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

W. F. Meyers, et al

Livingston Electronic Corporation
Montgomeryville, Pennsylvania

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SECOND QUARTERLY REPORT

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

10 September 1964 to 9 December 1964

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LIVINGSTON ELECTRONIC CORPORATION
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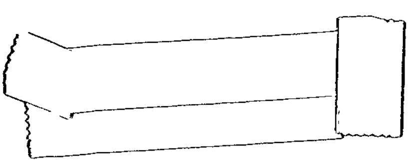

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SUMMARY

A number of organic liquids have been studied in order to evaluate their applicability as electrolyte solvents in Li - CuF_2 or Li - $CuCl_2$ cells.

The conductivity of $LiClO_4$ solutions was consistantly higher than that of $AlCl_3$ solutions in the solvents studied. In dimethyl sulfoxide, lithium chloride also produced strongly conductive solutions (5×10^{-3} mho/cm at 75 g/l).

Lithium fluoride was found to be soluble in nitromethane and in n-butyl formate to the extent of 5.0 g/l and 6.5 g/l, respectively; but the specific conductances of the resultant solutions did not vary significantly from those of the pure solvents.

Lithium metal stability tests in the pure solvents and in solutions of several electrolytes were conducted. The lowest rate of attack on the metal was observed in pure (no solute) propylene carbonate, dimethyl sulfoxide, butyrolactone, and acetic anhydride (listed in order of increasing reactivity); no other solvents tested were judged adequately compatible with lithium metal for extended contact periods (7 days). Drying of the solvents with calcium oxide (except acetic anhydride) improved the stability of the systems. The presence of solutes in the test solutions increased the rate of attack on the lithium; this effect was more pronounced with $LiClO_4$ than with the other salts tested.

The four solvents listed in the previous paragraph were compared in cell discharge tests using $LiClO_4$ as the solute in Li - CuF_2

and Li - MnO_2 cells. Performance of cells built with the most recent filter-pad positive electrode construction was best with propylene carbonate and dimethyl sulfoxide electrolyte solvents. The capacity of acetic anhydride cells was markedly inferior being limited by electrolyte attack on the lithium electrode.

Other Li - CuF_2 cells were tested with 2.3 M $LiClO_4$ - methyl formate electrolyte. In positive-limiting cells discharged at 1 mA/cm^2, electrochemical efficiency of the CuF_2 electrode was generally in the range 60 to 80 per cent measured to 50 per cent cell voltage drop. In view of the high conductivity (3.0×10^{-2} mho/cm with 2.2 M $LiClO_4$) and good cathode efficiency achieved with this material, methyl formate continues to be of prime interest as an electrolyte solvent though there is a moderate rate of chemical attack on the lithium anode.

1. INTRODUCTION

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

On the basis of rather extensive work performed by this contractor and by other researchers in the field, lithium has emerged as the most desirable anode material for a high energy density, organic electrolyte system. Other candidate materials such as magnesium, calcium, or sodium have either shown significantly more positive potentials compared to lithium (Mg by ca. 1.9 volts; Ca by ca. 0.7 volt) in the organic electrolytes, or have much higher equivalent weights (Na = 23; Li = 7). In addition to the above considerations, lithium also appears to be the most desirable material from the viewpoint of electrode manufacture and handling, since it is only moderately reactive with the atmosphere and does not react with either dry oxygen or dry nitrogen (Reference 1). Lithium electrodes can be manufactured by shaping the fairly malleable metal into molds.

A substantial number of aprotic electrolyte solvents which could be useful in a Li anode system have been studied by this contractor and by other researchers in the field and have been described in various reports and in the literature. It was decided to select a number of the solvents on the basis of the reported test results and to evaluate their utility for use in a Li anode, $CuCl_2$, or CuF_2 cathode cell system. As a result, the chemical stability of lithium metal, and the solubility and conductivity of solutions of the cathode-active materials $CuCl_2$ and CuF_2, cathode discharge products LiF and LiCl, and supporting electrolytes $LiClO_4$ and $AlCl_3$ were studied in twelve solvents.

In addition to being acceptable on the basis of the above properties, the electrolyte solvent in a high energy battery will also have to be conducive to a high level of positive active material utilization, and to a low and constant level of cell polarization during discharge. Consequently, the solvents which appeared most promising from the lithium stability, conductivity, and solubility tests were compared in Li-CuF_2 and Li-MnO_2 cells under identical cell construction and discharge conditions. At the completion of these tests, propylene carbonate and dimethyl sulfoxide appeared to be of primary interest for further development of the battery.

Methyl formate continues to be of primary interest as an electrolyte solvent for the Li-CuF_2 system because of demonstrated ability to allow high electrochemical efficiency to be obtained from the present cathode constructions at moderately high (30-hour) rates.

2. DISCUSSION OF EXPERIMENTAL WORK

2.1. ELECTROLYTE SYSTEMS STUDIES

2.1.1. Solubility and Conductivity Tests

The solubility of a number of salts in the candidate electrolyte solvents and the specific conductance of the solutions were determined and are presented in Table I, page 4. Copper chloride and copper fluoride were included in the test series for the purpose of attempting a correlation between the solubility of the cathode-active material with their performance in cell tests. Lithium chloride and lithium fluoride were included in order to attempt to correlate the solubility of the cathodic discharge product with the performance of the cell, since a positive discharge reaction of the type

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

is anticipated.

Solubility of $LiClO_4$ and $AlCl_3$ in the solvents was studied in order to evaluate their usefulness as supporting electrolytes in the various systems.

Several unexpected results were recorded in the course of the above investigations. Lithium fluoride was found to have considerable solubility in both n-butyl formate (6.5 grams/liter) and nitromethane (5.0 grams/liter). The conductivity of these solutions did not differ significantly from that of the pure solvents, indicating that the solute ions remain strongly assoicated in the solution phase.

Lithium chloride was found to be only moderately soluble in methyl formate (10.8 grams/liter) and butyrolactone (33.3 grams/liter),

TABLE III

CONDUCTIVITY OF ELECTROLYTE SOLUTIONS IN VARIOUS SOLVENTS

Solvent	Solute	Concentration (g/Liter)	Conductivity (ohm^{-1} cm^{-1})	Remarks
Methyl Formate	$CuCl_2$	10.5 (sat'd)	1.48×10^{-5}	Dark green solution, brown salt
Methyl Formate	CuF_2	.500 (sat'd)	1.97×10^{-6}	Colorless solution, blue-green salt
Methyl Formate	LiCl	10.80 (sat'd)	1.93×10^{-4}	Pale yellow solution, white salt
Methyl Formate	LiF	.500 (sat'd)	1.7×10^{-6}	Colorless solution, white salt
n-Butyl Formate	$AlCl_3$	200	6.25×10^{-4}	Exothermic, dark purple solution
n-Butyl Formate	$CuCl_2$	500 (sat'd)	1.04×10^{-6}	Pale yellow solution, brown salt
n-Butyl Formate	CuF_2	500 (sat'd)	$.3 \times 10^{-8}$	Colorless solution, grey salt
n-Butyl Formate	LiCl	.500 (sat'd)	3×10^{-8}	Colorless solution, white salt
n-Butyl Formate	$LiClO_4$	160	3.72×10^{-3}	Exothermic, colorless solution
n-Butyl Formate	LiF	6.500 (sat'd)	2×10^{-8}	Clear solution
Nitromethane	$CuCl_2$	.500	2.7×10^{-5}*	Amber-green solution
Nitromethane	CuF_2	.500 (sat'd)	1.6×10^{-5}*	Yellow-green solution, blue-green salt
Nitromethane	LiCl	.500 (sat'd)	7.3×10^{-6}*	Colorless solution, white salt
Nitromethane	LiF	5.000 (sat'd)	2.8×10^{-6}*	Clear solution
N-Methyl 2-Pyrrolidone	CuF_2	.500 (sat'd)	4×10^{-6}*	Colorless solution, grey salt
N-Methyl 2-Pyrrolidone	LiCl	1.00	1.6×10^{-4}*	Colorless solution
N, N-Dimethyl Formamide	CuF_2	.500 (sat'd)	1.4×10^{-5}*	Yellow solution, grey salt
N, N-Dimethyl Formamide	LiCl	1.00 (sat'd)	2.1×10^{-4}*	Colorless solution
Propylene Carbonate	$AlCl_3$	200	4.38×10^{-3}	Exothermic, dark brown solution
Propylene Carbonate	$CuCl_2$	5.00 (sat'd)	1.76×10^{-4}	Amber-black solution
Propylene Carbonate	$CuCl_2$	5.00 (sat'd)	1.7×10^{-4}*	Amber-black solution
Propylene Carbonate	CuF_2	.500 (sat'd)	1.85×10^{-5}	Colorless solution, grey salt
Propylene Carbonate	CuF_2	.500 (sat'd)	1.4×10^{-5}*	Colorless solution, grey salt
Propylene Carbonate	LiCl	.500	1.37×10^{-4}	Colorless solution
Propylene Carbonate	LiCl	.500	1.4×10^{-4}*	Colorless solution
Propylene Carbonate	$LiClO_4$	160	4.04×10^{-3}	Exothermic, colorless solution
Propylene Carbonate	LiF	.500 (sat'd)	1.26×10^{-6}	Colorless solution, white salt
Propylene Carbonate	LiF	.500 (sat'd)	2×10^{-6}*	Colorless solution, white salt

*20,000 CPS

TABLE I. Continued

CONDUCTIVITY OF ELECTROLYTE SOLUTIONS IN VARIOUS SOLVENTS

Solvent	Solute	Concentration (g/Liter)	Conductivity (ohm^{-1} cm^{-1})	Remarks
Pyridine	CuF_2	.500 (sat'd)	9×10^{-6}*	Yellow-green solution, blue-green salt
Pyridine	LiCl	2.500 (sat'd)	9×10^{-5}*	Yellow solution
Acetic Anhydride	$AlCl_3$	200 (sat'd)	2.70×10^{-4}	Exothermic, two solute phases
Acetic Anhydride	$CuCl_2$	.500 (sat'd)	3.06×10^{-5}	Green solution, blue-green salt
Acetic Anhydride	$CuCl_2$	.500 (sat'd)	1.6×10^{-5}*	Green solution, blue-green salt
Acetic Anhydride	CuF_2	.500 (sat'd)	4.32×10^{-6}	Yellow-green solution, blue-green salt
Acetic Anhydride	CuF_2	.500 (sat'd)	4.1×10^{-6}*	Yellow-green solution, blue-green salt
Acetic Anhydride	LiCl	.500	8.7×10^{-5}	Colorless solution
Acetic Anhydride	LiCl	.500	7.6×10^{-5}*	Colorless solution
Acetic Anhydride	$LiClO_4$	160 (sat'd)	6.07×10^{-3}	Exothermic, colorless solution
Acetic Anhydride	LiF	5.000 (sat'd)	2.72×10^{-6}	Yellow solution, white salt
Acetic Anhydride	LiF	5.000 (sat'd)	1.8×10^{-6}*	Yellow solution, white salt
2-Butanone	CuF_2	.500 (sat'd)	1.3×10^{-5}*	Colorless solution, blue-green salt
2-Butanone	LiCl	.500 (sat'd)	3.1×10^{-5}*	Colorless solution, white salt
Butyrolactone	$AlCl_3$	200	4.37×10^{-3}	Exothermic, dark tan solution
Butyrolactone	$CuCl_2$	.500	7.30×10^{-5}	Amber solution
Butyrolactone	$CuCl_2$	.500	6.7×10^{-5}*	Amber solution
Butyrolactone	CuF_2	.500 (sat'd)	9.44×10^{-6}	Yellow solution, grey salt
Butyrolactone	CuF_2	.500 (sat'd)	7.6×10^{-6}*	Yellow solution, grey salt
Butyrolactone	LiCl	33.30 (sat'd)	8.27×10^{-5}	Colorless solution, tan 3 wks. later
Butyrolactone	LiCl	33.30 (sat'd)	7.4×10^{-4}*	Colorless solution, tan 3 wks. later
Butyrolactone	$LiClO_4$	160	9.44×10^{-3}	Exothermic, colorless solution
Butyrolactone	LiF	.500 (sat'd)	2.04×10^{-6}	Colorless solution, white salt
Butyrolactone	LiF	.500 (sat'd)	1.9×10^{-6}*	Colorless solution, white salt
Dimethyl Sulfoxide	$AlCl_3$	200 (sat'd)	3.73×10^{-4}	Viscous white suspension, exothermic
Dimethyl Sulfoxide	$CuCl_2$	27.76 (sat'd)	1.06×10^{-3}	Bilious green solution
Dimethyl Sulfoxide	$CuCl_2$	27.76 (sat'd)	1.0×10^{-3}*	Bilious green solution
Dimethyl Sulfoxide	CuF_2	.500 (sat'd)	1.35×10^{-5}	Colorless solution, grey salt
Dimethyl Sulfoxide	CuF_2	.500 (sat'd)	1.3×10^{-5}*	Colorless solution, grey salt

*20,000 CPS

TABLE I: Continued

CONDUCTIVITY OF ELECTROLYTE SOLUTIONS IN VARIOUS SOLVENTS

Solvent	Solute	Concentration (g/Liter)	Conductivity (ohm^{-1} cm^{-1})	Remarks
Dimethyl Sulfoxide	LiCl	75.00 (sat'd)	4.56×10^{-3}	Colorless solution
Dimethyl Sulfoxide	LiCl	75.00 (sat'd)	5.0×10^{-3}*	Colorless solution
Dimethyl Sulfoxide	$LiClO_4$	160	7.1×10^{-3}	Exothermic, colorless solution
Dimethyl Sulfoxide	LiF	.500 (sat'd)	3.51×10^{-6}	Colorless solution, white salt
Dimethyl Sulfoxide	LiF	.500 (sat'd)	2.7×10^{-6}*	Colorless solution, white salt
Ethyl Formate	CuF_2	.500 (sat'd)	9×10^{-7}*	Blue-green solution, blue-green salt
Ethyl Formate	LiCl	.500 (sat'd)	2×10^{-6}*	Colorless solution, white salt

*20, 000 CPS

but the saturated solution in dimethyl sulfoxide (75 grams/liter) had a specific conductance almost as high as that of the 1.5 M $LiClO_4$ solution in the same solvent.

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

2.1.2. Lithium Compatibility Tests

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 Li ribbon (Foote Mineral Company) and were embossed on one side with a piece of expanded nickel screen. The samples were submerged in a test tube containing the test solution; the test tubes were stoppered, and changes in appearance of the Li metal and of the solution were observed.

Of the twelve solvents listed in Table II, page 8, propylene carbonate only appeared definitely to have acceptable stability (code letter "a") with respect to lithium in presence of dissolved lithium perchlorate; the remaining solvents were either slowly (code letter "b") or rapidly (code letter "c") decomposed. Of the latter, dimethyl sulfoxide, butyrolactone, and acetic anhydride appeared to be least reactive towards lithium and were selected in addition to propylene carbonate for further evaluation.

TABLE II

SUMMARY OF LITHIUM COMPATIBILITY STUDIES

	No Solute	$LiClO_4$	$AlCl_3$	$LiCl$	LiF	CuF_2	$CuCl_2$
1. Butyrolactone	a	b	b	a	b	a	c
2. Propylene Carbonate	a	a	b	a	a	b	c
3. Dimethyl Sulfoxid	a	b		a	a	a	c
4. Acetic Anhydride	a	b	b	a	a	b	c
5. Methyl Formate	a	b					
6. Nitromethane	b			c	b	c	c
7. Dimethyl Formamide	c						
8. Pyridine	c						
9. n-Butyl Formate	b	c	b				
10. 2-Butanone	c						
11. Ethyl Formate	b						
12. N-Methyl 2-Pyrrolidone	c						

a slight or no attack after 24 to 168 hours; definitely acceptable

b moderate attack after 24 hours, heavy attack after 168 hours; doubtful acceptability

c strong attack in 2 to 24 hours; definitely unacceptable

The tests with methyl formate had to be performed in hermetically sealed test tubes because of the high vapor pressure of the decomposition products. During the test with the pure solvent, a pressure of 55 pounds per square inch gauge was developed in the test tube, but the pressure disappeared when the test tube was cooled to -5°C.

No additional decomposition or pressure build-up was observed when a new lithium test sample was immersed in the liquid resulting from the above test. When the lithium stability test was performed with $LiClO_4$ solution, a pressure of 120 pounds per square inch gauge was observed, but the gas was again condensible at the lower temperature.

It appears from the present test results that propylene carbonate is the best electrolyte solvent from the standpoint of compatibility with the lithium anode, with dimethyl sulfoxide, butyrolactone, and acetic anhydride as the next possible choices. Methyl formate appears to be sufficiently stable only for short-time, reserve-activated applications.

Results of the compatibility tests are more thoroughly described in Table A of the Appendix.

2.1.3. Decomposition Potential Studies of Binary Electrolyte Solutions

A number of electrolyte solvents which appeared promising from the tests described in Sections 2.1.1. and 2.1.2. were electrolyzed between smooth platinum electrodes in the presence of 1.5M $LiClO_4$ as the supporting electrolyte. A lithium metal reference electrode was employed, which showed reproducible behavior in all solvents tested, except for acetic anhydride, where it tended to discolor and lose its activity.

Results of the electrolysis tests are presented in Table III, page 11. The dc potential was applied in steps of about 1.4 volts, and the cell current was obtained by measuring the forward voltage drop across a calibrated silicon diode. The electrolysis cells had cylindrical platinum electrodes of 1 mm diameter, spaced 10 mm apart, and had cell constants of about 1.0 cm^{-1}.

At each potential step, electrolysis was continued until steady-state conditions were approached at which time the potential and current values were recorded, and the next higher (or lower) potential step was applied.

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 overvoltage (ca. 0.1 volt) at the current densities employed.

TABLE III

DECOMPOSITION POTENTIALS 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	
		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	

*Decreased applied potential

TABLE III Continued

DECOMPOSITION POTENTIALS 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 #5 - Dimethyl Sulfoxide + 1.78 M $LiClO_4$ Continued			
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	
		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	

*Decreased applied potential

TABLE III Continued

DECOMPOSITION POTENTIALS OF VARIOUS SOLUTIONS ON SMOOTH PLATINUM ELECTRODES

Reference Electrode: Li/Li^+

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	
		Run #9 - Methyl Formate + 1.5 M $LiClO_4$ Con't.			
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	3.00	1.88	
21.25	25.4	2.50	2.33	0.15	Replaced reference electrode
23.25	190	3.58	3.48	-0.13	Gelatinous yellow-orange deposit on Li
23.75	1590	4.60	4.05	-0.54	Darkening on cathode
24.25	700	6.10	3.98	-2.20	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

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

Time, hrs.	C. D. $\mu a/cm^2$	Potential, Volts Cell	Anode	Cathode	Remarks
Run #13 - N, N-Dimethyl Formamide (CaO dried) + 1.0 M $LiClO_4$ + Ammonia					
Reference Electrode: None					
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	

2.1.4. Conductivity and Decomposition Potential of Selected Ternary Electrolyte Systems

A number of ternary electrolyte solutions were selected for verification of previous observations (Reference 2) and for further study of the properties of these systems; results of the conductivity and decomposition potential studies for two systems are presented in Table III, page 11 and Table IV, page 16.

During the tests, the conductivity and electrolysis cells were filled with the salt ($LiClO_4$) solution and sealed in pressure chambers. After purging with argon, the full vapor pressure of the ligand gas was applied to the chamber, and the supply tank was shut off. Thus, the amount of ligand absorbed by the cells could be calculated from the known volume of the test chamber and the observed decrease in vapor pressure over the solution. The specific resistance of the solution was monitored until either its value became constant, or no further ligand atmosphere could be observed.

In both dimethyl formamide and dimethyl sulfoxide, addition of the ligand atmosphere reduced the specific resistance of the solution by about 50 per cent. However, the decomposition potential of both systems was lowered significantly; hence, it appears that neither of the two systems will be useful in building lithium-anode cells having activated stand or long discharge life requirements.

2.1.5. Specific Conductance of $LiClO_4$ Solutions in Propylene Carbonate and Dimethyl Sulfoxide at Room Temperature

The specific conductance-concentration characteristics for $LiClO_4$ solutions in propylene carbonate and dimethyl sulfoxide were

TABLE IV

VARIATION OF SPECIFIC RESISTANCE WITH LIGAND PRESSURE

Run #13 - N, N-Dimethyl Formamide (CaO dried) + 1.0 M $LiClO_4$ + Ammonia

Elapsed Time Hours	Temperature °F	Gauge Pressure lbs/in.^{2}	Specific Resistance Ω cm
	75	Atmospheric	49.7
	75	Argon	51.0
0	Argon released - ammonia introduced into chamber		
.58	72	118	--
.75	70	115	--
1.50	72	108	51.1
16.92	78	87	36.6
18.17	76	87	36.6
22.33	78	84	33.2
24.75	78	84	32.2
65.33	79	72	25.7
72.33	69	68	26.4
113.08	78	68	24.8
116.00	Start of decomposition potential tests*		

*See page 14, Run #13

TABLE IV Continued

VARIATION OF SPECIFIC RESISTANCE WITH LIGAND PRESSURE

Run #14 - Dimethyl Sulfoxide + 1.0 M $LiClO_4$ + SO_2

Elapsed Time Hours	Temperature °F	Gauge Pressure lbs/in.^{2}	Specific Resistance Ω cm
	70	100 (Argon)	98.9
	Argon released - SO_2 introduced into chamber		
			88.1
	70	26	79.4
	SO_2 introduced into chamber		
0	70	30	--
3.67	77	37	79.4
	SO_2 introduced into chamber		
5.09	80	46	74.5
5.92	80	44	--
69.17	72	38	78.2
69.42	73	38	78.2
70.59	Start of decomposition potential test*		
71.84	72	38	77.1
73.67	72	38	78.7
74.59	73	38	79.1
75.51	End of decomposition potential test *		
76.18	75	38	78.5
93.60	77	38	79.5
94.02	Discharged chamber of SO_2		
99.60	77	0	79.5

*See page 14, Run #14

NOTE: Initial solution 5.5 cc

TABLE IV Continued

VARIATION OF SPECIFIC RESISTANCE WITH LIGAND PRESSURE

Run #15 - Dimethyl Sulfoxide + 1.0 M $LiClO_4$ + SO_2

Elapsed Time Hours	Temperature °F	Gaug Pressure lbs/in.^{2}	Specific Resistance Ω cm	Moles SO_2 per Mole DMSO
	72	120 (Argon)	111	
	Argon released - SO_2 introduced into chamber			
0	72	30	--	
.17	72	17	84.4	
.42	72	11	83.9	
.67	73	10	86.0	.32
	SO_2 introduced into chamber			
.75	74	33	83.9	
.92	74	20	64.7	
1.17	73	15	63.9	
1.75	74	12	64.6	.83
	SO_2 introduced into chamber			
1.83	74	35	63.3	
2.17	75	21	57.5	
2.50	76	19	57.0	
3.08	77	17	56.6	
3.75	77	16	56.5	
19.08	78	16	56.8	1.2
19.50	Start of decomposition potential test*			
26.75	77	16	56.9	
26.75	End of decomposition potential test*			
27.58	73	Atmospheric	60.4	
48.58	80	Atmospheric	62.6	

*See page 14, Run #15

NOTE: Initial solution 4.5 cc

determined and are presented in Figure 1, page 21. The conductivity maximum in both systems was observed to occur at a concentration of about 1.0 mole/liter. The maximum conductivity was 7×10^{-3} for the dimethyl sulfoxide and 5×10^{-3} for the propylene carbonate solution.

2.1.6. Electrode Potentials of Metals in PC-$LiClO_4$ and MF-$LiClO_4$ Solutions

The relative potentials of several metals were measured in 1.5 M PC-$LiClO_4$ and MF-$LiClO_4$ solutions with respect to the lithium metal-lithium ion potential. The test materials were commercially available metal samples, which had been cleaned with steel wool and degreased before immersion in a test tube containing the solution and a lithium-on-nickel reference electrode.

Results of the potential comparison are listed in Table V, page 22. The values shown are the potentials observed immediately after immersion; a VTVM having an internal resistance of 11 megohms was used for the measurements.

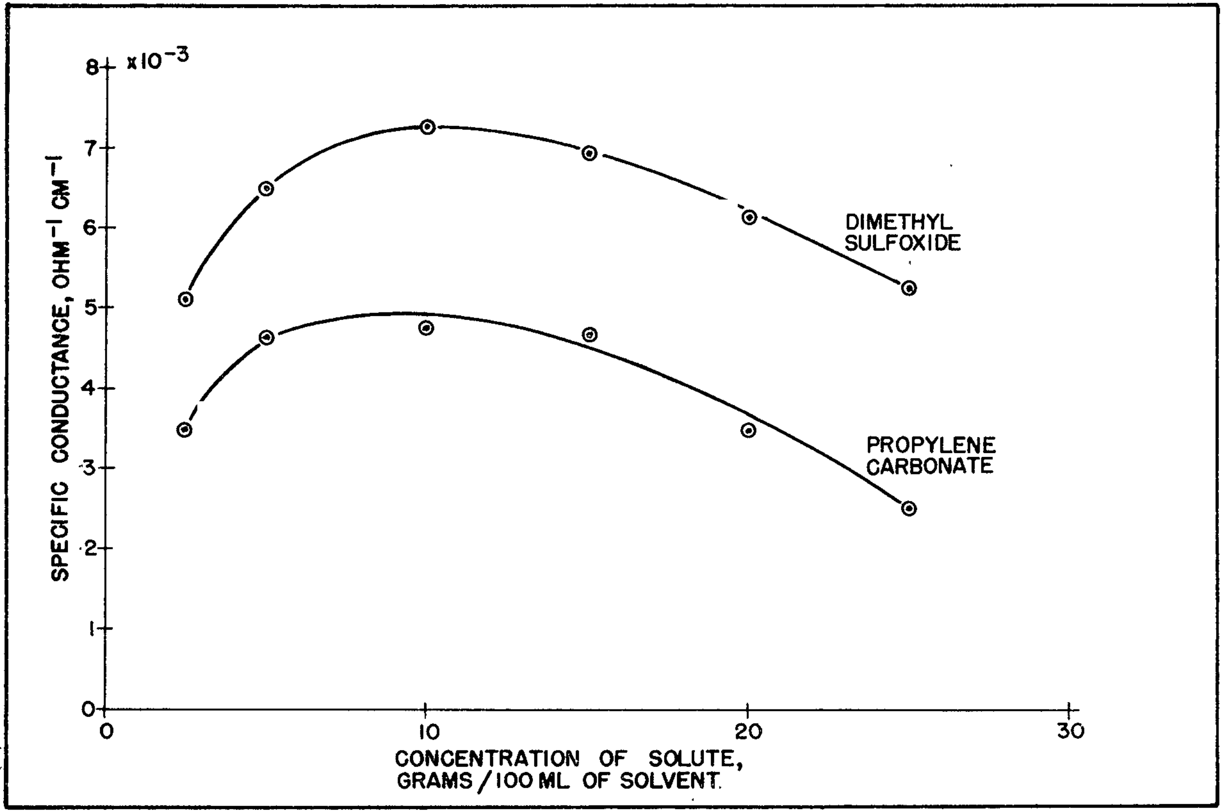

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FIGURE 1

SPECIFIC CONDUCTANCE OF $LiClO_4$ SOLUTIONS IN DIMETHYL SULFOXIDE AND PROPYLENE CARBONATE AT ROOM TEMPERATURE

TABLE V

ELECTRODE POTENTIALS OF METALS IN 1.5 M $LiClO_4$ SOLUTIONS IN PROPYLENE CARBONATE AND METHYL FORMATE

Electrode	Propylene Carbonate	Methyl Formate
Ni/L	0	0
Ca	0.7	0.7
Mg	1.9	1.9
Al	2.3	2.3
Zn	2.4	2.4
Pb	2.5	2.5
Ni	2.6	2.8
Cu	2.8	2.9
Ag	3.0	3.1

2.2. CELL SYSTEMS STUDIES

2.2.1. Evaluation of Electrolyte Solvents in Experimental Cells

Twenty-four "experimental" cell tests were conducted in order to compare the performance of cells constructed with acetic anhydride (ACAN), dimethyl sulfoxide (DMSO), butyrolactone (BL), and propylene carbonate (PC) electrolyte solvents. The cathode materials employed in the study were CuF_2 and MnO_2; lithium was the anode material in all cells.

Lithium perchlorate was used as the electrolyte, either at the consentration of 0.5 mole/liter, which corresponds to the saturated solution in ACAN, or at 1.0 mole/liter, which corresponds to the conductivity maximum in DMSO and PC. In the latter series, the saturated ACAN solution was used.

Copper metal reference electrodes were incorporated in the test cells for the purpose of estimating the relative contribution of the positive and negative electrodes toward the potential drop of the cell with load. In the two-plate cells, the reference electrode was a solid copper sheet positioned on the opposite side of the cathode and separated from it by a layer of separator material. In the two-negative, one-positive cells, the reference electrode was a copper wire protected by a Teflon tube except for the end opening which was placed at the outer edge of the positive electrode.

The cells were activated with the corresponding electrolyte solutions and were allowed to remain on open circuit for 15 minutes to two hours, at which time potential drop with various applied loads was measured. The loads were applied in order of decreasing ohmic value; and the cell and reference potentials were measured after 15 seconds, at which time the next higher load was applied. At the end of the scan, the cells were returned to open circuit for an additional active stand period. Results of the polarization tests are presented in Table VI, page 25.

At the end of the polarization tests, the cells were placed on discharge at constant current; and the cell potentials were monitored continuously on a strip chart recorder (Brown "Electronik"). The discharges were performed at either room temperature or at 115°F. The higher temperature was chosen because DMSO has a melting point very close to room temperature (18°C).

Results of the discharge tests are shown in Table VI, page 25 and Figure 2, page 35. In the test cells having CuF_2 cathodes, propylene carbonate gave the best cathode efficiency (78 per cent in 88 hours, Cell No. E92). Butyrolactone and dimethyl sulfoxide gave approximately the same efficiency with BL giving generally higher discharge potentials. There were some reversals to this trend in the first eight cells which had cathodes made by the dry-press technique (which has been superseded by the filter-pad technique). Use of the kerosene vehicle filter pad construction generally improved the reproducibility of cell discharge results and increased the utilization efficiency of the cathode-active material. In the case of the cells having MnO_2 cathodes, the highest capacity was recorded in the cells having DMSO electrolyte solvent, the highest efficiency figure being 56 per cent in 200 hours on the basis of two electron changes per mol.

Reference electrode measurements showed that the positive electrode limited capacity in the BL, DMSO, and PC cells; but in the ACAN

TABLE VI

CELL PERFORMANCE TESTS

Cell Nos. 1 - 4 (E70 - E73)

A. Construction Data

Cathode: 76 per cent CuF_2, 6 per cent graphite, 6 per cent fiber; dry-pressed at 2,000 pounds per square inch, 0.92 ampere hours theoretical capacity

Anode: Lithium pressed onto expanded Ni screen, 2.85 ampere hours theoretical capacity

Separation: Blotter paper, 0.6 mm thick

Electrolyte: Lithium perchlorate, 0.5 moles/liter

Electrode Area: 14.4 cm^2

Reference Electrode: Cu sheet

Electrolyte Solvent: Cell 1 (E-70) Acetic Anhydride
Cell 2 (E-71) Butyrolactone
Cell 3 (E-72) Dimethyl Sulfoxide
Cell 4 (E-73) Propylene Carbonate

B. Polarization Data

Test Temperature: 76°F

Time	Load, Ω	Potential							
		Cell 1		Cell 2		Cell 3		Cell 4	
		P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.
0	4.0 cc of electrolyte solution added to cells.								
1.6 hrs.	11M	3.26	0.15	3.30	0.08	3.28	0.11	3.30	0.12
	10K	3.40	0.14	3.28	0.08	3.26	0.10	3.26	0.12
	1K	3.35	0.09	3.25	0.05	3.23	0.06	3.17	0.08
	333	3.15	0.02	3.14	0.01	3.05	0.00	2.90	0.05
	100	2.72	-0.10	2.84	-0.03	2.80	-0.07	2.35	0.03
	33	1.97	-0.33	2.16	-0.09	2.11	-0.15	1.35	0.00

TABLE VI Continued

C. Discharge Data

Test Temperature: 115°F; Current: 17 mA

Time, hrs.	Cell Potential			
	Cell 1	Cell 2	Cell 3	Cell 4
0	Cells put in discharge; time from activation: 3.0 hrs.			
4	2.44	2.80	2.40	2.86
8	1.80	2.68	2.10	2.60
10	1.50	2.60	1.75	2.34
12	0.85	2.36	0.00	2.06
14		1.00		1.80
16				1.50

TABLE VI Continued

CELL PERFORMANCE TESTS

Cell Nos. 5 - 8 (E74 - E77)

A. Construction Data

Cathode: 80% CuF_2, 6.6% graphite, 6.6% paper fiber, 6.6% AgCl, dry-pressed at 2,000 pounds per square inch. Theoretical capacity 0.92 ampere hours.

Anode: Lithium pressed onto expanded nickel screen. Theoretical capacity 2.85 ampere hours.

Separation: Microporous rubber, 1.1 mm thick

Electrolyte: Lithium Perchlorate, .5 moles/liter

Electrode Area: 14.4 cm^2

Reference Electrode: Cu sheet

Electrolyte Solvent: Cell 5 (E74) Acetic Anhydride
Cell 6 (E75) Butyrolactone
Cell 7 (E76) Dimethyl Sulfoxide
Cell 8 (E77) Propylene Carbonate

B. Polarization Data

Test Temperature: 72°F

Time	Load, Ω	Potential							
		Cell 5		Cell 6		Cell 7		Cell 8	
		P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.
0	7.0 cc of electrolyte solution added to cells								
1 hr.	11M	3.54	0.26	3.43	0.25	3.27	0.21	3.53	0.49
	10K	3.52	0.25	3.22	0.25	3.19	0.19	3.30	0.47
	1K	3.36	0.17	2.94	0.21	2.64	0.14	2.96	0.40
	333	3.10	0.07	2.44	0.16	2.18	0.08	2.36	0.34
	100	2.62	-0.14	1,43	0.11	1.63	0.00	1.34	0.26
	33	1.79	-0.48	0.62	0.08	0.90	-0.08	0.60	0.21

TABLE VI Continued

B. Polarization Data Continued

Test Temperature: 72°F

Time	Load, Ω	Potential							
		Cell 5		Cell 6		Cell 7		Cell 8	
		P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.	P. to Neg.	P. to Ref.
1.25 hr.	all cells place in oven at 115°F								
3 hr.	10K	3.48	0.10	3.42	0.07	3.35	0.09	3.40	0.15
	1K	3.37	0.04	3.20	0.04	3.22	0.03	3.05	0.11
	333	3.16	-0.09	3.05	0.00	3.00	-0.06	2.74	0.06
	100	2.80	-0.39	2.65	-0.07	2.62	-0.18	2.00	-0.05
	33	1.85	-0.93	1.98	-0.19	2.02	-0.39	1.05	

C. Discharge Data

Test Temperature: 115°F; Current: 6 mA

Time, hrs.	Cell Potential			
	Cell 5	Cell 6	Cell 7	Cell 8
0	Cells put on discharge 3.25 hrs. after activation			
6	2.90	3.20	3.10	3.15
12	2.70	3.14	2.90	3.06
15	2.66	3.08	2.82	3.06
18	2.60	3.00	2.74	3.02
21	2.15	2.88	2.68	2.98
24	2.00	2.60	2.55	2.90
27	2.20	2.74	2.86	2.94
30	2.10	2.35	2.83	2.86
33	2.00	0.80	2.78	2.76
36	1.78	0.00 (37.5 hrs)	2.54	2.54
39	0.00 (38.5 hrs)		2.28	1.86
42			2.20	1.00
45			1.50	0.00 (43.5 hrs)
48			1.14 (47.5 hrs)	

TABLE VI Continued

CELL PERFORMANCE TESTS

Cell Nos. 9 - 16 (E86 - E93)

A. Construction Data

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: 28.8 cm^2

Reference Electrode: Cu wire

Electrolyte Solvent: Cells 9 and 10 (E86 and E87) Acetic Anhydride
Cells 11 and 12 (E88 and E89) Butyrolactone
Cells 13 and 14 (E90 and E91) Dimethyl Sulfoxide
Cells 15 and 16 (E92 and E93) Propylene Carbonate

B. Polarization Data

Test Temperature: 77°F

Time	Load, Ω	Potential							
		Cell		Cell		Cell		Cell	
		9	10	11	12	13	14	15	16
.5 hrs.	11M		3.59	3.48	3.46	3.35	3.27	3.55	3.56
	10K	3.60	3.58	3.41	3.38	3.33	3.22	3.50	3.42
	1K	3.56	3.55	3.03	3.00	3.22	2.85	3.20	2.94
	333	3.49	3.50	2.64	2.40	3.06	2.15	2.82	2.30
	100	3.30	3.35			2.65		2.0	
	33	2.93	3.02						

TABLE VI Continued

B. Polarization Data Continued

Test Temperature: 77°F

Time	Load, Ω	Potential							
		Cell		Cell		Cell		Cell	
		9	10	11	12	13	14	15	16
1 hr.	11M	3.39	3.37	3.44	3.39	3.30	3.20	3.53	3.55
	10K	3.38	3.36	3.38	3.35	3.28	3.17	3.45	3.35
	1K	3.33	3.33	3.19	3.13	3.12	2.92	3.18	2.96
	333	3.26	3.27	2.91	2.82	2.91	2.55	2.86	2.54
	100	3.06	3.10	2.30	2.10	2.50		2.20	
	33	2.70	2.80						
4.5 hr	11M	3.27	3.24	3.45	3.43	3.18	3.16	3.50	3.51
	10K	3.26	3.23	3.44	3.42	3.17	3.15	3.49	3.47
	1K	3.22	3.19	3.32	3.29	3.11	3.09	3.36	3.16
	333	3.13	3.11	3.13	3.11	3.01	3.00	3.16	3.01
	100	2.93	2.93	2.65	2.61	2.73	2.71	2.88	2.48
	33	2.58	2.61					2.19	

C. Discharge Data

Test Temperature: 77°F; Current: 17 mA

Time, hrs.	Potential							
	Cell		Cell		Cell		Cell	
	9	10	11	12	13	14	15	16
0	Cells put on discharge; time from activation: 5 hrs.							
3	2.90	2.94	2.96	3.18	2.84	2.78	2.52	1.55
6	2.95	2.95	3.18	3.24	2.95	2.95	2.73	1.94
9	2.96	3.00	3.22	3.24	2.95	2.95	3.08	2.64
12	2.96	3.00	3.24	3.24	2.95	2.90	3.10	2.68
15	2.93	3.00	3.25	3.22	2.93	2.88	3.14	2.75
18	2.90	2.95	3.20	3.20	2.86	2.86	3.12	2.70
21	2.88	2.92	3.20	3.17	2.86	2.83	3.11	2.70
24	2.86	2.94	3.18	3.12	2.78	2.82	3.08	2.65
27	2.60	2.60	3.10	3.00	2.54	2.30	3.00	2.53
30	2.40	2.50	3.02	2.92	2.20	1.60	3.02	2.60
33	2.50	2.50	2.98	2.90	1.80	2.28	3.05	2.69
36	2.45	2.45	2.88	2.75	1.16	1.70	3.00	2.68
39	2.45	2.45	2.78	2.65	0.95	1.30	3.04	2.70

TABLE VI Continued

C. Discharge Data Continued

Test Temperature: 77°F; Current: 17 mA

Time, hrs.	Potential							
	Cell		Cell		Cell		Cell	
	9	10	11	12	13	14	14	16
42	2.20	2.30	2.60	2.20	0.75	0.95	3.05	2.65
45	1.35	2.10	1.25	0.50	0.40	0.55	3.05	2.53
46.2	1.70	2.00	1.00	0.00	0.35	0.50		
50							2.95	1.87
55							2.87	1.40
60							2.87	0.50
65							2.77	0.00
70							1.90	
75							1.50	
80							0.80	
85							0.25	
							0.00 (88.2 hrs)	

TABLE VI Continued

CELL PERFORMANCE TESTS

Cell Nos. 17 - 24 (E78 - E85)

A. Construction Data

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: 28.8 cm^2

Reference Electrode: Cu wire

Electrolyte Solvent: Cells 17 and 18 (E78 and E79) Acetic Anhydride
Cells 19 and 20 (E80 and E81) Butyrolactone
Cells 21 and 22 (E82 and E83) Dimethyl Sulfoxide
Cells 23 and 24 (E84 and E85) Propylene Carbonate

B. Polarization Data

Time	Load, Ω	Potential							
		Cell		Cell		Cell		Cell	
		17	18	19	20	21	22	23	24
0	8.0 cc of electrolyte solution added to cells								
1.0 hr.	10K	3.60	3.60	3.54	3.56	3.55	3.55	3.42	3.42
(76°F)	1K	3.52	3.52	3.32	3.32	3.38	3.32	3.05	3.02
	333	3.40	3.43	3.28	3.25	3.23	3.18	2.80	2.75
	100	3.16	3.22	3.00	2.94	2.88	2.66	1.76	1.58
	33	2.75	2.86	2.60	2.46	1.88	1.56	0.85	0.72
21 hrs.	10K	3.62	3.64	3.48	3.46	3.50	3.55	3.58	3.60
(72°F)	1K	3.45	3.45	3.30	3.28	3.48	3.52	3.48	3.42
	333	3.32	3.32	3.20	3.00	3.43	3.46	3.32	3.25
	100	3.15	3.15	2.82	2.82	3.30	3.31	3.05	2.92
	33	2.82	2.90	2.35	2.40	2.98	3.30	2.75	2.53

TABLE VI Continued

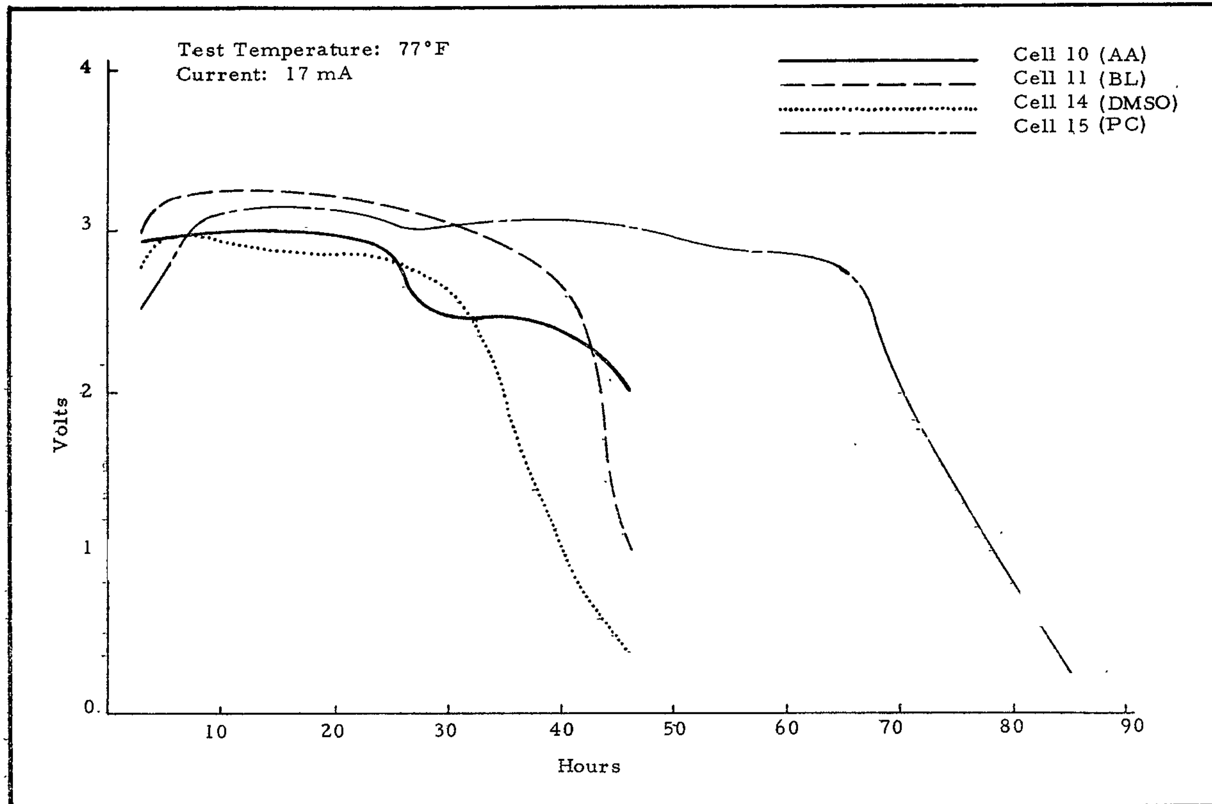
B. Polarization Data Continued

Time	Load, Ω	Potential							
		Cell		Cell		Cell		Cell	
		17	18	19	20	21	22	23	24
69 hrs.	10K	3.62	3.62	3.27	3.30	3.42	3.47	3.52	3.52
(71°F)	1K	3.38	3.40	3.15	3.15	3.40	3.45	3.48	3.48
	333	3.15	3.25	2.80	2.92	3.37	3.42	3.35	3.36
	100	3.15	3.05	2.50	2.60	3.23	3.26	3.06	3.05
	33	2.58	2.66	1.70	2.05	2.90	2.95	2.65	2.65

C. Discharge Data

Test Temperature: 115°F; Current: 11 mA

Time, hrs.	Potential							
	Cell		Cell		Cell		Cell	
	17	18	19	20	21	22	23	24
0	Cells put on discharge; time from activation: 71 hours							
10	3.22	3.22	2.90	2.90	3.02	3.02	3.05	3.05
20	3.22	3.20	2.66	2.66	2.95	3.00	3.00	3.02
30	2.55	2.75	1.30	0	2.82	2.92	2.85	2.90
40	0	0			2.72	2.88	2.75	2.80
50					2.63	2.88	2.58	2.72
60					2.48	2.80	2.30	2.55
70					2.34	2.80	2.10	2.36
80					2.10	2.70	1.40	2.20
90					1.82	2.60	0.80	1.84
100					1.62	2.54	0.40	1.25
110					1.40	2.43	0.22	1.08
120					1.20	2.33	0.10	0.70
130					1.05	2.16	0.0	0.56
140					1.00	1.98		0.45
150					0.98	1.80		0.32
160					0.94	1.50		0.14
170					1.10	1.52		
180					0.91	1.23		
190					0.90	1.10		
200					0.83	0.97		



FORM FM-101

FIGURE 2

DISCHARGE CHARACTERISTICS OF $Li-CuF_2$ CELLS

cells, the negatives became polarized to limit capacity. Upon returning the cells to open circuit, the potentials of the ACAN cells recovered instantaneously to near their original open circuit values, while the recovery of the potential of positive-limiting cells was relatively slow.

2.2.2. Evaluation of Electrolyte Solvents in Research Cells

The four electrolyte solvents described in Section 2.2.1. were further evaluated using the "Research Cell" technique (Reference 2) which permits monitoring the potentials of the positive and negative electrodes, as well as changes in cell resistance during the discharge. Voltage-time curves for four cells built with the various electrolyte solvents are presented in Figures 3 to 6, pages 40 to 46. The electrochemical utilization of the positive active material was in the range 50 to 60 per cent at 1 mA/cm^2 (about 80-hour rate) for propylene carbonate and dimethyl sulfoxide, while for the butyrolactone cell, it was 25 per cent. The cell built with acetic anhydride electrolyte suffered negative polarization after about eight hours of discharge, which limited its capacity to less than ten per cent of the available CuF_2 in the positive electrode.

2.2.3. Evaluation of Cathode Construction Methods in Experimental Cells

A number of experimental cells were built and discharged in order to study the effect of several physical and chemical variables on the performance of the system.

Cells having flat-plate construction with an electrode area of about 30 cm^2 were continued to be used in the tests. The two-anode, one-cathode cells were designed to have an excess of negative capacity (3 - 6 ampere hours negative versus 1 - 2 ampere hours positive), making the cells positive-limiting; this assumption was substantiated by reference elctrode measurements on several cells.

The performance of the CuF_2 electrode improved substantially when kerosene-base filter pad construction was employed in place of the previously used dry-press technique. Further improvement in capacity and reproducibility of results was observed when polyethylene-coated cellulose fiber was substituted for paper pulp as the binder for the positive active material.

A summary of cell discharge tests performed during the quarter are presented in Table VII, page 49. A final cell voltage of about 1.5 volts was adopted for the electrochemical efficiency studies (versus 0 VF[1] employed in earlier work); this change was made because evidence of reduction of several solvents (DMSO and MF) was observed when the cell potential was allowed to decrease to 1.0 - 1.5 volts, giving erroneously high figures for the apparent efficiency of reduction of the CuF_2.

At the present, reduction efficiency of the CuF_2 electrode is about 80 per cent to 1.5 volts per cell at the 20- to 30-hour rate in methyl formate electrolyte at room temperature (Cells Nos. E115 and E117). The average discharge voltage under these conditions was 2.5 to 2.6 volts, which has been estimated to be equivalent to 160 to 170 watt hours per pound of cell (Reference 4) for the CuF_2 - Li system.

[1] 0 VF = zero volts final cut-off

LEGEND TO FIGURES 3 - 6

Research Cell Runs

1. Positive reference versus negative reference: working cell on open circuit

2. Positive reference versus negative reference: working cell on closed circuit

3. Positive working electrode versus the negative working electrode: working cell on open circuit

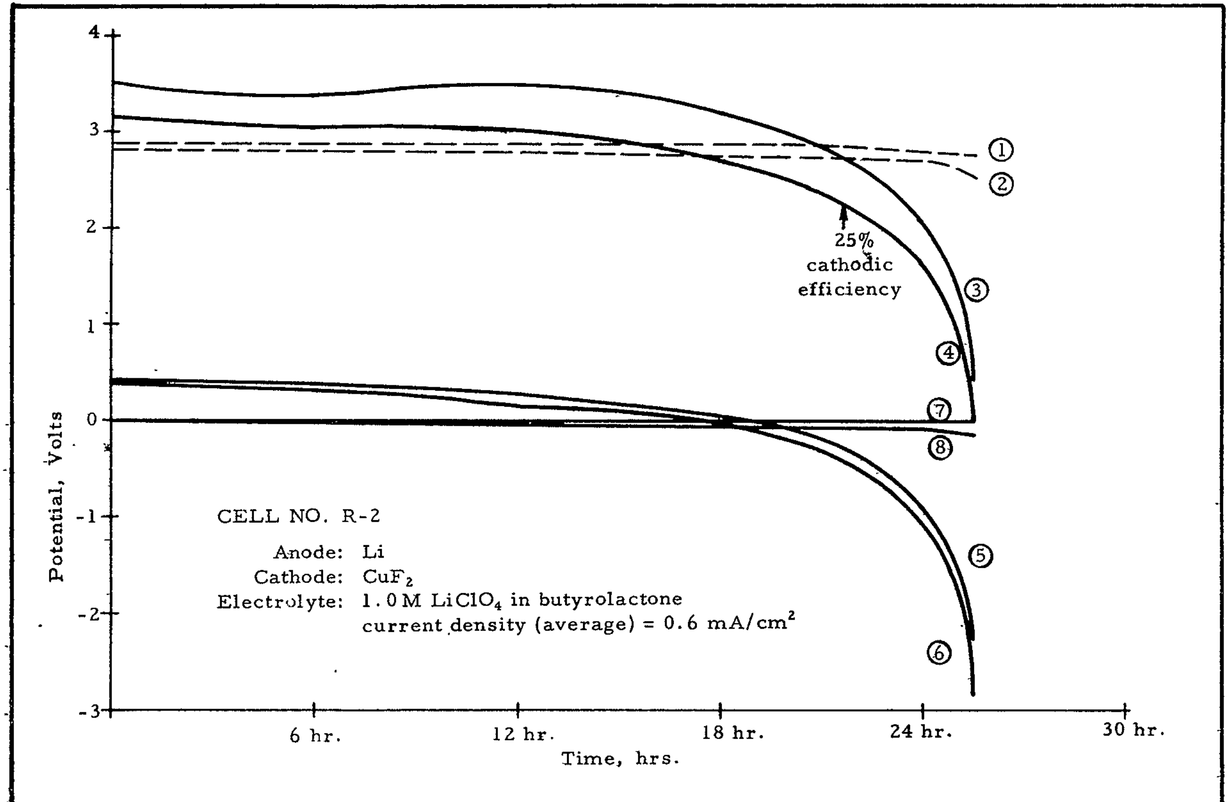
4. Positive working electrode versus the negative working electrode: working cell on closed circuit

5. Positive reference versus the positive working electrode: working cell on open circuit

6. Positive reference versus the positive working electrode: working cell on closed circuit

7. Negative working electrode versus the negative reference: working cell on open circuit

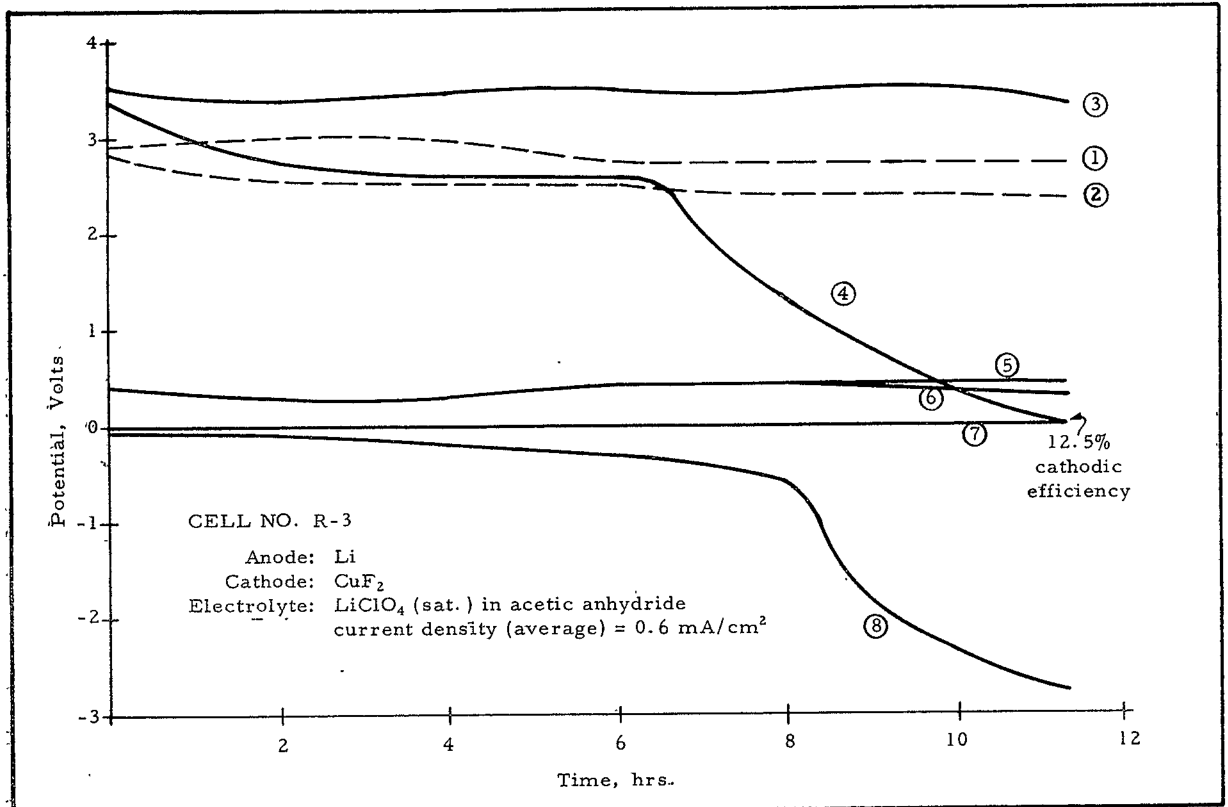
8. Negative working electrode versus the negative reference: working cell on closed circuit



FORM FM-101

FIGURE 3

DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL
WITH BUTYROLACTONE SOLVENT



FORM FM-101

FIGURE 4

DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL
WITH ACETIC ANHYDRIDE SOLVENT

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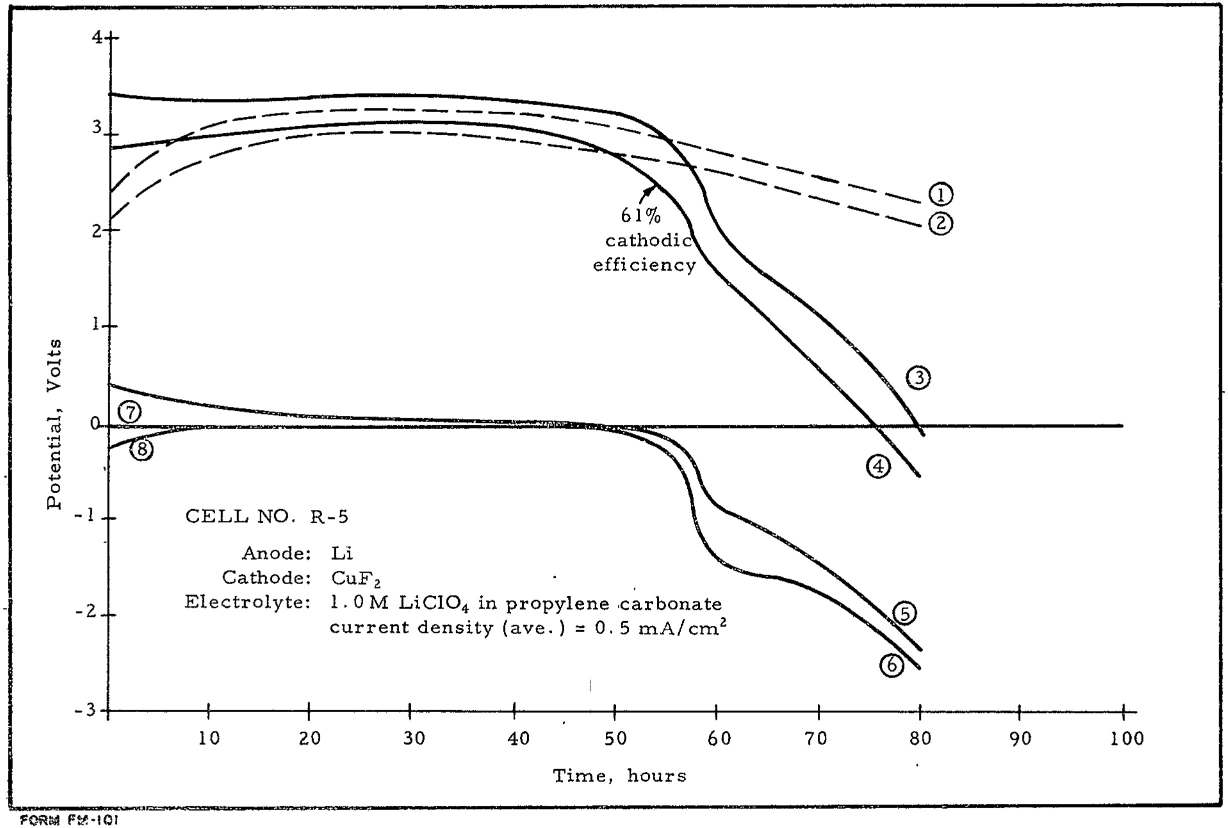

FIGURE 5

DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL
WITH PROPYLENE CARBONATE SOLVENT

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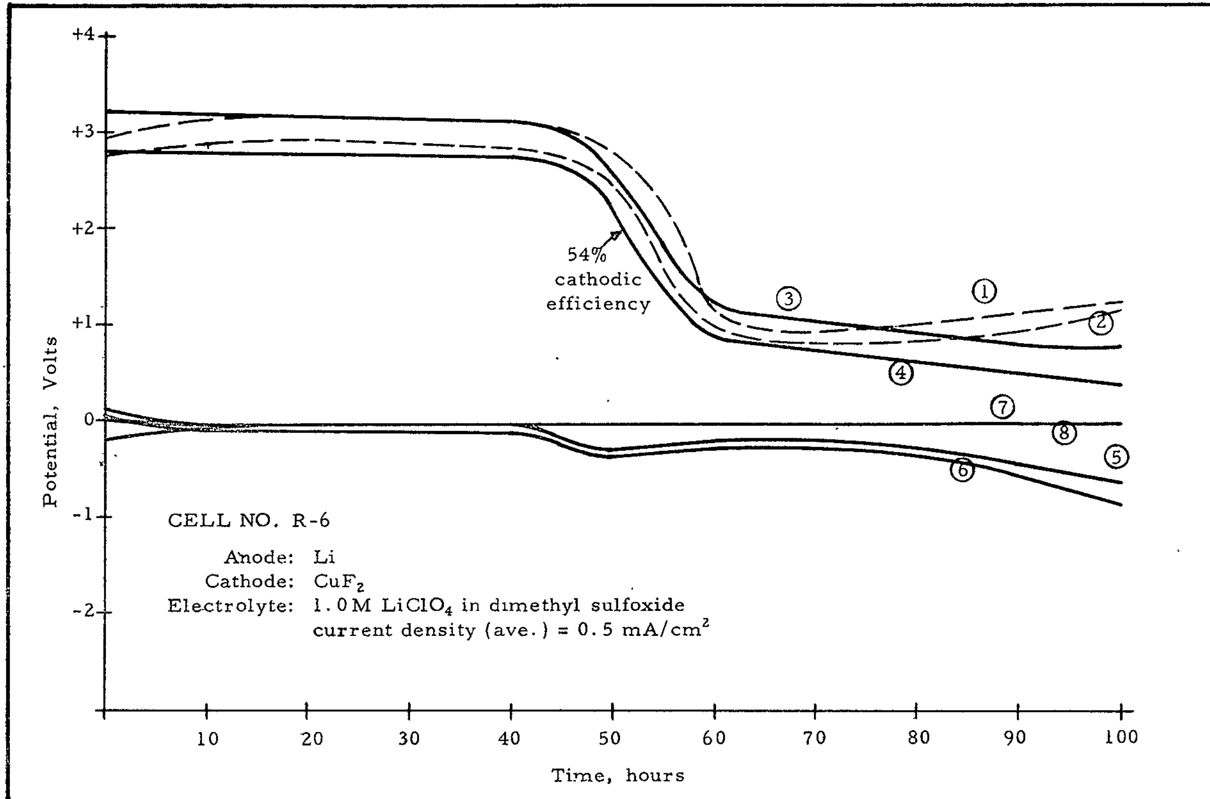

FORM FM-101

FIGURE 6

DISCHARGE CHARACTERISTICS OF Li-CuF_2 CELL
WITH DIMETHYL SULFOXIDE SOLVENT

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CODE TO TABLE VII

PP	- Paper Pulp
BP	- Blotter Paper
MPR	- Microporous Rubber
MF	- Methyl Formate
BL	- Butyrolactone
DMSO	- Dimethyl Sulfoxide
WP	- Water Pad
DP	- Dry Pressed
FP	- Filter Paper, Whatman #50
nBF	- n-Butyl Formate
AA	- Acetic Anhydride
PC	- Propylene Carbonate
THF	- Tetrahydrofuran
KP	- Kerosene Pad
N	- Nalcon

*Electrochemical equivalent of CuF_2-MnO_2 cells based on 2 electron change/mol CuF_2 an 1 electron change/mol MnO_2

TABLE VII

SUMMARY OF

Cell No.	CATHODE Active Material	Construction	Binder	Wt. of mix, gram	Theoretical A. H.	ANODE Material	Wt. of Li, gram	A. H.	SEPARATION Material	Thickness, mm
E-66	MnO_2	WP	PP	8.5	1.72*	Li	1.2	4.63	FP	
E-67	CuO	WP	PP	8.5	3.82*	Li	1.2	4.63	FP	
E-68	MnO_2	WP	PP	8.5	1.72	Li	1.2	4.63	FP	
E-69	MnO_2	WP	PP	8.5	1.72	Li	1.2	4.63	FP	
E-70	CuF_2	DP	PP	2.0	.92	Li	.75	2.9	BP	.6
E-71	CuF_2	DP	PP	2.0	.92	Li	.75	2.9	BP	.6
E-72	CuF_2	DP	PP	2.0	.92	Li	.75	2.9	BP	.6
E-73	CuF_2	DP	PP	2.0	.92	Li	.75	2.9	BP	.6
E-74	CuF_2	DP	PP	2.0	.92	Li	.75	2.9	MPR	1.1
E-75	CuF_2	DP	PP	2.0	.855	Li	.75	2.9	MPR	1.1
E-76	CuF_2	DP	PP	2.0	.855	Li	.75	2.9	MPR	1.1
E-77	CuF_2	DP	PP	2.0	.855	Li	.75	2.9	MPR	1.1
E-78	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-79	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-80	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-81	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-82	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-83	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-84	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6
E-85	MnO_2	WP	PP	8.0	1.97	Li	1.5	5.7	BP	.6

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Volume	Solute	Open Circuit Potential	Load, mA	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H./to Final Voltage	
DMSO	8	$LiClO_4$	3.60	11	3.40	1.50	133	1.46	
DMSO	8	$LiClO_4$	3.10	11	2.30	1.50	38	.42	
nBF	8	$AlCl_3$	4.07	5	3.20	1.50	3.0	.015	
AA	8	$LiClO_4$	3.07	25	3.25	1.50			
AA	5	$LiClO_4$	3.26	17	2.75	1.50	10	.17	
BL	5	$LiClO_4$	3.30	17	3.00	1.50	14	.238	
DMSO	5	$LiClO_4$	3.28	17	2.76	1.50	5.8	.099	
PC	5	$LiClO_4$	3.30	17	1.90	1.50	16	.272	
AA	7	$LiClO_4$	3.54	6	2.88	1.50	30.5	.183	
BL	7	$LiClO_4$	3.43	6	3.18	1.50	25.1	.151	
DMSO	7	$LiClO_4$	3.27	6	3.04	1.50	39	.234	
PC	7	$LiClO_4$	3.53	6	3.10	1.50	33.5	.205	
AA	9.5	$LiClO_4$	3.60	11	3.43	1.50	37	.407	
AA	9	$LiClO_4$	3.60	11	3.46	1.50	36.5	.400	
BL	7	$LiClO_4$	3.54	11	3.18	1.50	29.4	.324	
BL	8	$LiClO_4$	3.56	11	3.20	1.50	27	.297	
DMSO	9	$LiClO_4$	3.55	11	3.25	1.50	104.1	1.145	58% efficiency
DMSO	10	$LiClO_4$	3.55	11	3.28	1.50	160	1.76	89.5%efficiency
PC	11	$LiClO_4$	3.42	11	3.30	1.50	78.8	.865	
PC	12	$LiClO_4$	3.42	11	3.32	1.50	95.8	1.055	53.5%efficiency

TABLE VII

SUMMARY OF

	CATHODE					ANODE			SEPARATOR	
Cell No.	Active Material	Construction	Binder	Wt. of mix, gram	Theoretical A. H.	Material	Wt. of Matrl. gram	A. H.	Material	Thickness, mm
E- 86	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 87	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 88	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 89	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 90	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 91	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 92	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 93	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 94	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 95	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 96	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 97	CuF_2	KP	N	5.2	1.91	Li	1.5	5.7	MPR	1.1
E- 98	V_2O_5	DP	N	5.0		Li	1.5	5.7	MPR	1.1
E- 99	V_2O_5	DP	N	5.0		Li	1.5	5.7	MPR	1.1
E-100	V_2O_5	DP	N	5.0		Li	1.5	5.7	MPR	1.1
E-101	CuF_2	DP	N	5.0	1.84	Mg	4.3	8.6	MPR	1.1
E-102	CuF_2 MnO_2 1 : 1	DP	N	5.0	1.62*	Li	1.5	5.7	Glass	1.0
E-103	CuF_2 MnO_2 1 : 1	DP	N	5.0	1.62	Li	1.5	5.7	MPR	1.1

Continued

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Volume	Solute	Open Circuit Potential	Load, mA	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H./to Final Voltage	
AA	8	$LiClO_4$		17	3.10	1.50	44.7	.760	
AA	9	$LiClO_4$	3.59	17	3.10	2.00	46.2	.785	
BL	9	$LiClO_4$	3.48	17	3.05	1.50	45.9	.780	
BL	9	$LiClO_4$	3.46	17	2.96	1.50	44.7	.760	
DMSO	8	$LiClO_4$	3.35	17	2.90	1.50	35.2	.600	
DMSO	9	$LiClO_4$	3.27	17	2.80	1.50	38.7	.658	
PC	8	$LiClO_4$	3.55	17	3.10	1.50	76.5	1.30	68% efficiency
PC	8	$LiClO_4$	3.56	17	2.50	1.50	55.9	.95	
MF	7	$LiClO_4$	3.46	195	2.60	1.50	3.75	.732	
MF	7	$LiClO_4$		15	3.20	1.50	17.64	.262	test temp.-40°C
MF	7	$LiClO_4$		15	3.20	1.50	17.64	.262	test temp.-40°C
MF	7	$LiClO_4$		50Ω	2.95	1.50	15.3	.688	test temp.-40°C
PC	7	$LiClO_4$	3.55	15	3.00	1.50	11.7	.175	
MF	7	$LiClO_4$	3.46	25	3.05	1.50	41.2	.03	
PC	7	$LiClO_4$	3.40	5	3.00	1.50	31.75	.159	
NH_3		$LiClO_4$	2.30	100Ω	1.93	1.50	1.2		test temp.-40°C
THF	7	$LiClO_4$	3.95	25	3.75	1.50	32.5	.814	50.2%efficiency
MF	7	$LiClO_4$	3.90	25	2.70	1.50	62.4	1.56	96.5%efficiency

TABLE VII

SUMMARY OF

	CATHODE					ANODE			SEPARATION	
Cell No.	Active Material	Construction	Binder	Wt. of mix, gram	Theoretical A.H.	Material	Wt. of Matrl., gram	A. H.	Material	Thickness, mm
E-104	CuF_2 · MnO_2 1 : 1	DP	N	5.0	1.62	Li	1.5	5.7	MPR	1.1
E-105	CuF_2	KP	N	7.3	1.84	Li	1.2	4.63	Glass	1.0
E-106	CuO	WP	PP	10.3	3.82*	Li	1.2	4.63	MPR	1.1
E-107	CuF_2 · MnO_2 1 : 1	WP	N	13	3.01	Li	1.5	5.7	MPR	1.1
E-108	CuF_2	KP	N	4.1	1.51	Li	1.2	4.63	Glass	1.0
E-109	CuF_2 · MnO_2 1 : 1	WP	N	9.0	3.01	Li	1.5	5.7	MPR	1.1
E-110	CuF_2 · MnO_2 1 : 1	WP	N	13.0	3.01	Li	1.5	5.7	MPR	1.1
E-111	CuF_2	KP	N	7.4	2.70	Li	1.5	5.7	MPR	1.1
E-112	CuO	WP	PP	4.0	1.91	Mg	2.0	4.0	MPR	1.1
E-113	CuF_2	KP	N	3.75	1.38	Li	1.5	5.7	MPR	1.1
E-114	CuF_2	KP	N	4.00	1.48	Li	1.5	5.7	MPR	1.1
E-115	CuF_2	KP	N	3.53	1.30	Li	1.5	5.7	MPR	1.1
E-116	CuF_2 · MnO_2 1 : 1	KP	N	19.0	6.81	Li	3.0	11.4	Glass	1.0
E-117	CuF_2	KP	N	4.17	1.54	Li	1.5	5.7	MPR	1.1

Continued

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Volume	Solute	Open Circuit Potential	Load, mA	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H./to Final Voltage	
MF	7	$LiClO_4$	4.10	25	4.00	1.50	64.7	1.62	100% efficiency
THF	10	$LiClO_4$	3.55	25	3.20	1.50	36.1	1.40	76.5%efficiency
THF	10	$LiClO_4$	3.40	10	2.50	1.40	40	.400	
THF	7	$LiClO_4$	3.75	15	3.25	1.50	15.88	.238	
THF	10	$LiClO_4$	3.62	25	3.18	1.75	30	.750	49.6%efficiency
MF	8	$LiClO_4$	3.75	21	3.54	1.50	67.1	1.41	
MF	8	$LiClO_4$	3.75	21	3.58	1.50	90	1.89	62.8%efficiency
MF	7	$LiClO_4$	3.55	25	3.42	1.50	58.8	1.46	54% efficiency
AA	10	$LiClO_4$	2.04	25	1.66	1.50	1.20	.030	
MF	8	$LiClO_4$	3.53	25	1.70	1.50	17.8	.445	
MF	8	$LiClO_4$	3.56	25	2.90	1.50	24.2	.605	
MF	8	$LiClO_4$	3.50	50Ω	3.17	1.50	20.6	1.03	79.3%efficiency
MF	13	$LiClO_4$	3.80	21 17	3.76 1.85	1.74 1.50	180 35	4.30	63.3%efficiency
MF	8	$LiClO_4$	3.60	50Ω	3.20	1.50	24.7	1.26	81.7%efficiency

3. ACTIVITY PLANNED FOR THE THIRD QUARTER

The following activity has been planned for the 7th, 8th, and 9th months of the contract period:

1. Further evaluation of the filter-mat construction of the CuF_2 electrode with consideration of both processing and composition variables.

2. Study of electrolyte drying methods and the effect of water concentration in MF, PC, and other electrolytes on cell performance.

3. Further study of the properties of selected ternary (ligand) electrolyte systems.

4. Study of cathode materials other than CuF_2.

4. APPENDIX

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

TABLE A

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 1

Solvent: Butyrolactone, Antara (General Aniline & Film Corp.)

Result: Gassing, Li discolored after five hours; Li heavily discolored after 24 hours.

Test No. 2

Solvent: Butyrolactone, Antara, CaO dried for 60 hours

Result: Li discoloration after 72 hours, heavy discoloration after 168 hours except where not backed with Ni. No further change after three weeks.

Test No. 3

Solvent: Butyrolactone, Matheson, Coleman & Bell

Result: Similar to Test No. 2.

Test No. 4

Solvent: : Butyrolactone, Aldrich

Result: Similar to Test No. 1, except no discoloration where no. with Ni.

Test No. 5

Solvent: Propylene Carbonate, Eastman

Result: Heavy discoloration of Li in 24 hours.

Test No. 6

Solvent: Propylene Carbonate, Jefferson

Result: Similar to Test No. 5, except no discoloration where not backed with Ni.

Test No. 7

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Result: Moderate discoloration after 168 hours; no further change after three weeks.

Test No. 8

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Result: No Li corrosion after three weeks, solvent strongly yellowed.

TABLE X Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 9

Solvent: Acetic anhydride, Merck

Result: Translucent film on Li after 168 hours; slight Li discoloration after three weeks; solvent slightly yellowed.

Test No. 10

Solvent: Methyl Formate, Matheson, Coleman & Bell

Result: White corrosion product after two hours; moderate gassing.

Test No. 11

Solvent: Methyl Formate, Matheson, Coleman & Bell, CaO dried

Result: Similar to Test No. 10.

Test No. 12

Solvent: Nitromethane, Matheson, Coleman & Bell

Result: Moderate Li discoloration after 24 hours, heavy after 168 hours.

Test No. 13

Solvent: N, N-Dimethyl Formamide, Matheson, Coleman & Bell, CaO dried

Result: Solvent yellowed after six hours; yellow deposit on Li after 24 hours; system solidified after 48 hours (gelled).

Test No. 14

Solvent: Pyridine, Fisher

Result: Reddish brown film formed immediately on Li surface; system solidified in six hours.

Test No. 15

Solvent: n-Butyl Formate, Eastman

Result: No discoloration after eight hours; moderate discoloration after 24 hours; no change after 48 hours; white film on Li after 168 hours.

TABLE A Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 16

Solvent: 2-Butanone, Matheson, Coleman & Bell

Result: White decomposition product on Li after ten minutes; after two hours, yellow product on Li; white precipitate in solution.

Test No. 17

Solvent: Ethyl Formate, Matheson, Coleman & Bell

Result: Traces of yellow condensate on Li after two hours; heavily decomposed after six hours.

Test No. 18

Solvent: N-Methyl 2-Pyrrolidone, Antara

Result: Moderate Li discoloration, solvent pink after 24 hours; heavy discoloration after 48 hours, solvent amber. After 168 hours, heavy decomposition.

Test No. 19

Solvent: N-Methyl 2-Pyrrolidone, Antara, CaO dried

Result: Moderate Li discoloration, solvent pink after 48 hours. Yellow film on Li after 168 hours.

Test No. 20

Solvent: N-Methyl 2-Pyrrolidone, Matheson, Coleman & Bell

Result: Heavy Li discoloration after 24 hours, solvent deep rose. Heavy corrosion after 168 hours.

Test No. 21

Solvent: Butyrolactone, Antara, CaO dired

Solute: $LiClO_4$, 160 g/liter of solvent

Result: Gassing on Ni after 24 hours, Li slightly discolored; Li heavily discolored after 168 hours.

TABLE A Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS
AND ELECTROLYTE SOLUTIONS

Test No. 22

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: $LiClO_4$, 160 g/liter

Result: No apparent reaction after 168 hours

Test No. 23

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Solute: $LiClO_4$, 180 g/liter

Result: Gas bubbles on Ni after four hours; no discoloration after 24 hours. Moderate Li discoloration after three weeks.

Test No. 24

Solvent: Acetic Anhydride, Merck

Solute: $LiClO_4$, 50 g/liter

Result: No apparent decomposition after 24 hours; greyish discoloration after 48 hours; whitish translucent film after 60 hours.

Test No. 25

Solvent: n-Butyl Formate

Solute: $LiClO_4$, 160 g/liter

Result: Immediate reaction, solvent truned dark red.

Test No. 26

Solvent: Butyrolactone, Antara, CaO dried

Solute: $AlCl_3$, saturated (ca. 67 g/liter)

Result: Greyish film on Li after 24 hours; no further change after 168 hours.

Test No. 27

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: $AlCl_3$, 67 g/liter

Result: Grey deposit on Li after 24 hours; no further change after 168 hours.

TABLE A Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS
AND ELECTROLYTE SOLUTIONS

Test No. 28

Solvent: Acetic Anhydride

Solute: $AlCl_3$, saturated

Result: Greyish deposit on Li after 24 hours; solution cloudy, white precipitate after 168 hours.

Test No. 29

Solvent: n-Butyl Formate, Eastman

Solute: $AlCl_3$, 67 g/liter

Result: Li covered with white film after 70 hours; white precipitate on bottom of test tube.

Test No. 30

Solvent: Butyrolactone, Antara, CaO dried

Solute: LiCl, 33.3 g/liter, saturated

Result: Gas bubbles on Ni after four hours; slight Li discoloration on Ni side after three weeks; solution light tan.

Test No. 31

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: LiCl, 0.5 g/liter

Result: Gas bubbles on Ni after four hours; heavy Li discoloration after three weeks, white precipitate on bottom of test tube.

Test No. 32

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Solute: LiCl, 75 g/liter (saturated)

Result: No reaction after 24 hours; moderate Li corrosion on Ni side after three weeks

Test No. 33

Solvent: Acetic Anhydride

Solute: LiCl, 0.5 g/liter

Result: No reaction after 24 hours; translucent film on Ni side of Li after three weeks.

TABLE A Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 34

Solvent: Nitromethane, Matheson, Coleman & Bell

Solute: LiCl, <0.5 g/liter, saturated

Result: Li discoloration after four hours, heavy Li discoloration after 24 hours.

Test No. 35

Solvent: Butyrolactone, Antara, CaO dried

Solute: LiF, <0.5 g/liter, saturated

Result: Li discoloration after 24 hours; heavy discoloration on Ni side after three weeks.

Test No. 36

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: LiF, <0.5 g/liter, saturated

Result: Similar to Test No. 35.

Test No. 37

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Solute: LiF, <0.5 g/liter, saturated

Result: Similar to Test No. 35

Test No. 38

Solvent: Acetic Anhydride, Merck

Solute: LiF, 5 g/liter, saturated

Result: No reaction after 24 hours; after three weeks, translucent film on Li, moderate discoloration on Ni side.

Test No. 39

Solvent: Nitromethane, Matheson, Coleman & Bell

Solute: LiF, 5 g/liter, saturated

Result: Slight Li discoloration after four hours; heavy Li discoloration after 24 hours

TABLE A Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 40

Solvent: Butyrolactone, Antara, CaO dried

Solute: CuF_2, <0.5 g/liter, saturated

Result: Gas on Ni after 24 hours; after three weeks, discoloration on Ni side and Li side opposite Ni screen only.

Test No. 41

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: CuF_2, <0.5 g/liter, saturated

Result: Slight Li discoloration after four hours; heavy discoloration after 24 hours.

Test No. 42

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Solute: CuF_2, <0.5 g/liter, saturated

Result: No apparent reaction after 168 hours. Moderate Li discoloration on Ni side only after three weeks.

Test No. 43

Solvent: Acetic Anhydride

Solute: CuF_2, <0.5 g/liter, saturated

Result: Solution initially green; white deposit on Li after 24 hours; after 168 hours, solution colorless.

Test No. 44

Solvent: Nitromethane, Matheson, Coleman & Bell

Solute: CuF_2, <0.5 g/liter, saturated

Result: Li discoloration after four hours; heavy discoloration after 24 hours After 168 hours, solution colorless.

Test No. 45

Solvent: Butyrolactone, Antara, CaO dried

Solute: $CuCl_2$, 0.5 g/liter

Result: Amber solution turned colorless after 168 hours; Li severely discolored (Cu deposits).

TABLE A. Continued

STABILITY OF Ni/Li SAMPLES IN VARIOUS SOLVENTS AND ELECTROLYTE SOLUTIONS

Test No. 46

Solvent: Propylene Carbonate, Matheson, Coleman & Bell

Solute: $CuCl_2$, 5 g/liter

Result: Dark amber solution turned colorless after 168 hours; severe Li discoloration; solution gelled.

Test No. 47

Solvent: Dimethyl Sulfoxide, Crown Zellerbach

Solute: $CuCl_2$, 25 g/liter, saturated

Result: Dark green solution turned amber in 168 hours; no Li remaining; Ni grid copper plated.

Test No. 48

Solvent: Acetic Anhydride, Merck

Solute: $CuCl_2$, <0.5 g/liter, saturated

Result: Green solution turned colorless in 168 hours; Li heavily discolored (Cu plating).

Test No. 49

Solvent: Nitromethane, Matheson, Coleman & Bell

Solute: $CuCl_2$, 0.5 g/liter, saturated

Result: Heavy Li discoloration in 24 hours. Solution remained dark green after 168 hours.

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2. NAS 3-2775 Final Report (CR-54083) p. II-5.

3. *Ibid.*, p. III-16.

4. *Ibid.*, pp. III-17 to III-25.

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[illegible]

TABLE	VI.	[illegible]	
FIGURE	2.	Discharge [illegible] Cells	
FIGURE	3.	Discharge Characteristics of [illegible] Cell in [illegible] Solvent	
FIGURE	[illegible]	[illegible]	
FIGURE	[illegible]	Discharge Characteristics of [illegible] Cell with [illegible] Solvent	
FIGURE	6.	Discharge Characteristics of [illegible] Cell with [illegible] Solvent	
TABLE	VII.	Summary of "Experimental" Cell Data	
TABLE	A.	Stability of [illegible] Samples in Various Solvents and Electrolyte Solutions	61

[illegible]

The four solvents [illegible] in the previous paragraph were compared in cell discharge tests using [illegible] as the solute in [illegible]

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10) by William F. Meyers and Sandora G. Abens.

11) 9 Dec 64, (12) 84p (14) -

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