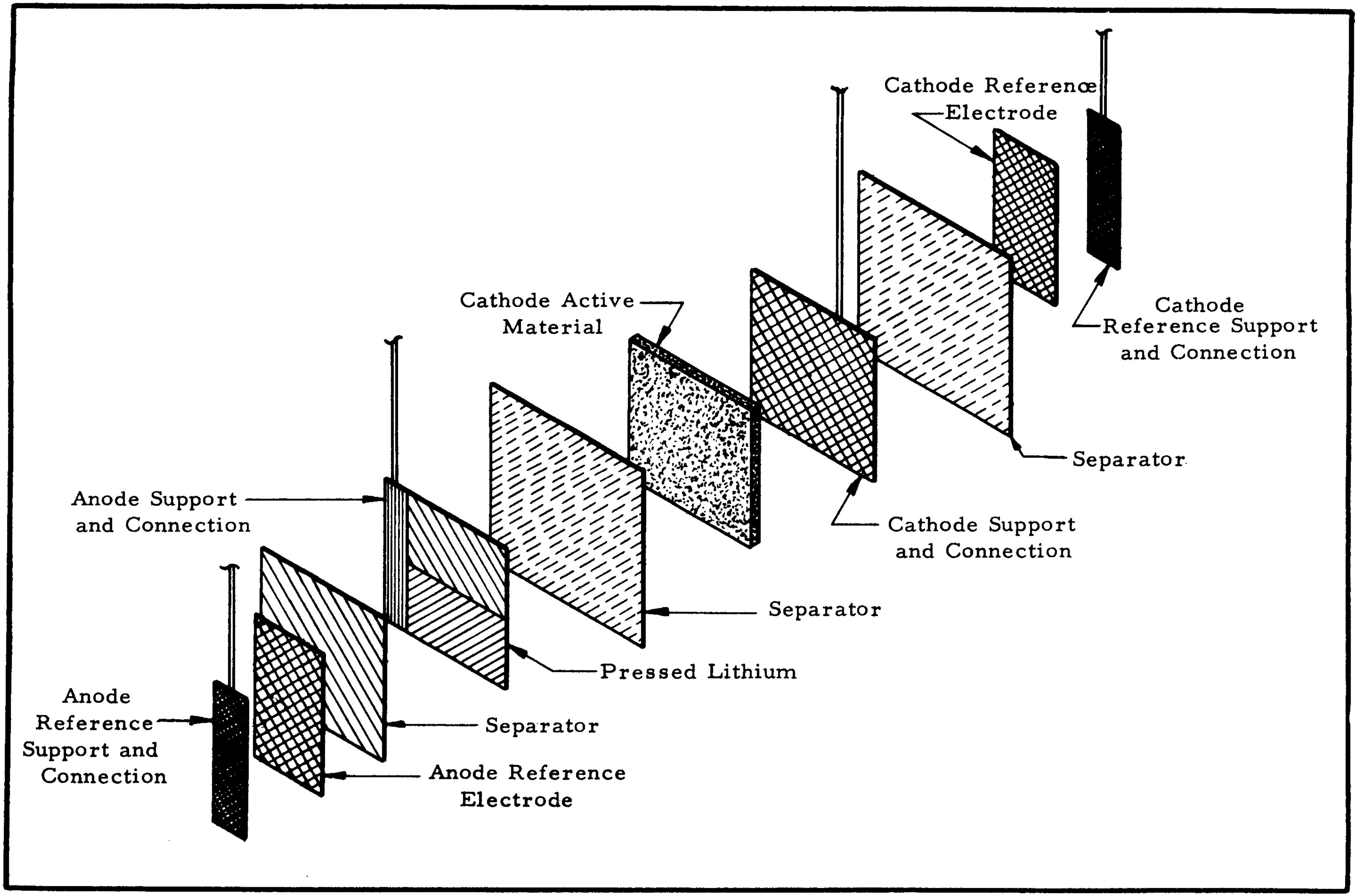
In order to study the behaviour of the lithium and copper fluoride electrodes during discharge, cells having two working and two reference electrodes as shown in Figure 5, page 41 , were built and tested. The lithium electrode was a flat sheet of the metal pressed onto an expanded metal (Ag or Ni) support, while the copper fluoride electrodes were constructed by the filter-mat method described in Section 4.4. The reference electrodes were, in most cases, identical to the positive electrode of the working cell — i.e., Cu/CuF_2 electrodes. Lithium was used as the negative reference electrode in a few cells; however, for the purpose of a uniform presentation of the discharge data in Table VI, page 42 , these readings are given with respect to a Cu/CuF_2 reference electrode (taking the CuF_2/Cu electrode 3.4 volts positive to the Li electrode).

The working electrodes had a cross-sectional area of about 15 cm^2 and were separated by commercial microporous rubber 1.1 mm thick. The same separation was used between the reference and the working electrode at both the cathode and the anode of the cell. Since the positive electrode was the prime objective of the study, the thickness of the lithium working electrode was of sufficient thickness to give approximately a three-fold excess of theoretical capacity compared to that of the CuF_2 working electrode.

The cells were discharged on the "Research Cell Recorder" circuit developed during the previous contract period (See page III-32, NASA CR54083). With this equipment, the discharge current is supplied in eleven-second on-off intervals, the on-cycle being chopped at 120 cps for the purpose of measuring the ac resistance of the working cell.

In general, capacity to a final working cell potential of 2.0 volts was limited by polarization of the CuF_2 electrode. The lithium electrode potential generally remained constant throughout the discharge. An exception to this condition was found in cells having MF electrolyte solvent (Cells R-16 to R-21), where strong polarization of the lithium electrode was observed. This condition was, however, traceable to loss of mechanical contact between the lithium and the expanded metal support used.

The best CuF_2 utilization (78-85%) was obtained with propylene carbonate electrolyte. The utilization also appeared to improve when the water content of the electrolyte solution was reduced by drying with Li powder (Cells R-7 to R-10).



FORM FM-101

EXPLODED VIEW OF R-CELL CONSTRUCTION

FIGURE 5

TABLE VI

SUMMARY OF REFERENCE ELECTRODE CELL TESTS

Cell No.	Electrolyte Solution: $LiClO_4$	Cell (loaded) Voltage			Anode (loaded) Potential vs CuF_2:graphite/Cu			Cathode (loaded) Potential vs CuF_2:graphite/Cu			Average Current Density: mA/cm^2	IR Drop in volts			Percent CuF_2 Utilization
		Initial	Final	Average	Initial	Final	Average	Initial	Final	Average		Initial	Final	Average	
R-1	10g/100 ml PC	3.1	2.0	2.8	-3.4	-3.4	-3.4	-0.1	-1.0	-0.3	0.7	0.2	0.4	0.3	30
R-2	10g/100 ml PC	2.6	2.0	2.5	-3.4	-3.2	-3.3	-0.6	-0.8	-0.6	1.0	0.2	0.4	0.2	35
R-3	15g/100 ml BL	3.2	2.0	2.8	-3.4	-3.4	-3.4	-0.1	-1.2	-0.4	0.5	0.1	0.2	0.2	26
R-4	5g/100 ml Acan	3.2	2.0	2.6	-3.4	-2.4	-2.9	0.0	-0.1	-0.1	0.5	0.2	0.3	0.2	10
R-5	10g/100 ml DMSO	2.8	2.0	2.7	-3.0	-3.2	-3.2	-0.0	-0.9	-0.3	0.5	0.2	0.3	0.2	55
R-6	15g/100 ml PC H_2O = 2000 ppm	2.9	2.0	2.9	-3.4	-3.4	-3.4	-0.1	-1.2	-0.2	0.5	0.4	0.2	0.3	63
R-7*	15g/100 ml PC H_2O = 2000 ppm	3.0	2.0	2.8	-3.4	-3.4	-3.4	-0.1	-1.0	-0.3	0.5	0.3	0.4	0.3	78
R-8**	15g/100 ml PC H_2O = 430 ppm	3.0	2.0	2.8	-3.3	-3.3	-3.3	-0.1	-1.1	-0.3	0.5	0.2	0.2	0.2	83
R-9	15g/100 ml PC H_2O = 400 ppm	3.0	2.0	2.9	-3.4	-3.4	-3.4	-0.1	-1.0	-0.2	0.5	0.3	0.4	0.3	80
R-10**	15g/100 ml PC H_2O = 200 ppm	3.0	2.0	2.8	-3.3	-3.3	-3.3	0.0	-1.1	-0.3	0.5	0.3	0.2	0.2	85

* Changeover from the kerosene pad to the heptane pad:

** Li powder treated electrolyte solution

Cells R-1 through R-6 employed kerosene cathode pads
Cells R-7 through R-21 employed heptane cathode pads

TABLE VI Continued

SUMMARY OF REFERENCE ELECTRODE CELL TESTS

Cell No.	Electrolyte Solution: $LiClO_4$	Cell (loaded) Voltage			Anode (loaded) Potential vs CuF_2:graphite/ Cu			Cathode (loaded) Potential vs CuF_2:graphite/ Cu			Average Current Density; mA/cm^2	IR Drop in volts			Percent CuF_2 Utilization
		Initial	Final	Average	Initial	Final	Average	Initial	Final	Average		Initial	Final	Average	
R-11	15g/100ml BL H_2O = 615 ppm	3.0	2.0	2.6	-3.2	-3.0	-3.0	0.0	-0.5	-0.3	1.0	0.2	0.5	0.5	62
R-12*	15g/100ml BL H_2O = 615 ppm	2.9	2.0	2.6	-3.2	-3.0	-3.1	-0.1	-0.6	-0.3	1.0	0.2	0.4	0.2	45
R-13	15g/100ml BL H_2O = 600 ppm	3.1	2.0	2.9	-3.3	-3.3	-3.3	-0.1	-1.2	-0.3	0.5	0.1	0.1	0.1	69
R-14	15g/100ml BL sat. with CuF_2 H_2O = 600 ppm	3.1	2.0	2.9	-3.3	-3.3	-3.3	-0.1	-1.2	-0.3	0.5	0.1	0.1	0.1	83
R-15	sat. $LiClO_4$ in Acan H_2O <15 ppm	2.8	2.0	2.4	-3.4	-2.5	-2.8	-0.1	-0.1	0.0	0.5	0.5	0.4	0.4	11
R-16	50g/100ml MF H_2O = 780 ppm	2.8	2.0	2.4	-3.1	-2.4	-2.7	-0.1	-0.2	-0.1	3.3	0.2	0.2	0.2	34

* Changeover in pad ratio: Cells R-1 through R-11, CuF_2/graphite/nalcon = 70/20/10
Cells R-11 through R-21, CuF_2/graphite/nalcon = 82.6/11.6/5.8

TABLE VI Continued

SUMMARY OF REFERENCE ELECTRODE CELL TESTS

Cell No.	Electrolyte Solution: $LiClO_4$	Cell (loaded) Voltage			Anode (loaded) Potential vs CuF_2:graphite/Cu			Cathode (loaded) Potential vs CuF_2:graphite/Cu			Average Current Density: mA/cm^2	IR Drop in volts			Percent CuF_2 Utilization
		Initial	Final	Average	Initial	Final	Average	Initial	Final	Average		Initial	Final	Average	
R-17	50g/100 ml MF H_2O = 780 ppm	2.8	2.0	2.4	-3.1	-2.4	-2.7	-0.1	-0.2	-0.1	3.3	0.2	0.2	0.2	30
R-18	37.5g/100 ml MF H_2O = 800 ppm	3.0	2.0	2.4	-3.3	-2.4	-2.8	-0.2	-0.2	-0.2	3.3	0.1	0.2	0.2	23
R-19	37.5g/100 ml MF H_2O = 800 ppm	3.0	2.0	2.4	-3.3	-2.4	-2.8	-0.2	-0.2	-0.2	3.3	0.1	0.2	0.2	19
R-20	25g/100 ml MF H_2O = 820 ppm	3.0	2.0	2.3	-3.3	-2.4	-2.6	-0.2	-0.3	-0.2	3.3	0.1	0.1	0.1	10
R-21	25g/100 ml MF H_2O = 820 ppm	3.0	2.0	2.3	-3.3	-2.4	-2.6	-0.2	-0.3	-0.2	3.3	0.1	0.1	0.1	12

4.2. EVALUATION OF CuF_2-Li AND MnO_2-Li CELLS WITH VARIOUS ELECTROLYTE SOLVENTS

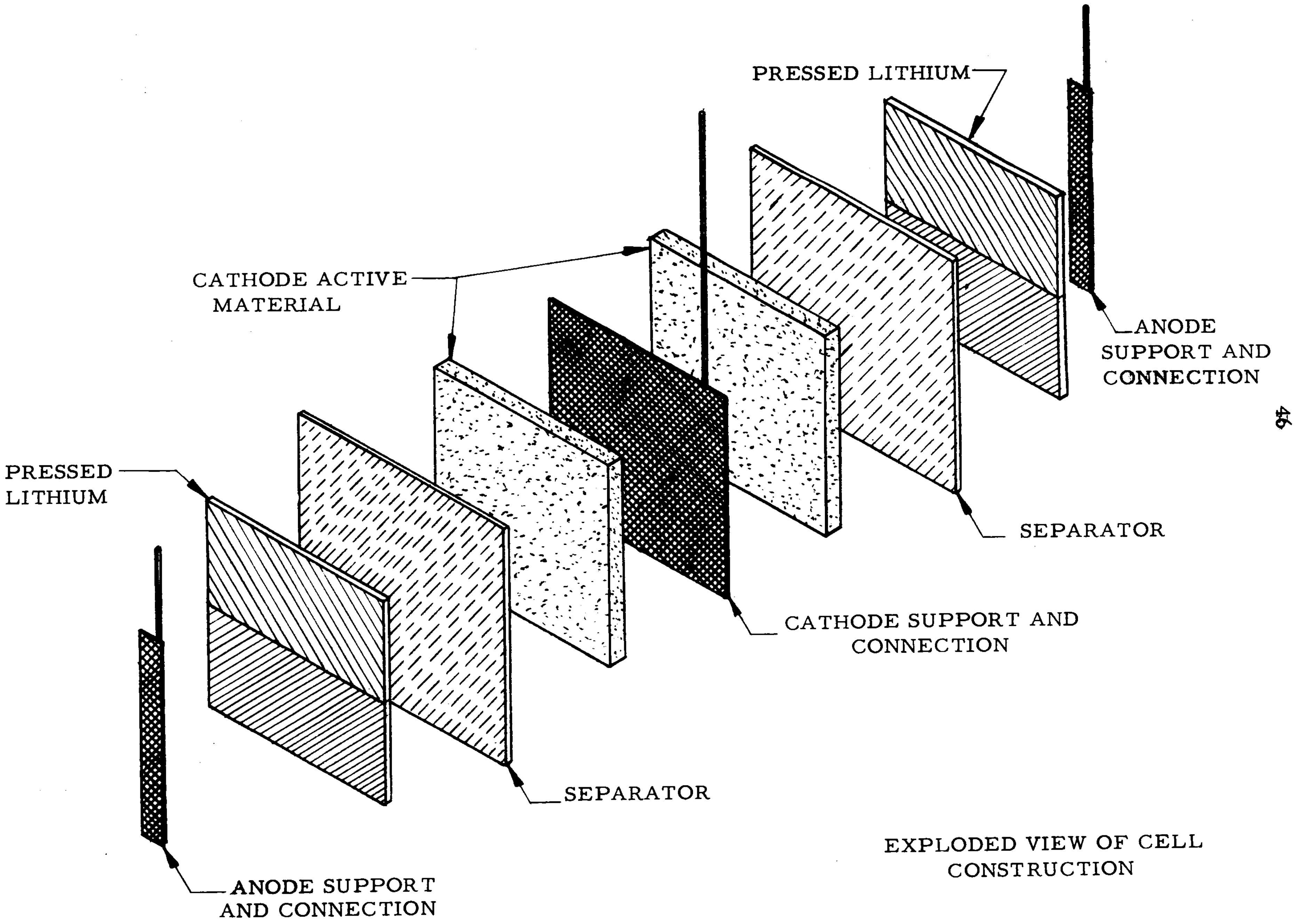
Cell discharge tests were conducted for the purpose of comparing cells constructed with acetic anhydride, dimethyl sulfoxide, butyrolactone, and propylene carbonate as the electrolyte solvents, and with lithium perchlorate as the solute. Flat-plate cells having two lithium negatives and one positive were constructed. The positive active materials used in this study were MnO_2 and CuF_2, and the filter-mat electrode construction was employed. A view of the test cell assembly is shown in Figure 6, page 46 (except for changes in materials, this type of test cell construction was employed for flat-plate cells throughout the program).

After the cells were activated with the electrolyte solutions and given an initial open-circuit stand period, the potential drop with various applied loads was determined. The cells were then discharged and the voltage-time data were continuously monitored. The CuF_2 cells were put in discharge five hours after addition of the electrolyte, while the MnO_2 cells were allowed to stand 71 hours in the activated state before discharge was started.

Construction data for the CuF_2 and MnO_2 cells given in Tables VII and VIII, pages 47 and 48; the polarization versus current, and voltage-time data for the discharges are presented in Figures 7 to 13, pages 49 to 55. In the test cells having CuF_2 positive electrodes, the best cathodic efficiency was obtained in propylene carbonate. Butyrolactone, acetic anhydride, and dimethyl sulfoxide gave approximately equal cathodic efficiency with BL giving somewhat higher discharge potentials. In the cells having MnO_2 positives, the cells with dimethyl sulfoxide solvent gave the longest discharge times, followed by propylene carbonate; the capacity of the acetic anhydride and butyrolactone cells was decidedly less probably because of a more extensive attack on the anodes during the open-circuit stand period.

Use of kerosene filter pad construction generally improved the reproducibility of cell discharge results and increased the utilization of the cathode active materials. Reference electrode (Cu wire) measurements indicated positive limitation in all cells except those with acetic anhydride electrolyte solvent, where the Li negatives became polarized and limited the cell capacity.

On the basis of the above test results, CuF_2 with propylene carbonate-$LiClO_4$ electrolyte appeared to hold the most promise for use in a high energy cell.



EXPLODED VIEW OF CELL CONSTRUCTION

FIGURE 6

TABLE VII

CONSTRUCTION OF CuF_2-Li TEST CELLS

Cell Nos. 1-8 (E86 - E93)

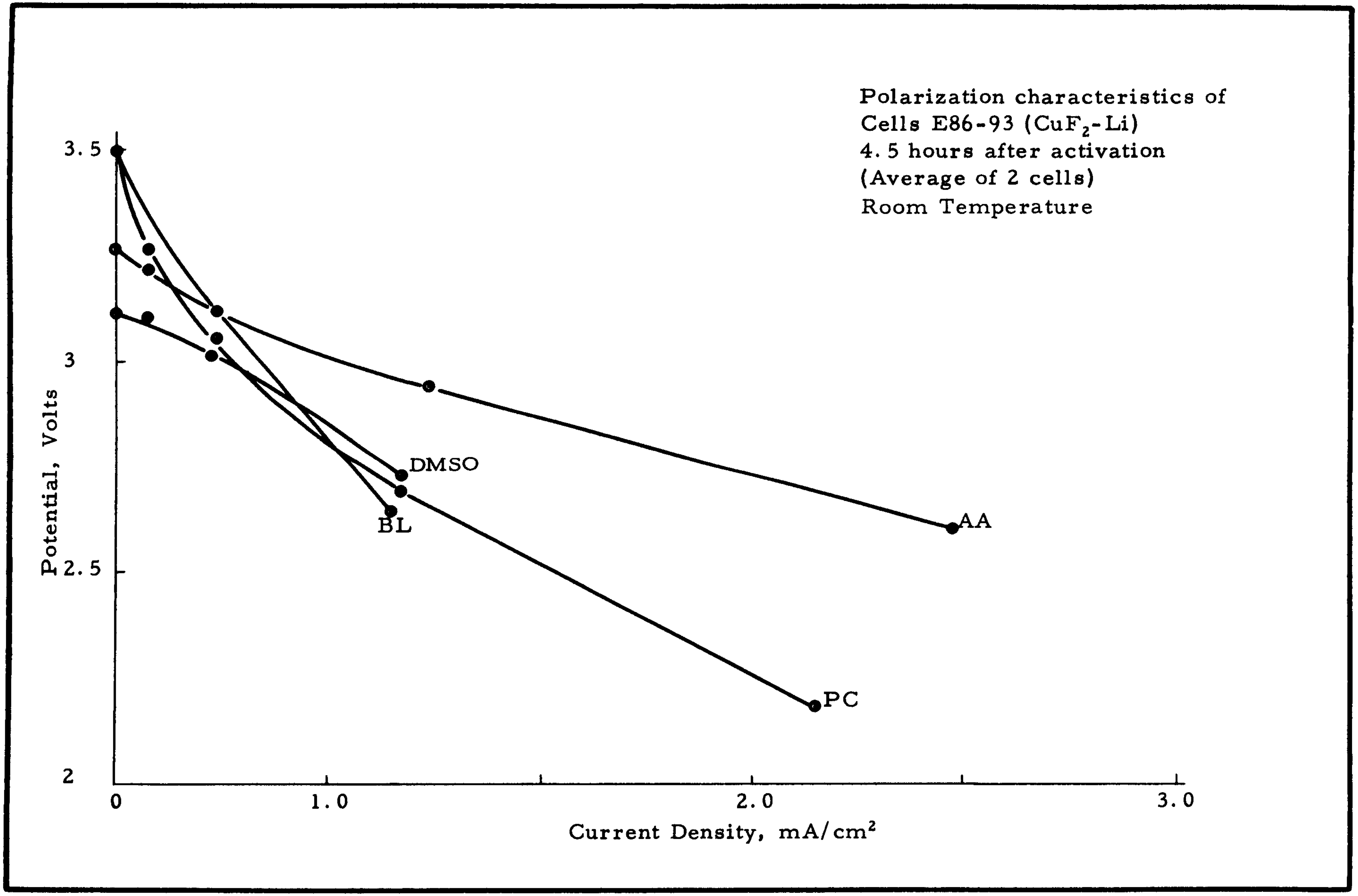
Cathode:	70% CuF_2, 20% graphite, 10% Nalcon Fiber (National Lead Company). Filter-mat construction, kerosene vehicle, pressed at 5.0 pounds per square inch; 1.91 ampere hours theoretical capacity.
Anode:	Lithium pressed onto expanded Ni screen. Theoretical capacity 5.7 ampere hours.
Separation:	Microporous rubber, 1.1 mm thick
Electrolyte:	Lithium perchlorate, 1 mole/liter except Acetic Anhydride saturated.
Electrode Area:	30 cm^2
Reference Electrode:	Cu wire
Electrolyte Solvent:	Cells 1 and 2 (E86 and E87) Acetic Anhydride Cells 3 and 4 (E88 and E89) Butyrolactone Cells 5 and 6 (E90 and E91) Dimethyl Sulfoxide Cells 7 and 8 (E92 and E93) Propylene Carbonate

TABLE VIII

CONSTRUCTION OF MnO_2-Li TEST CELLS

Cell Nos. 9-16 (E78 - E85)

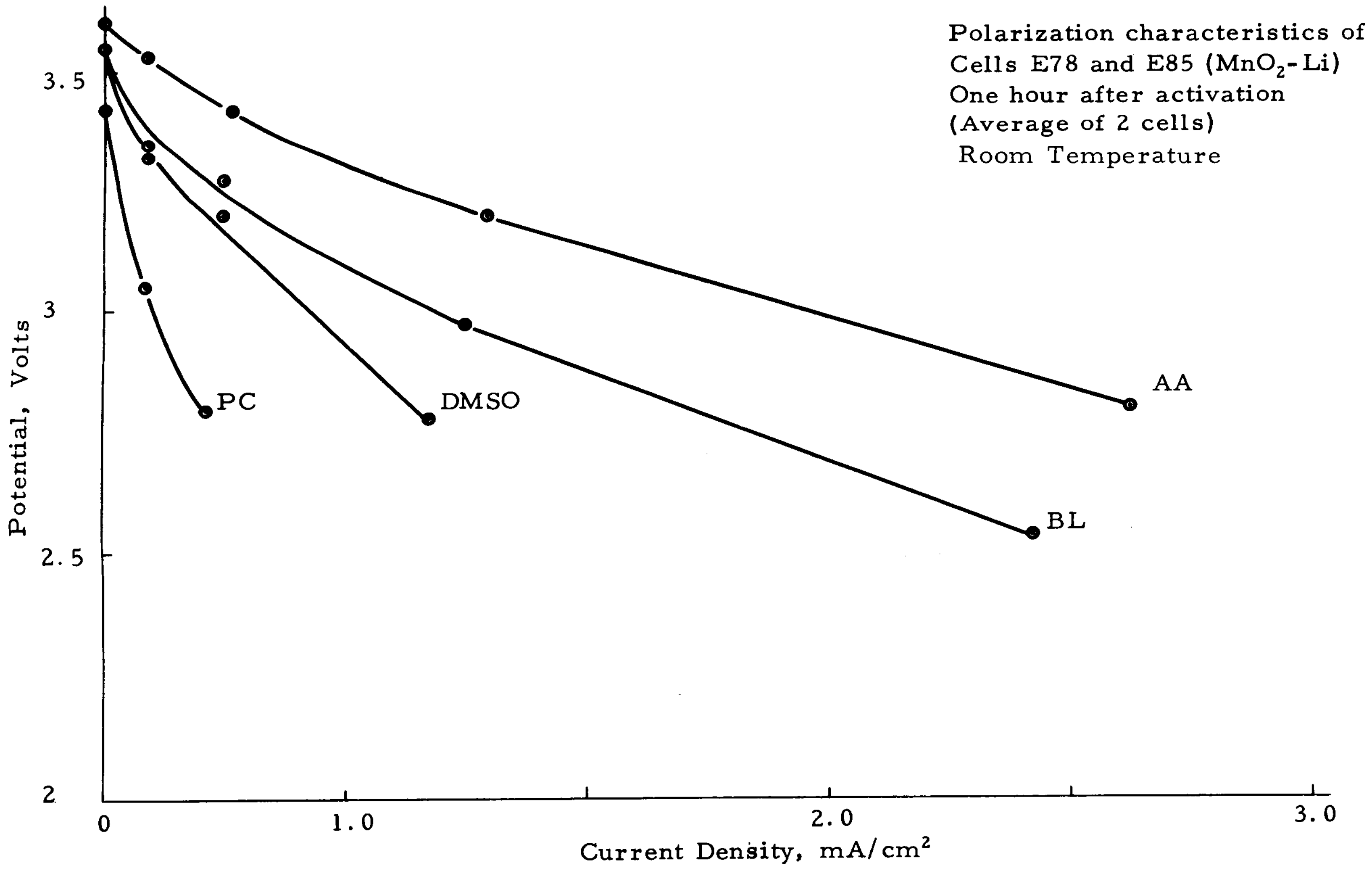
Cathode:	80% MnO_2, 15% graphite, 5% paper fiber, filter-mat construction, water vehicle, compressed at 5 pounds per square inch, 1.97 ampere hours theoretical capacity for 1 faraday/mole.
Anodes:	Two lithium anodes pressed onto Ni screen, 5.7 ampere hours theoretical capacity.
Separation:	Blotter paper, 0.6 mm
Electrolyte:	Lithium perchlorate, 0.5 mole/liter
Electrode Area:	30 cm^2
Reference Electrode:	Cu wire
Electrolyte Solvent:	Cells 9 and 10 (E78 and E79) Acetic Anhydride Cells 11 and 12 (E80 and E81) Butyrolactone Cells 13 and 14 (E82 and E83) Dimethyl Sulfoxide Cells 15 and 16 (E84 and E85) Propylene Carbonate



FORM FM-101

POLARIZATION CHARACTERISTICS OF CuF_2-Li CELLS

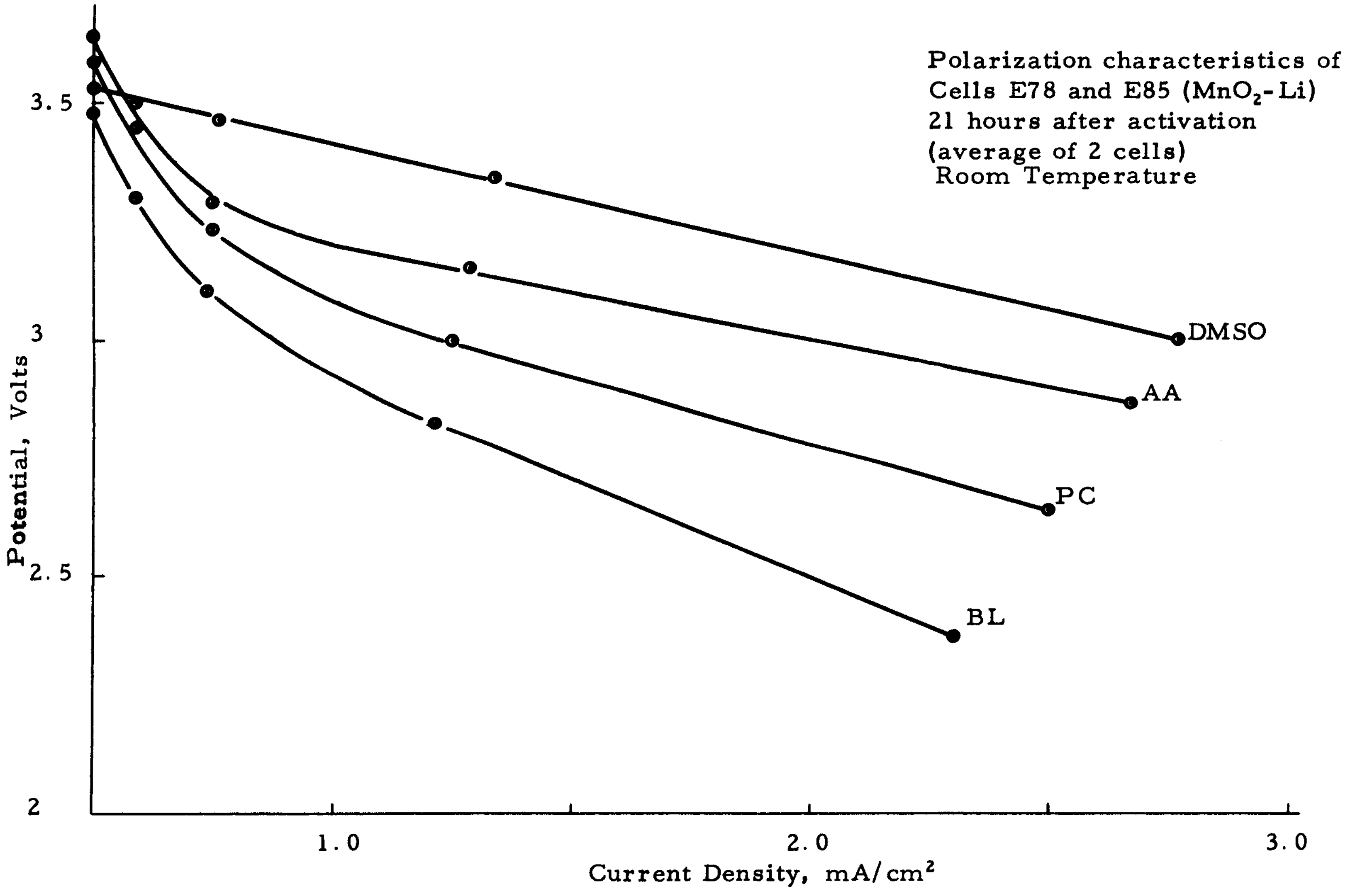
FIGURE 7



FORM FM-101

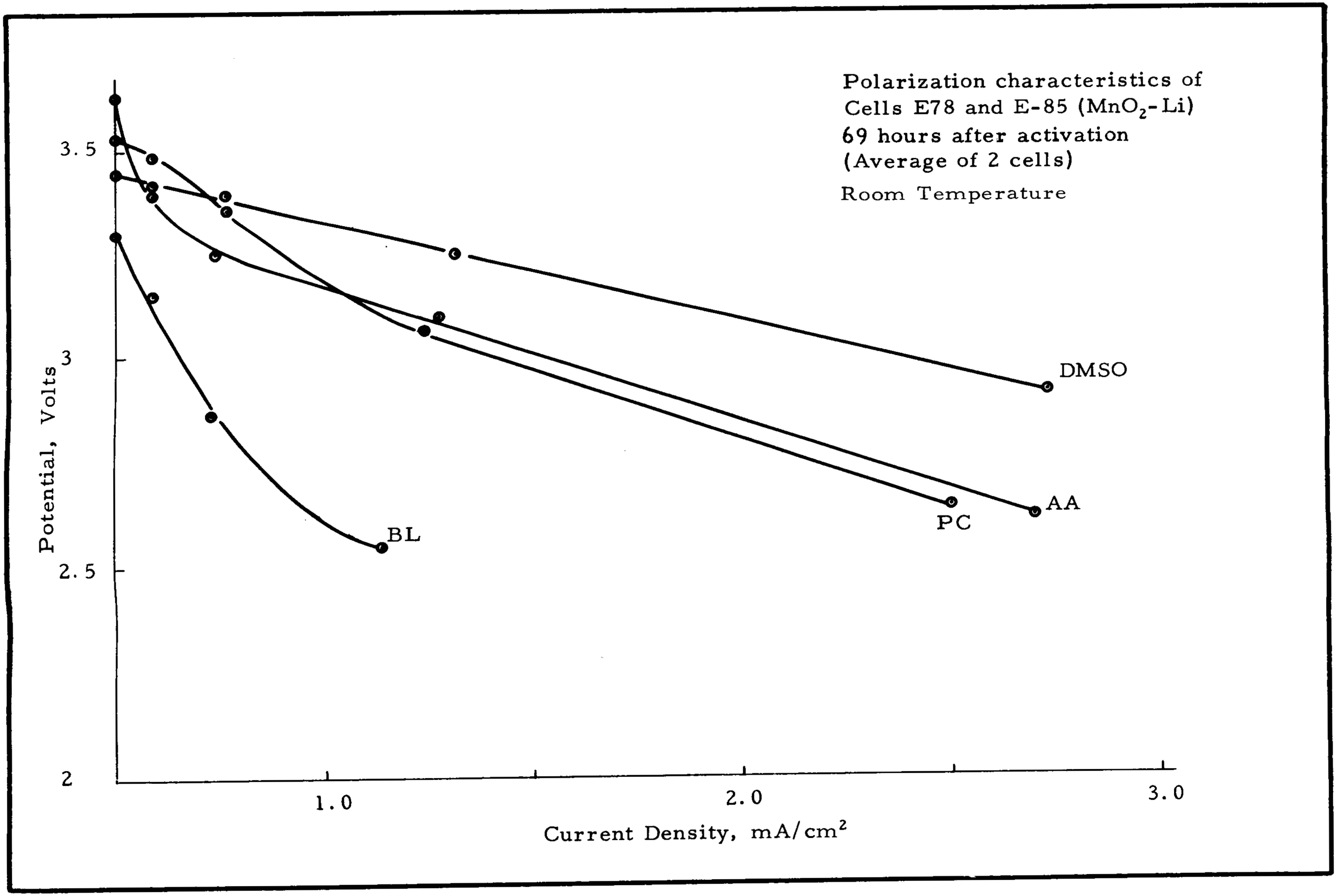
POLARIZATION CHARACTERISTICS OF MnO_2-Li CELLS

FIGURE 8



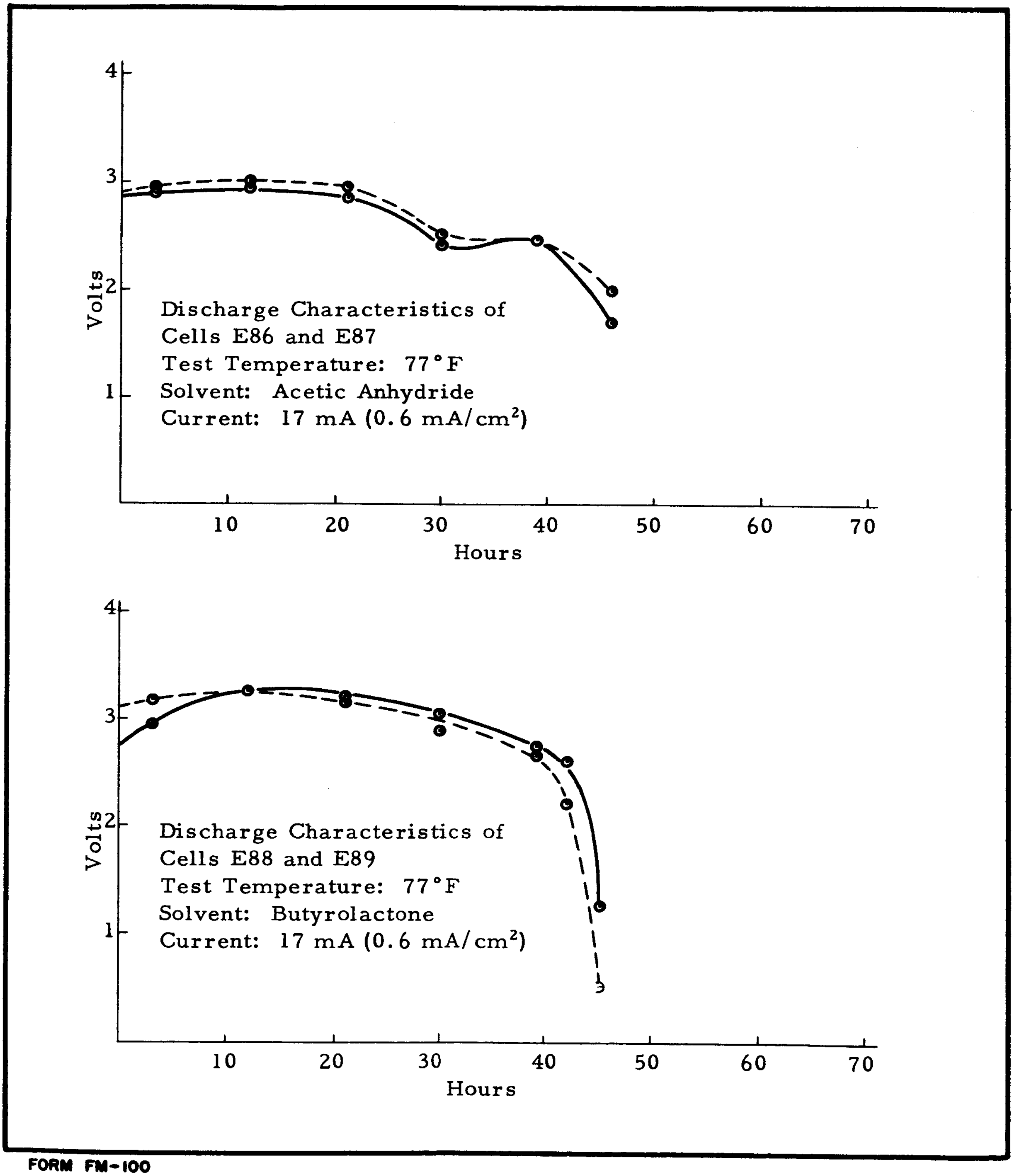
POLARIZATION CHARACTERISTICS OF MnO_2-Li CELLS

FIGURE 9



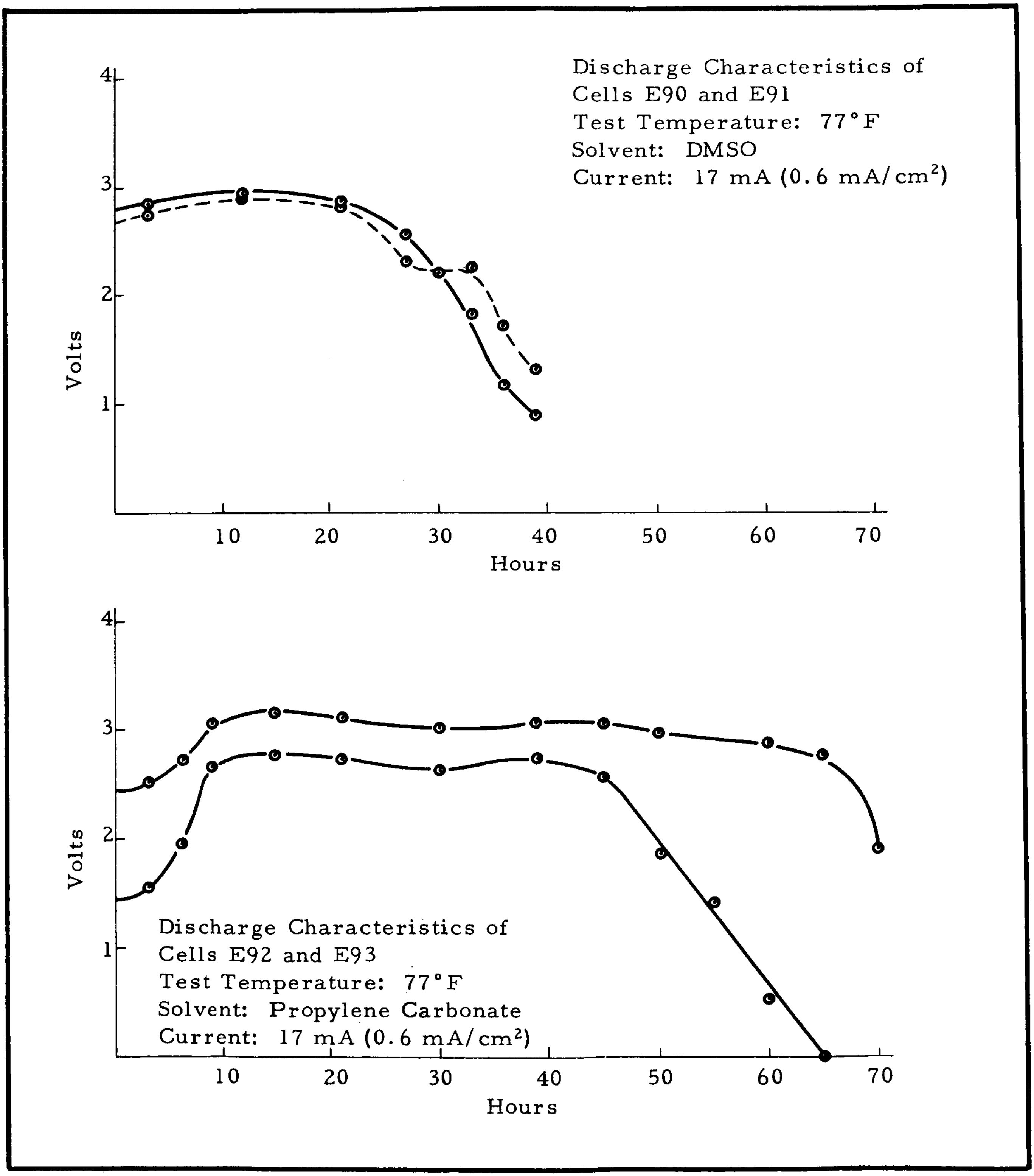
POLARIZATION CHARACTERISTICS OF MnO_2-Li CELLS

FIGURE 10



CHARACTERISTICS OF CuF_2-Li CELLS

FIGURE 11



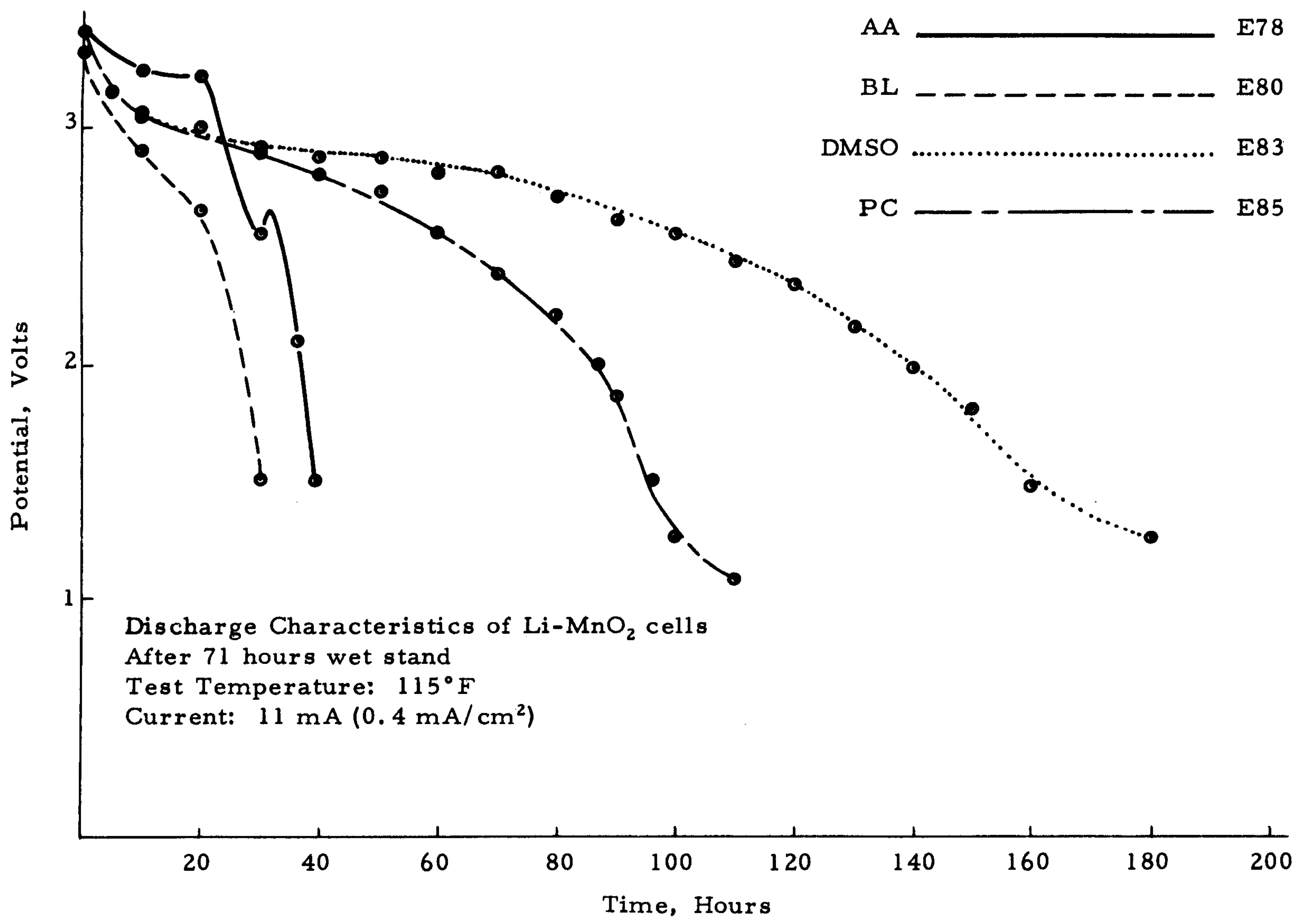
Discharge Characteristics of
Cells E90 and E91
Test Temperature: 77°F
Solvent: DMSO
Current: 17 mA (0.6 mA/cm^2)

Discharge Characteristics of
Cells E92 and E93
Test Temperature: 77°F
Solvent: Propylene Carbonate
Current: 17 mA (0.6 mA/cm^2)

FORM FM-100

CHARACTERISTICS OF CuF_2-Li CELLS

FIGURE 12



Discharge Characteristics of Li-MnO_2 cells
After 71 hours wet stand
Test Temperature: 115°F
Current: 11 mA (0.4 mA/cm^2)

CHARACTERISTICS OF MnO_2-Li CELLS

FIGURE 13

4.3. EVALUATION OF CATHODE REACTANTS IN POSITIVE LIMITING CELLS

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 source and manufacturer's grade designation for the materials are listed in the Appendix.

Only initial, short contact period stability tests were considered necessary to eliminate potentially hazardous combinations from cell tests. About 100 milligrams of the material was placed in a test tube, and 4 milliliters of the solvent (propylene carbonate or methyl formate) were added. The compatibility tests were performed in an inert atmosphere chamber under argon.

After observing the test samples for 24 hours, a quantity of lithium perchlorate was added to the test tubes to give a solution 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 57. 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 materials appeared to be compatible with the electrolyte solutions.

Electrodes were constructed from the materials which appeared to be 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 slurring was thinned with additional perchloroethylene and 0.5 grams of acid-washed asbestos fibers (powminco) were added. The mixture was suction-filtered on a 55 mm 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		1.5 M $LiClO_4$	
	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	R.	R.	--	--
12. TICA*	Sol.	N.R.	--	N.R.
13. K-DIC**	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 separators. 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

Discharge Current: 22 mA (0.7 mA/cm^2)

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 were poor compared with other cell tests at equivalent discharge conditions. This indicated that an optimum electrode and cell construction had not been obtained, and, therefore, the cell discharge data for the other materials probably was 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 with a reduction efficiency to 1.90 volts of 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 (0.57 mA/cm^2)

	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: 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.

Because of the apparently inconclusive results of the above discharge tests, a second test cell series was prepared. In order to produce more comparable electrode structures from the various materials, a constant volume (rather than weight) ratio of active material to graphite was employed. Using the available handbook density data, electrodes having the composition:

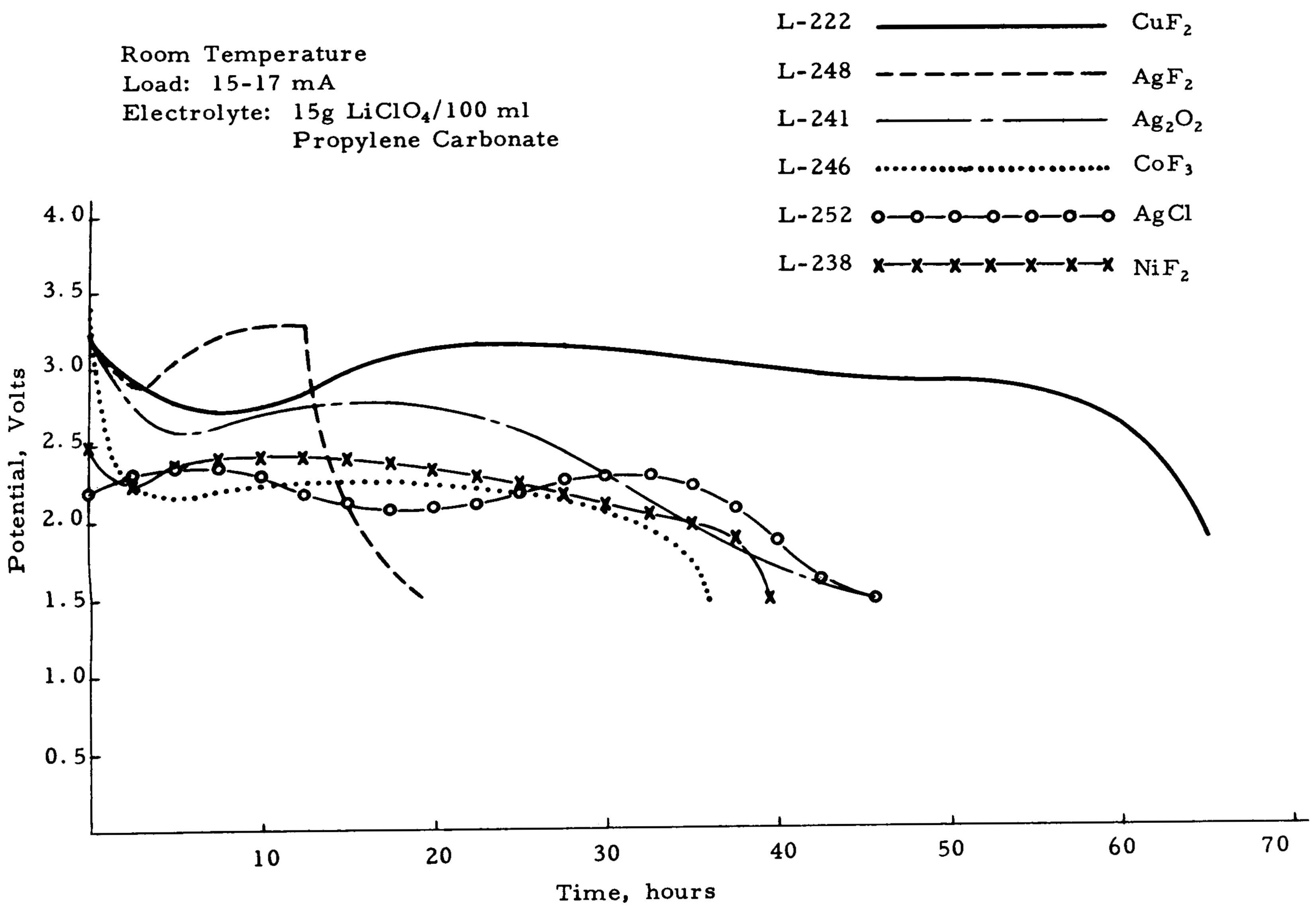
active material	0.83 cm^3
graphite	1.0 gram
Nalcon fiber	0.5 gram

were prepared by using the kerosene-vehicle filter pad construction method. This composition corresponds to the 7:2;1 CuF_2:graphite:fiber weight ratio employed in other CuF_2 electrode tests. Cell construction was similar to that shown in Figure 6, page 46 , and the construction details of the individual cells were as listed in Table XII, page 63.

Discharges were performed in methyl formate electrolyte at 27.5 mA (ca. 0.9 mA/cm^2), and in propylene carbonate electrolyte at 16 mA (ca. 0.5 mA/cm^2). Capacities of the individual cells to an arbitrarily chosen cut-off point of 2.0V, and the calculated cathodic efficiencies are presented in Table XIII, page 65. The voltage-time data for some of the cells (those showing the higher capacity) have been plotted in Figure 14, page 62.

Of the materials studied, Silver II fluoride showed the highest load potential (3.5 volts vs Li at 0.6 mA/cm^2). This material was not stable in methyl formate, and in propylene carbonate the electrochemical efficiency was low compared to that observed for CuF_2 cells. The latter may have been caused by a low Silver II content in the material used in the test as indicated by the varying coloration in the sample (presence of yellow color indicates Silver I fluoride). The other materials tested showed generally poor characteristics and do not appear promising as cathode reactants in the present construction.

On the basis of the results of the two test series, further emphasis on CuF_2 as the cathode material appears warranted. Other materials which may be of future interest because of their high potentials are Silver II fluoride and TICA. These, however, will probably be useful only in short life, reserve-activated cells.



DISCHARGE CHARACTERISTICS OF VARIOUS CATHODE MATERIALS VS LITHIUM ANODE IN PROPYLENE CARBONATE

FIGURE 14

TABLE XII

EXPERIMENTAL CELL CONSTRUCTION DATA

Cell No.	Material	Specific* Gravity	Grams of mat'l per 1.0 gram Graphite	Theoretical Capacity, AH	Electrolyte Solvent	Electrolyte Grams $LiClO_4$ per 100 ml solvent
L-208	CuF_2	4.23	3.51	1.61	MF	25
L-209				1.62		
L-210	NiF_2	4.63	3.85	1.65	MF	25
L-211				1.49		
L-212	$CuF_2 \cdot MnO_2$[1]	4.63	3.85	1.33	MF	25
L-213				1.51		
L-214	V_2O_5	3.36	2.79	3.56	MF	25
L-215				3.56		
L-216	Ag_2O_2	7.44	6.17	2.23	MF	25
L-217				1.79		
L-93	CoF_3	3.88	3.22	1.71	MF	25
L-94				1.71		
L-95	AgF_2	4.67	3.88	0.95	MF	25
L-96				0.83		
L-250	AgCl	5.56	4.61	0.39	MF	25
L-251				0.59		
L-238	NiF_2	4.63	3.85	1.96	PC	15
L-239				1.95		
L-240	Ag_2O_2	7.44	6.17	2.54	PC	15
L-241				3.31		

TABLE XII (Continued)

EXPERIMENTAL CELL CONSTRUCTION DATA

Cell No.	Material	Specific* Gravity	Grams of mat'l per 1.0 gram Graphite	Theoretical Capacity, AH	Electrolyte Solvent	Electrolyte Grams $LiClO_4$ per 100 ml solvent
L-242	V_2O_5	3.36	2.79	4.02	PC	15
L-243				4.50		
L-244	$CuF_2 \cdot MnO_2$[1]	4.63	3.85	1.95	PC	15
L-245				1.68		
L-246	CoF_3	3.88	3.22	1.65	PC	15
L-247				1.59		
L-248	AgF_2	4.67	3.88	0.86	PC	15
L-249				0.86		
L-252	AgCl	5.56	4.61	0.44	PC	15
L-253				0.68		

[1] Equal parts by weight

* <u>Handbook of Chemistry and Physics</u>, Chemical Rubber Publishing Company, 44th Edition

TABLE XIII

CATHODIC EFFICIENCY OF VARIOUS MATERIALS IN LITHIUM-ANODE CELLS

	CATHODE			ELECTROLYTE				
Cell No.	Active Material	Wt. of a.m., gms.	Theoretical Capacity, AH	Solvent	gms $LiClO_4$ per 100 ml Solvent	Dischg. Current mA	Capacity to 2.0v/cell, A.H.	Cathodic Efficiency, %
L-208	CuF_2	3.05	1.61	MF	25	27.5	1.05	63.7
L-209		3.09	1.62			27.5	--- [1]	---
L-210	NiF_2	2.97	1.65	MF	25	27.5	0.08	5.0
L-211		2.70	1.49			27.5	0.08	5.4
L-212	$CuF_2:MnO_2$ [2]	3.20	1.33	MF	25	27.5	0.11	8.3
L-213		3.60	1.51			27.5	0.11	7.3
L-214	V_2O_5	2.51	3.56	MF	25	27.5	0.13	3.7
L-215		2.51	3.56			27.5	0.08	2.2
L-216	Ag_2O_2	5.15	2.23	MF	25	27.5	0.41	18.4
L-217		4.15	1.79			27.5	0.34	19.0
L-93	CoF_3	2.43	1.71	MF	50	27.5	0.00 [3]	0
L-94		2.44	1.71			27.5	0.00	0
L-95	AgF_2	2.55	0.95	MF	50	27.5	0.00	0
L-96		2.26	0.83			27.5	0.00	0
L-238	NiF_2	3.52	1.96	PC	15	16.0	0.54	27.5
L-239		3.51	1.95			16.0	0.48	24.6

TABLE XIII (Continued)

CATHODIC EFFICIENCY OF VARIOUS MATERIALS IN LITHIUM-ANODE CELLS

	CATHODE			ELECTROLYTE				
Cell No.	Active Material	Wt. of a.m., gms.	Theoretical Capacity, AH	Solvent	gms. $LiClO_4$ per 100 ml Solvent	Dischg. Current mA	Capacity to 2.0v/cell A.H.	Cathodic Efficiency, %
L-240	Ag_2O_2	5.87	2.54	PC	15	16.0	0.38	14.9
L-241		7.65	3.31			16.0	0.66	19.9
L-242	V_2O_5	2.73	4.02	PC	15	17.0	0.24	6.0
L-243		3.06	4.50			17.0	0.29	6.5
L-244	CuF_2:MnO_2 [2]	4.66	1.95	PC	15	17.0	0.12	6.2
L-245		4.02	1.68			17.0	0.15	9.0
L-246	CoF_3	2.38	1.65	PC	15	17.0	0.55	33.3
L-247		2.28	1.59			17.0	0.43	27.0
L-248	AgF_2	2.36	0.86	PC	15	17.0	0.26	30.0
L-249		2.36	0.86			17.0	0.25	29.1
L-250	AgCl	2.07	0.39	MF	50	26.0	0.34	86.5
L-251		3.16	0.59			26.0	0.49	83.0
L-252	AgCl	2.34	0.44	PC	15	12.0	0.43	92.5
L-253		3.62	0.68			12.0	0.42	61.7

[1] No print-out (ink supply exhausted)

[2] 1:1 weight ratio

[3] Negligible above 2.0 volts

4.4. STUDY OF PRISMATIC CuF_2 ELECTRODE CONSTRUCTION

All of the prismatic CuF_2 electrodes studied on this program were prepared by mixing the active reagent with a conductor such as graphite and a fibrous material, and pressing the mixture to make a porous, coherent electrode. During the early part of the program, dry-mixing was employed, and the mixture was pressed in a steel mold at about 5000 psi onto an expanded metal support. A typical electrode composition of this type was:

CuF_2	12 parts by weight
Graphite	1 part " "
Paper Fibers	1 part " " .

It was found that with electrodes of this type slow and non-uniform wetting with the electrolyte solution often resulted. The above composition was modified by adding three parts of $LiClO_4$ (the electrolyte salt) to the dry mixture. Although this method produced electrodes having better characteristics, the procedure was abandoned because of the hazard of mixing dry components in the presence of the perchlorate salt.

A filter-mat electrode construction (developed by Livingston for organic electrodes) was adapted for construction of the positive electrode matrix. The active material and the conductor (graphite) were jar-milled with an inert solvent such as heptane, blended with paper or other fibers, and filtered in a paper sheet mold. After most of the solvent was removed, the mat was pressed at the desired pressure (usually 60 psi) between flat plates, cut to the desired size, and vacuum dried.

Since copper fluoride was found to have the most desirable discharge characteristics among the materials studied in the early comparative tests, it was the only material used in the electrode construction studies. Both graphite and acetylene black were investigated as the conducting additives, and S & S Filter Paper Pulp, and Nalcon fibers (National Lead Company) were used as the binding media.

The electrodes were evaluated by constructing and discharging 3-plate cells (See Figure 6, page 46). Lithium anodes and lithium perchlorate electrolyte solute were used in all tests; both methyl formate and propylene carbonate were employed as the electrolyte solvents. The cells were designed with about a three-fold excess of theoretical negative capacity to insure positive limitation at the end of discharge.

A series of tests was performed in order to evaluate the minimum ratio of conductor-to-active material needed for good electrochemical efficiency and voltage regulation of the positive electrode. A series of electrodes with both acetylene black and graphite at various concentrations were prepared keeping the ratio of active material-to-fiber constant at 14 grams of fiber/100 grams of CuF_2. Results of the cell discharge tests using methyl formate and propylene carbonate solvents are shown in Tables XIV and XV, pages 69 and 70.

Although the agreement between replicate cells in the series was fair, a clearly defined relationship between the concentration of the additives and electrode performance was not evident. Acetylene black was about as effective as graphite, but produced thicker electrodes (which hold more electrolyte solution and, therefore, appear less desirable). Reduction of the ratio of acetylene black to CuF_2 from 14:100 to 7:100 reduced the utilization efficiency considerably in propylene carbonate, but not in methyl formate.

It appears, however, that the electrode can contain over 80 percent of CuF_2 without affecting the electrochemical efficiency adversely.

The effect of compression of the filter mat on the discharge characteristics of the CuF_2 electrodes was also studied; results of these tests are shown in Table XVI, page 71 . Increasing the pressure from 60 psi to 500 psi reduced the tendency for an initial voltage "dip" in propylene carbonate cells as shown in Figure 15, page 72 . The overall performance of the electrodes did not appear to be sensitive to the amount of compression in this region. A pressure of 500 psi was found to give electrodes of good strength and was adopted as a temporary standard value.

TABLE XIV

DISCHARGE EFFICIENCY OF CuF_2 ELECTRODES IN METHYL FORMATE ELECTROLYTE

Cell No.	Weight of Carbon, grams/100g CuF_2		Theoretical Capacity, AH	Electrolyte Volume, cc	Efficiency Percent	Ampere hrs. to 2V. F.	Ampere hrs. per gram of electrode
	Graphite	Acetylene Black					
E-118	42	--	1.81	8	65.7	1.19	.220
E-119	42	--	1.98	8	54.5	1.08	.184
E-120	--	10.5	1.83	8	60.6	1.11	.255
E-121	--	10.5	1.81	8	65.2	1.18	.274
E-124	--	42	2.18	10.5	68.8	1.50	.232
E-125	--	42	1.85	10.5	57.0	1.06	.192
E-159	28	--	2.13	8	77.8	1.66	.292
E-160	28	--	2.23	8	71.4	1.59	.267
E-161	14	--	2.32	8	51.3	1.19	.211
E-162	14	--	2.12	8	31.5	.665	.129
E-165	--	7	2.92	8	56.8	1.66	.247
E-166	--	7	2.82	8	44.0	1.24	.191

TABLE XV

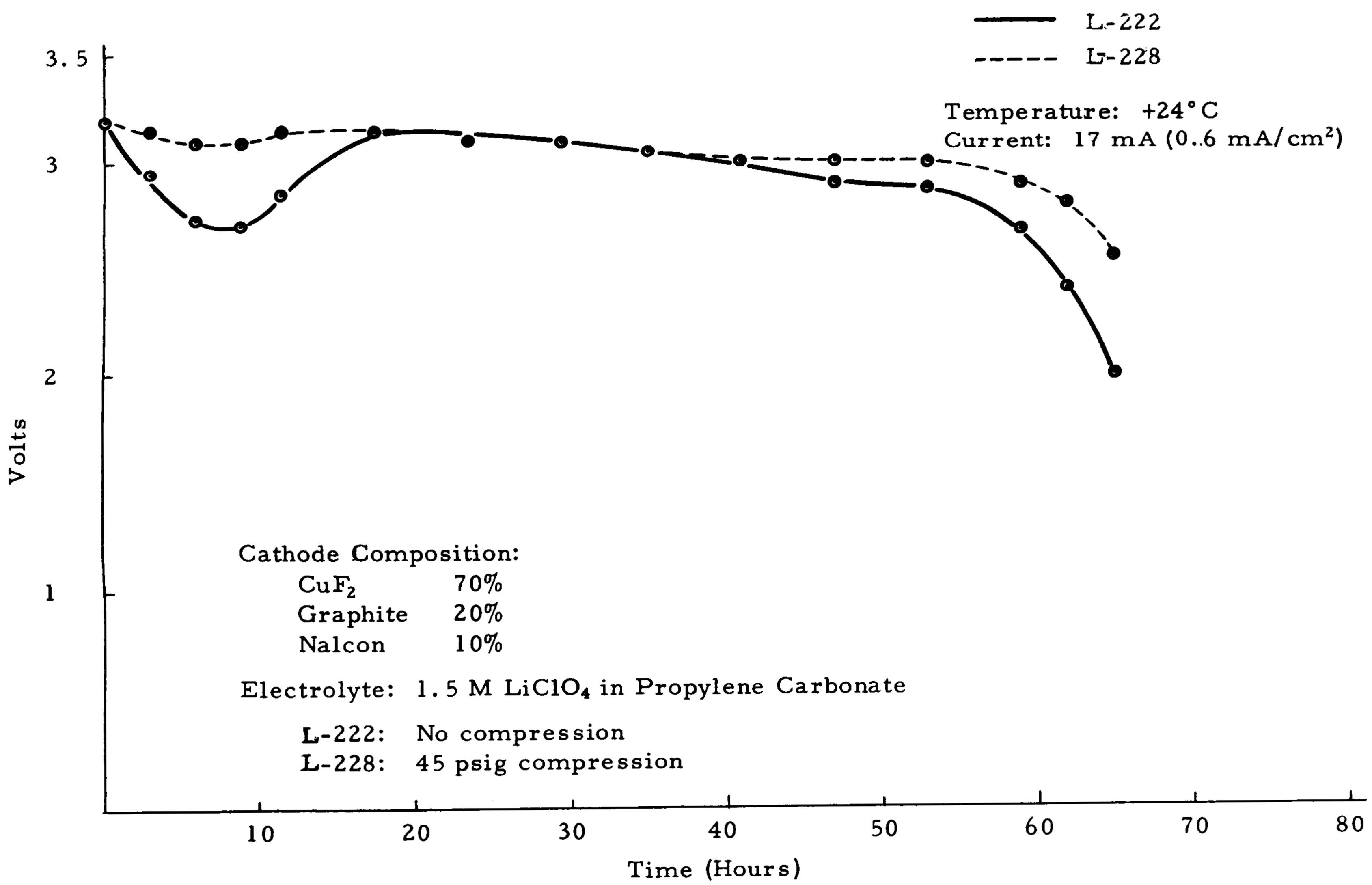
DISCHARGE EFFICIENCY OF CuF_2 ELECTRODES IN PROPYLENE CARBONATE ELECTROLYTE

Cell No.	Weight of Carbon grams/100g CuF_2		Theoretical Capacity, AH	Ampere hrs. to 2.0V.F.	Efficiency Percent	Ampere hrs. per gram of electrode
	Graphite	Acetylene Black				
E-135	28	--	2.11	1.18	56	.206
E-136	28	--	1.93	1.18	61	.226
E-143	28	--	1.78	1.05	59	.216
E-144	28	--	2.00	1.21	60	.223
E-145	28	--	2.14	1.35	63	.232
E-146	28	--	2.15	1.29	60	.221
E-137	14	--	2.45	1.32	54	.221
E-138	14	--	2.38	1.08	46	.186
E-147	14	--	2.24	1.05	47	.193
E-148	14	--	1.91	0.99	52	.213
E-139	--	14	2.37	1.11	47	.192
E-140	--	14	2.53	1.05	42	.169
E-149	--	14	2.63	1.25	48	.195
E-150	--	14	2.56	1.09	43	.175
E-141	--	7	2.34	0.62	26	.115
E-142	--	7	2.32	0.66	28	.124
E-151	--	7	2.48	0.75	30	.133
E-152	--	7	2.21	0.77	34	.152

TABLE XVI

EFFECT OF COMPRESSION OF FILTER-MAT ON ELECTRODE PERFORMANCE

Cell No.	Grams Additive Per 100 grams of CuF_2		Compression psig	Theoretical Capacity, AH	Discharge Rate	Ampere hrs. to 2.0V. F.	Efficiency Percent
	Graphite	Nalcon					
L-222	20	10	60	2.00	17.5 mA	1.27	63.5
L-223	20	10	60	1.86	17.5 mA	1.11	59.6
L-230	11.5	6	60	1.79	200 Ω	1.30	72.6
L-231	11.5	6	60	1.95	200 Ω	1.44	74
L-228	20	10	534	1.96	17.5 mA	1.19	60.7
L-229	20	10	534	1.99	17.5 mA	1.08	54.3
L-236	11.5	6	534	1.94	200 Ω	1.50	77.5
L-237	11.5	6	534	1.94	200 Ω	1.53	79
L-224	20	10	4450	1.95	17.5 mA	0.96	49.2
L-225	20	10	4450	2.30	17.5 mA	1.27	55.3
L-232	11.5	6	4450	1.88	200 Ω	1.45	77.2
L-233	11.5	6	4450	1.93	200 Ω	1.33	69
L-226	20	10	5340	1.95	17.5 mA	1.15	59
L-227	20	10	5340	1.97	17.5 mA	0.99	50.3
L-234	11.5	6	5340	1.99	200 Ω	1.50	75.5
L-235	11.5	6	5340	1.83	200 Ω	1.37	75



CHARACTERISTICS OF Li-CuF_2 CELLS

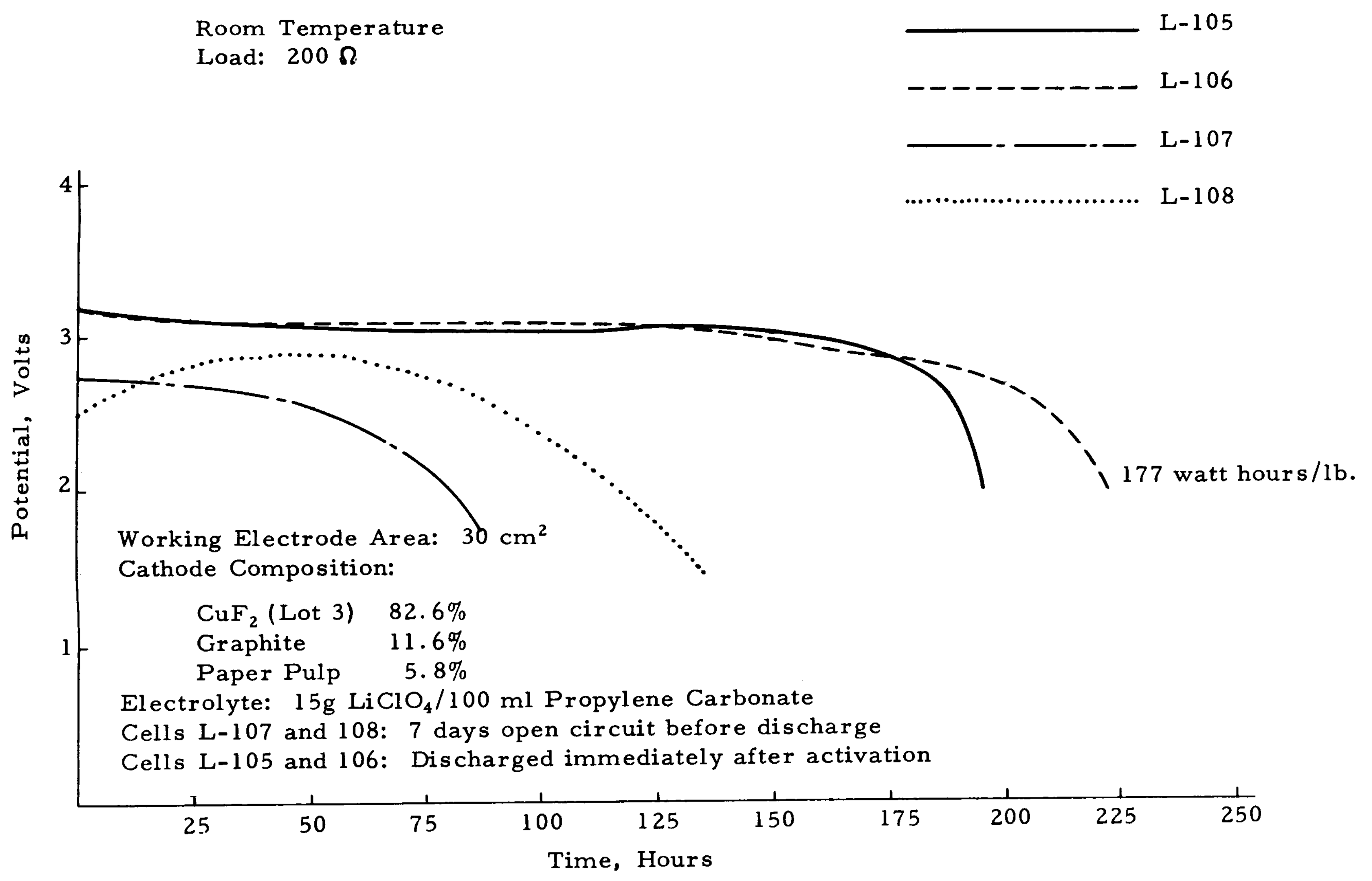
Figure 15

4.5. STUDY OF SELF-DISCHARGE IN CuF_2-Li CELLS

A series of CuF_2-Li cells were built and discharged in order to study the self-discharge characteristics of this couple in propylene carbonate-$LiClO_4$ electrolyte. The three-plate cells were built with one positive and two negative plates as shown in Figure 6, page 46 . The theoretical capacity of the CuF_2 electrode was about 4.0 AH, while the two negatives had a combined capacity in the range of 5.5 to 6.0 AH. The separation was 1.1 mm thick microporous rubber veneer, and the external case was a polyethylene envelope laterally supported between rigid blocks.

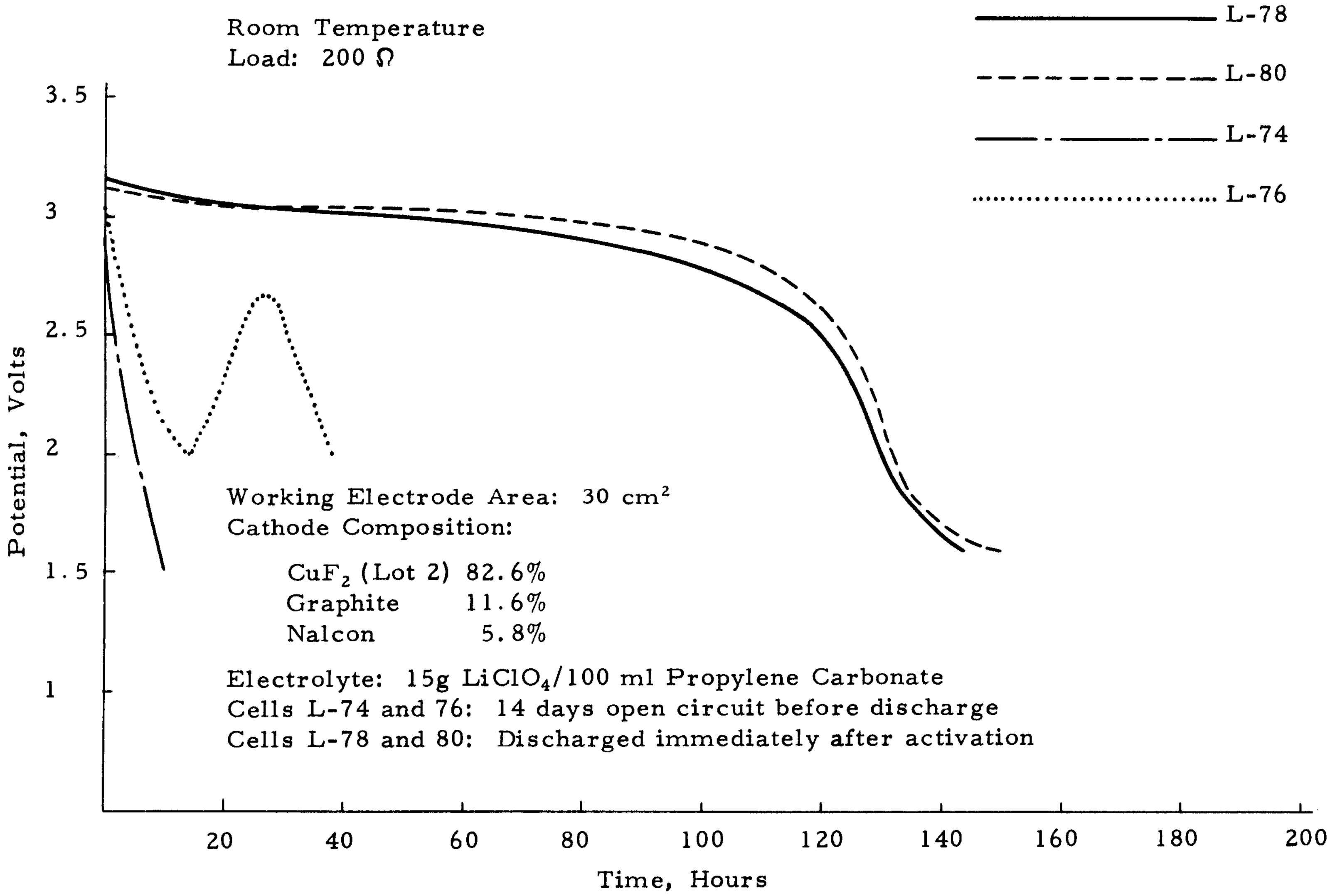
As can be seen from the voltage-time data presented in Figures 16 through 18, pages 74 through 78 , a considerable decrease in capacity resulted even after a one-week stand at room temperature. Vacuum-drying of the cells for 16 hours before activation with electrolyte solution did not appreciably improve the shelf life characteristics. During the stand period, a green coloration gradually developed in the electrolyte solutions as viewed through the translucent polyethylene envelopes. Since the green coloration is most likely due to dissolved copper compounds, the shelf life capability of the system is greatly affected by the solubility of the cathode material. This assumption was further substantiated by the presence of copper-colored deposits on the lithium anodes of the cells upon inspection of the discharged cells.

Since only very low solubility of CuF_2 in propylene carbonate had been observed in the specific conductance and solubility tests described in Section 3.3, the amount of CuF_2 which passes into solution must be affected by the presence of the $LiClO_4$ and/or impurities such as water. It will be necessary to study these phenomena extensively in order to produce CuF_2-Li cells with extended shelf life capabilities.



EFFECT OF OPEN CIRCUIT STAND ON DISCHARGE CHARACTERISTICS OF CuF_2-Li CELLS

FIGURE 16

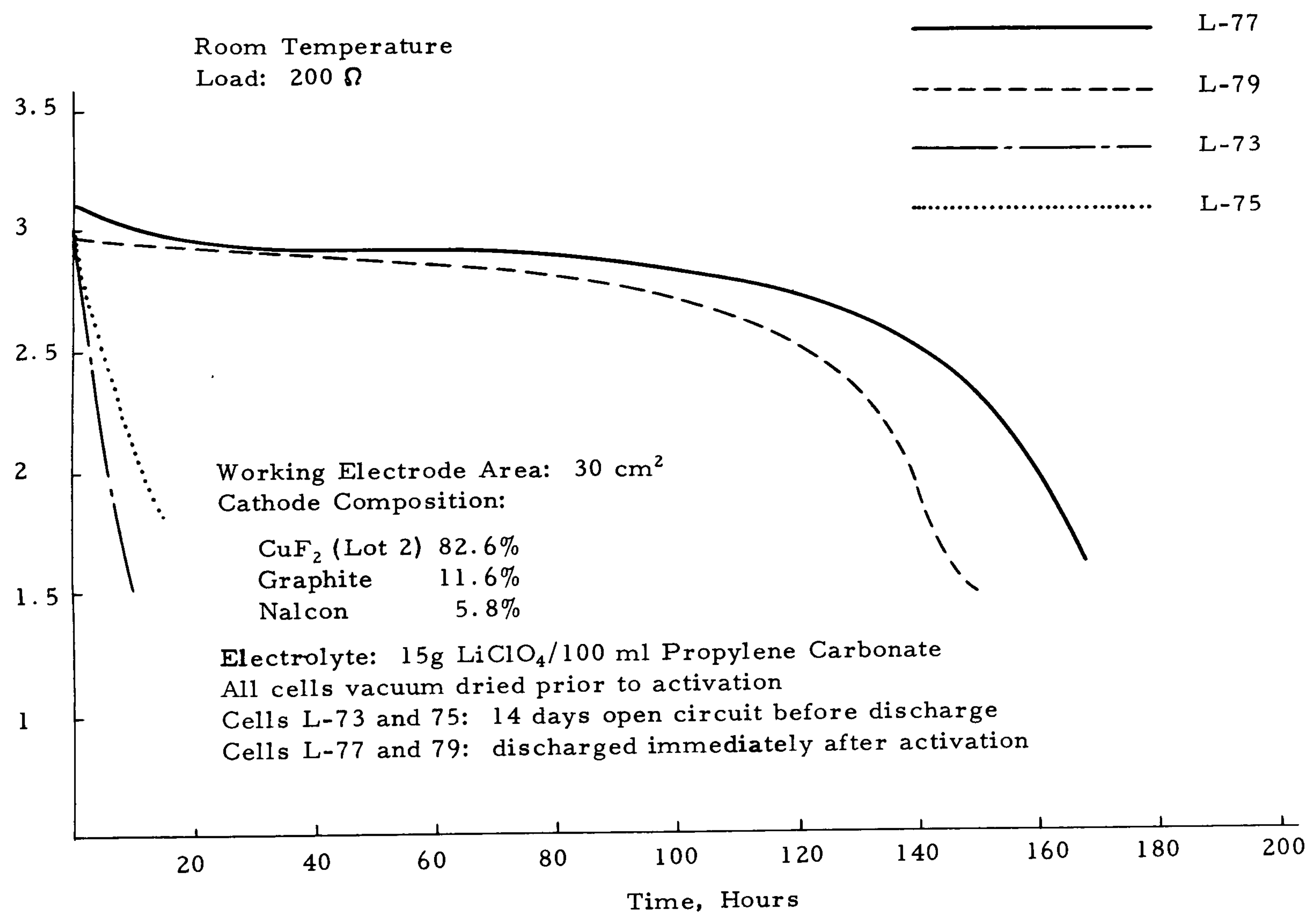


FORM FM-101

EFFECT OF OPEN CIRCUIT STAND ON DISCHARGE CHARACTERISTICS OF CuF_2-Li CELLS

(Vacuum Dried)

FIGURE 17



FORM FM-101

EFFECT OF OPEN CIRCUIT STAND ON DISCHARGE CHARACTERISTICS OF CuF_2-Li CELLS

(Not Vacuum Dried)

FIGURE 18

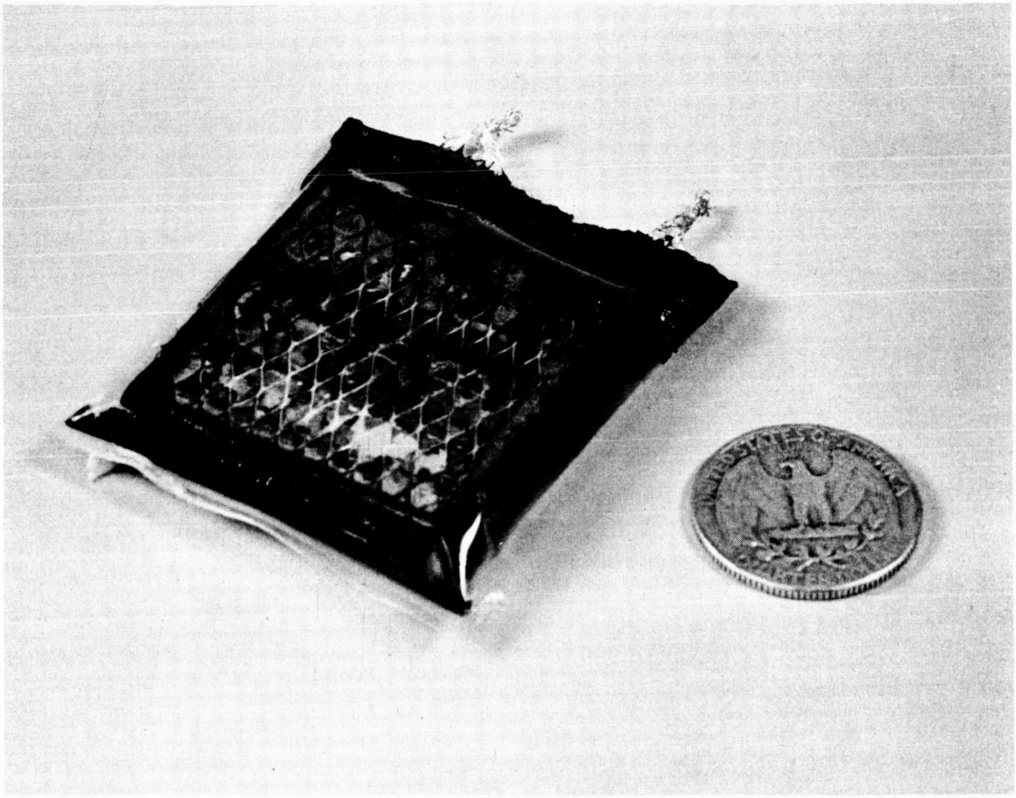
4.6. PROTOTYPE CELL TESTS

Thirty prototype cells were constructed and discharged in accordance with Section I. B. 8 of the contract, and direction from NASA Project Manager. The three-plate cells had construction similar to that described in Section 4. 5. The positive electrodes had the composition

CuF_2	100 parts (by wt.)
Graphite	14 parts (by wt.)
Paper Fiber	7 parts (by wt.)

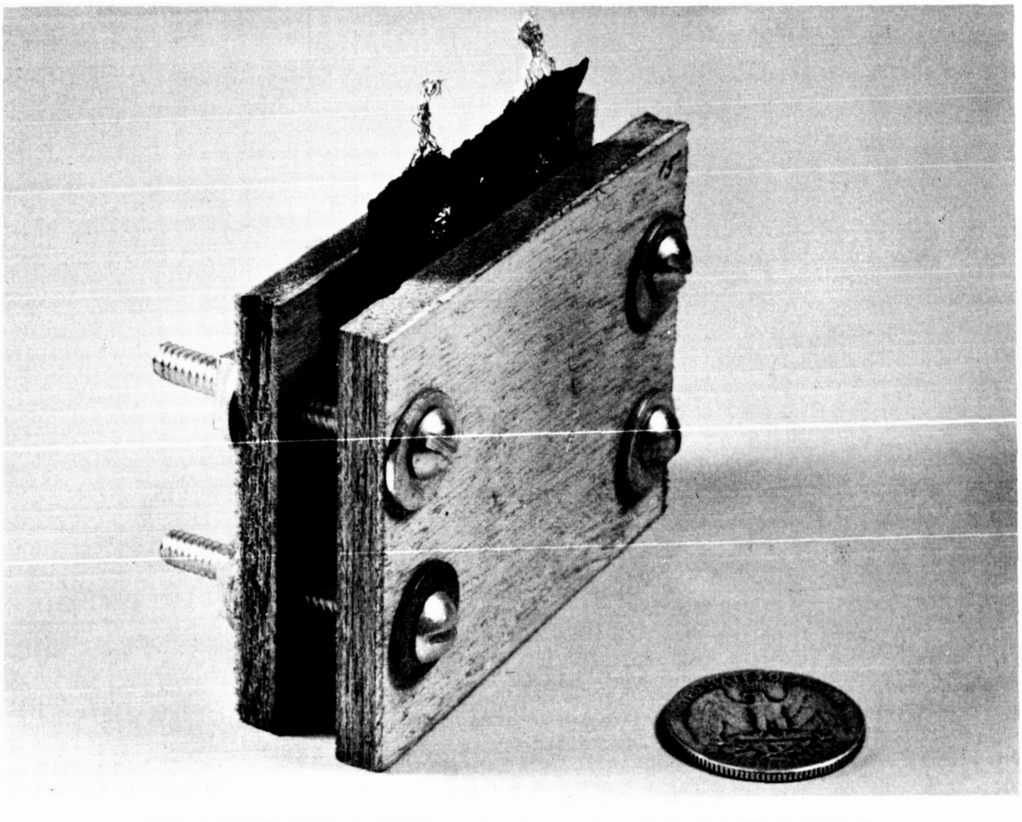
and had a theoretical capacity of 3 to 5 ampere hours. The two lithium negatives had a combined theoretical capacity of 4 to 6 ampere hours. Expanded silver was used to make connection to both the positive and the negative electrodes, and 0.03 inch thick microporous rubber separation was employed. As the external case, polyethylene envelopes having a film thickness of .005 inches were used. A completed cell is pictured in Figure 19, page 78, while Figure 20, page 78 shows the cell supported between blocks to provide lateral compression during discharge.

Construction data for the prototype cells listing theoretical electrode capacity, electrolyte solution and volume, and active material (CuF_2 and Li) and total cell weights are presented in Table XVII, page 79. The weights of the individual components in a representative cell are shown in Table XVIII, page 80.



CuF_2-Li PROTOTYPE CELL

FIGURE 19



PROTOTYPE CELL DISCHARGE ASSEMBLY

FIGURE 20

TABLE XVII

PROTOTYPE CELL CONSTRUCTION DATA

Cell No.	Theo. Electrode Capacity, AH Li	Theo. Electrode Capacity, AH CuF_2	Electrolyte*	Volume, cc	Active Material Wt., grams**	Cell Wt., grams
1	5.18	3.85	MF	6.0	8.61	21.0
2	5.53	3.67	MF	6.0	8.35	20.6
3	4.52	3.90	MF	6.0	8.53	20.9
4	5.26	3.75	MF	6.0	8.58	20.9
5	4.52	3.66	MF	6.0	8.08	20.4
6	4.32	3.73	MF	5.0	8.17	19.2
7	5.68	3.76	MF	5.0	8.57	19.6
8	4.36	3.33	MF	5.0	7.41	18.3
9	4.75	3.51	MF	5.0	7.85	18.8
10	4.91	3.84	MF	5.0	8.52	19.6
11	5.25	3.80	MF	5.0	8.53	19.6
12	7.72	3.14	MF	5.0	7.92	18.7
13	5.40	3.80	MF	5.0	8.57	19.7
14	5.40	3.84	MF	5.0	8.66	19.8
15	4.63	3.50	MF	5.0	7.81	18.8
16	4.79	4.89	PC	8.0	10.47	26.1
17	4.83	4.31	PC	7.0	9.39	23.4
18	5.72	4.86	PC	7.0	10.65	24.9
19	4.86	4.09	PC	7.0	8.98	22.9
20	5.10	4.97	PC	7.0	10.69	25.0
21	5.44	4.00	PC	6.0	8.96	21.8
22	5.40	3.71	PC	6.0	8.40	21.1
23	4.48	4.42	PC	7.0	9.51	23.8
24	5.06	5.09	PC	7.5	10.93	26.1
25	5.56	4.60	PC	7.0	10.12	24.5
26	4.64	4.85	PC	6.0	10.35	23.5
27	4.98	4.37	PC	6.0	9.55	22.6
28	4.96	4.57	PC	6.0	9.92	23.0
29	4.67	4.28	PC	6.0	9.29	22.2
30	4.91	4.44	PC	6.0	9.65	22.6

* 50g $LiClO_4$/100 ml MF
15g $LiClO_4$/100 ml PC

** CuF_2 + Li

TABLE XVIII

COMPONENT WEIGHTS OF PROTOTYPE CELL NO. 20

	Wt., grams	Percent
Positive Electrode (1)		
CuF_2	9.4	37.6
Graphite	1.3	5.2
Paper Pulp	0.7	2.8
Ag Screen	0.3	1.2
Negative Electrodes (2)		
Li	1.3	5.2
Ag Screen	0.6	2.4
Electrolyte (7 ml, density 1.33)	9.3	37.2
MPR Separators (2)	1.3	5.2
Polyethylene Envelope	0.8	3.2
TOTAL	25.0	100

Discharge data for the thirty prototype cells are presented in Table XIX, page 82 and voltage-time data are plotted in Figures 21 to 28, pages 84 to 91 for the best run in each group. The best performance in terms of energy density was obtained from cells having propylene carbonate electrolyte solvent and discharged at the 250-hour rate at 35°C (Cells 16-20). Of the five cells in this group, four delivered in excess of 200 watt-hours per pound of total cell weight. The highest energy density figure was obtained for Cell No. 20, which gave 223 watt-hours per pound of cell weight, and 522 watt-hours per pound of active materials (CuF_2 and Li) weight. These figures were considerably lower for cells discharged at the approximately 100-hour rate (100-154 watt-hours per pound of cell weight at 35°C, and 71-144 watt-hours per pound of cell weight at 50°C).

With methyl formate-$LiClO_4$ electrolyte the energy density (per pound of cell weight) for discharges run at -15°C ranged from 111 to 124 WH/lb. at the ca. 70-hour rate and from 47 to 94 WH/lb. at the ca. 30-hour rate. At 35°C, the energy density was in the range of 38-83 WH/lb. at the ca. 20-hour rate.

The CuF_2-Li system with propylene carbonate-lithium perchlorate electrolyte shows good promise for low rate applications. At the present time, the main drawback of the system appears to be the lack of shelf life capability.

With methyl formate-$LiClO_4$ electrolyte, the CuF_2-Li couple should allow construction of cells for moderately high rate applications (1-hour rate). However, a more appropriate cell construction (thinner prismatic electrodes) would need to be developed to produce cells having the required discharge rate capability.

TABLE XIX

PROTOTYPE CELL DISCHARGE DATA

Methyl Formate Cells

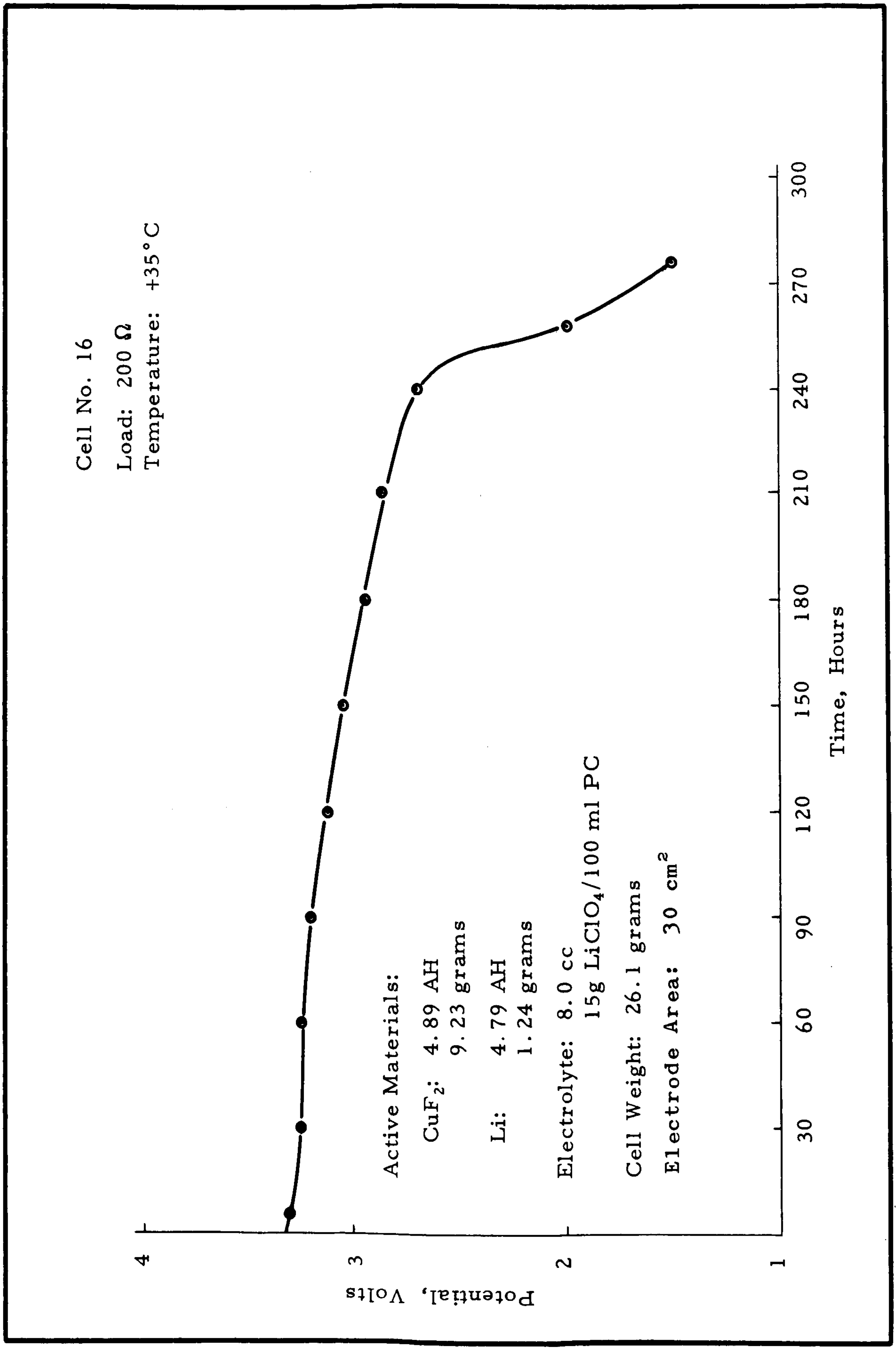
Cell No.	Load, ohms	Discharge Temp., °C	Time to 2.0VF, hrs.	Average Voltage to 2.0VF	Watt hrs. to 2.0VF	Watt hrs. per lb. of active mat'l	Watt hrs. per lb. of cell wt.
1	100	-15	77.6	2.72	5.74	302	124
2	100	-15	67.1	2.74	5.04	274	111
3	100	-15	77.6	2.70	5.71	302	123
4	100	-15	74.7	2.72	5.50	293	120
5	100	-15	70.0	2.71	5.13	289	114
6	50	-15	32.9	2.46	3.98	221	94
7	50	-15	20.6	2.63	2.84	151	66
8	50	-15	25.9	2.66	3.67	224	91
9	50	-15	28.2	2.61	3.84	220	93
10	50	-15	13.5	2.74	2.06	108	47
11	50	+35	12.0	2.60	1.62	88	38
12	50	+35	22.0	2.68	3.16	182	77
13	50	+35	20.0	2.73	2.98	158	69
14	50	+35	14.0	2.67	2.00	105	46
15	50	+35	24.0	2.67	3.42	200	83

TABLE XIX (Continued)

PROTOTYPE CELL DISCHARGE DATA

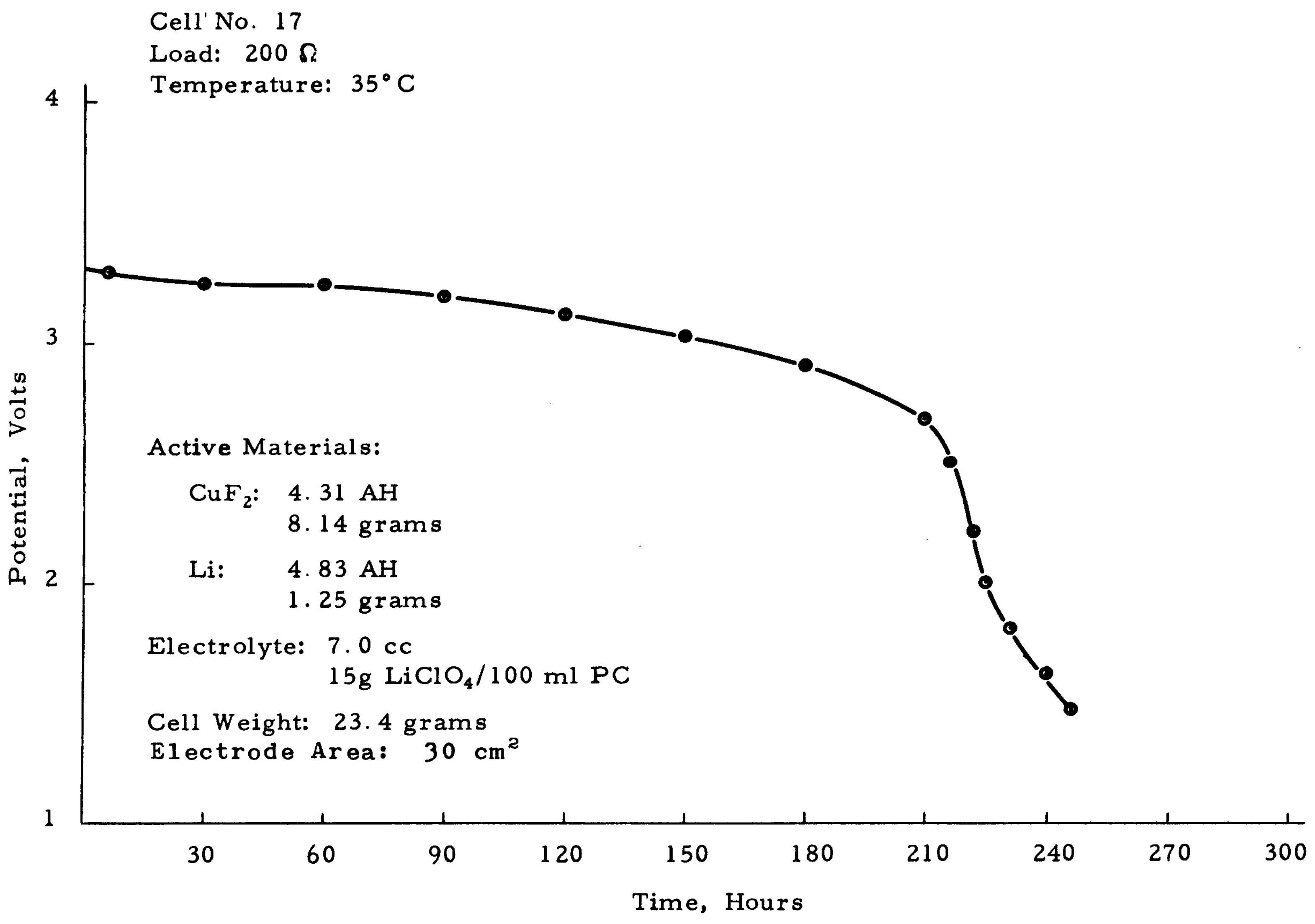
Propylene Carbonate Cells

Cell No.	Load, ohms	Discharge Temp. °C	Time to 2.0VF, hrs.	Average Voltage to 2.0VF	Watt hrs. to 2.0VF	Watt hrs. per lb. of active mat'l	Watt hrs. per lb. of cell wt.
16	200	+35	259.0	3.04	11.90	512	207
17	200	+35	225.0	3.04	10.46	502	201
18	200	+35	256.0	2.99	11.32	489	208
19	200	+35	210.0	3.07	9.86	498	195
20	200	+35	265.0	3.05	12.20	522	223
21	100	+35	86.0	2.79	6.40	341	140
22	100	+35	94.0	2.76	7.15	387	154
23	100	+35	80.0	2.68	5.73	273	109
24	100	+35	72.0	2.82	5.73	238	100
25	100	+35	84.0	2.80	6.58	296	122
26	100	+50	87.1	2.83	6.96	304	134
27	100	+50	60.0	2.93	5.15	247	104
28	100	+50	84.1	2.95	7.32	335	144
29	100	+50	82.4	2.89	6.88	335	140
30	100	+50	42.9	2.87	3.54	166	71



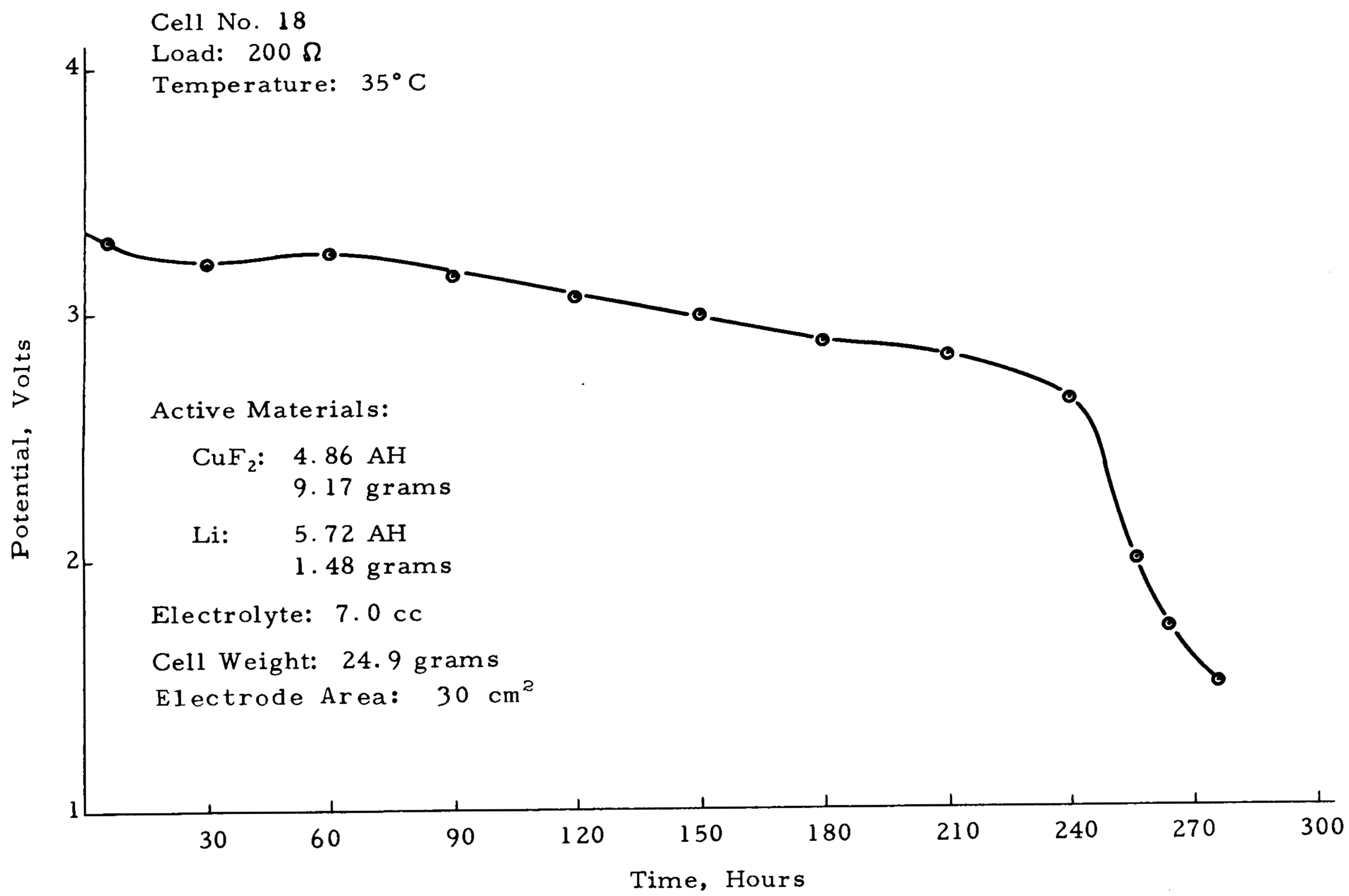
DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS

FIGURE 21



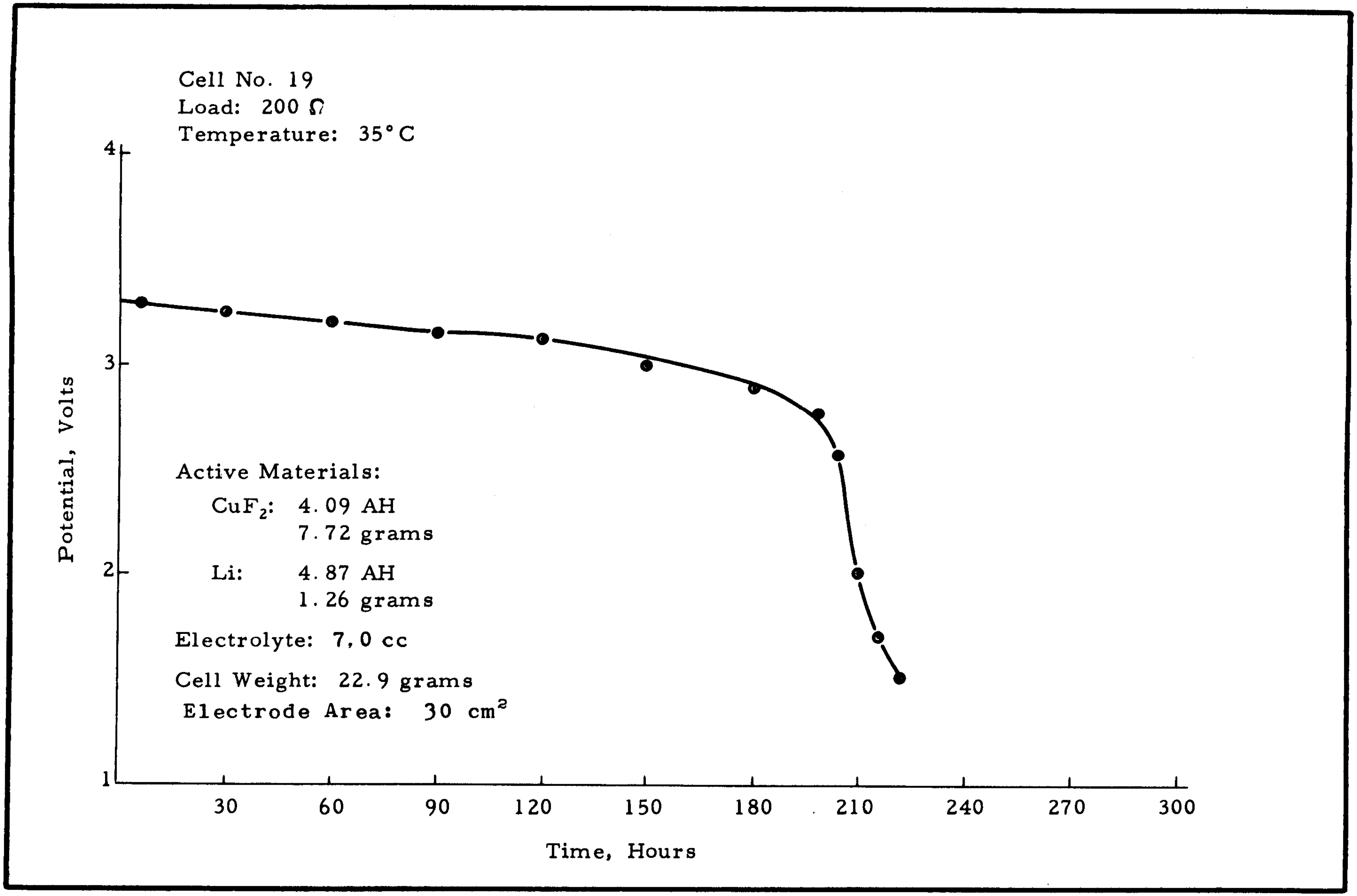
DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS

FIGURE 22



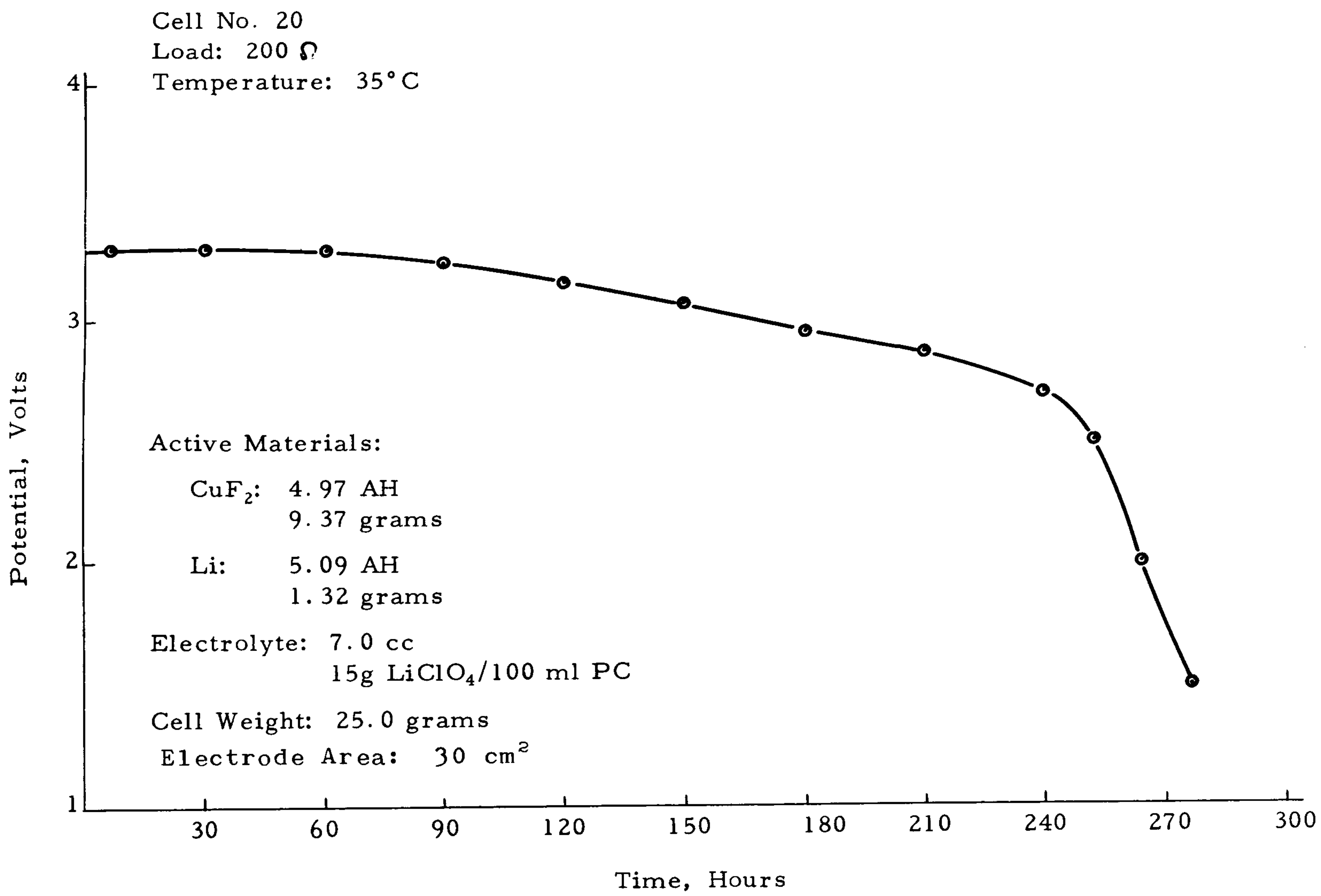
DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS

FIGURE 23



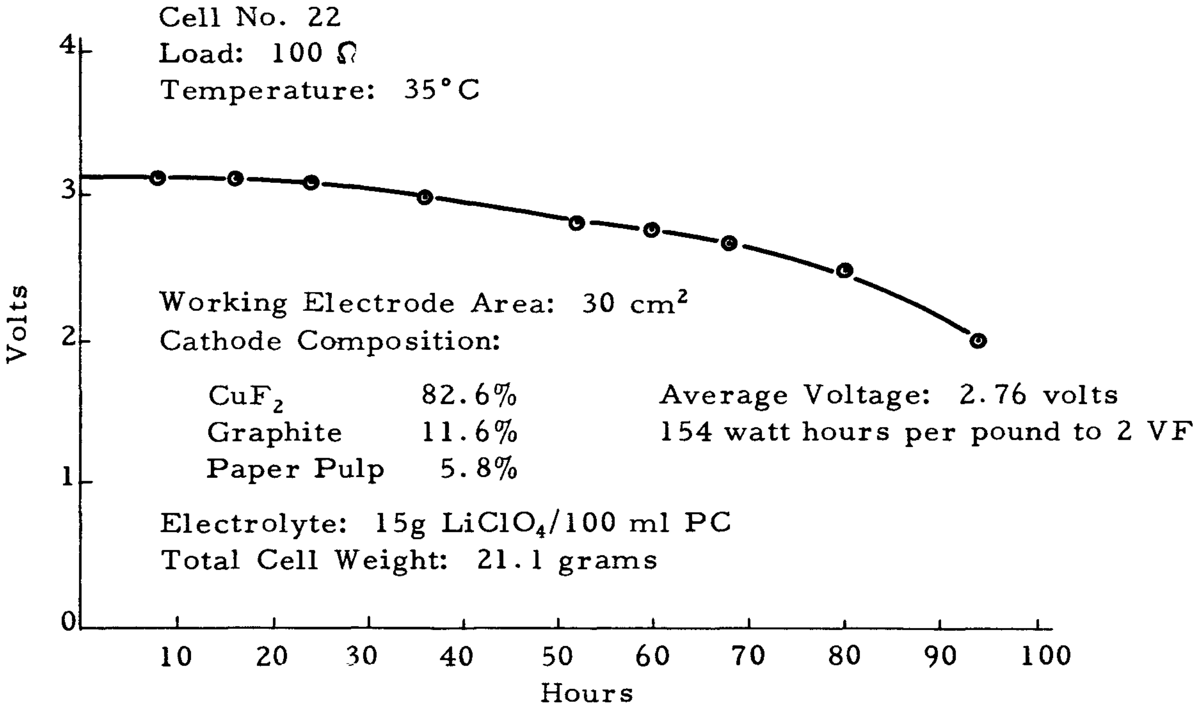
DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS

FIGURE 24



DISCHARGE CHARACTERISTICS OF PROTOTYPE CELLS WITH PROPYLENE CARBONATE ELECTROLYTE

FIGURE 25



Cell No. 22
Load: 100 Ω
Temperature: 35°C

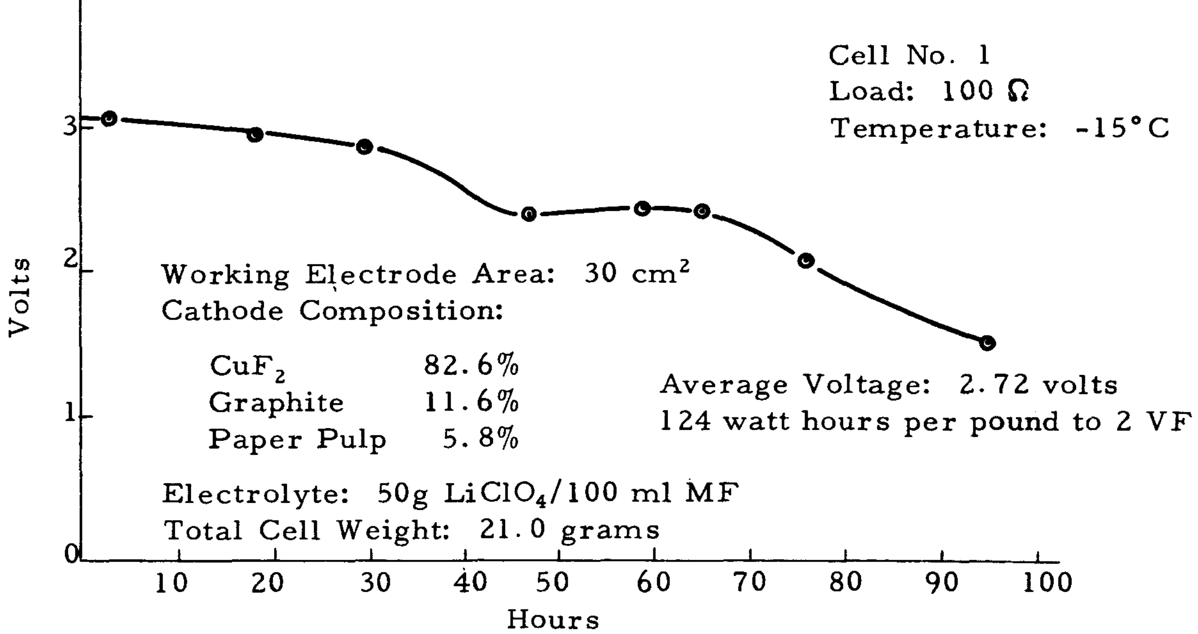
Working Electrode Area: 30 cm^2
Cathode Composition:

CuF_2	82.6%
Graphite	11.6%
Paper Pulp	5.8%

Average Voltage: 2.76 volts
154 watt hours per pound to 2 VF

Electrolyte: 15g $LiClO_4$/100 ml PC
Total Cell Weight: 21.1 grams

DISCHARGE CHARACTERISTICS OF CuF_2-Li CELL IN PROPYLENE CARBONATE (80 hour rate)



Cell No. 1
Load: 100 Ω
Temperature: -15°C

Working Electrode Area: 30 cm^2
Cathode Composition:

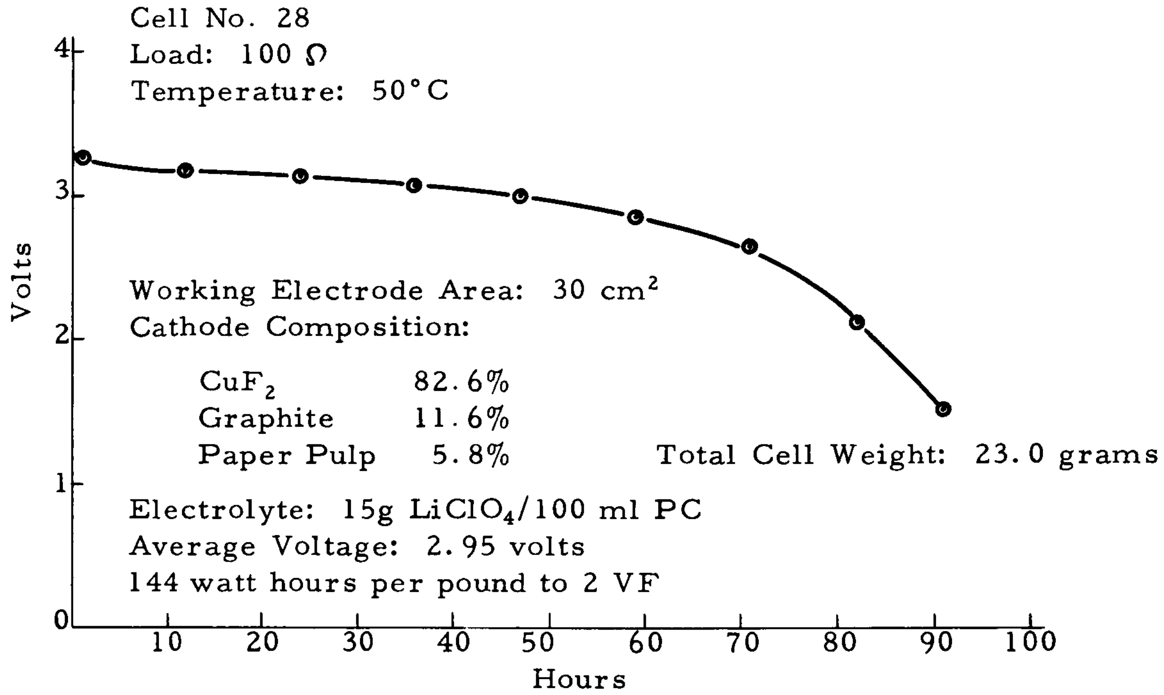
CuF_2	82.6%
Graphite	11.6%
Paper Pulp	5.8%

Average Voltage: 2.72 volts
124 watt hours per pound to 2 VF

Electrolyte: 50g $LiClO_4$/100 ml MF
Total Cell Weight: 21.0 grams

DISCHARGE CHARACTERISTICS OF CuF_2-Li CELL IN METHYL FORMATE (70 hour rate)

FIGURE 26



Cell No. 28
Load: 100 Ω
Temperature: 50°C

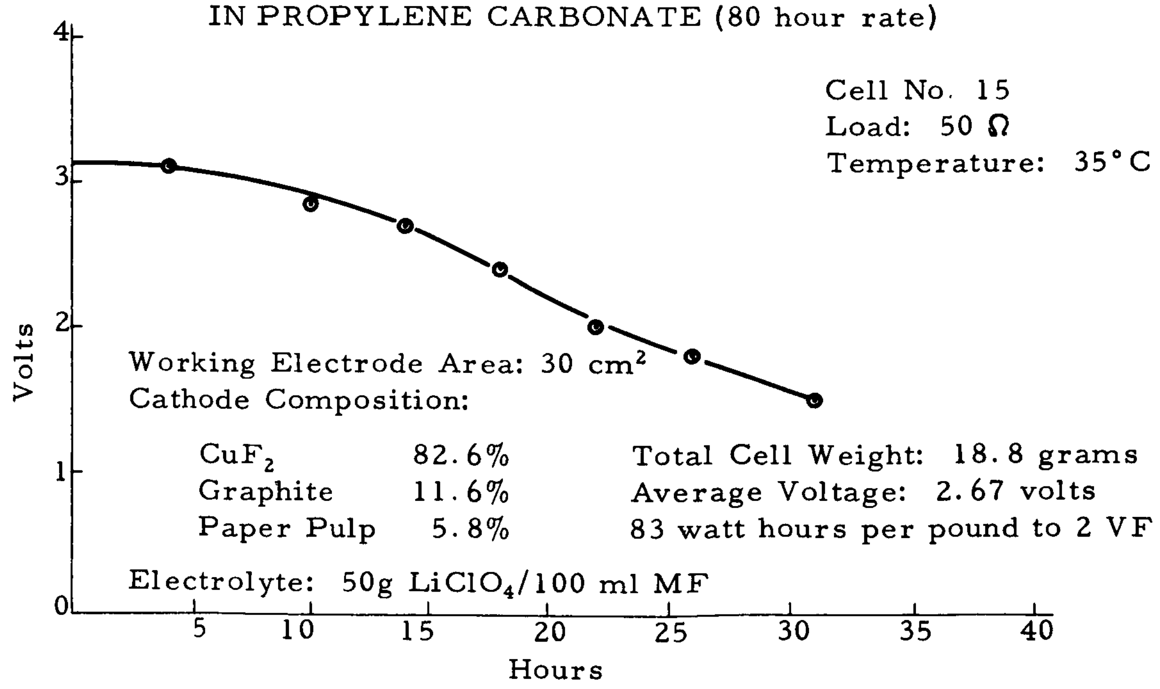
Working Electrode Area: 30 cm^2
Cathode Composition:

CuF_2	82.6%
Graphite	11.6%
Paper Pulp	5.8%

Total Cell Weight: 23.0 grams

Electrolyte: 15g $LiClO_4$/100 ml PC
Average Voltage: 2.95 volts
144 watt hours per pound to 2 VF

DISCHARGE CHARACTERISTICS OF CuF_2-Li CELL IN PROPYLENE CARBONATE (80 hour rate)



Cell No. 15
Load: 50 Ω
Temperature: 35°C

Working Electrode Area: 30 cm^2
Cathode Composition:

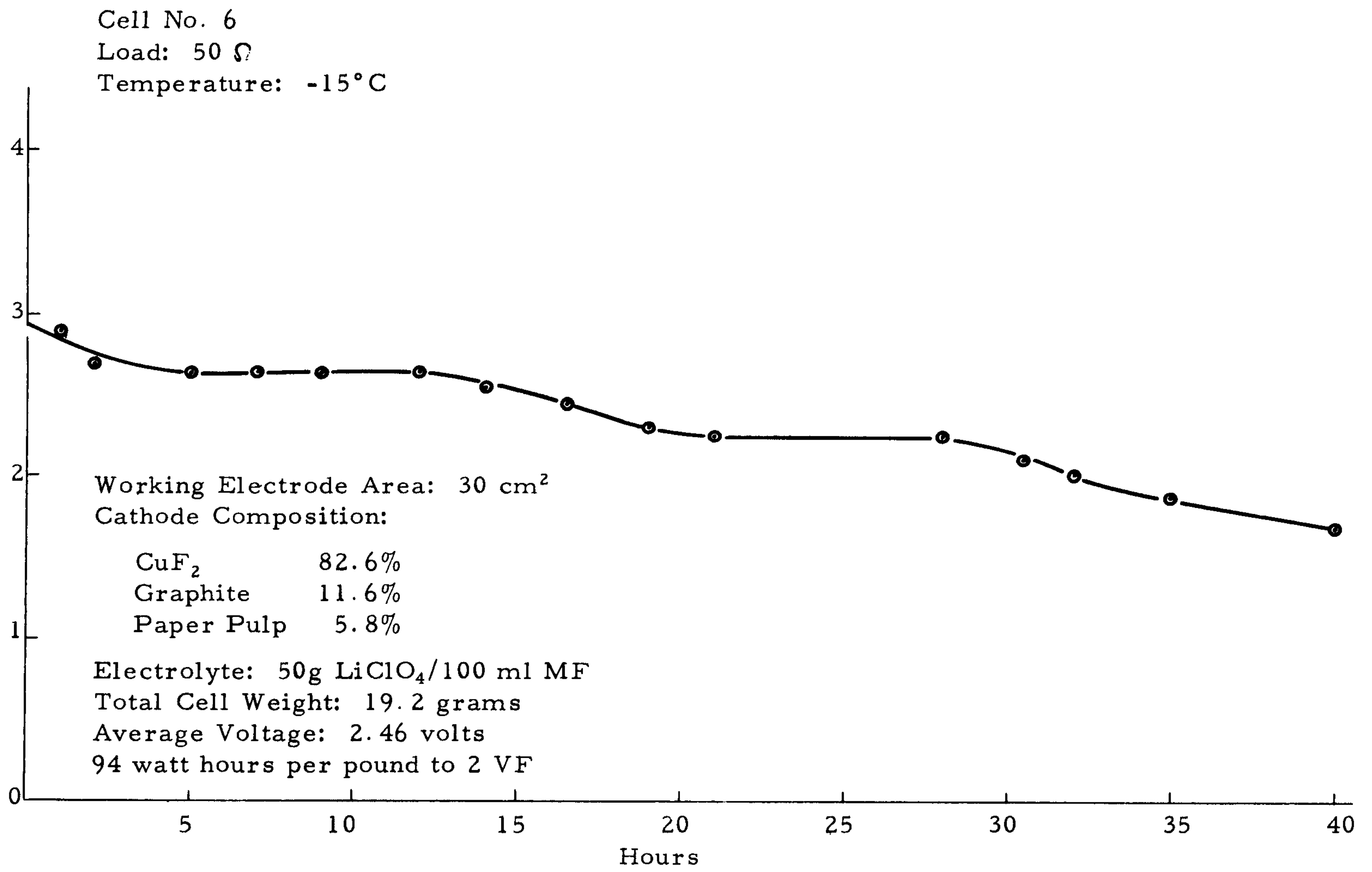
CuF_2	82.6%
Graphite	11.6%
Paper Pulp	5.8%

Total Cell Weight: 18.8 grams
Average Voltage: 2.67 volts
83 watt hours per pound to 2 VF

Electrolyte: 50g $LiClO_4$/100 ml MF

DISCHARGE CHARACTERISTICS OF CuF_2-Li CELL IN METHYL FORMATE (20 hour rate)

FIGURE 27



DISCHARGE CHARACTERISTICS OF CuF_2-Li CELL IN METHYL FORMATE
(30 hour rate)

FIGURE 28

5. APPENDIX

5.1. LIST OF MATERIALS

Solvent	Source	Cat. No.	Remarks
Acetic Anhydride	Fisher Scientific Co.	A-10	Certified reagent
Acetic Anhydride	Merck & Co., Inc.	7109	Reagent (ACS)
Acetone	Fisher Scientific Co.	A-19	Spectroanalyzed
Acetone	Matheson, Coleman & Bell	AX-115	Spectroquality
2-Butanone	Matheson, Coleman & Bell	BX-1670	
n-Butyl Formate	Eastman Organic Chem.	55	
Butyl Butyrate	Eastman Organic Chem.	364	
Butyrolactone	Matheson, Coleman & Bell	BX-2185	
Butyrolactone	General Aniline & Film Corp.		
Butyrolactone	Aldrich Chem. Co., Inc.		
Diethyl Ether	Fisher Scientific Co.	E-138	Anhydrous
Dimethyl Ether	Air Products & Chem., Inc.		99^{+}% Pure
Dimethyl Formamide	Matheson, Coleman & Bell	DX-1725	Spectroquality
Dimethyl Sulfoxide	Crown Zellerbach Corp.		Sample
Dimethyl Sulfoxide	Fisher Scientific Co.	D-128	Certified reagent
1, 2 Epoxypropane	Eastman Organic Chem.	2068	
Ethyl Acetate	Matheson, Coleman & Bell	EX-245	Spectroquality
Ethyl Acetoacetate	Eastman Organic Chem.	111	
Ethyl Formate	Matheson, Coleman & Bell	EX-595	Spectroquality
Heptane	Fisher Scientific Co.	H-20	Laboratory chemical

LIST OF MATERIALS (Continued)

Solvent	Source	Cat. No.	Remarks
Kerosene	Phillips "66"		
Methyl Acetate	Matheson, Coleman & Bell	MX-628	Practical
Methyl Alcohol	Fisher Scientific Co.	A-142	Certified reagent
Methyl Chloroform	Fisher Scientific Co.	T-391	Certified reagent
Methyl Formate	Matheson, Coleman & Bell	MX-1040	Spectroquality
1-Methyl-2-Pyrrolidone	Matheson, Coleman & Bell	MX-1395	
1-Methyl-2-Pyrrolidone	General Aniline & Film Corp.		
Nitromethane	Matheson, Coleman & Bell	NX-613	Spectroquality
Perchlorethylene	Globe Solvents		
Propylene Carbonate	Matheson, Coleman & Bell	PX-1705	
Propylene Carbonate	Jefferson Chem. Co., Inc.		Sample
Propylene Carbonate	Eastman Organic Chem.	P7050	Practical
Pyridene	Fisher Scientific Co.	P368	Certified reagent
Tetrahydofuran	Matheson, Coleman & Bell	TX-280	
Toluene	Fisher Scientific Co.	T-324	Certified reagent

LIST OF MATERIALS (Continued)

Solutes	Source	Cat. No.	Remarks
Aluminum Chloride	Fisher Scientific Co.	A-575	Certified reagent
Aluminum Fluoride	Olin Matheson Chem.		Sample
Lithium Bromide	Bios Laboratories, Inc.		Anhydrous
Lithium Chloride	Fisher Scientific Co.	L-121	Certified reagent
Lithium Fluoride	J. T. Baker Chem. Co.	2380	Analyzed reagent
Lithium Iodide	Mallinkrodt Chem. Works	1056	
Lithium Perchlorate	Foote Mineral Co.		H_2O <0.3W%
Potassium Acetate	Matheson, Coleman & Bell	PX-1330	Reagent
Potassium Chloride	Fisher Scientific Co.	P-217	Certified reagent
Potassium Fluoride	Fisher Scientific Co.	P-238	Certified reagent
Potassium Iodide	Fisher Scientific Co.	P-256	Certified reagent
Potassium Thiocyanate	Fisher Scientific Co.	P-317	Certified reagent
Potassium Trichloroacetate	G. & W. H. Corson		
Sodium Chloride	Fisher Scientific Co.	S-271	Certified reagent
Sodium Fluoroborate	Stauffer Chem. Co.		Sample
Sodium Trichloroacetate	G. & W. H. Corson		

LIST OF MATERIALS (Continued

Oxidant	Source	Cat. No.	Remarks
Chromic Anhydride	Merck & Co., Inc.	01532	N. F. X.
Cupric Chloride	Fisher Scientific Co.	C-456	Certified reagent
Cupric Fluoride	A. D. MacKay, Inc.		C. P.
Cupric Fluoride	Ozark Mahoning Co.		
Iodine Pentoxide	K & K Laboratories		
Lithium Peroxide	Foote Mineral Co.		
Manganese Dioxide	E. J. Lavino & Co.		Lavinor "F"
Manganic Fluoride	Harshaw Chem. Co.		Technical
Nickelous Fluoride	Varlacoid Chem. Co.		Anhydrous
Nickelous Fluoride Tetrahydrate	Allied Chem. Corp.	2024	Technical
Potassium Dichloroisocyanurate	FMC Corp.		Sample
Potassium Superoxide	MSA Research Corp.		
Silver Chloride	Fisher Scientific Co.	S-174	Certified reagent
Silver Difluoride	City Chemical Corp.	SA935	Technical
Silver Oxide	Fisher Scientific Co.	S-184	Purified
Silver Peroxide	City Chemical Co.	VA736	Purified
Sodium Superoxide	MSA Research Corp.		
Sulfur	Stauffer Chem. Co.		
Trichloroisocyanuric Acid	FMC Corp.		Sample
Vanadium Pentoxide	Fisher Scientific Co.	V-7	Certified reagent

LIST OF MATERIALS (Continued)

Material	Source	Cat. No.	Remarks
Acetylene Black	Shawinigan Products Co.		
Ammonia	National Ammonia Co.		
Argon	Burdett Oxygen Co.		
Asbestos Fiber	Arthur H. Thomas Co.		
Calcium Metal	Beryllium Corp.		
Calcium Oxide	G. & W. H. Corson		
Calcium Oxide (High Ca.)	G. & W. H. Corson		
Chloroplatinic Acid	Fisher Scientific Co.	P-154	Reagent (ACS)
Carbon Dioxide	Burdett Oxygen Co.		
Copper Exmet	Exmet Corp.		
Copper Metal	Fisher Scientific Co.	C-428	Purified
Copper Powder	Fisher Scientific Co.	C-431	Purified
Distilled Nat. Water	Sunbeam Water Co.		
Efficiency Blotter Paper No. 1698	Lansdale Office Supply		
Glass Mat Filter	Carl Schleicher & Schuell Co.	24	0.040" thickness
Glass Mat Filter Sheet	Whatman Drawing & Filter Papers	GF-A	0.008" thickness
Graphite, Airspun	Joseph Dixon Crucible Co.	200-44	
Graphite, Felt	H.I. Thompson Fiber Glass Co.	SS1558	
Hydrochloric Acid (Conc.)	Fisher Scientific Co.	A-144	Reagent (ACS)
Hydrofluoric Acid (48%)	Fisher Scientific Co.	A-147	Reagent (ACS)
Karl Fisher Stabilized Reagent	Fisher Scientific Co.	SO-K-3	Reagent (ACS)

LIST OF MATERIALS (Continued)

Material	Source	Cat. No.	Remarks
Lead, Exmet	Exmet Corp.		
Lead, Metal	Fisher Scientific Co.	L-27	Purified
Lithium, $\frac{1}{2}$" Ribbon	Foote Mineral Co.		
Lithium, Hexane Dispersion	Foote Mineral Co.		
Magnesium Metal	Fisher Scientific Co.	M-11	
Mercury	Fisher Scientific Co.	M-140	Redistilled, N.F.
Microporous Rubber	American Hard Rubber		0.045" - 0.030" thk.
Microthene	U. S. Industrial Chem. Co.		Powdered Polyethylene
Nalcon Fiber	National Lead Co.		Polyethylene Encapsulted Cellulose Fiber
Nickel, Exmet	Exmet Corp.		
Nickel, Flake	Electric Storage Battery Co.		
Nitric Acid	Fisher Scientific Co.	A-200	Reagent
Paper Pulp, Filter	Carl Schleicher & Schuell Co.	289	Analytical, Ash Free
Platinum Wire (0.040" dia.)	Arthur H. Thomas Co.	8303	
Polyethylene Envelopes	Seal-Tite Bag Co.		
Rubber to Metal Cement	Kravex Mfg. Corp.		
Silver Exmet	Exmet Corp.		
Silver Metal	Fisher Scientific Co.	S-166	Purified
Silver Powder	Fisher Scientific Co.	S-167	Certified reagent
Sodium Tartrate Dihydrate	Fisher Scientific Co.	S-435	Certified reagent (ACS)

LIST OF MATERIALS (Continued)

Material	Source	Cat. No.	Remarks
Sulfuric Acid (Conc.)	Fisher Scientific Co.	A-300	Reagent (ACS)
Sulfur Dioxide	Virginia Chemical & Smelting Co.		
Teflon Covered Glass	General Lab. Supply Co.		0.003" thk., 2-7μ Pore size
Triton X-100	Rohm & Haas Co.		
Zinc Metal	Fisher Scientific Co.	Z-9	

5.2. LIST OF SUPPLIERS

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New York 38, New York

Air Products & Chemicals, Inc.
Specialty Gas Department
P.O. Box 538
Allentown, Pennsylvania

Aldrich Chemical Co., Inc.
2369 North 29th
Milwaukee, Wisconsin

Allied Chemical Corp.
(Baker & Adamson)
61 Broadway
New York 6, New York

American Hard Rubber
7 Ace Road
Butler, New Jersey

Arthur H. Thomas Company
P.O. Box 779
Philadelphia, Pennsylvania

Beryllium Corp.
Tuckerton Road
Reading, Pennsylvania

Bios Laboratories, Inc.
19 West 60th Street
New York 23, New York

Burdett Oxygen Company
6 Swede Street
Norristown, Pennsylvania

Carl Schleicher & Schuell Company
Keene, New Hampshire

City Chemical Corporation
130 West 22nd Street
New York, New York

Commercial Plastics
548 Rising Sun Avenue
Philadelphia, Pennsylvania

Crown Zellerbach Corporation
1 Bush Street
San Francisco, California

Eastman Organic Chemical Products, Inc.
65 Concord Street
Framingham, Massachusetts

E. J. Lavino & Company
Philadelphia, Pennsylvania

Electric Storage Battery Company
Rising Sun & Adams Avenues
Philadelphia 20, Pennsylvania

Exmet Corporation
123 Marbledale Road
Tuckahoe, New York

Fisher Scientific Company
Gulph Road (Route 23)
King of Prussia, Pennsylvania

FMC Corporation
161 East 42nd Street
New York 17, New York

Foote Mineral Company
Route 100
Exton, Pennsylvania

General Aniline & Film Corp. (Antara)
435 Hudson Street
New York 14, New York

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Joshua Road & Stenton Avenue
Plymouth Meeting, Pennsylvania

General Laboratory Supply Co.
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Patterson, New Jersey

Globe Solvents
7th and Fisher Ave.
Philadelphia, Pennsylvania

Harshaw Chemical Company
1933 East 97th Street
Cleveland 6, Ohio

H.I. Thompson Fiber Glass Co.
1600 West 135th Street
Pasadena, California

Jefferson Chemical Company, Inc.
1121 Walker
Houston, Texas

Joseph Dixon Crucible Company
Division 48-C
Jersey City 3, New Jersey

J. T. Baker Chemical Company
North Broad Street
Phillipsburg, New Jersey

K & K Laboratories
Plainview, New York

Kravex Mfg. Corporation
Brooklyn 16, New York

Lansdale Office Supply
213 West Main Street
Lansdale, Pennsylvania

Mallinkrodt Chemical Works
Second and Mallinkrodt Streets
St. Louis 7, Missouri

Merck & Co., Inc.
1935 Lincoln Avenue
Rahway, New Jersey

MSA Research Corporation
Mars Road
Callery, Pennsylvania

Matheson, Coleman & Bell
Jackson & Swanson Streets
Philadelphia, Pennsylvania

National Ammonia Company
Tacony & Van Kirk Streets
Philadelphia 24, Pennsylvania

National Lead Company
1050 State Street
Perth Amboy, New Jersey

Olin Matheson Chemical Corp.
Metal Division
400 Park Avenue
New York 22, New York

Ozark Mahoning Company
310 West Sixth
Tulsa, Oklahoma

Phillips Petroleum Company
Bartlesville, Oklahoma

Rohm & Haas Company
Washington Square
Philadelphia 5, Pennsylvania

Seal-Tite Bag Company
3000 Reed Street
Philadelphia, Pennsylvania

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Empire State Building
350 Fifth Avenue
New York 1, New York

Stauffer Chemical Company
Agricultural Chemicals Division
380 Madison Avenue
New York 17, New York

Sunbeam Water Company
Tennis Avenue
Ambler, Pennsylvania

U.S. Industrial Chemicals Company
P.O. Box 208
Tuscola, Illinois

Varlacoid Chemical Company
116 Broad Street
New York, New York

Virginia Chemical & Smelting Company
West Norfolk, Virginia

H. Reeve Angel & Company
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