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APL-TDR-64-59

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LIMITED-CYCLE SECONDARY BATTERY USING LITHIUM ANODE

TECHNICAL DOCUMENTARY REPORT NO. APL-TDR-64-59
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AF Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 8173, Task No. 817304-20

(Prepared Under Contract AF 33(657)-11709 by the
Lockheed Missiles & Space Company, Palo Alto,
California; H. Bauman, author)

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FOREWORD

This is the Final Report prepared by the Electrochemistry Group, Materials Sciences Laboratory, Lockheed Missiles & Space Company, Palo Alto, California, under Air Force Contract No. AF 33(657)-11709, Project No. 8173, Task No. 817304, entitled "Lithium Anode Limited-Cycle Secondary Battery Investigation." This work was administered under the direction of the Flight Vehicle Power Branch, Air Force Aero Propulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. The assistance of Mr. Wayne S. Bishop, Task Engineer for the Aero Propulsion Laboratory, is acknowledged. The work reported covers the period June 1963 through March 1964.

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ABSTRACT

The lithium–cupric fluoride and lithium–cobaltic fluoride electrochemical systems were investigated with eventual battery development as the goal. Specific conductivities of $13.4 \times 10^{-3} \Omega^{-1} cm^{-1}$ and $6.8 \times 10^{-3} \Omega^{-1} cm^{-1}$ were experimentally determined for solutions of sodium hexafluorophosphate in butyrolactone and propylene carbonate. Both of these electrolytes showed little structural change as indicated by infrared spectra change after 60 days at 165°F in contact with cupric fluoride or cobaltic fluoride. Both cupric fluoride and cobaltic fluoride are insoluble in the electrolyte solutions under similar conditions. Aluminum, silver, stainless steel, polyolefins, and fluorinated polyolefins are inert in these electrolytes.

Cells with reference electrodes showed lithium anode polarization of 70 mv during a 100-hr discharge at 1 ma/in.^{2} in $NaPF_6$–propylene carbonate and 150 mv under similar conditions with $NaPF_6$–butyrolactone electrolyte. Approximately 90-percent utilization of lithium was achieved in these tests.

Cupric fluoride cathodes were prepared from cupric fluoride–silver flake blends. Utilization of 72 percent was achieved for cupric fluoride to 1.5-v polarization, which is approximately equivalent to a 2.0-v cell endpoint.

Values of 128 w-hr/lb of electrodes or 24 w-hr/lb of electrodes and electrolyte actually used were obtained during these tests.

Aluminum-cased cells discharged with a profiled load rate had lower weight-to-energy figures than the previous test cells. Figures of 4 to 15 w-hr/lb of electrode and electrolyte were obtained at 1.2 to 0.6 ma/in.^{2} current density to a 2.0-v endpoint.

A successful cobalt fluoride cathode was not made. Theoretical voltage was obtained on open circuit, but none of the electrodes constructed would sustain significant discharge at 1 ma/in.^{2}

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INTRODUCTION

A continuing need exists for batteries with higher energy-to-weight ratios for portable power supplies for applications such as satellite power supplies where logistics limits the weight and volume that are allowable for batteries. Systems with higher theoretical energy-to-weight figures than aqueous electrolyte systems may be utilized with organic solvent-based electrolytes. Work on such systems has been reported in Technical Documentary Reports No. ASD-TDR-62-1, January 1962, and ASD-TDR-62-837, September 1962, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

This program was concerned with the lithium–cupric fluoride and lithium–cobaltic fluoride electrochemical systems that have a theoretical energy-to-weight value of 746 and 970 w-hr/lb. These systems have a theoretical potential of 3.5 v. A maximum of 120 w-hr/lb may be obtained from presently available cells.

The objective of this experimental investigation of high-energy batteries was development of a cell capable of meeting a specific space-flight application. Significant goals were a battery discharging between 22 and 30 v within a temperature range of 30° to 100°F and delivering 300 w-hr/lb. The steady discharge rate was 14.4 amp with an additional 12-amp load imposed for 10 min every 90 min. A recharge and additional discharge were required from the battery.

Achievement of the ultimate goals of this project would triple the useful flight time of a space vehicle using a primary battery power system or would allow the equivalent increase in instrument load weight.

Manuscript released by author May 1964 for publication as an RTD Technical Documentary Report.

Section 2

DISCUSSION OF EXPERIMENTAL WORK

2.1 ELECTROLYTE STUDIES

The electrolyte for an electrochemical cell must be stable in contact with the active cell material, exhibit low solubility for the active material, have high specific conductivity, and have desirable physical characteristics within the range in which the cell must operate. Both the advantages and the disadvantages which a nonaqueous solvent cell system has over an aqueous cell system are derived from the electrolyte; the nonreaction of the nonaqueous solvent electrolyte with high potential anodic and cathodic material; and the low specific conductivity of nonaqueous solvent electrolytes. The physical properties of water and some of the nonaqueous solvents considered in this study are shown in Table 1. The wide liquid range of the organic solvents is an advantage in expanding the operating range of the system.

Previous work has indicated the value of propylene carbonate, nitromethane, and butyrolactone as solvents.* These solvents are generally unreactive with lithium, and solutions of salts in these solvents have relatively high conductivity. Preliminary testing of dimethylsulfoxide was initiated at the end of the program.

Water is a common impurity in the solvents under discussion and probably the most harmful. Although the specific effects of water in the electrolyte have not been determined, it probably reacts with the lithium anode in the cell to form lithium hydroxide and hydrogen, and also forms hydrated salts or reacts with the cathodic material. The lithium hydroxide, in turn, may affect the stability of the electrolyte solvent. By reflux distillation of butyrolactone or propylene carbonate, water contents of 20 ppm may be obtained. Water removal from butyrolactone was attempted with dehydrating agents. Water content as received was 2,500 ppm; $CaSO_4$ reduced it to 50 ppm, barium oxide increased it to 4,400 ppm, and molecular sieve reduced it to 10 ppm. The decrease in water content did not result in a proportional increase in resistance of the solvent (0.5 to 1.4 megohm), probably because of salt leaching from the dehydrating agent. Water content in the described tests was made by a standard Karl Fisher titration, which is adequate for water contents above 10 ppm. For water contents below this figure, apparatus must be used that will not expose the solvent or reagents to the atmosphere.

By a combination of dehydration with molecular sieve followed by reflux distillation at reduced pressure, the water content of butyrolactone was reduced from 2,500 to 10 ppm, propylene carbonate from 395 to 11 ppm, and dimethylsulfoxide from 75 to 12 ppm. The nitromethane used for solution preparation was spectrographic grade and was used without additional purification.

2.1.1 Conductivity and Concentration of Electrolyte Solutions

Initial electrolyte solutions were prepared with propylene carbonate and nitromethane as solvents. Work with nitromethane was later discontinued because of its general instability, but data are included as a matter of interest. Because CuF_2 and

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*<u>New Cathode-Anode Couples Using Nonaqueous Electrolytes</u>, Contract No. AF 33(616)-7957, Tech. Doc. Report ASD-TDR-62-1, Apr 1962; and Contract No. AF 33(616)-7952, Quarterly Tech. Progress Report No. 1 15 Dec 1962.

COMPARISON OF PHYSI
AND NONAQUEO

Solvent	Molecular Weight	Melting Point (° C)	Boiling Point (° C)	Dielectr Consta
Water	18	0	100	78
Propylene Carbonate	102	-49	242	64.4
Butyrolactone	86	-43	204	39.1
Nitromethane	61	-29	101	38
Dimethyl-sulfoxide	78	18.4	189	46.7

Table 1

SICAL PROPERTIES OF AQUEOUS
EOUS SOLVENTS AT 25° C

ctric tant	Viscosity Centipoise	Specific Conductivity $(r^{-1}cm^{-1})$	Equivalent Conductivity of 1:1 Electrolyte at Infinite Dilution $(r^{-1}cm^{2}\ eq^{-1})$	Density (gm/cm^{3})
	1.0	10^{-8}	150	1.0
4	2.53	10^{-7}	31	1.20
1	1.75	10^{-7}	46	1.13
	0.62	10^{-8}	121	1.38
7	1.96	2×10^{-8}	–	1.096

and CoF_3 were being investigated as cathodic material, fluorine complex salts were of particular interest as electrolyte salts to facilitate reversibility of the cathode.

A common test procedure was used in the electrolyte tests. Ten grams of salt were added to 100 cc of the electrolyte and agitated intermittently over a 16-hr period. Unless otherwise noted, this amount of salt was not soluble. The clear solution was then used for determination of conductivity. Resistance was measured in a glass conductivity cell with a 1,000-cycle bridge, and specific conductivity was calculated from this value. Purchased anhydrous salts were used in all cases and, except for the $AlCl_3$-LiCl electrolytes, salts were opened and stored in an argon atmosphere box. Table 2 shows the specific conductivity of a variety of salts dissolved in propylene carbonate and nitromethane.

Solutions of nitrosyl salts in nitromethane were found to react with lithium, so no additional work was done with these salts.

Both ammonium and quaternary ammonium salts dissolved in nitromethane or propylene carbonate may form the free radical when a cell with such an electrolyte solution is charged. Therefore, the primary interest was the alkali metal salts.

Solubility and conductivity measurements were made of lithium tetrafluoroborate ($LiBF_4$) and lithium hexafluorophosphate ($LiPF_6$) dissolved in butyrolactone, propylene carbonate, and nitromethane. A summary of the conductivities of saturated solutions of these salts with $NaPF_6$ as a comparison is given in Table 3. A dimethylsulfoxide solution of $NaPF_6$ is also included in this table. From these tests, propylene carbonate and butyrolactone solutions of $NaPF_6$ were selected for more intensive evaluation.

2.1.2 Properties of Propylene Carbonate–Sodium Hexafluorophosphate Solutions

The conductivity of $NaPF_6$–propylene carbonate solutions with varying concentration of $NaPF_6$ was experimentally determined. A maximum conductivity is obtained at less than saturation for $AlCl_3$-LiCl-propylene carbonate, and it is possible that $NaPF_6$ solutions would behave similarly. Figure 1, which plots the results of these tests, shows that maximum conductivity is obtained at maximum salt concentration. Evidently, the solubility of the $NaPF_6$ is so low that the viscosity of such solutions is not great enough to affect conductivity adversely. The concentration of salt was obtained by measuring the Na^+ present by flame photometry. The results were similar to those obtained by gravimetric measurement of the PF_6^- precipitated with tetraphenylarsonium chloride.*

The effect of temperature on the conductivity of $NaPF_6$–propylene carbonate solutions is shown for two $NaPF_6$ concentrations in Figure 2. A linear temperature-conductivity relationship exists over the range 0° – 65°C; an increased slope is observed for the more concentrated solution.

2.1.3 Properties of Butyrolactone–Sodium Hexafluorophosphate Solutions

The effect of concentration of $NaPF_6$ in butyrolactone on the conductivity of these solutions is shown in Figure 3. As with propylene carbonate–$NaPF_6$ solutions, no

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*H. E. Affsprung and V. S. Archer, "Gravimetric Determination of Hexafluorophosphate as Tetraphenylarsonium Hexafluorophosphate," Analytical Chemistry, Vol. 35, No. 12, Nov 1963, 1912–13.

Table 2

SPECIFIC CONDUCTANCE OF VARIOUS SALT SOLUTIONS IN PROPYLENE CARBONATE AND NITROMETHANE

Salt	Specific Conductance ($\Omega^{-1}cm^{-1}$)	
	Propylene Carbonate	Nitromethane
Nitrosyl hexafluorophosphate $NOPF_6$ (unsat.)	7.97×10^{-3}	2.35×10^{-2}
Ammonium hexafluorophosphate NH_4PF_6	6.92×10^{-3}	1.23×10^{-2}
Sodium hexafluorophosphate $NaPF_6$	6.80×10^{-3}	1.23×10^{-2}
Potassium hexafluorophosphate KPF_6	3.12×10^{-3}	5.91×10^{-3}
Tetramethylammonium hexafluorophosphate $(CH_3)_4NPF_6$	2.76×10^{-3}	8.30×10^{-3}
Nitrosyl tetrafluoroborate $NOBF_4$	3.88×10^{-3}	1.56×10^{-3}
Tetramethylammonium tetrafluoroborate $(CH_3)NBF_4$	2.76×10^{-3}	8.60×10^{-3}
Ammonium fluorosulfonate NH_4FSO_3	3.98×10^{-4}	1.79×10^{-4}
Ammonium hexafluorotitanate $(NH_4)_2TiF_6$	1.35×10^{-7}	2.32×10^{-5}
Aluminum chloride–lithium chloride $AlCl_3$-LiCl(a)	6.57×10^{-3}	4.70×10^{-2}
$AlCl_3$-LiCl(a) + $NOPF_6$	6.92×10^{-3}	4.95×10^{-2}
$AlCl_3$-LiCl(a) + NH_4PF_6	7.87×10^{-3}	–
$AlCl_3$-LiCl(a) + $NaPF_6$	6.61×10^{-3}	Gelled
$AlCl_3$-LiCl(a) + $NOBF_4$	5.90×10^{-3}	–

(a) 10 gm of $AlCl_3$/100 gm of propylene carbonate saturated with LiCl.

Table 3

CONDUCTIVITIES OF SATURATED SALT SOLUTIONS IN BUTYROLACTONE, DIMETHYLSULFOXIDE, PROPYLENE CARBONATE, AND NITROMETHANE AT 24°C

Salt	Solvent	Concentration (moles/liter)	Specific Conductivity (ohm^{-1} cm^{-1})
$LiBF_4$	Butyrolactone	0.25	3.40×10^{-3}
$LiPF_6$	Butyrolactone	0.22	4.07×10^{-3}
$NaPF_6$	Butyrolactone	1.14	13.40×10^{-3}
$LiBF_4$	Propylene Carbonate	0.42	2.54×10^{-3}
$LiPF_6$	Propylene Carbonate	0.55	4.49×10^{-3}
$NaPF_6$	Propylene Carbonate	0.86	6.8×10^{-3}
$LiBF_4$	Nitromethane	0.11	0.23×10^{-3}
$LiPF_6$	Nitromethane	0.23	6.78×10^{-3}
$NaPF_6$	Nitromethane	--	12.3×10^{-3}
$NaPF_6$	Dimethylsulfoxide	1.36	10.0×10^{-3}

maximum is observed, but the slope is quite low at maximum concentration. The conductivity of the saturated butyrolactone solution is almost twice that of the propylene carbonate solution.

The effect of temperature on the conductivity of butyrolactone $NaPF_6$ solutions is shown in Figure 4. The relationship is linear between 0° and 55°C, with a steeper slope for the more concentrated solutions.

2.1.4 Properties of Dimethylsulfoxide–Sodium Hexafluorophosphate Solutions

The change in conductivity with concentration for the more concentrated solutions of sodium hexafluorophosphate in dimethylsulfoxide is shown in Figure 5. With these solutions, a maximum conductivity is reached at about 0.9 moles/liter. The decrease in conductivity as a saturated solution is approached is probably the result of increasing viscosity.

2.1.5 Solubility of Cupric Fluoride and Cobaltic Fluoride in Electrolyte Solutions

For extended cell stand time, the active electrode materials must be insoluble in the electrolyte. Solubility of active material would result in reactant diffusion and direct reaction with the counter electrode. Solubility tests of cobalt trifluoride and cupric fluoride were made in nitromethane, propylene carbonate, butyrolactone, and

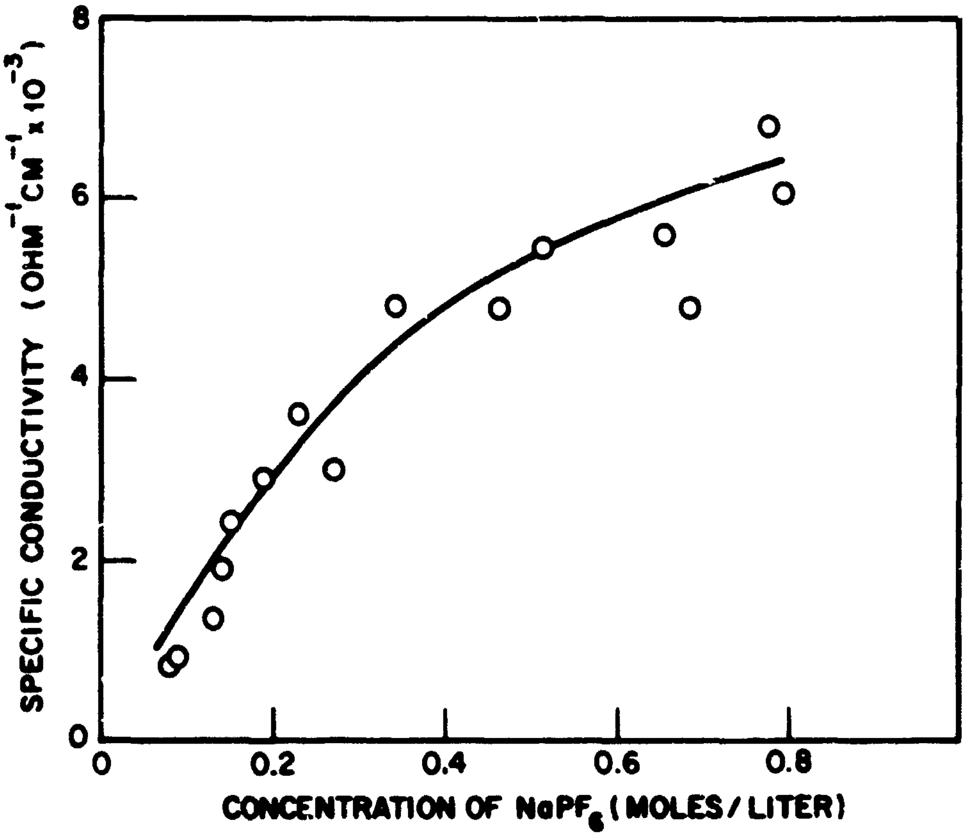

Figure 1. Conductivity Versus Concentration for $NaPF_6$ in Propylene Carbonate at 24°C

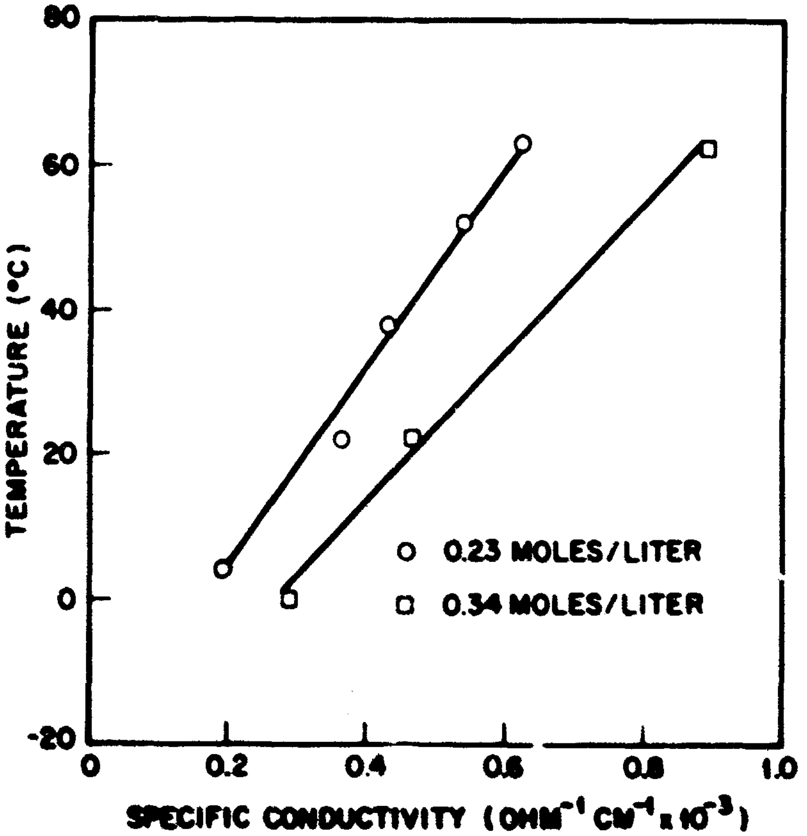

Figure 2. Variation in Conductivity of $NaPF_6$ – Propylene Carbonate Solutions With Temperature

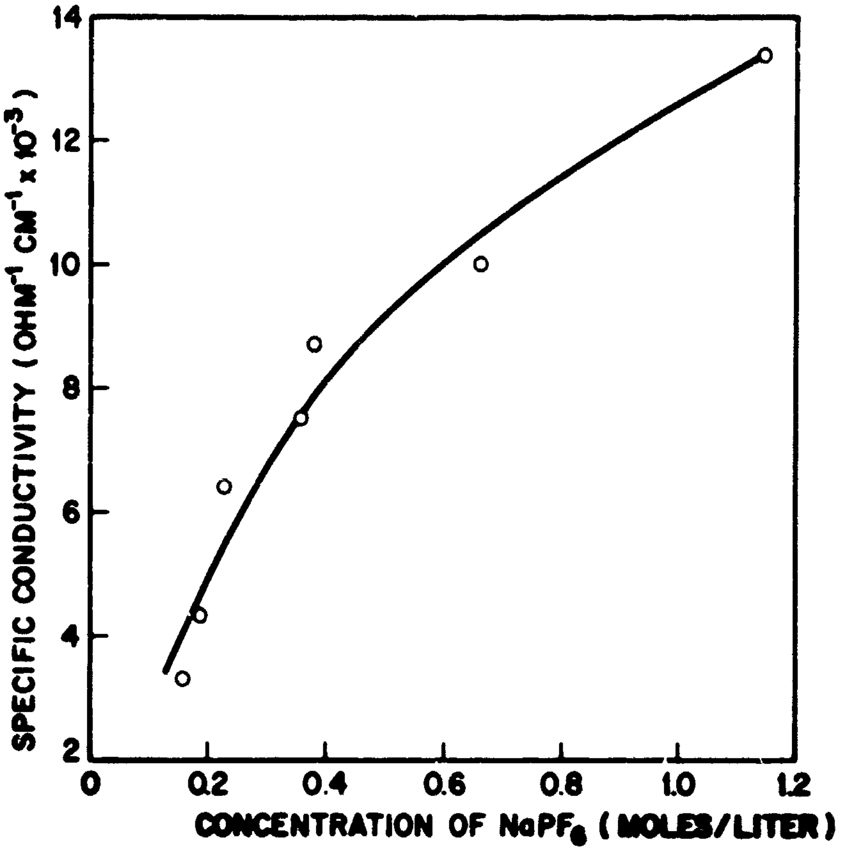

Figure 3. Conductivity Versus Concentration for $NaPF_6$ in Butyrolactone at 24°C

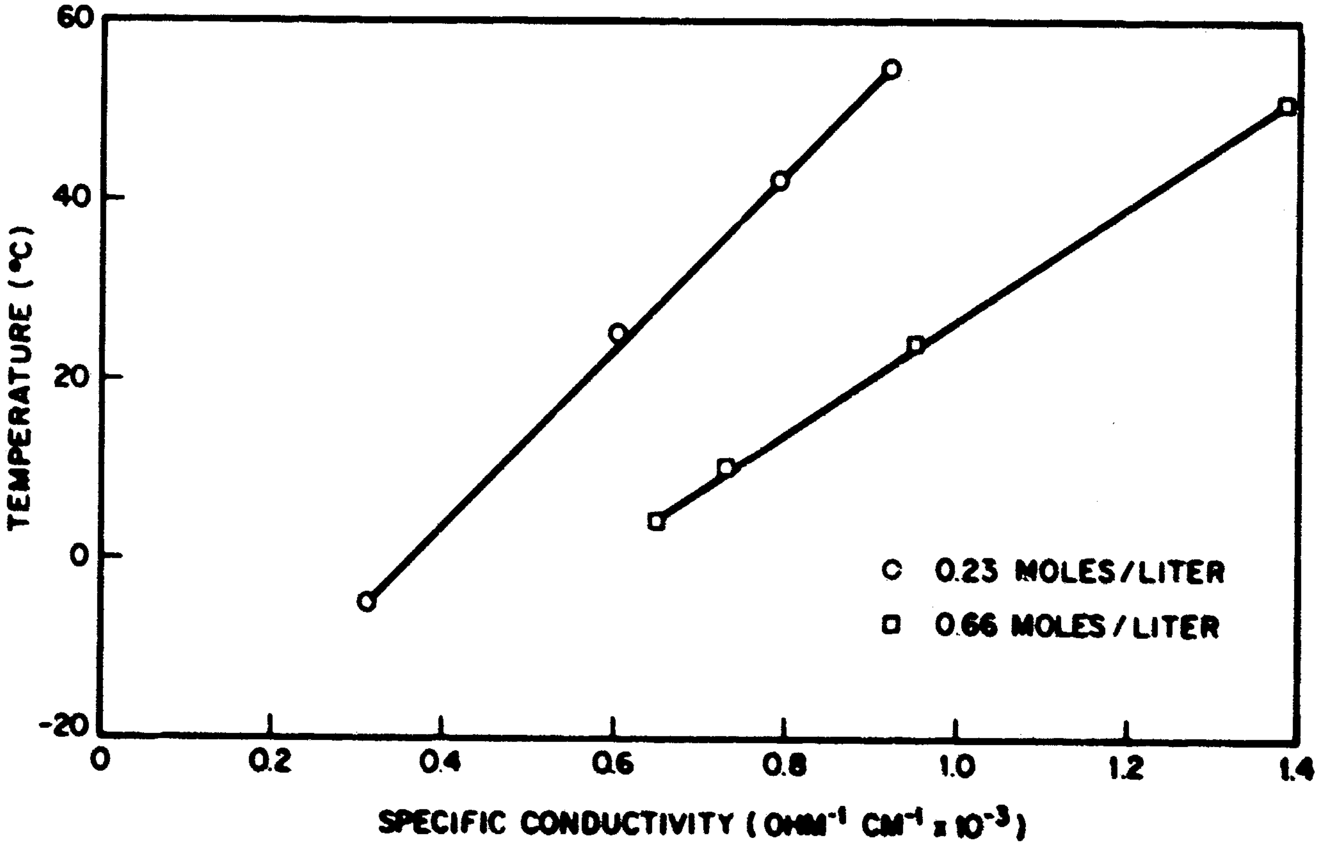

Figure 4. Variation in Conductivity of $NaPF_6$ – Butyrolactone Solutions With Temperature

dimethylsulfoxide alone and in $NaPF_6$ solutions in these solvents. The results of these tests are shown in Table 4. Cupric ion was measured in these experiments by a semiquantitative spot test with $K_4FE(CN)_6$.* Cobalt was measured by a semiquantitative color test with thiocyanate ion.** Both cupric fluoride and cobalt trifluoride are insoluble in $NaPF_6$ solutions in propylene carbonate or butyrolactone.

2.1.6 Stability of Electrolyte With Materials of Construction

Tests were made to determine the stability of $NaPF_6$ solutions in propylene carbonate and butyrolactone when in contact with materials of construction. This series of tests was made at 165° F using glass bottles. The corrosion of metals by $NaPF_6$–propylene carbonate electrolyte is shown in Table 5, for $NaPF_6$ butyrolactone in Table 6, and for $NaPF_6$ dimethylsulfoxide in Table 7. Subsequent tests were made in polyethylene bottles because the glass bottles were attacked by the electrolyte. Corrosion of metals is reduced with the drier electrolyte. Aluminum, silver, and stainless steel appear unattacked by the $NaPF_6$ solutions. Preliminary tests had shown the polyolefins and fluorinated polyolefins to be inert to the electrolyte.

The infrared spectra of the electrolyte solutions was measured before and after 60 days of storage at 165° F with lithium and CuF_2 for indications of structural degradation of the solvent. There was little change in the spectra, and decomposition, if any, was minor.

2.2 SEPARATOR STUDIES

2.2.1 Separator Stability in Electrolyte

Various separator materials that had been found useful in nonaqueous electrolyte at room temperature were tested for stability at 165° F. The materials selected could be dried free of water and could be obtained in porous forms. Table 8, which summarizes the tests, indicates that polyester and polyolefin nonwoven fabrics withstand exposure to the electrolyte and should be useful as separators in cells with $NaPF_6$–propylene carbonate and $NaPF_6$–butyrolactone electrolytes. The yellowing of solution in these tests resulted from the use of solvent as received from the manufacturer in the preparation of electrolyte and from the use of glass sample bottles.

2.2.2 Resistance of Separator Material

The resistance of the separator material increases the impedance of a cell and its voltage regulation and should be kept to a minimum. The resistance of separator material wet with electrolyte was measured in a small jig between two parallel silver-plated plates. The jig was designed to receive a standard circular sample of separator and was enclosed to standardize the electrolyte present. The measurement was made with a 1-kc AC bridge and the resistance calculated from the bridge measurements which included a capacitive element. The results of these measurements are shown

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*Wilfred W. Scott, Standard Method of Chemical Analysis, Van Nostrand, 6th ed., 1962.

**W. F. Hillebrand, Applied Inorganic Analysis, Wiley, 1953.

Table 4

SOLUBILITY OF CUPRIC FLUORIDE AND COBALTIC FLUORIDE IN SOLVENTS AND SALT SOLUTIONS

Solution	Cu^{++} (moles/liter)	Co^{+++} (moles/liter)
Butyrolactone	0.0015	0.00025
Butyrolactone + $NaPF_6$	Neg. test	Trace
Propylene carbonate(a)	0.005	0.0006
Propylene carbonate + $NaPF_6$(a)	Negative	0.00125
Nitromethane(a)	Negative	Negative
Nitromethane + $NaPF_6$	0.021	0.0062
Dimethylsulfoxide	0.043	0.021
Dimethylsulfoxide + $NaPF_6$	0.031	-

(a) Solution sample at 165° F for 60 days before test.

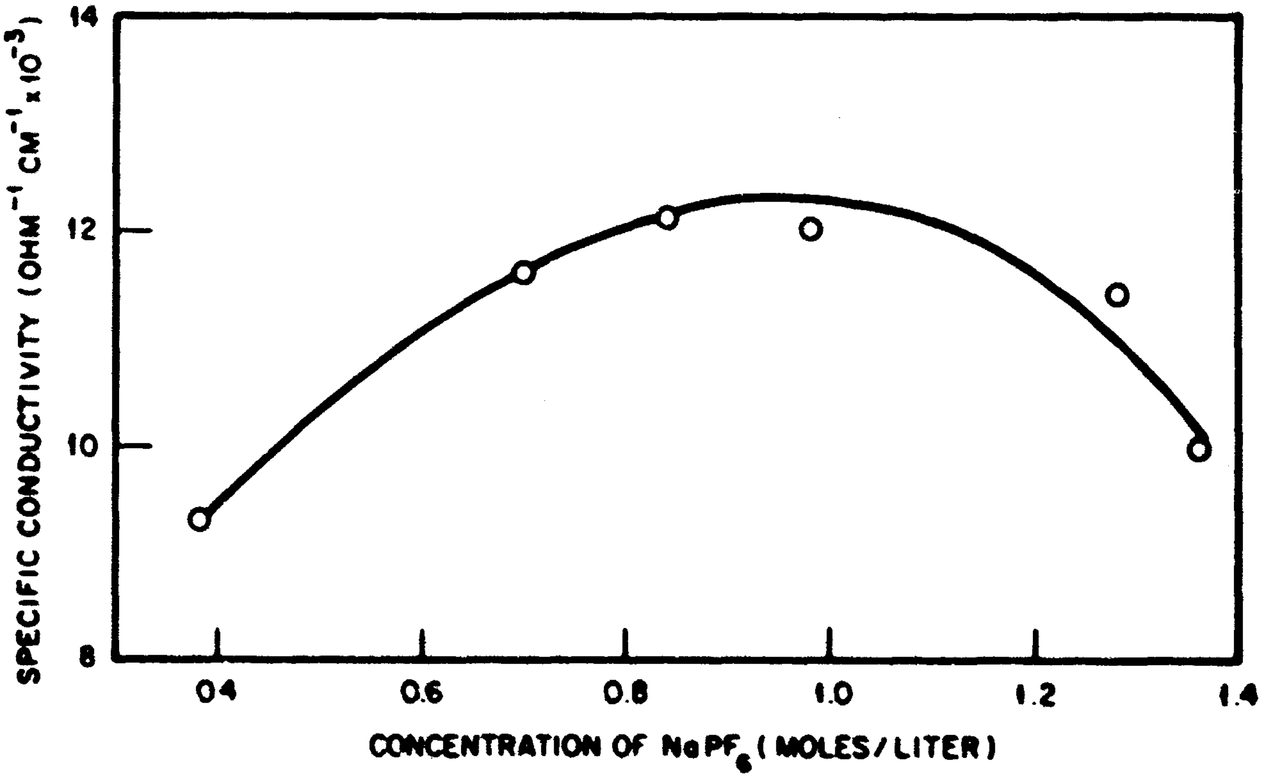

Fig. 5 Conductivity Versus Concentration of $NaPF_6$ in Dimethylsulfoxide at 24°C

Tabie

CORROSION OF METALS IN NaPF$_6$–PROPYLEN

Material	Form	Original Weight	Original Area	Weight Los 12 Days' S	
				mg	mg/
Copper	Sheet	1.2944	0.531	7.1	
Copper	Sheet	1.3463	0.531	7.7	
Nickel	Sheet	0.1[illegible]70	0.505	3.2	
Nickel	Sheet	0.1978	0.505	3.4	
Silver	Sheet	0.0858	0.502	6.3	
Silver	Sheet	0.0828	0.502	5.9	
Aluminum	Sheet	0.2571	0.524	0	
Aluminum	Sheet	0.2858	0.524	0	
Soft Solder	Sheet	2.3376	0.570	23.7	
Soft Solder	Sheet	2.5054	0.570	22.4	
Stainless Steel	Machined Ring	0.9826		+00.1	
Stainless Steel	Screen	0.0757		0.1	
Hard Solder	Wire	0.9209	0.389	3.1	
Hard Solder	Wire	0.9108	0.389	3.4	

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ENE CARBONATE ELECTROLYTE AT 165°F

Loss After s' Storage	Weight Loss After 22 Days' Storage		Weight Loss After 60 Days' Storage	
g/in.^{2}/day	mg	mg/in.^{2}/day	mg	mg/in.^{2}/day
1.11	12.6	1.08	23.4	0.74
1.21	13.6	1.16	23.4	0.74
0.53	9.4	0.85	23.8	0.79
0.61	10.1	0.90	24.7	0.82
1.05	9.8	0.89	15.8	0.53
0.98	10.4	0.94	15.7	0.53
0	1.1	0.01	0.4	.00
0	0.1	.00	0.5	.00
3.46	41.2	3.29	66.6	1.95
3.28	41.8	3.33	66.0	1.93
0	0	0	0.4	0
0	0.1	0	0.1	0
0.67	7.1	0.83	9.8	0.42
0.73	9.0	1.05	19.8	0.85

Table

CORROSION OF METALS IN $NaPF_6$-BUTY

Material	Form	Original Weight	Original Area	Weight Lo 12 Days'	
				mg	mg
Copper	Sheet	1.1746	0.531	67.8	
Copper	Sheet	1.1710	0.531	54.8	
Nickel	Sheet	0.1952	0.505	11.8	
Nickel	Sheet	0.1970	0.505	11.8	
Silver	Sheet	0.0873	0.502	5.0	
Silver	Sheet	0.0937	0.502	4.9	
Aluminum	Sheet	0.2190	0.524	0.6	
Aluminum	Sheet	0.2748	0.524	0.3	
Soft Solder	Sheet	2.1152	0.570	15.2	
Soft Solder	Sheet	2.1073	0.570	13.7	
Stainless Steel 316	Machined Ring	0.9857	–	+0.2	
Stainless Steel 304	Screen	0.0734	–	+0.2	
Hard Solder	Wire	0.9226	0.389	1.9	
Hard Solder	Wire	0.9500	0.389	2.3	

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TYROLACTONE ELECTROLYTE AT 165°F

Loss After ys' Storage	Weight Loss After 22 Days' Storage		Weight Loss After 60 Days' Storage	
mg/in.^{2}/day	mg	mg/in.^{2}/day	mg	mg/in.^{2}/day
10.6	75.8	6.5	87.5	2.8
8.3	57.4	4.9	69.3	2.2
1.95	32.4	2.9	36.7	1.2
1.95	33.3	3.0	35.3	1.2
0.8	10.5	0.95	11.4	0.38
0.8	11.5	1.05	12.2	0.40
0.1	2.4	0.21	5.5	0.17
0.05	2.0	0.17	6.7	0.21
2.21	47.7	3.80	65.9	1.93
2.00	34.7	2.76	46.6	1.36
0	0.1	0	0.2	0
0	0	0	0.1	0
0.41	10.5	1.23	22.6	0.97
0.49	10.0	1.17	21.6	0.93

Table 7

CORROSION OF METALS IN $NaPF_6$-DIMETHYLSULFOXIDE ELECTROLYTE AT 165°F

Material	Form	Original Weight	Original Area	Weight Change After 11 Days Storage		Appearance
				mg	mg/in.^{2}/day	
Silver	Sheet	0.2141	0.510	0.0	0.0	Discolored
Nickel	Sheet	0.2006	0.530	+ 2.6	+0.445	Discolored
Aluminum	Sheet	0.2328	0.543	+ 0.7	+0.117	Discolored
Copper	Sheet	1.1029	0.566	-53.4	-8.59	Discolored
Stainless Steel	Machined Ring	9.7558	–	0.0	0	No Change

in Table 9. Although glass fiber paper was attacked by the electrolyte at 165°F, it was stable during cell tests at room temperature and was used for the testing program because of its low resistance.

2.3 LITHIUM ANODE STUDIES

The potential loss at the lithium anode, because of polarization during discharge, and the amount of lithium used electrochemically are of interest for cell design. The polarization loss affects voltage regulation, and the utilization shows what amount of lithium above theoretical must be added to the electrode to secure a specific discharge time.

The lithium electrodes for all experiments were prepared by rolling sheet lithium on one side of a grid of expanded silver mesh. The final electrodes were 2 in. × 2 in. × 0.015 to 0.025 in. thick. Initially, test cells were assembled with two lithium electrodes and the cells driven by a constant-current power supply, making one electrode anodic and one cathodic. The results of tests with $NaPF_6$-propylene carbonate electrolyte at 10 ma/in.^{2} are shown in Figure 6. The electrodes had sufficient lithium for approximately 120 hr of discharge at this rate. Approximately 90-percent utilization was achieved with polarization levels below 200 mv. The polarization on the graph is the increase from the initial closed-circuit reading. The change between anode and reference at open-circuit conditions and initial reading contains both the activation polarization of the electrode and the IR drop caused by solution resistance between the anode and the reference electrode, and these values were not determined.

Similar polarization tests were made with nitromethane-$AlCl_3$-LiCl electrolyte. The open cells were discharged in an inert-atmosphere glove box, and there was some loss of solvent which was replaced as needed to maintain electrolyte level. Figure 6 shows the change in potential with time. The end of the discharge, where polarization increased rapidly, was obtained from a recorder tape that measured cell voltage only.

Tabl

STABILITY OF SEPARATOR MATERIAL I

Sample No.	Material	Form	Propylene Saturated V
			24 hr
1	Glass	Fiber Matt	Disintegrated & soluble; soln yel
2	Polyester	Fiber Matt	Material ok; soln br
3	Polyester	Fiber Matt	↓
4	Polyester	Fiber Matt	↓
5	Polyester	Film	Material ok; soln br
6	Polyamide	Fiber Woven	Material solid; soln yel
7	Polyamide	Fiber Matt	↓
8	Polyamide	Fiber Matt	↓
9	Acrylic	Fiber Matt	Material solid; soln yel
10	Asbestos	Fiber Matt	Material ok; soln yel
11	Polyolefin	Porous Sheet	↓
12	Polyolefin	Woven Screen	↓
13	Polyolefin	Porous Sheet	↓
14	Polyolefin	Fiber Matt	↓
15	Fluorinated Polyolefin	Woven Screen	↓
16	Acrylic	Fiber Matt	↓
17	Acrylic	Fiber Matt	↓

able 8

L IN ELECTROLYTE SOLUTIONS AT 165° F

ylene Carbonate ted With $NaPF_6$		Butyrolactone Saturated With $NaPF_6$	
	14 days	48 hr	14 days
d & yel	-	Disintegrated & soluble; soln br	-
	Material ok; soln br	Material ok; soln br	-
	-	Material ok; soln lt br	-
	-	Material ok; soln yel	Material curled; soln dk br
	Material ok; soln br	Material ok; soln br	-
id;	-	Material ok; soln yel	Material solid; soln yel
	-	Material solid; soln br	-
	-	Material solid; soln br	-
ıd;	-	Material solid; soln br	-
	Material disint or solid	Material disint or solid	-
	Material ok; soln yel	Material ok; soln br	Material ok; soln br
	↓	↓	↓
	↓	Material ok; soln br	Material ok; soln br
	↓	Material ok; soln yel	Material ok; soln yel
	↓	Material soluble	-
	↓	Material soluble	-

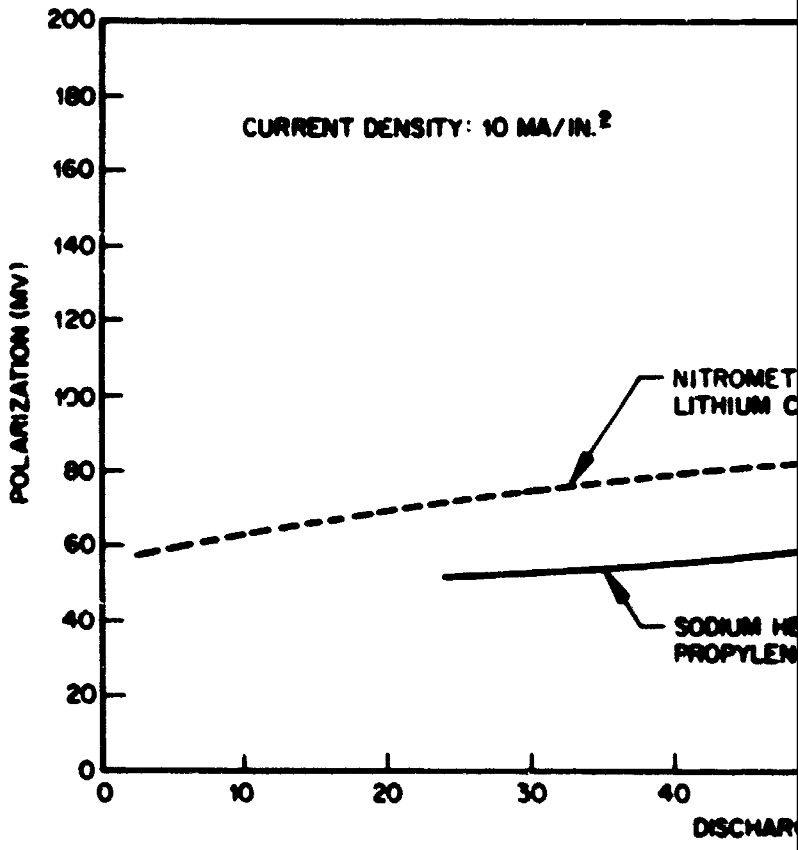
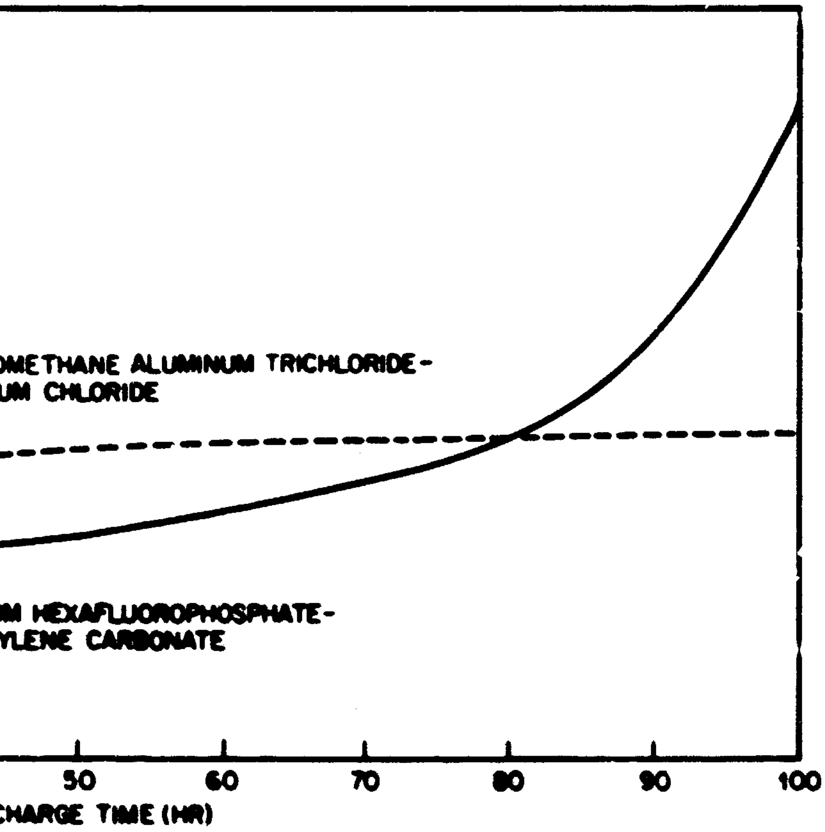


Figure 6. Polarizatio



ation of Lithium Anode

Table 9

RESISTANCE OF SEPARATOR MATERIAL WET WITH $NaPF_6$-PROPYLENE CARBONATE ELECTROLYTE

Material	Thickness (mil)		Resistance
	Dry	Wet	(ohm/in.^{2})
Polyethylene Nonwoven Fabric 14 PN	11.35	11.25	3.38
Glass Fiber Paper No. 934	12.05	12.0	1.01
Polyester Nonwoven Fabric EM 346	1.35	1.25	1.49
Polyester Nonwoven Fabric EM 345	2.0	2.0	2.27
Polyester Woven Fabric	3.83	3.75	0.66
Polyester Nonwoven Fabric EM 343	3.75	3.75	4.57
Polyester EM 345; 60 Days in Electrolyte at 165° F	–	5.5	4.68
Polyester Woven Fabric After 60 Days in Electrolyte at 165° F	–	4.5	0.61
Irradiated Film	8.0	7.0	98.00

The lithium present on the electrodes as weighed was sufficient for 140 hr of discharge at the 10 ma/in.^{2} rate. The discrepancy with that actually obtained is probably the result of inaccuracies in weighing in the glove box.

Periodically during the discharge of these cells, the load was increased in steps to obtain polarization at higher discharge levels and then decreased in similar steps. Polarization curves obtained after 4, 49, and 100 hr of discharge are shown in Figure 7. The decrease in polarization between 49 and 100 hr of discharge occurred with both cells and is shown by the points in the figure. These data indicate that polarization of less than 200 mv is obtained with short-time higher current rates during a significant part of the discharge.

Later, polarization tests were made in plastic-cased cells consisting of a sheet lithium anode rolled on expanded silver metal, various CuF_2 cathodes, and a lithium-wire reference electrode insulated from the working electrodes with glass-fiber separator material. These cells were discharged at a manually maintained constant current primarily for cathode studies, but anodic polarization was also recorded. In these tests, shown in Figure 8, anodic polarization at 1 ma/in.^{2} was usually less than 70 mv during discharges lasting over 100 hr with propylene carbonate-$NaPF_6$ electrolyte. Polarization of lithium in butyrolactone-$NaPF_6$ was approximately 150 mv at this current density. With both electrolytes, polarization was initially higher after the cell had been on open circuit. The results of increasing the load stepwise at

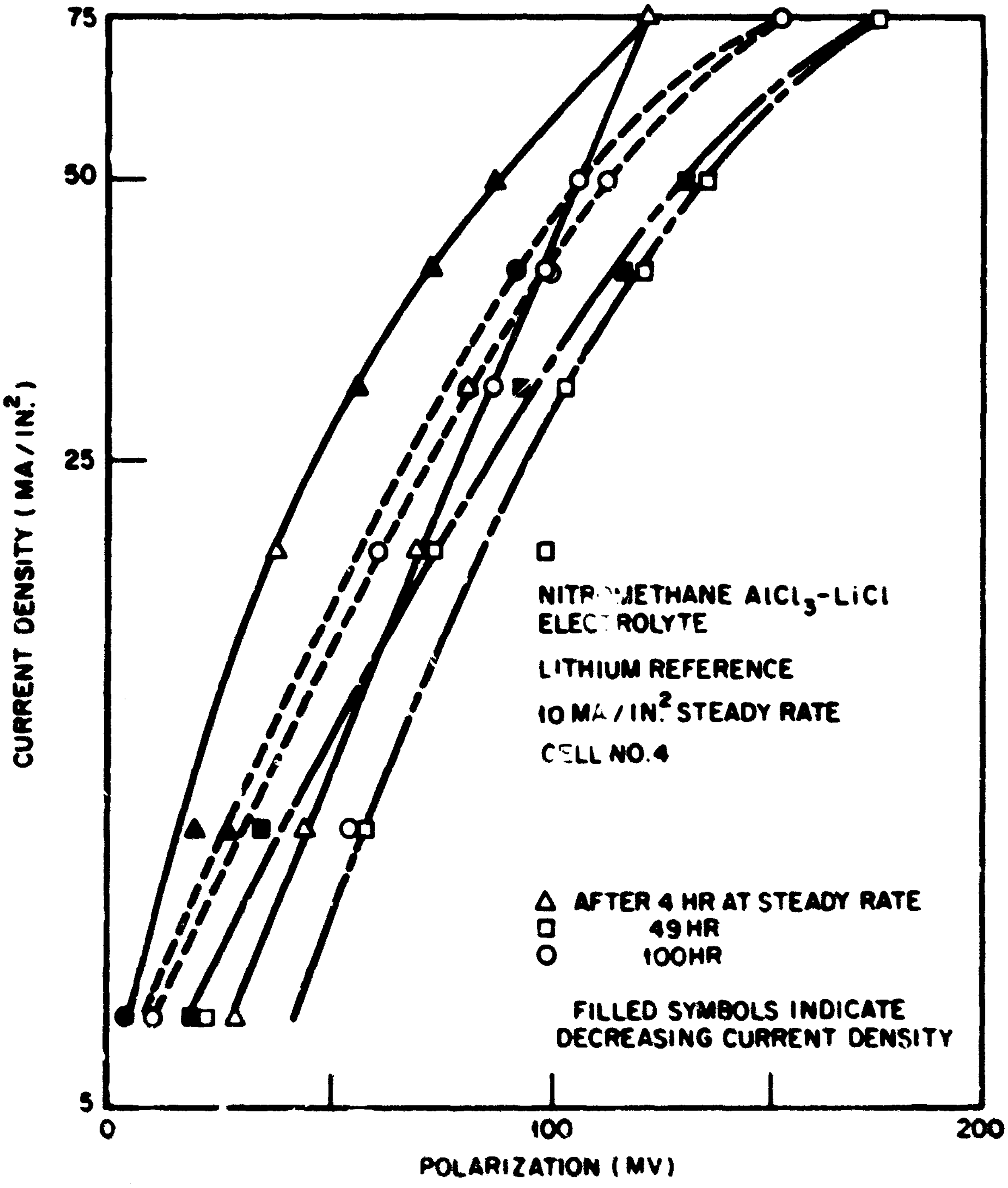


Fig. 7 Polarization Versus Current Density for Lithium Anode in Nitromethane-$AlCl_3$ - LiCl Electrolyte

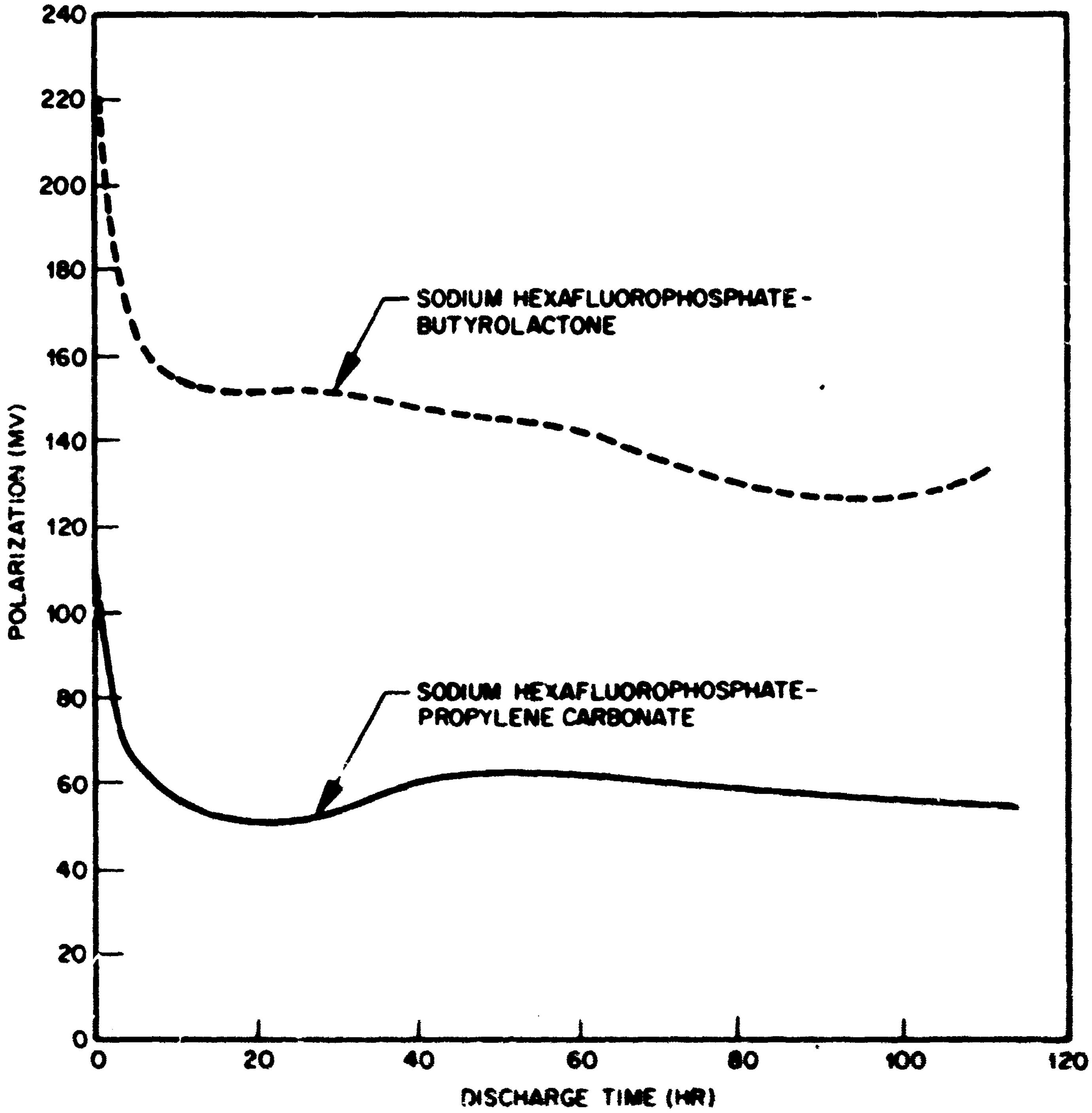


Fig. 8 Polarization of Lithium During Low Rate Discharge

intervals during a long-time discharge are shown in Figure 9. These tests were made at lower current density than those of Figure 7 but show higher polarization. This may be because of the different electrolyte used in the two tests or because of the difference in cell conditions. Polarization with butyrolactone-$NaPF_6$ electrolyte is somewhat higher than with propylene carbonate$-NaPF_6$ over the current range. Both of these electrolytes have the common Na^+ and PF_6^- ions, and the difference is not large. From these limited tests, it appears that the electrolyte composition will greatly affect the polarization of lithium during discharge, and at high current densities the anodic polarization losses must be considered.

.4 CUPRIC FLUORIDE CATHODE STUDIES

Copper fluoride is a poor electronic conductor; consequently the characteristics of a thick massive copper fluoride cathode for use in a cell would be quite poor. Generally, cathodic materials used in electrochemical cells are finely powdered to increase the surface area and mixed with an electronic conductor to increase the points at which electrons can be supplied for the cathodic reaction. Another consideration in making the electrode is the mechanical strength that will maintain the shape of the electrode and the contact between reaction sites and current-carrying grid. Cathodes for this contract have been fabricated by cold-pressing of dry powder; by pasting the cathode mixture with added colloidal graphite suspended in mineral spirits as a binder; by pasting a cathode mixture containing finely powdered thermoplastic resin, drying, and pressing above the flow point of the resin; by heating without pressure a mix containing a thermoplastic resin binder; and by low-temperature sintering of a CuF_2-Ag flake or a CuF_2-Cu powder mix without binder. In the last case, dried xylene was used to prepare a wet mix for pasting on the grid. All mixes were ball-milled 16 hr and, with a few exceptions in the earliest work, were sieved after milling. The prepared cathodes were assembled with an anode of sheet lithium rolled on a silver expanded metal grid and a lithium reference electrode centrally situated between the electrodes. Glass fiber paper was used to separate the electrodes in the solution. Propylene carbonate$-NaPF_6$ electrolyte was used for all tests unless indicated otherwise. These cells were of the same construction as those described in subsection 2.3.

Cold-pressed cathodes were prepared by placing the metal grid and uniformly distributed cathode powder in a steel die in an inert atmosphere, sealing the assembly in aluminum foil, and then removing it from the inert atmosphere. Pressure was applied in a hydraulic press. Uniform distribution of dry material was difficult and resulted in nonuniform pressure distribution in the pressing operation, particularly with thin electrodes, although some spots that maintained good adhesion and cohesion during discharge were found on these electrodes. Electrodes fabricated in this manner with CuF_2-graphite mixes for discharges of 100 hr reached 1.5-v cathode polarization in less than 10 hr. Somewhat better results were obtained with $CuF_2$$-$silver flake mixes.

Cathodes prepared from CuF_2-graphite mixtures and pasted with colloidal graphite in mineral spirits as binder showed similar results. Adhesion was very poor, and cathodes removed from discharged cells were swollen and mushy.

Resin-bonded electrodes (polyethylene) were made to improve adhesion. These electrodes did not swell as did the pasted electrodes, but adhesion to the grid was poor and cathode mix could be flaked from the grid. The 1.5-percent polyethylene-bonded cathodes had too high a resistance to sustain discharge, but the results obtained from the 0.4-percent and the 0.75-percent resin content cathodes were favorable. The best cell with this type of cathode construction discharged 45 hr before cathode polarization was greater than 1.5 v.

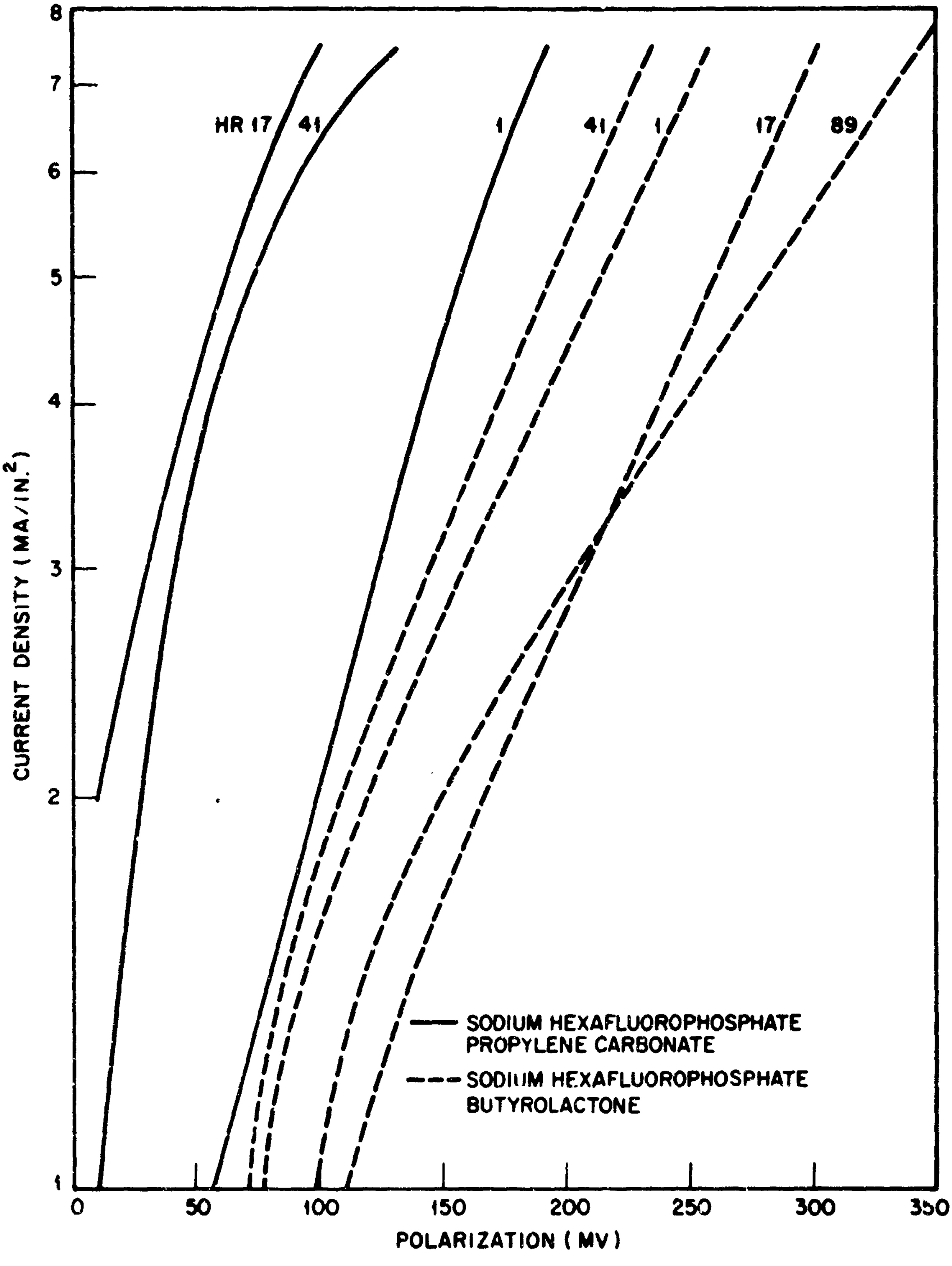


Figure 9. Polarization Versus Current Density for Lithium Anode

Cathodes were also prepared by sintering a similar mix containing powdered polyethylene. The mix was pasted on grids with an acrylic binder in xylene. In these tests, the electrodes, after pasting and vacuum drying, were heated to 150°C, which is above the softening point of the resin. Results from these electrodes show a long flat discharge after a rapid drop at the beginning of discharge. In later tests at 1.0 ma/in.^{2} in which no secondary binder was used, the voltage drop did not occur as quickly. Higher binder concentrations may be used with this method than by hot pressing.

Another approach to cathode improvement was made by preparing a sintered metal matrix with the copper fluoride in place. To maintain the anhydrous condition of copper fluoride, it must not be exposed to the atmosphere. An Inconel container with a water-cooled "O" ring seal was prepared that could be filled in the glove box and then passed out and placed in a furnace for the sintering operation. Valved holes in the container allowed gas flow through the container during sintering.

It was found that any binder in the cathode mix decomposed the CuF_2 during sintering, so electrodes were made by pasting the ball-milled cathode mix with dried xylene on screen or expanded metal mesh. The cathodes were vacuum dried at 80°C to remove the solvent and then sintered at various temperatures in a flowing stream of argon. When silver powder was used in the dry mix, silver was used as grid material; when copper powder was the additive, the electrode grid was of copper. A characteristic of cells with these cathodes was a rapid drop to between 2.5 to 2.0 v and then a long discharge at this level. Cell voltage and reference-cathode voltage are similar in these tests because of the small anode polarization. Two hundred hours of discharge were obtained to a 2.0-v endpoint with one cell which was equivalent to 57-percent utilization of CuF_2. Even at this low discharge rate (1 ma/in.^{2}), a calculated 96 w-hr/lb (for electrodes and electrolyte) could be obtained with minimum electrolyte.

The most successful cathodes as evaluated by cell tests were prepared by pasting 70 percent CuF_2 and 30 percent silver flake wet with xylene on expanded silver mesh and baking at 200°C after vacuum drying at 85°C. Polarization with discharge time is shown for cells prepared from these cathodes in Figure 10. The reason for the decrease in polarization after the first rise is not known. Polarization at higher current during the discharge is shown in Figure 11. It is of interest that, after the initial cathodic polarization, the subsequent increase with higher current is slight. The best of the cells in this group used 72 percent of the available CuF_2 in discharging at 1 ma/in.^{2} to a 2.0-v endpoint. This is equivalent to 128 w-hr/lb of the electrodes used, or 24 w-hr/lb of electrodes and electrolyte. Excess electrolyte was used, as the test cell was a standard case and the spacers used did not completely fill the unneeded space.

2.5 COBALTIC FLUORIDE STUDIES

Some cobaltic fluoride electrodes were prepared by pasting with graphite in mineral spirits as binder by the same technique as the CuF_2 electrodes and suffered similarly from poor adhesion and cohesion. These electrodes did not recover their open-circuit voltage to the same extent as the CuF_2 electrodes when current was interrupted for extended times during discharge.

As the problems of preparing a CoF_3 cathode were so similar to those of preparing a CuF_2 cathode, the greatest effort was with CuF_2 cathodes which had earlier shown favorable results. Electrodes were prepared by pasting mixtures of CoF_3 and silver flake and xylene and then sintering after vacuum drying. The CoF_3 was quite active.

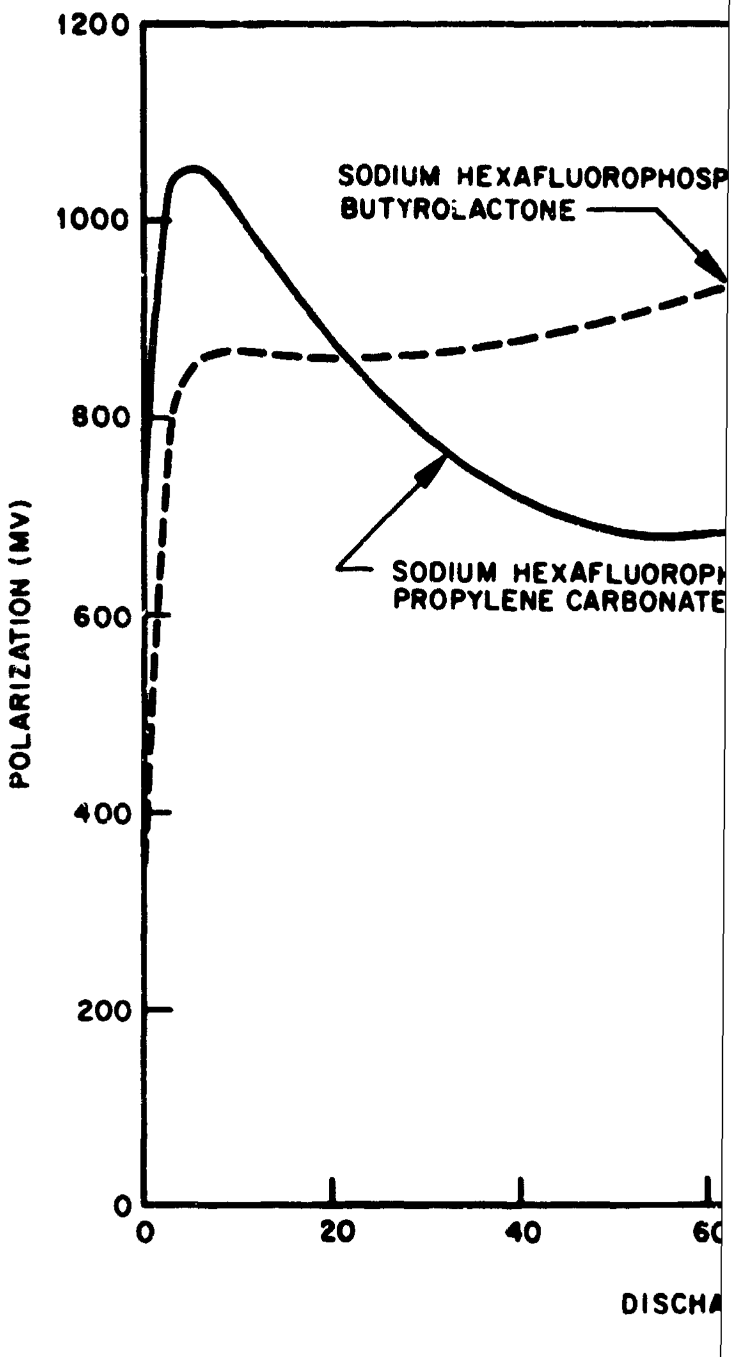
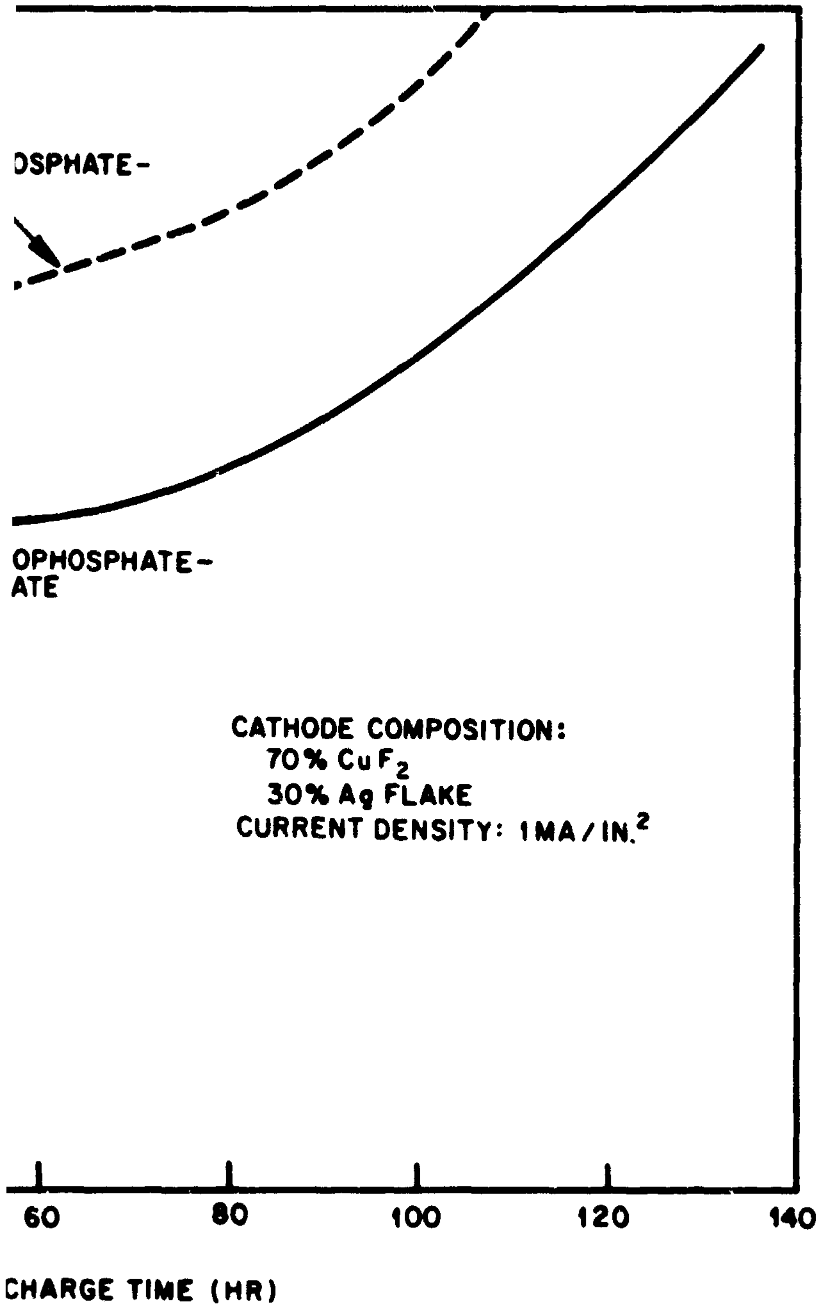


Figure 10. Polarization of CuF_2



$_2$ Cathode During Low Rate Discharge

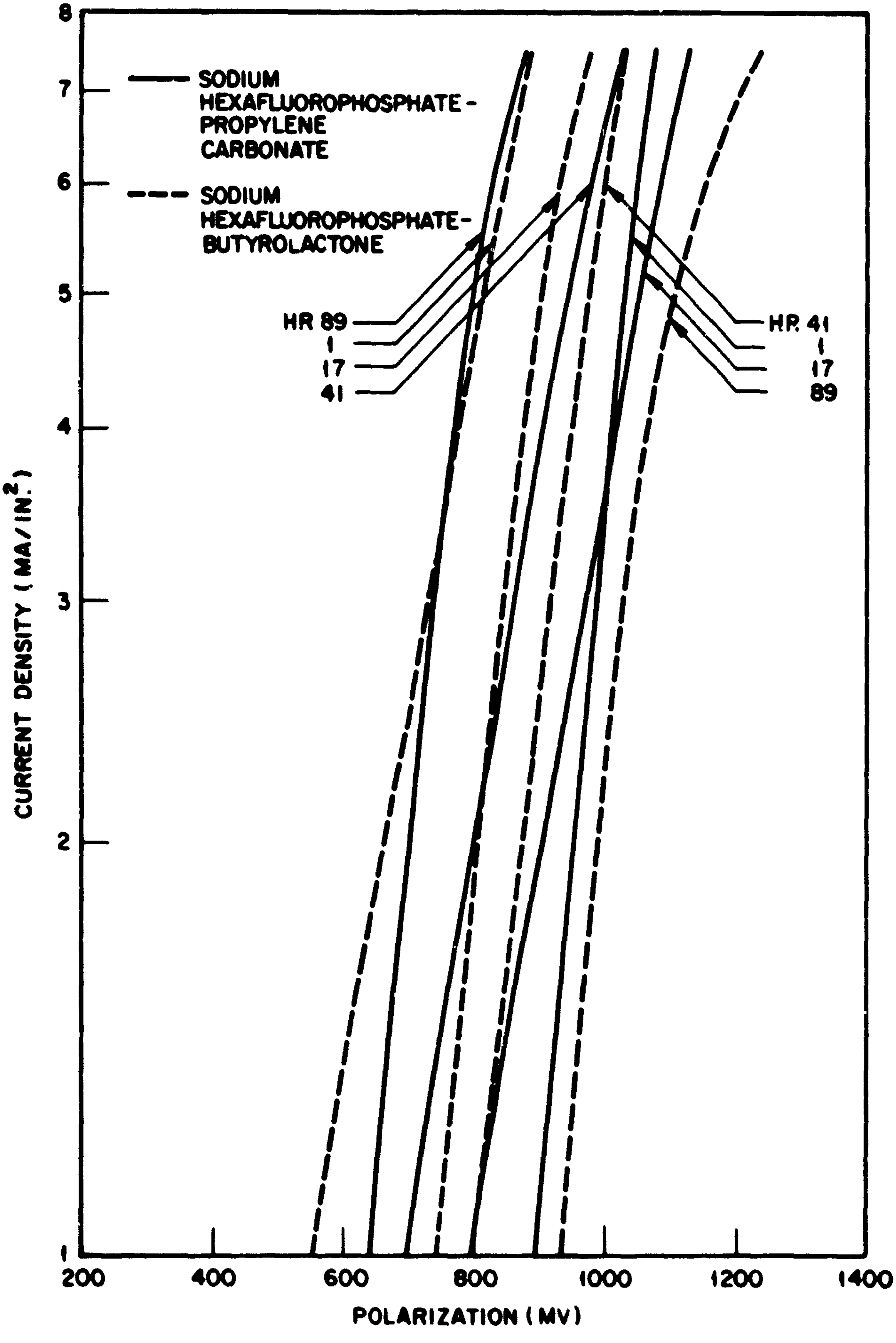


Figure 11. Polarization Versus Current Density for CuF_2 Cathodes

and there were indications of decomposition during sintering. Cells were prepared with these electrodes and discharged on profile discharge equipment, as described in subsection 2.6.

2.6 CELL TESTS WITH A PROFILED DISCHARGE

2.6.1 Discharge Equipment

A goal of this project was a cell that would discharge at the 100-hr rate (14.4 amp) with a superimposed load of 12 amp for 10 min once every 90 min. Equipment was designed and built that would put the equivalent load on cells of lower ampere-hour capacity than the design goal. A solid-state regulator was included to maintain constant current during both discharge levels. The schematic of the circuit, shown in Figure 12, has elements common to previously designed discharge equipment.* A cam timer is used to switch a periodic load in addition to the normal discharge rate. A solid-state regulator maintains constant current, and a switching relay allows the recording of both voltage and current on a single recorder. Figure 13 shows the back of the equipment with four discharge positions in use. The individual load regulators were mounted on plug-in panels for additional flexibility.

2.6.2 Cell Design for Test Assemblies

A packaging design was required to test larger cells on a profiled discharge. Drawn aluminum cans available as stock items were used for the outer case. Top closure was made with a polytetrafluoroethylene cover, which also served to insulate the terminals. This top was clamped against the can by six studs with nuts. The terminals were sealed to the cover with "O" rings. Two of these cells are shown being discharged in Figure 14.

2.6.3 Results of Profiled Discharge Tests

Cells with the Li-CoF_3 system. Two cells of similar construction were prepared for the profile test. The anodes were of lithium rolled on silver expanded metal mesh. The cathodes were prepared from a ball-milled mix of 60 percent CoF_3 and 40 percent silver flake wet with dried xylene and pasted on silver expanded metal mesh. The cathodes were vacuum dried 30 min at 50°C, vacuum dried 30 min at 100°C, and sintered at 250°C for 1 hr in flowing argon. Three of these cathodes were assembled with four anodes in a cell and the cell filled with $NaPF_6$–propylene carbonate electrolyte. Both cells were discharged at 13 ma steady rate corresponding to 0.5 ma/in.^{2} and 26 ma during the pulse.

The voltage of one of the cells dropped below 2.0 v on the first cycle; the second cell ran seven cycles (10.5 hr) before its voltage was below 2.0.

The poor cell discharge characteristics of the Li-CoF_3 couple parallel earlier experiments with this couple. In addition, HF evolved during the sintering, indicating some decomposition. Additional experimental work would undoubtedly improve the CoF_3 electrode, but at present the characteristics of the CuF_2 electrode are superior.

Cells with the Li-CuF_2 system. These cells were assembled in the cases and with lithium anodes of the type previously described. The cathodes were prepared from

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*Quarterly Technical Progress Report No. 2, Contract AF 33(616)-7957, 15 Apr 1963.

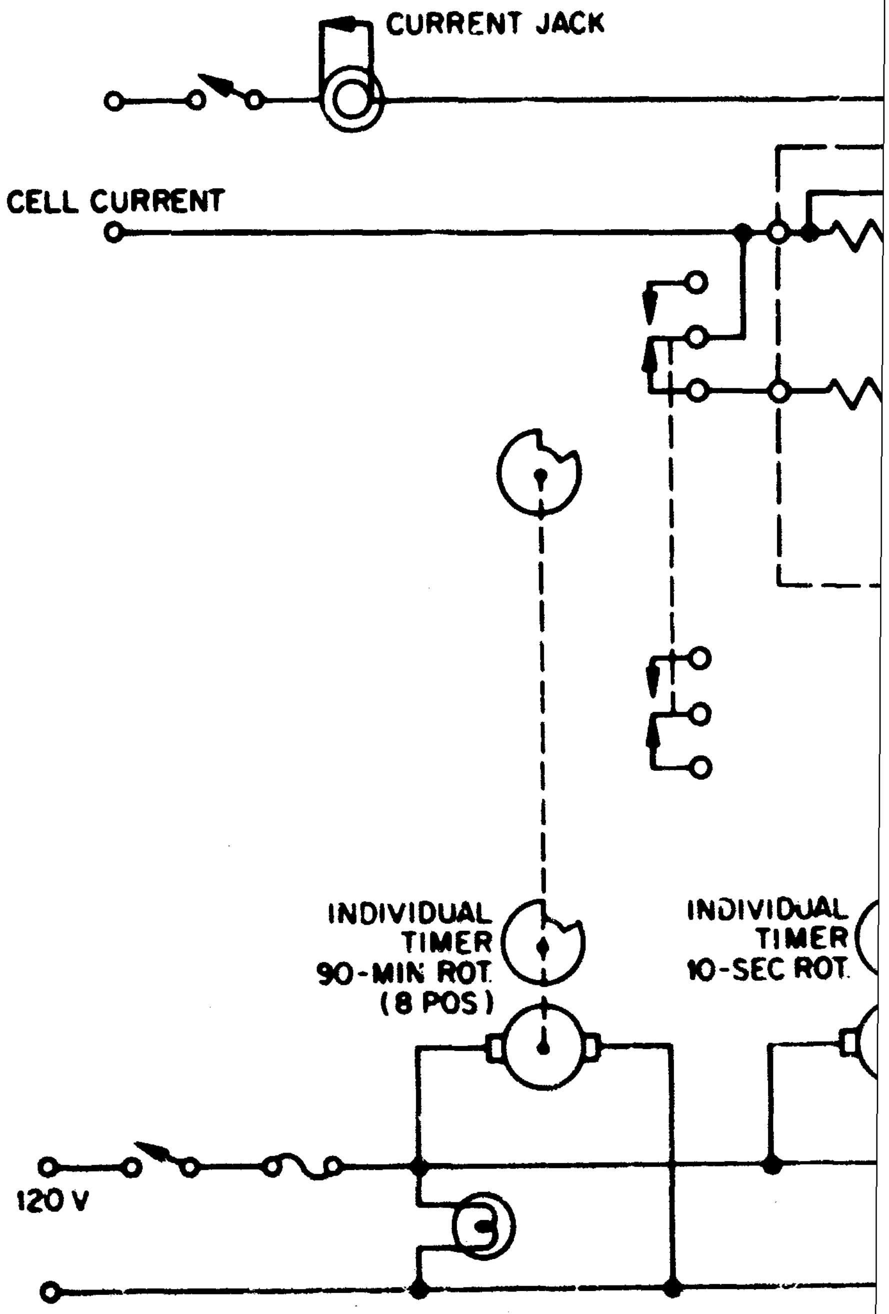
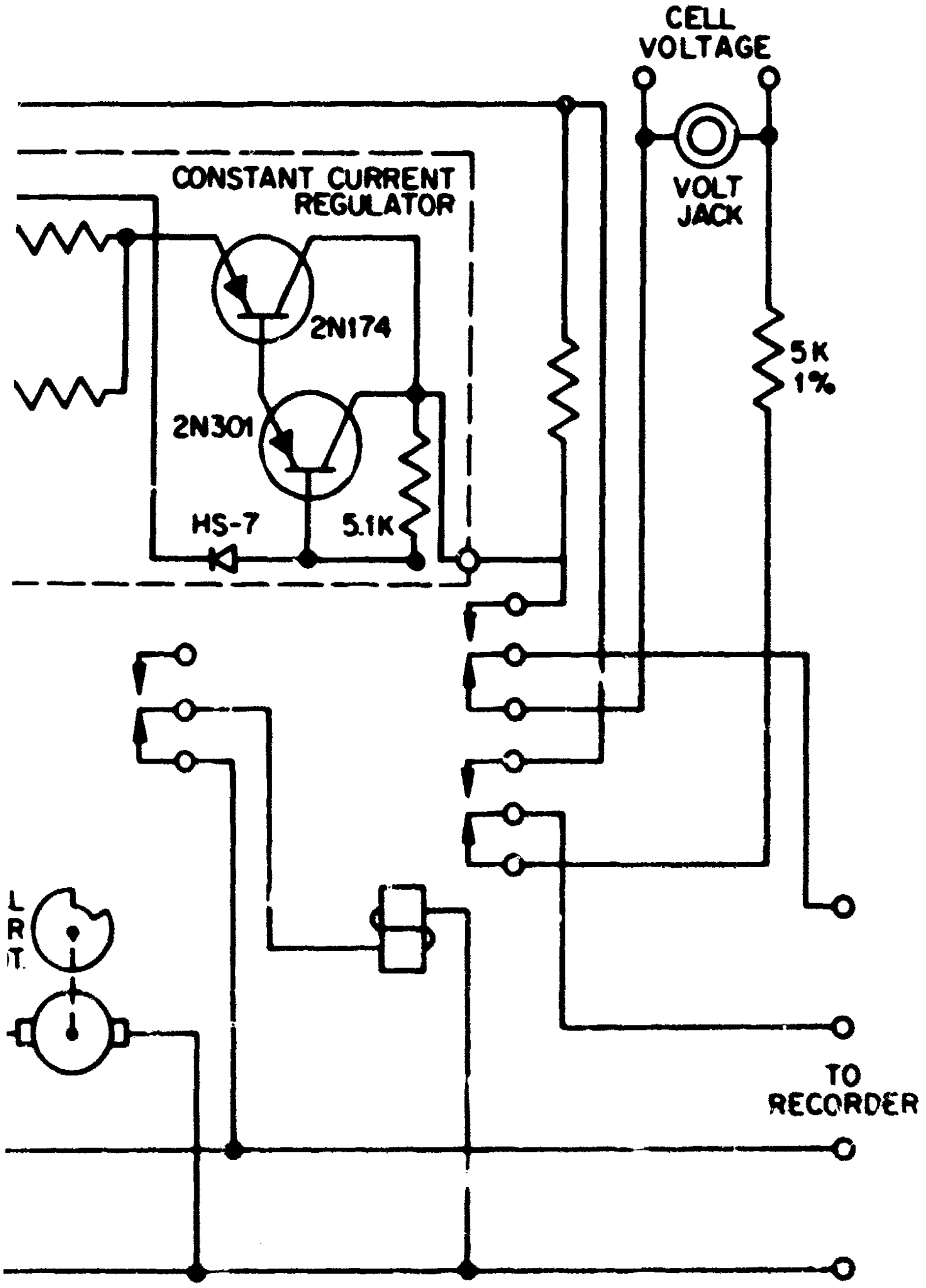


Fig. 12 Programmed



ned Discharge Unit

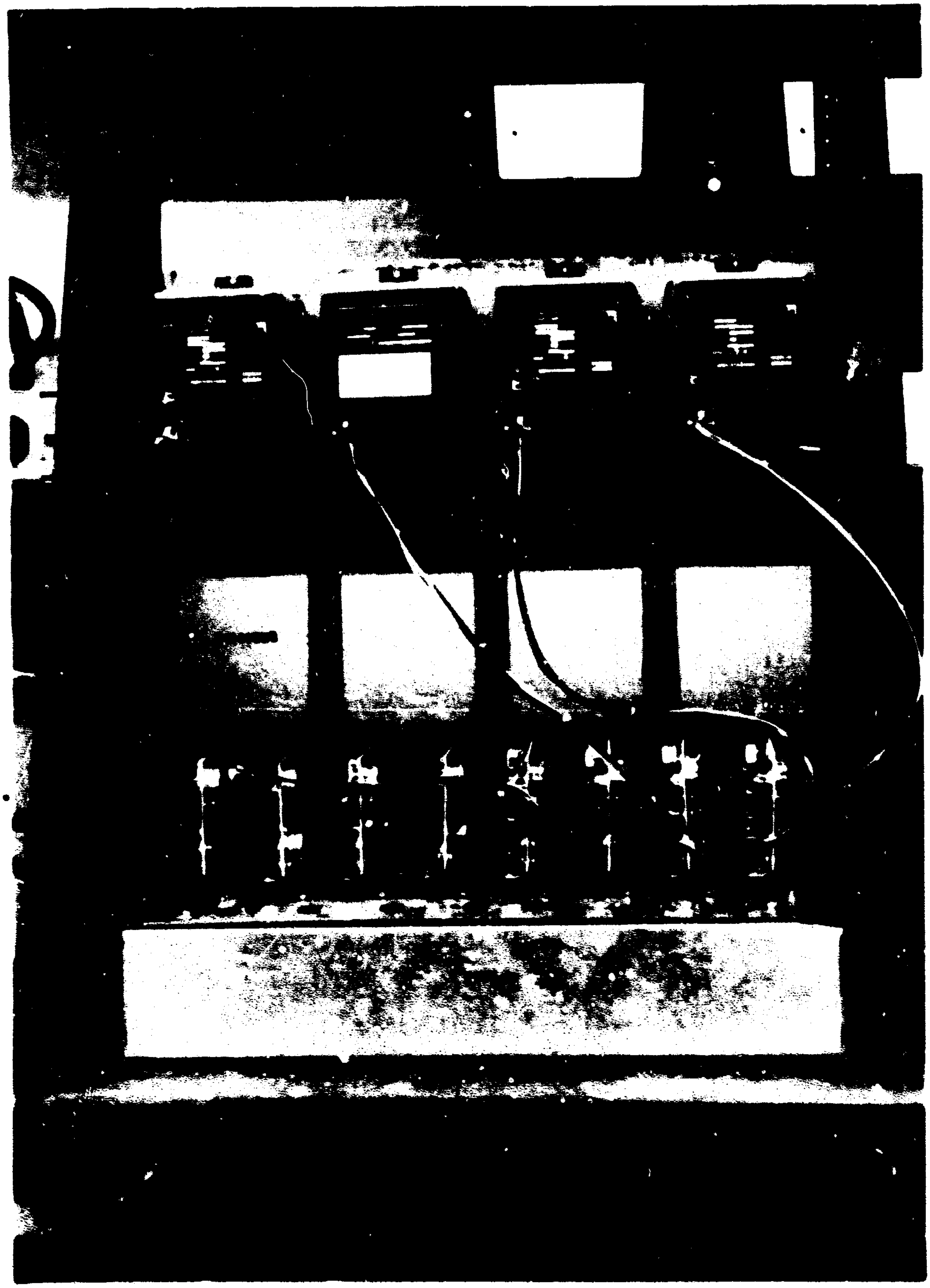


Figure 13. Back of Eight-Position Profile Discharge Unit

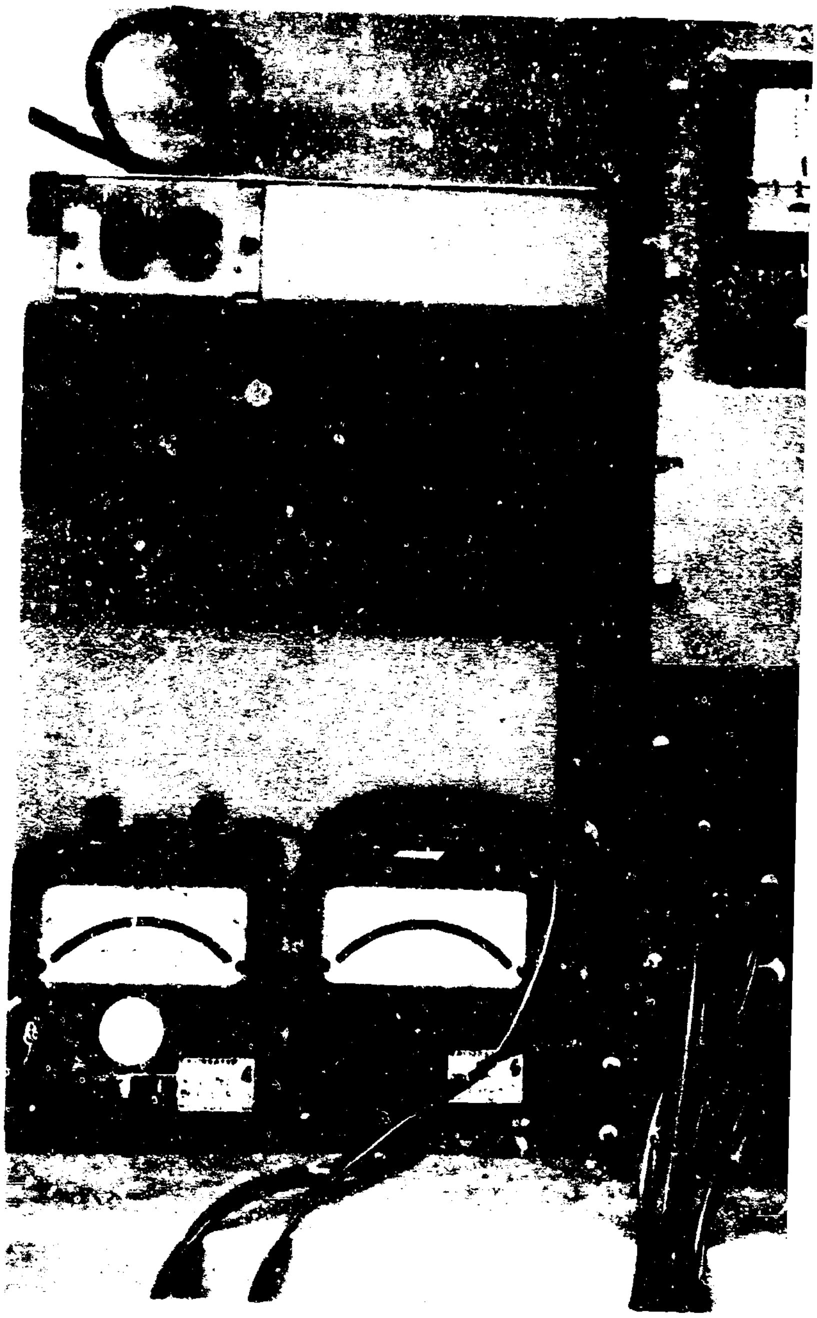
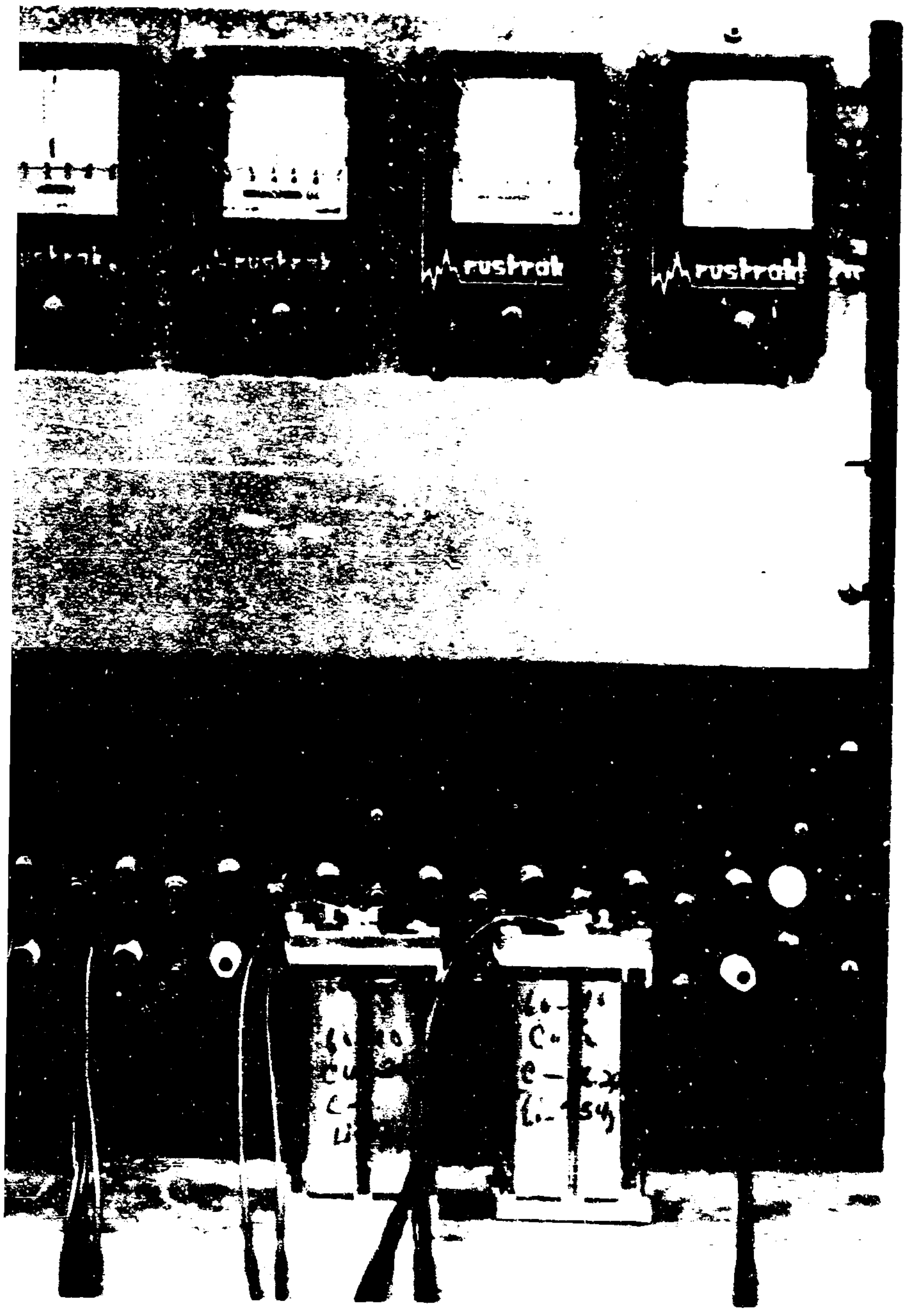


Figure 14. Test Cells



lls on Profile Discharge Unit

dry ball-milled CuF_2-silver flake blends wet with xylene for pasting on silver expanded mesh grids. The grids were vacuum dried at 100°C or dried at 100°C in flowing argon and then sintered at 250°C in flowing argon. The cells were then assembled with glass-fiber separators and one extra anode so that both sides of the cathodes were subject to discharge. From two to five cathodes were used in a cell.

Energy-to-weight values obtained with typical cells were quite dependent upon the current density. At 1.3 ma/in.^{2}, 4 w-hr/lb of electrodes and electrolyte were achieved; at 1 ma/in.^{2}, 8 w-hr/lb; and at 0.6 ma/in.^{2}, 15 w-hr/lb. A 2.0-v endpoint during the steady rate discharge was taken as an endpoint for these cells. The energy-to-weight figures for these cells did not approach that obtained with plastic-cased cells used for polarization tests.

Several reasons for failure to obtain higher energy-to-weight figures are evident. From 60 to 75 percent of the weight of these cells is electrolyte. Probably not all of this electrolyte is required, but the amount necessary has not been determined.

Adhesion of cathodic material was poor in all cases, and chipping was more of a problem with the larger electrodes (1.75 × 2.5 in.) used for the profiled discharge test than for the smaller (2 × 2 in.) electrodes used in the polarization tests.

It was suggested that there may have been reaction between the active cell material and the aluminum cans, but some cells were made with the electrodes and electrolyte encased in a plastic bag without significantly different discharge. The major factor is probably the quality of the electrodes, which are difficult to reproduce consistently.

It was intended that the cells used for profile discharge tests be recharged, but utilization was at too low a figure to allow separation of the additional energy received from recharge and that still remaining in the system after the first discharge.