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MULTIFUNCTIONAL EXPLOSIVE BATTERY

LOCKHEED MISSILES AND SPACE COMPANY, INC

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Multifunctional Explosive Battery

Hubert F. Bauman

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FOREWORD

This report documents work accomplished from June 1971 through December 1972 by the Electrochemistry Laboratory of the Lockheed Palo Alto Research Laboratory, Lockheed Missiles & Space Company, Inc., Palo Alto, California, under Air Force Contract F08635-71-C-0179 with the Air Force Armament Laboratory, Eglin Air Force Base, Florida. The program was monitored by Captain Larry D. Berry (DLKM) of the Armament Laboratory.

Lockheed Missiles & Space Company, Inc., personnel chiefly responsible for the performance of this work were Mr. H. F. Bauman, Staff Scientist; Dr. J. E. Chilton, Research Scientist; and Mr. J. Troendle, Staff Engineer.

This technical report has been reviewed and is approved.

Donald R. [illegible]

For ROBERT L. REAGAN, Colonel, USAF Chief,
Clusters, Bombs, and Mines Division

ABSTRACT

This report covers work on an explosive battery whose feasibility was established during an earlier program. On the present program, the lithium vanadium pentoxide couple with a nitromethane-ethylene carbonate lithium perchlorate-aluminum chloride electrolyte was selected for battery fabrication and evaluation. Batteries were discharged at rates from 4 to 400 mA and at temperatures from -40° to 160F. Energy densities of over 40 Whr/lb were obtained with discharges at -10 and 70° F. Batteries survived drop tests without significant damage. Detonation was demonstrated over a temperature range of -60 to 160° F, but the test fixture did not allow complete evaluation. High temperature storage results in electrolyte gelling, but this could be prevented in reserve cells by storing the solvent system in a reservoir and having the electrolyte salts present in the separator.

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SECTION I

INTRODUCTION

This program is concerned with development of a battery that not only delivers electrical power but is capable of being detonated. Such a battery would be used in a munition in which electrical power would be needed for fuzing and sensing functions, and the explosive capability would be used to augment the main explosive charge or as a booster in the firing train. The feasibility of such a battery was demonstrated on an initial program (Air Force Contract FO8635-70-C-0115) entitled "Multifunctional Explosive Battery Concept." The battery developed to demonstrate the concept included lithium and copper hydroxyfluoride as the active electrode materials and an electrolyte based on nitromethane. The electrolyte is the primary explosive element in the battery. A problem area developed on this program involved interaction between the electrolyte and the lithium anode.

The current program has as its goal the definition of compatible elements for a battery and the fabrication, assembly, and test of batteries. The program was divided into two tasks to encompass these goals. The first task was definition of suitable elements for a battery and the design of a battery. The second task was the actual fabrication of 50 batteries and subjecting them to electrical, explosive, and sensitivity tests. Although a reserve-type remotely activated battery would be needed to meet ultimate requirements, the current program was concerned only with the cell pack that would be used in such a battery.

SECTION II

SYSTEM EVALUATION

1. EVALUATION

a. Evaluation Criteria

The purpose of this battery is, by definition, to supply electrical power and be capable of detonation; the predominant parameters to be used for evaluation are therefore those that affect the electrical power-producing properties of the battery and those that affect the explosive properties of the battery. Parameters which determine the practicality of the system are the ability of the selected system to meet temperature and other environmental conditions imposed by the end use of the battery and ease of fabrication and assembly.

The energy capability of the battery depends upon the theoretical energy density of the anode-cathode couple less electrical losses due to resistance and polarization, reduction in the theoretical power available because of the added weight of inert materials, and the inefficiency of the electrochemical reaction. What might be considered as efficiency of the electrochemical reaction is determined by the voltage regulation imposed on the battery. The anode losses contributing to decreasing electrical power involve resistance added in the path from the reaction site to the battery terminal and polarization losses suffered by the anode during discharge. The electrolyte holds a critical position in a battery. The conductivity of the electrolyte determines the resistance losses in the electrolyte while the stability and liquid range of the electrolyte largely limit the operational temperature range of the battery. Any direct reaction between the anode and the electrolyte and the solubility of the cathode material in the electrolyte affect the wet shelf life and the discharge life of the battery. The cathode is chosen for the longest discharge time per unit weight within the appropriate voltage level and regulation requirements. The electrochemically inert structural components are chosen for their inactivity with the cell components or, in the case of the conductive additive for the cathode, the conductivity per unit of volume and its physical properties when blended with the active cathode material.

Since the explosive capability of the battery under consideration on this program is localized in the electrolyte, the electrolyte must be considered in terms of explosive power and sensitivity. Nitromethane is the primary explosive in the electrolyte, but other solvents and salts that are added to alter the properties of the nitromethane or make the solution conductive alter or augment the explosive power. There are some theoretical guidelines for the effect of material added to the electrolyte, but the primary approach in this case is empirical and based on the increase in volume of a cavity in a metal block which occurs when a weighed amount of explosive is detonated in the cavity. This Trauzl test was used to compare electrolytes for explosive power. Sensitivity tests are made by dropping a weight from different heights upon the electrolyte sample in a modified Picatinny Arsenal apparatus.

b. Anode Selection

Lithium had been selected as anode material on the initial contract of this program; the major consideration of this immediate program was to determine what methods could be used in handling and assembly of lithium anodes into cells and whether any surface treatment of the lithium was necessary. Conventional tools operated in an argon atmosphere glove box were used effectively and cell tests indicated that the lithium strip extruded and stored in argon as supplied by the manufacturer could be used efficiently in cells. The lithium anode, although a critical component of the cell, is not considered troublesome; a minimum effort demonstrated the effective usefulness of this component in a cell.

c. Electrolyte Evaluation

The criteria used for evaluation of electrolyte systems include the conductivity, stability with lithium, solvation of cathode material, explosive power, freezing point, and reaction in a complete cell. The electrolyte solvent having explosive properties is nitromethane, and empirical tests indicate that up to 20% of another solvent could be used to alter the physical properties of the nitromethane without diminishing the explosive power excessively. An ionizing salt must be dissolved in the solvent system to secure conductivity, and the choice of this salt has a major effect not only on the conductivity of the electrolyte but also on the explosive power as well.

The conductivity of the electrolyte systems was measured in a glass cell with two parallel plane electrodes coated with platinum black. The resistance between the electrodes when immersed in the selected electrolyte was measured with a 1000-Hz AC bridge. The cell is standardized by measuring the conductivity of a 0.1-M potassium chloride solution for which literature values are readily available. From this standard value, a constant C can be calculated from the relationship

$$K = \frac{C}{R}$$

where K is the specific conductance in $\Omega^{-1}\mathrm{cm}^{-1}$, R is the resistance in ohms, and C is the cell constant in cm^{-1} (the cell constant can be derived from the area and spacing of the electrode from the expression

$$C = \left(\frac{\text{length (cm)}}{\text{area (cm}^2)}\right) \quad)$$

Solvents that were considered for use with nitromethane were 2-nitropropane, ethylene carbonate, methylchlorocarbonate, tetrahydrofuran, and dimethoxyethane. Salts considered for the solute in the electrolyte were lithium perchlorate, lithium aluminum chloride, lithium nitrate, and combinations of lithium perchlorate and aluminum chloride. It was found during the program that lithium nitrate was not sufficiently soluble to form solutions of reasonable conductivity. Lithium perchlorate was a most desirable solute because this salt was found to increase the explosive power of nitromethane solutions on the earlier program.

It was found that the addition of 20 percent (volume) of other solvents to the nitromethane could have a large effect on the conductance of lithium perchlorate solutions. Methyl chlorocarbonate and 2-nitropropane acted similarly to nitromethane itself as shown in Figure 1. However, solutions with 20 percent of ethylene carbonate, tetrahydrofuran, or dimethoxyethane resulted in conductance peaks at lower concentrations of lithium perchlorate and also increased conductance at increasing concentrations. Conductance of these solutions is shown in Figure 2, which also includes a curve showing the conductance of the ethylene carbonate mixture with both lithium perchlorate and aluminum chloride added. Conductance of this solution at temperatures from -13°F to 122°F is shown in Figure 3. The conductance values of solutions of lithium aluminum chloride in nitromethane are shown in Figure 4. It can be seen that these solutions have conductance values over twice that of the best lithium perchlorate solutions and that even at -58°F, the conductance is almost $10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Lithium does not appear to be attacked by nitromethane; when water is present in the nitromethane, corrosion products form on the lithium, but the nitromethane remains clear and evidently unchanged. With lithium perchlorate solutions in nitromethane, there is rapid evidence of attack as gas bubbles are formed and orange-brown products are formed in the solution within 24 hours. The results of a series of compatibility tests between lithium and electrolytes are given in Table I. The addition of tetrahydrofuran or ethylene carbonate to nitromethane appears to lend stability to its lithium perchlorate solutions. Aluminum chloride additions which improved conductance had no effect on the compatibility of lithium perchlorate solutions in nitromethane-ethylene carbonate.

The solubility of copper salts which were prospective cathode material in electrolytes is shown in Table II. The solubility of the cathodic material in the electrolyte is a criterion to be considered since soluble cathodic material can diffuse through the electrolyte to the anode and react chemically with consequent loss of active material available for electrical power. Increased corrosion and shorting can also occur because reduced cathodic material is deposited on the anode. The amount of solubility of cathode material that can be tolerated depends upon the mechanical construction (electrode spacing and separation) and the wet stand time which is required from the cell. The results in Table II are guidelines in the selection of electrolyte.

The explosive power of the various electrolytes was determined using a modification of a Trauzl test in which a weighed amount of explosive is detonated in a cavity in a metal block and the expansion in the volume of the cavity resulting from the explosion is used as a comparative value for comparison among other material. Two groups of tests were made; in the first group, aluminum alloy 6061 cylindrical blocks of 3 inches in diameter and 8 inches long with a 1-1/4-inch hole 5 inches deep were used to contain the explosive; in the second group, a similarly configured block of the softer 1100 aluminum alloy was used. The electrolyte in both tests was contained in a glass vial crimp sealed with a cap which had a tubular cavity to receive the detonator. The block cavity, after insertion of the vial-detonator assembly, was filled with dry sand. A No. 8 Engineers Special dynamite cap was used to initiate detonation in all cases. A Trauzl block and the electrolyte vial are shown in Figure 5. Composition C-4, a plastic explosive containing 91 percent RDX and 9 percent nonexplosive plasticizer, was used for comparison. This material has a listed power figure of 130 percent that of TNT on a ballistic mortar test and an estimated 120 percent that of TNT on the Trauzl test.

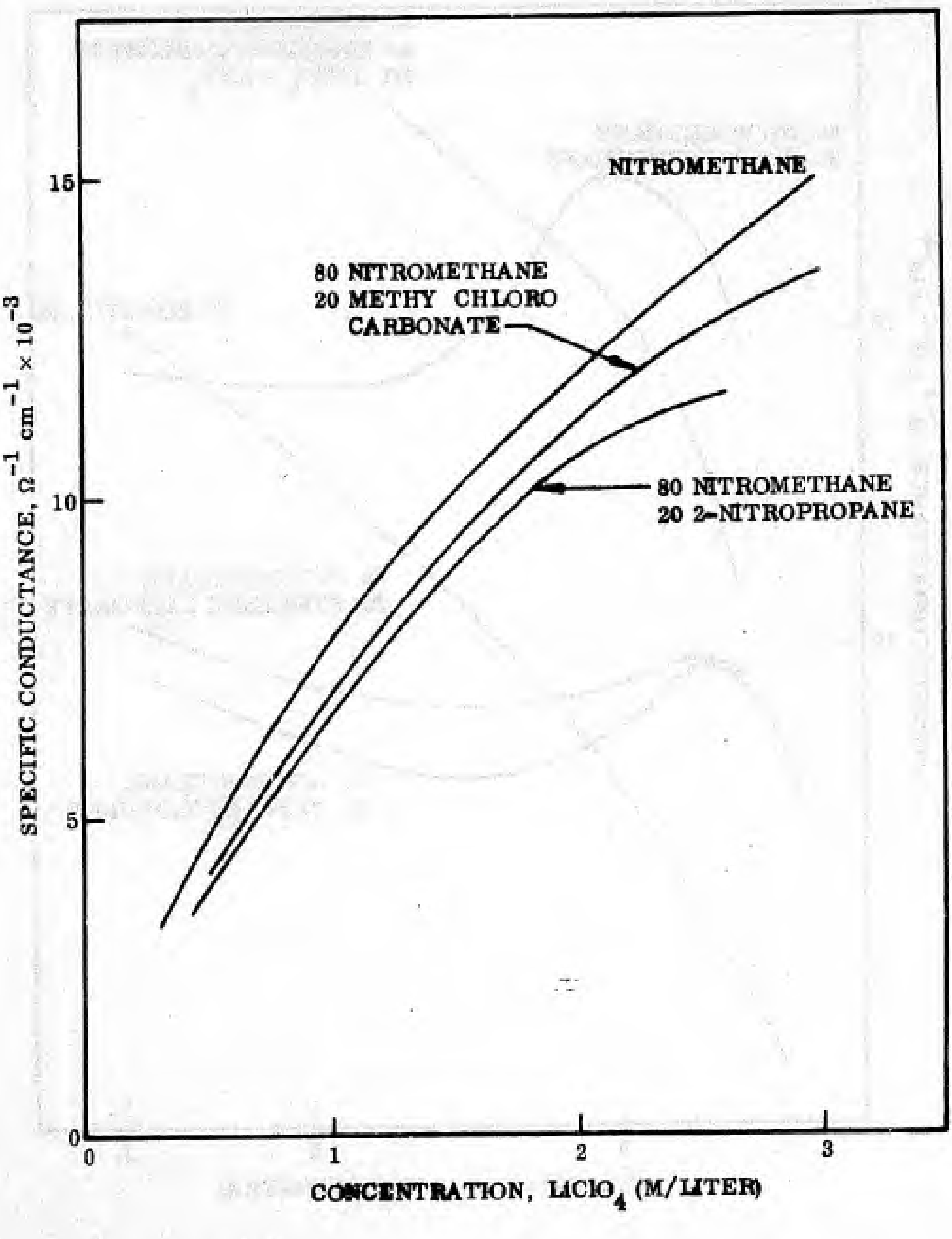


Figure 1. Conductivity of Lithium Perchlorate Solutions at 77°F

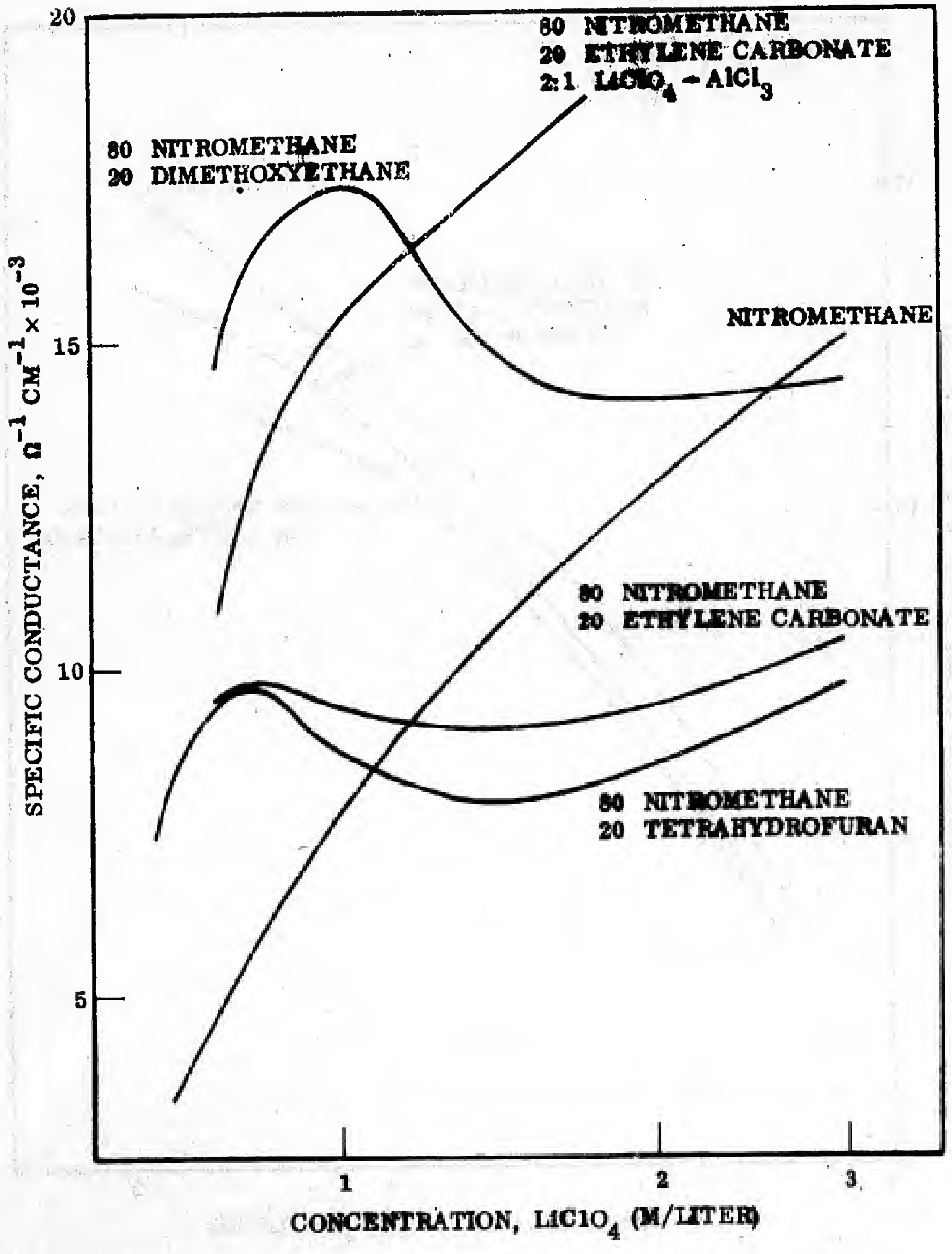


Figure 2. Conductivity of Lithium Perchlorate Solutions at 77°F

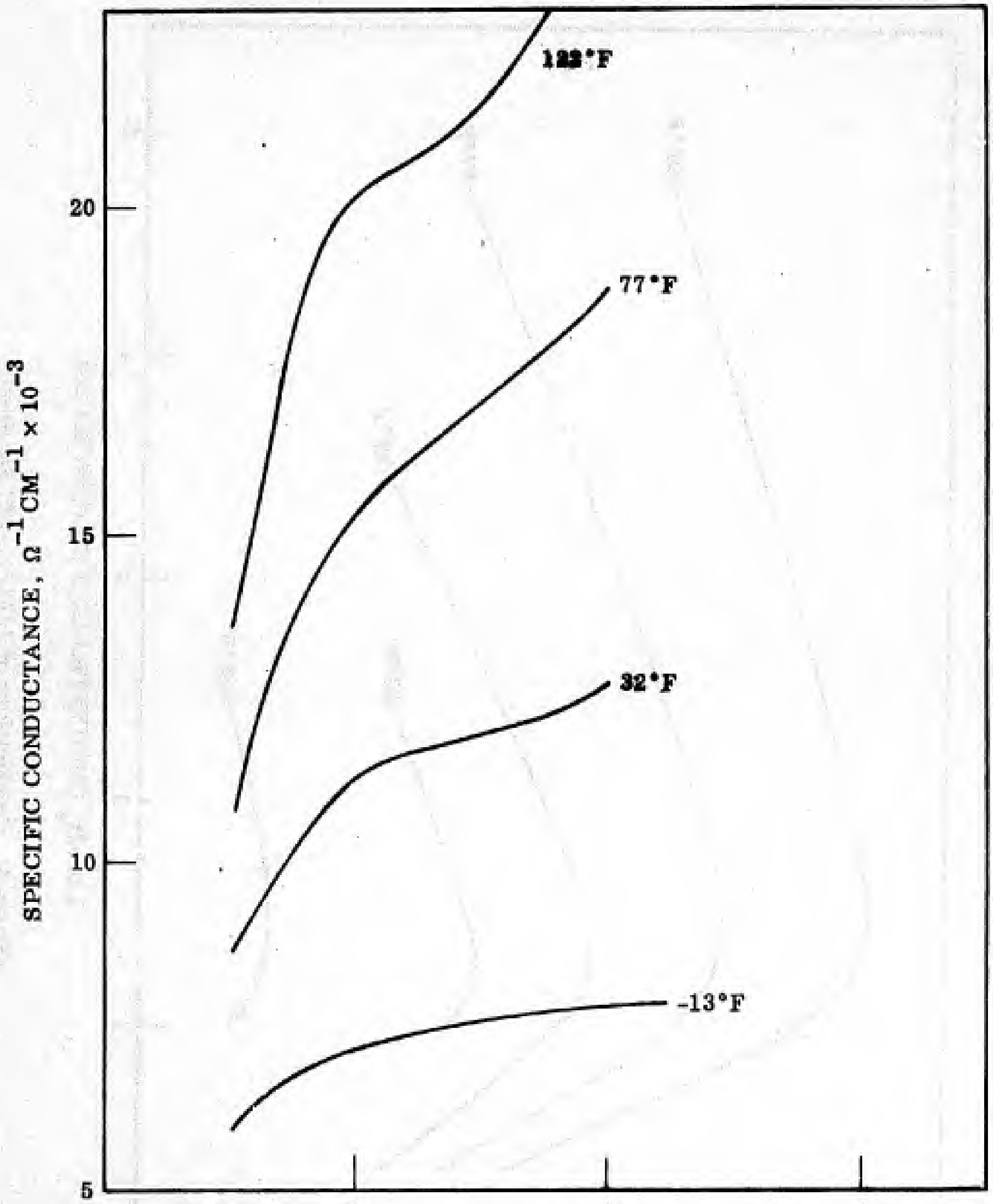


Figure 3. Conductivity of $LiClO_4$-$AlCl_3$-80 NM-20 EC Solutions

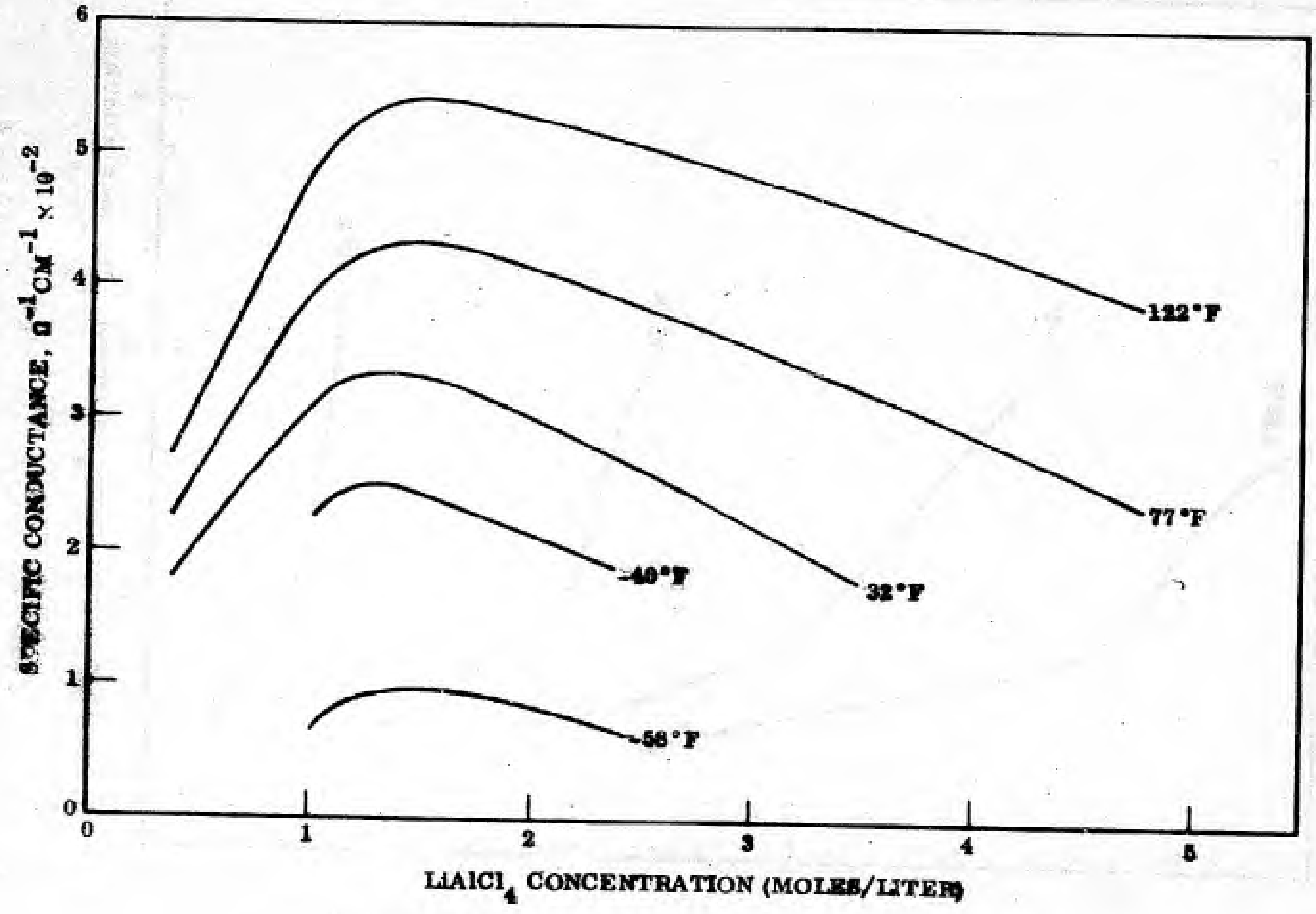


Figure 4. Conductivity of $LiAlCl_4$-NM Solutions

TABLE I. LITHIUM METAL-ELECTROLYTE COMPATIBILITY (Room Temperature)

System	Observation Time (day)	Lithium Metal	Solution
NM-2M $LiClO_4$ stored over lithiated molecular sieve	1	Initial gas bubbles	Orange solution Brown ppt
	18	Tan coating	Orange solid
NM-700 ppm H_2O	22	Black coating	Clear-colorless
NM-10,000 ppm H_2O	22	Orange-yellow	Clear
NM-$LiAlCl_4$	33	Coating-gassing	Colorless solution
		Clear-bright	Colorless solution
NM-EC-$LiClO_4$	33	Clear-bright	Clear colorless
NM-THF-$LiClO_4$	33	Clear-bright	Clear-colorless
NM-2NP-$LiClO_4$	33	Completely coated-gassing	Orange solid
NM-MCC-$LiClO_4$	33	White coating	Cloudy ppt
NM-2M $LiClO_4$-1M $AlCl_3$	30	Coated with white precipitate	Cloudy
NM-EC-2M $LiClO_4$-1M $AlCl_3$	30	Clean surface	Clear
NM-1M $LiClO_4$-1M $LiAlCl_4$	30	Coated with white precipitate	Cloudy

NM	Nitromethane
EC	Ethylene carbonate
THF	Tetrahydrofuron
2-NP	2-nitropropane
MCC	Methyl chlorocarbonate

TABLE II. ELECTROLYTE-CATHODE MATERIAL COMPATIBILITY
(5-Day Test at Room Temperature)

Specimen No.	Solid-Color	Solution-Color	Soluble Copper (gm atoms/liter)
1	CuF_2 white	nitromethane colorless	0
3	CuOHF green	nitromethane colorless	0
5	CuF_2 white	nitromethane colorless	3×10^{-3}
7	CuOHF green	+ 700 ppm H_2O colorless	0
9	CuF_2 white	NM+ 2M$LiClO_4$ green	3.05×10^{-2}
11	CuOHF blue	NM+ 2M$LiClO_4$ yellow-green	2.5×10^{-3}
13	CuF_2 white-brown underneath	NM+ 2M$LiAlCl_4$ yellow	1×10^{-3}
15	CuOHF white-brown underneath	NM+ 2M$LiAlCl_4$ deeper yellow	5×10^{-3}
17	CuF_2 white	NM+ THF+ $LiClO_4$ green	6.1×10^{-2}
19	CuOHF blue	NM+ THF+ $LiClO_4$ light yellow-green	3.5×10^{-3}
21	CuF_2 white	NM+ 2NP+ $LiClO_4$ green	5.1×10^{-2}
23	CuOHF blue	NM+ 2NP+ $LiClO_4$ yellow-green	3.5×10^{-3}
25	CuF_2 white	NM+ EC+ $LiClO_4$ light green	2.85×10^{-2}
27	CuOHF blue	NM+ EC+ $LiClO_4$ slightly green	2.5×10^{-3}
29	CuF_2 brown	NM+ MCC+ $LiClO_4$ light blue	1.1×10^{-2}
31	CuOHF brown	NM+ MCC+ $LiClO_4$ light yellow	1. $\times 10^{-3}$
	$CuSO_4 \cdot H_2O$ (dried 130° C) gray	NM-2M$LiClO_4$ green	3.5×10^{-3} Mole
	$CuSO_4$ (dried 250° C) gray	NM-2M$LiClO_4$ green	2.5×10^{-3} Mole
	$Cu_3(PO_4)_2$ green	NM-2M$LiClO_4$ colorless	0
	CuCl white	NM-2M$LiClO_4$ colorless	0

NM-nitromethane, THF-tetrahydrofuran, 2NP-2nitropropane, EC-ethylene carbonate, MCC-methyl chlorocarbonate, $LiClO_4$-lithium perchlorate, $LiAlCl_4$-lithium aluminum chloride

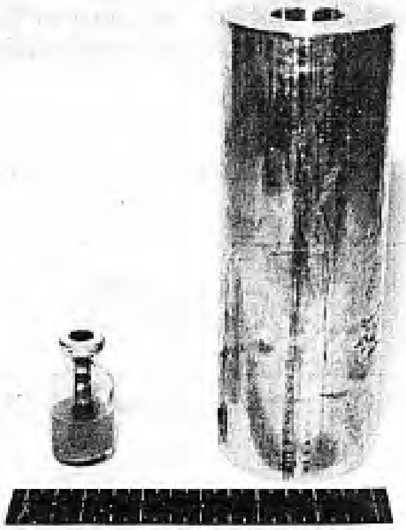


Figure 5. Trauzl Test Block and Electrolyte Vial Used in Explosive Testing

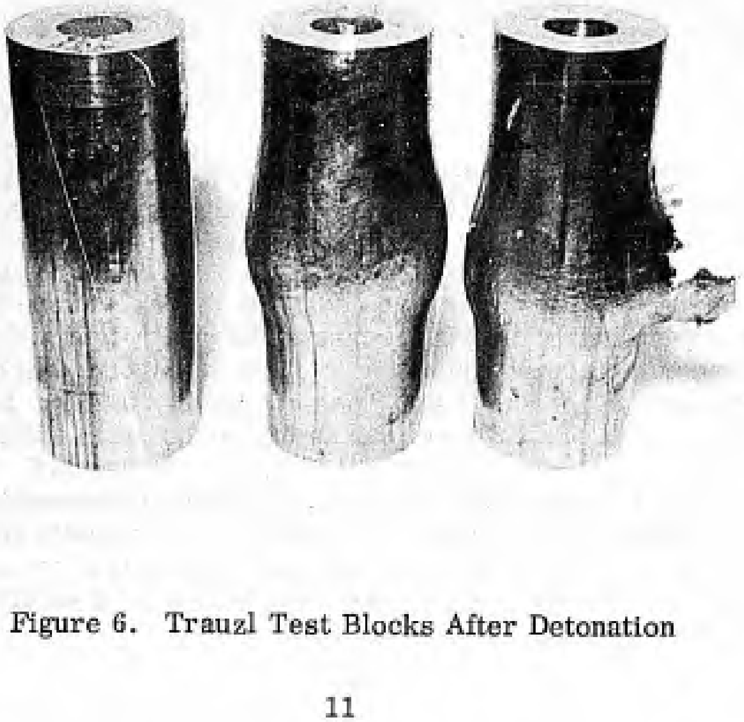


Figure 6. Trauzl Test Blocks After Detonation

Table III lists the results obtained on the first test series and shows that, with the exception of the tetrahydrofuran-containing electrolyte, all those with perchlorate had a higher volume expansion than the nitromethane alone and approximately 80 percent that of the C-4. The low volume expansion of the nitromethane-lithium aluminum chloride electrolyte is shown in this table.

TABLE III. PRELIMINARY TRAUZL BLOCK TEST[(a)]

Sample Number	Block Number	Electrolyte Composition	Volumetric Change (ml)
1	1-A	Nitromethane (NM) (2M)	46
2	2-A	NM-Li $AlCl_4$ (2M)	4
3	3-A	NM-$LiClO_4$ (2M)	84
4	4-A	NM-THF-$LiClO_4$ (2M)	5
5	5-A	NM-MCC-$LiClO_4$ (2M)	71
6	6-A	NM-2NP-$LiClO_4$ (2M)	64
7	7-A	NM-EC-$LiClO_4$	68
8	8-A	C-4 (Test Comparison)	94

(a) All tests samples were 13 grams by weight with Samples 2-A through 7-A composed of 80 percent NM and 20 percent other solvent by volume. Sample 1-A, nitromethane, contained 680 ppm H_2O. Sample 8 was 8 g by weight.

In the second series of tests shown in Table IV, a comparison was made between the two electrolytes that had the most favorable results on other tests, nitromethane-lithium aluminum chloride and nitromethane-ethylene carbonate-lithium perchlorate-aluminum chloride. Duplicate tests were made at room temperature; one test with each electrolyte made with the electrolyte cooled to -85°F, and one test with vanadium pentoxide added to the electrolyte. In all cases, the electrolyte with the lithium perchlorate showed an expansion equivalent to about 80 percent that of the C-4. This electrolyte, in the case of the -85°F test, was completely frozen. Sample 10 of Figure 4, which was a calibration shot, had an expansion value which did not agree with other expansion values and a repeat test was made on Test 14. The low-order expansion on sample 10 was probably the result of incomplete consolidation of the fragments of C-4 weighed for this test with consequent incomplete detonation. Sensitivity tests with a modified Picatinny Arsenal apparatus were made with a limited number of samples. Detonation did not take place with a 2-kg weight dropped from 170 cm, the maximum possible with the apparatus.

TABLE IV. TRAUZL TEST OF SELECTED ELECTROLYTES(a)

Sample No.	Block No.	Rockwell "E" Scale – Block Hardness	Sample Composition	Volumetric Change (ml)	Blast Notes
1	1-B	59	1.5 $LiAlCl_4$-NM at -85°F	6	Quiet Report
2	2-B	51	1.5 $LiAlCl_4$-NM	6	Quiet Report
3	3-B	54	1.5 $LiAlCl_4$-NM	7	Quiet Report
4	12-B	70	1.5 $LiAlCl_4$-V_2O_5	4	Quiet Report
5	5-B	62	2M $LiClO_4$-0.5M $AlCl_3$-80 NM-20EC at -85°F	68	Large Report
6	6-B	47	2M $LiClO_4$-0.5M $AlCl_3$-80 NM-20EC	86	Large Report
7	7-B	56	2M $LiClO_4$-0.5M $AlCl_3$-80 NM-20EC	76	Large Report
8	8-B	61	2M $LiClO_4$-0.5M $AlCl_3$-80 NM-20EC +V_2O_5	75	Large Report
9	9-B	55	Blasting Cap	2	Quiet Report
10	10-B	66	C-4 10 gr	40	Large Report
11	11-B	60	C-4 7.5 gr	76	Large Report
12	14-B	68	C-4 5.0 gr	32	Large Report
13	15-B	–	C-4 7.5 g	71	Large Report
14	16-B	–	C-4 10.0 g	133	Large Report Burst Block

(a) All samples 10 g

The results on tests of the electrolyte by itself showed that the nitromethane-lithium aluminum chloride was superior in conductance and probably in stability with lithium but had a low-order of explosive power. (See Table IV.) The nitromethane-ethylene carbonate-lithium perchlorate-aluminum chloride had reasonable stability and conductivity and was far superior in explosive power. Because of the criterion of explosive power, the latter electrolyte appeared to be the best selection, a selection which must be confirmed by cell tests discussed under the selection of the cathode.

d. Cathode Evaluation

The criteria for the selection of cathode material for this program are a high energy density per unit of weight, insolubility in the electrolyte, ease of drying, and the ability to be fabricated and handled when used with conductive material for the cathode mix. In addition to the cupric fluoride and the cupric hydroxyfluoride originally proposed, other materials were investigated. A list of material considered is given in Table V. Of the materials listed on the table, copper sulfate ($CuSO_4$) had appreciable solubility in electrolyte, copper phosphate $[Cu_3 (PO_4)_2]$ could not be successfully discharged, and cupric fluoride was difficult to prepare since it required a furnace dehydration in a hydrogen fluoride atmosphere. The carbon fluoride $C_{1.1}F$ has been used in cells

TABLE V. CATHODE MATERIALS FOR LITHIUM ANODE CELLS

Cathode Material	Proposed Cell Reaction	Theoretical Energy Density (W-hr/lb)	Theoretical Cell Voltage (V)	Actual No Load Cell Voltage (V)
CuF2	$2\ Li + CuF_2 \rightarrow 2\ LiF + Cu$	746	3.5	3.33
CuOHF	$2\ Li + CuOHF \rightarrow LiF + LiOH + Cu$	671	3.2	3.33
CuCl	$Li + CuCl \rightarrow LiCl + Cu$	313	2.8	3.30
$Cu_3(PO_4)_2$	$6\ Li + Cu_3(PO_4)_2 \rightarrow 2\ Li_3PO_4 + 3\ Cu$	530 Calc from ocv	3.1 (exp ocv)	3.122
$CuSO_4$	$2\ Li + CuSO_4 \rightarrow Li_2SO_4 + Cu$	480	3.4	—
$C_{1.1}F$	$Li + C_{1.1}F \rightarrow LiF + 1.1C$	950	3.0 (exp ocv)	3.09
MoO_3	$2\ Li + MoO_3 \rightarrow Li_2O + MoO_2$	289	2.0	3.24–3.13
V_2O_5	$2\ Li + V_2O_5 \rightarrow Li_2O + V_2O_4$	290	2.4	3.40

with reputedly good results. (It is the subject of an American patent by a Japanese national and hence was kept as a reserve material on the advice of the contract sponsor.) Discharge tests with this material, copper hydroxy fluoride, molybdenum trioxide, and vanadium pentoxide with lithium perchlorate electrolyte in cells sealed in a glass metal case are shown in Figure 7. Discharge curves for these materials are shown in Figure 8 and discharge curves of cells with cuprous chloride, molybdenum trioxide, with vanadium pentoxide, and with lithium aluminum chloride electrolyte are shown in Figure 9. It is evident that, with either electrolyte, the vanadium pentoxide discharges at a higher voltage level and for longer times. The weight of the cathode pellets used in these cells were of a similar weight except for the $C_{1.1}F$ which was of about one-half the weight of the others.

Groups of cells with 80 percent nitromethane ethylene carbonate-lithium perchlorate-aluminum chloride and nitromethane-lithium aluminum chloride electrolyte were discharged at 60°C (140°F), 25°C (77°F) and -25°C (-13°F). The discharge curves of these chells are shown in Figures 10 and 11. As was expected, the lithium aluminum chloride electrolyte performed best at room and low-temperature discharge, but at the high temperature discharge test, short discharges were obtained. In a separate test in which this electrolyte was stored with vanadium pentoxide at 140°F, there was an obvious reaction resulting in the formation of a gel-like mass in the electrolyte. This reaction between the electrolyte and the cathode was evidently the reason for the short time cell discharges obtained at 140°F with that electrolyte.

e. Material Compatibility

No specific compatibility tests of structural materials were made on this program since a backlog of this information was available and was used as a guide in selecting material for cell tests. The following material demonstrated stability in cells without apparent degradation during times as long as two weeks:

- Plastic Resins
  - Delrin (polyacetal)
  - Polyethylene
  - Polypropylene (structural and as nonwoven separator material)
  - Teflon (tetrafluoroethylene) (except in contact with lithium)
- Inorganic Material
  - Glass (structural and as paper separator)
  - Stainless steel No. 302 and No. 316
  - Nickel
  - Silver
  - Copper

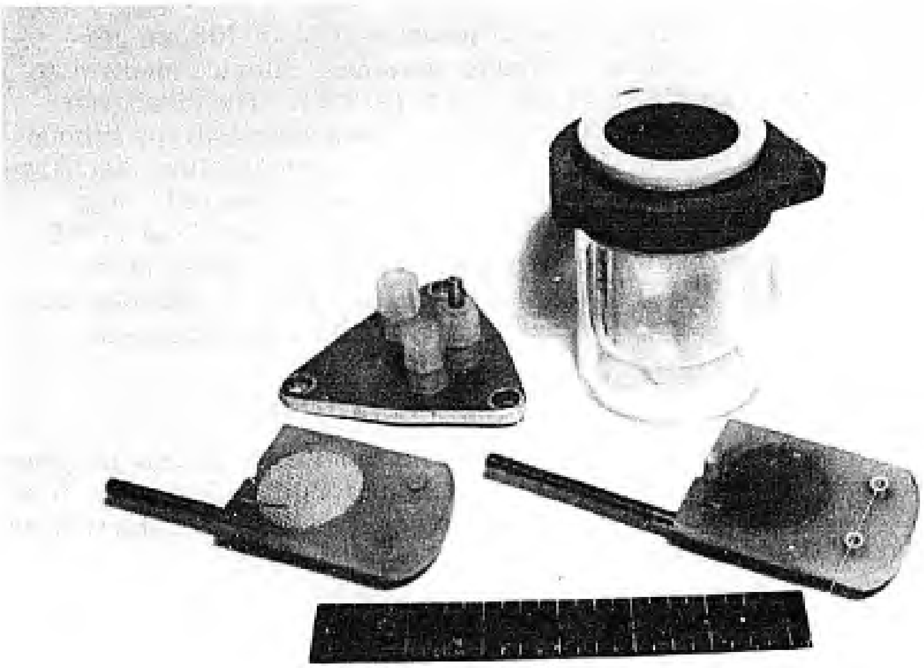


Figure 7. Test Cell With Internal Components

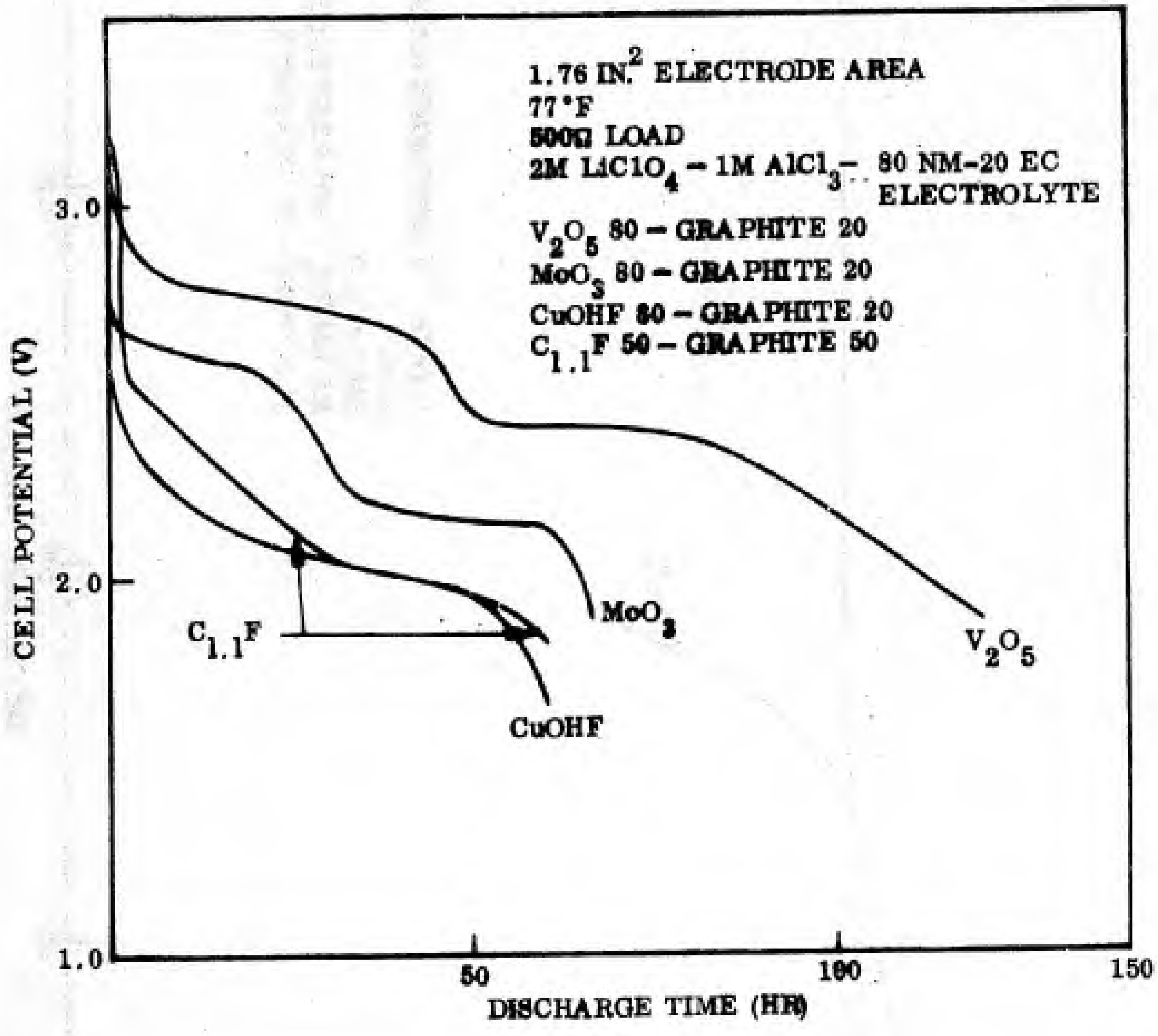


Figure 8. Discharge of Lithium Cells With LiClO$_4$-AlCl$_3$-NM-EC Electrolyte at 77 °F, With Various Cathodes

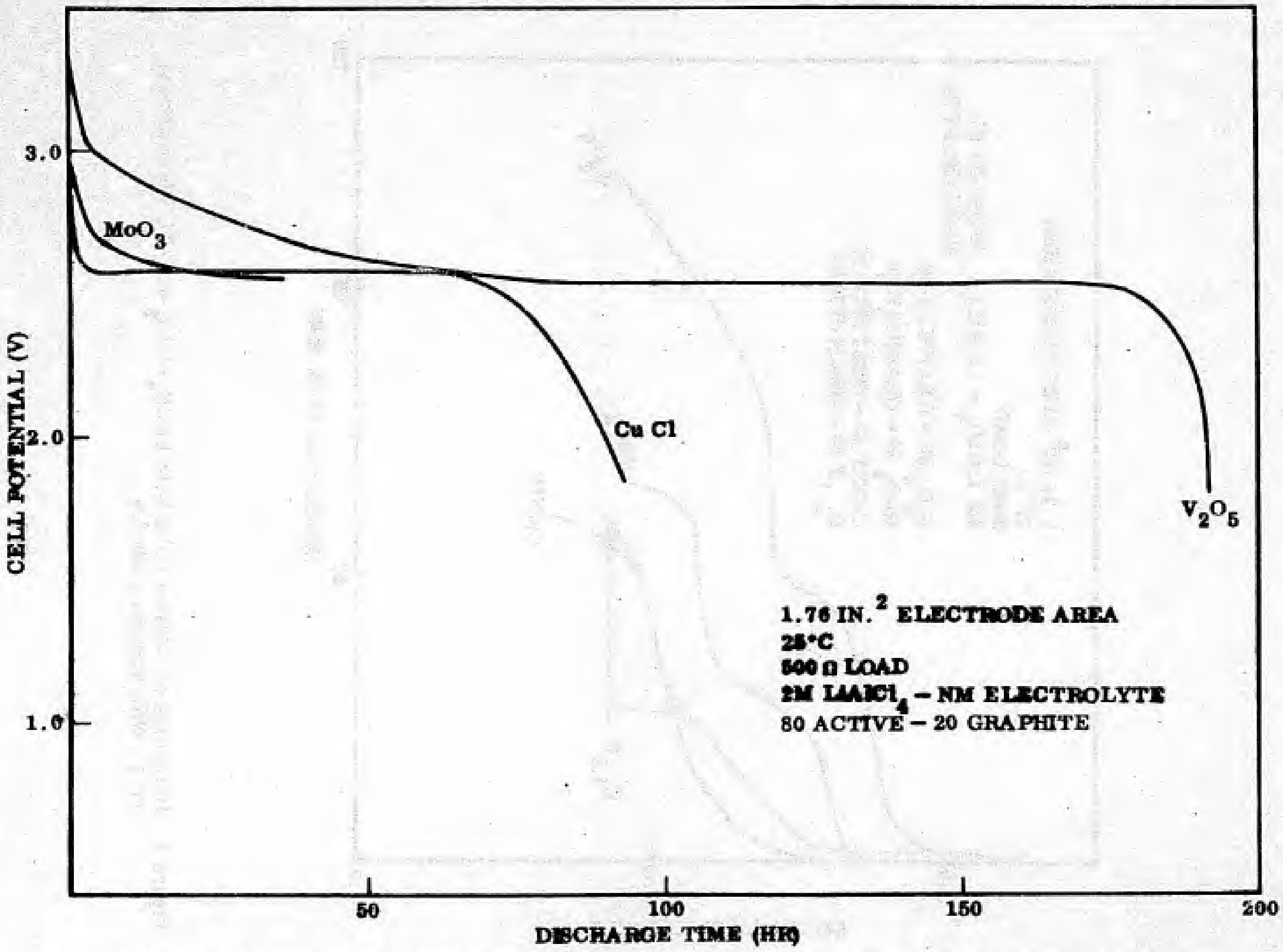


Fig. 9 Discharge of Lithium Cells With LiAlCl$_4$-NM Electrolyte at 77° F, With Various Cathodes

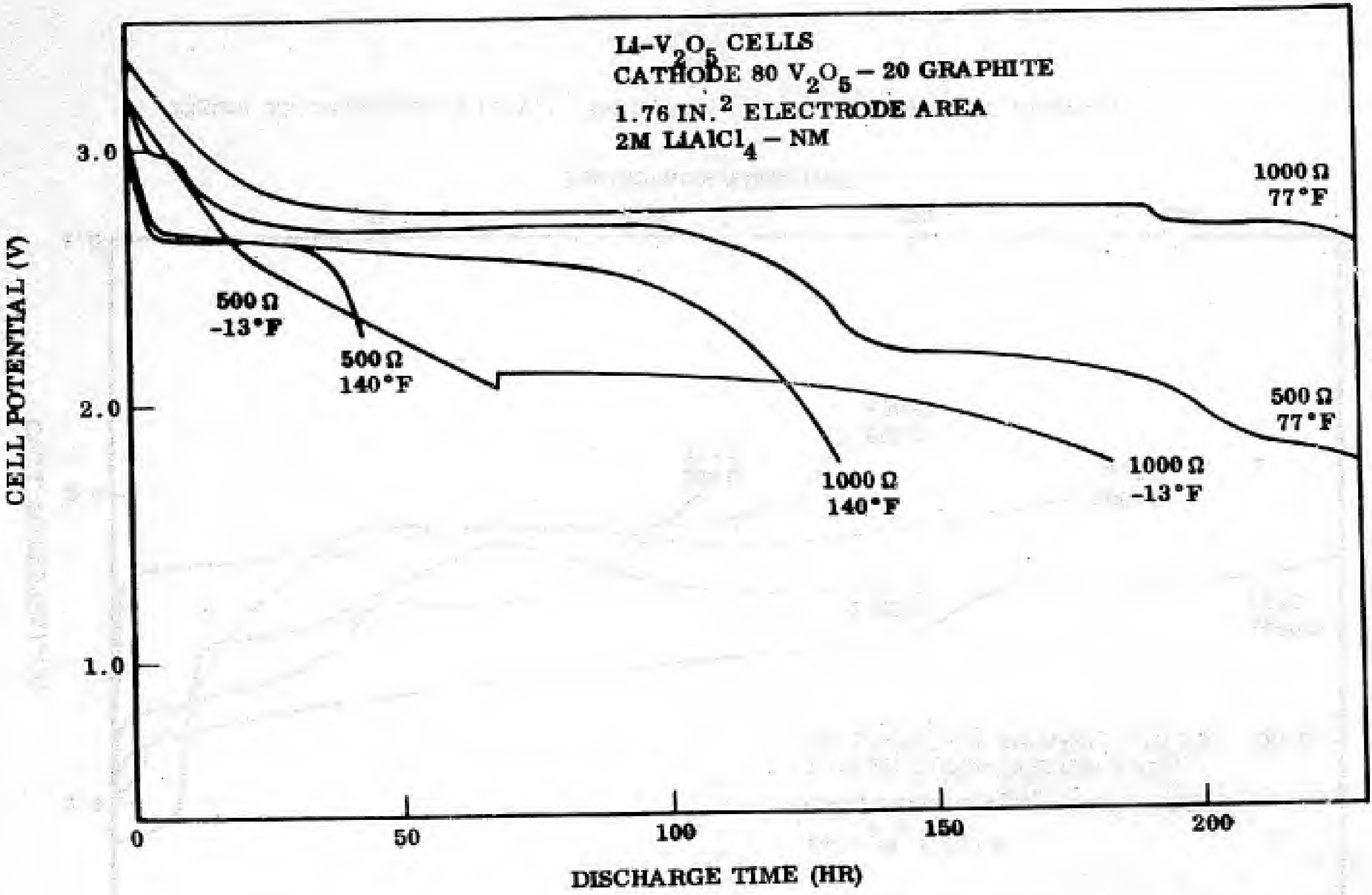


Figure 10. Discharge of Li-V_2O_5 Cells With $LiAlCl_4$-NM Electrolyte

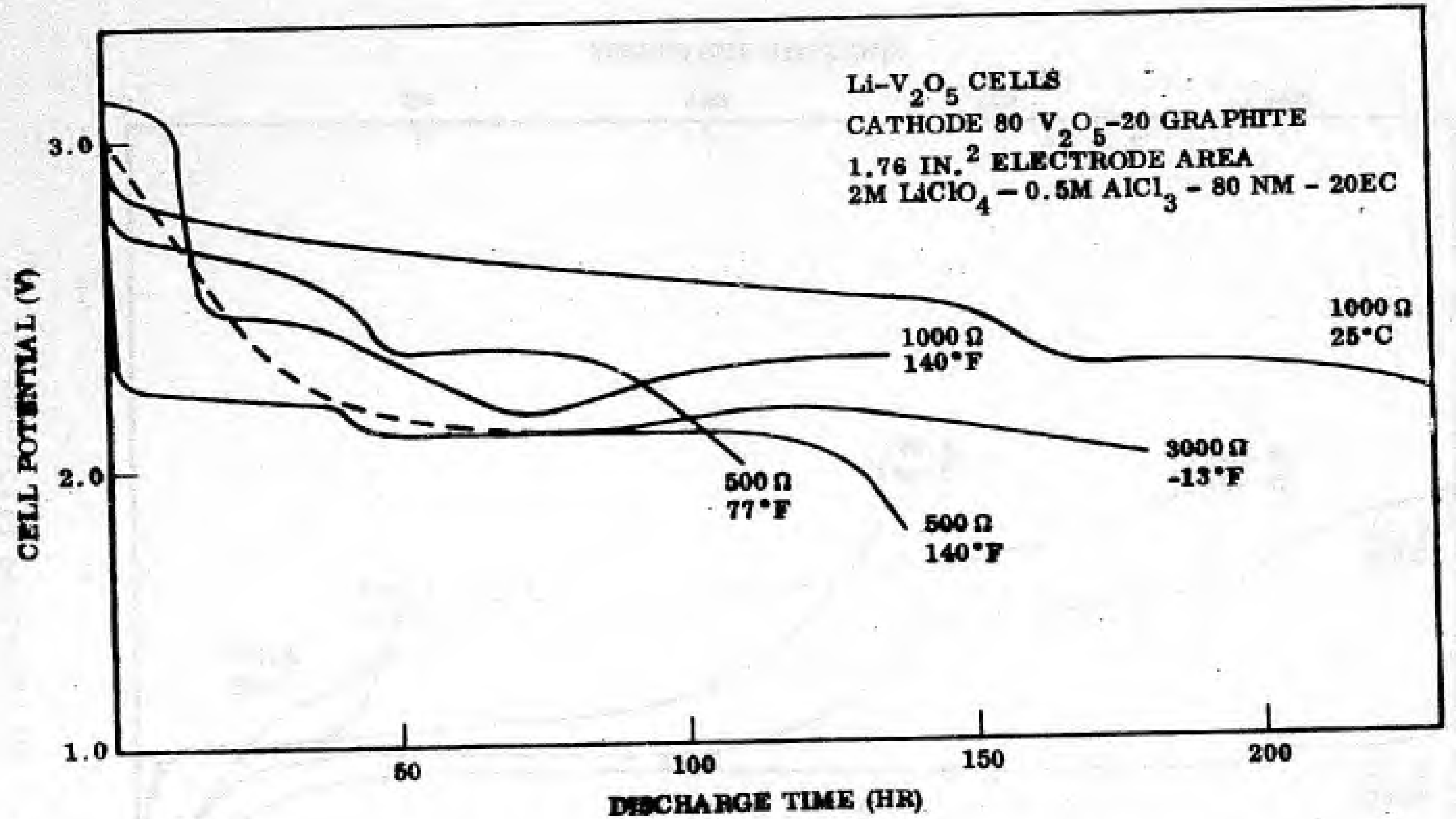


Figure 11. Discharge of Li-V_2O_5 Cells With $LiClO_4$-$AlCl_3$-NM-EC Electrolyte

2. BATTERY DESIGN

a. Components

The components that are active electrochemically in a cell and that have been chosen for cell design and fabrication are a lithium anode, 80 percent nitromethane-20 percent ethylene carbonate (volume)-2-M lithium perchlorate-0.5-M aluminum chloride electrolyte, and 80 percent vanadium pentoxide-20 percent graphite (weight) cathode. The anode was selected on the basis of previous work which was verified by cell tests on this contract; the electrolyte was selected because of its much superior explosive power and high temperature stability, combined with reasonable conductivity and good stability with lithium; the cathode was selected because of its higher discharge voltage and longer discharge time. A simplified block diagram of an electrochemical cell is shown in Figure 12. During discharge, the anode is oxidized with the release of electrons which pass through the external load to the cathode where reduction occurs. Current is conducted through the electrolyte by the ions formed from the salt dissolved in the electrolyte solvent. The reactions at the anode and cathode of the selected cell system may be hypothesized to be the following:

$$2\ Li \rightarrow 2\ Li^+ + 2e$$

$$V_2O_5 + 2e \rightarrow V_2O_4 + O^=$$

Since the reaction and the cathode products have not been characterized, the above reaction equations are simply an indication of the electron generation and valence change at the anode and cathode.

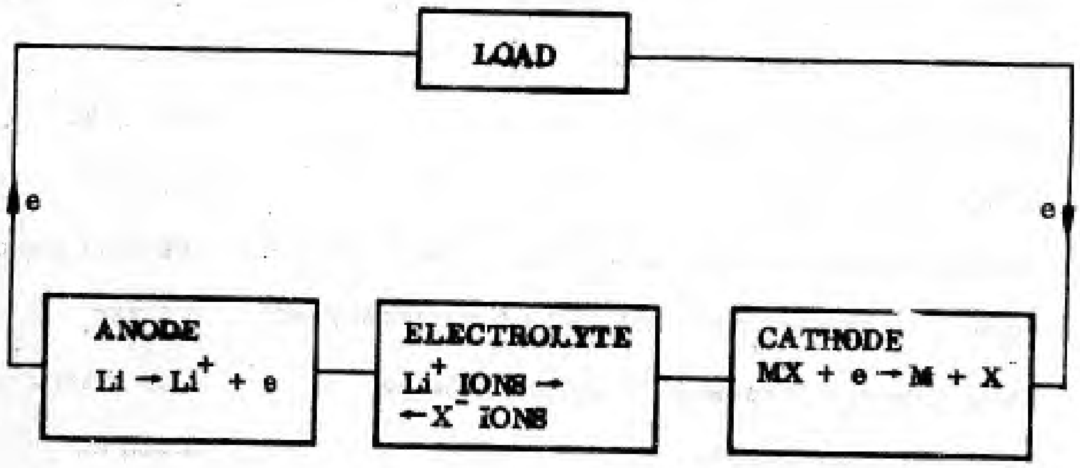


Figure 12. Diagram of Discharging Cell

b. Mechanical Design

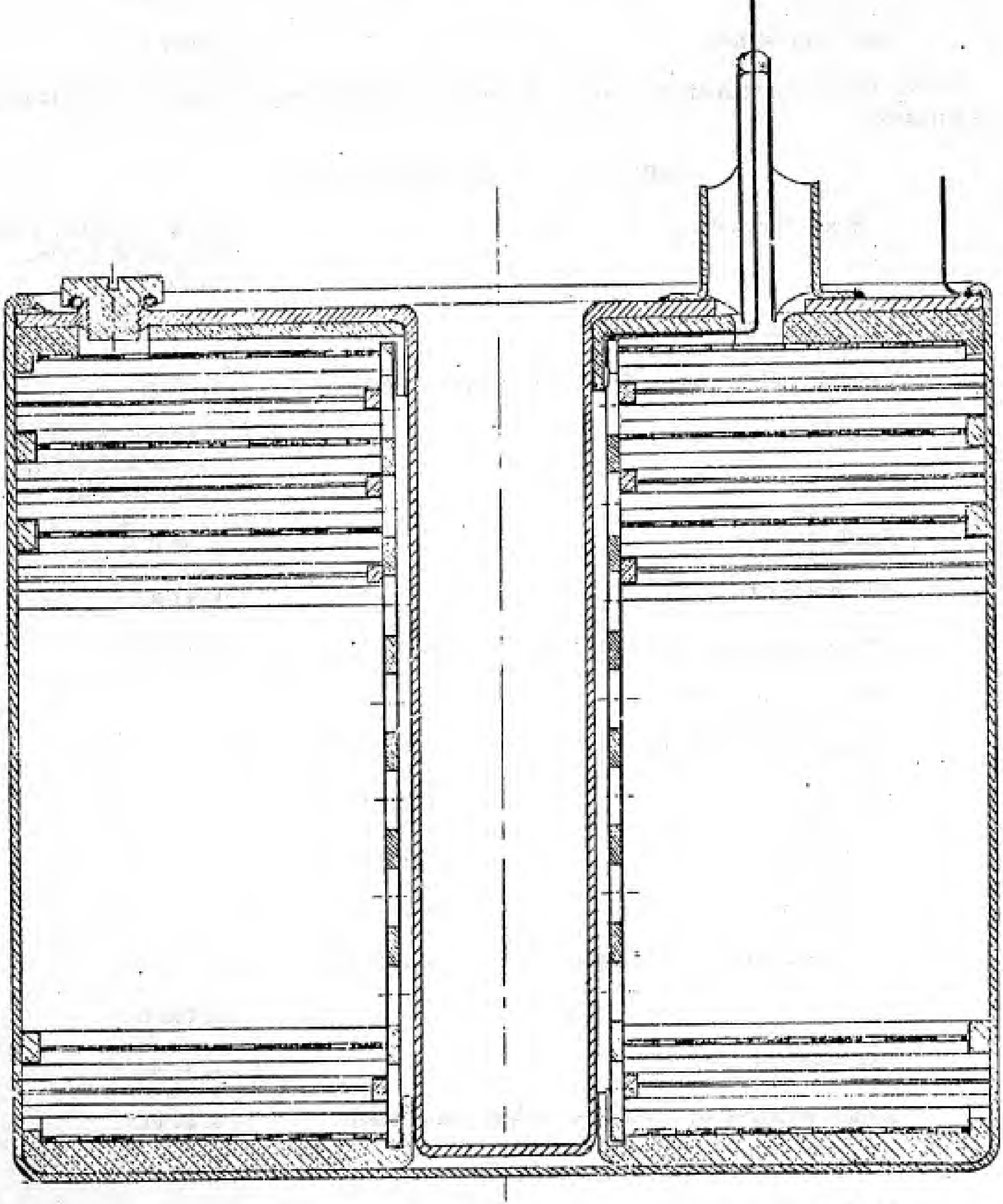
The goal of this contract is to fabricate and evaluate a single cell battery so that the discharge and explosive capability may be extrapolated for system use. For most applications, a reserve type battery with the electrolyte stored in a reservoir until use rather than in contact with the electrodes is necessary so that extended shelf life may be obtained. The reservoir and activation system were not considered on the present design except to make the packaging compatible with a reservoir-activation assembly.

The cell design chosen for this battery is shown in Figure 13. The unit cells consist of washer-shaped disks of cathode material contacting a nickel grid, a separator, and a lithium anode similarly shaped contacting a cathode grid. Six of these unit cells will be stacked and connected in parallel by allowing the anode grid to contact on its perimeter the metal can which is a container for the cell and the cathode grids to contact a centrally located contact tube. Delrin end insulators and anode and cathode insulators will be used to isolate the electrodes from the counterelectrode. The whole unit will be contained in a stainless steel can and sealed with a lid containing a reentrant detonator cavity by crimping and soft soldering to make a hermetic seal. The cathode lead will be carried through the can cover with a glass-metal hermetic seal and filling will be accomplished through a port which can be sealed with an O-ring and a threaded fastener.

Data used in preparing the design and estimating performance were obtained from test cells which were discharged during this program, and from measurements made on material intended for the cell design. The data in Table VI were directly measured or calculated:

TABLE VI. TEST CELL DATA

Dimension of V_2O_5-graphite cathode pellet in test cells	1.5 in. dia. by 0.075 in.
Average weight of cathode pellet	3.5 g
Density of cathode material	26.8 g/in.^{3}
Area of cathode pellet	1.76 in.^{2}
Average discharge time obtained from cathode to 2.0 V	100 hr at 5.0 mA
Ampere-hr capacity from cell with 3.5 g cathode pellet	0.5 Ahr
Current density of cathode for above discharge	2.83 mA/in.^{2}
Electrode grid thickness	0.005 in.
Electrode grid weight (1.5 in. dia.)	0.717 g
Anode thickness	0.020 in.
Anode weight (1.5 in. dia.)	0.306 g



Approx 3X

Figure 13. Cell Design

TABLE VI. (CONCLUDED)

Separator thickness (one layer each glass and polypropylene)	0.025 in.
Separator weight	0.007 g

For the proposed battery design, the data in Table VII were measured, calculated, or estimated:

TABLE VII. CELL DESIGN DATA

Cathode dimensions		1.93 in. O.D., 0.5 in. I.D. by 0.075 in. thick
Cathode area		2.75 in.^{2}
Cathode weight (ratio of test cell to design cell area)		5.35 g
Anode dimensions		2.027 in. O.D., 0.570 in. I.D. by 0.020 in. thick
Anode area		2.99 in.^{2}
Anode weight		0.47 g
Usable electrode area 1.93 in. O.D. 0.57 in. I.D.		2.70 in.^{2}
Unit cell thickness		
Anode grid (1/2 thickness)	0.0025 in.	
Anode	0.020 in.	
Separator	0.025 in.	
Cathode	0.075 in.	
Cathode grid (1/2 thickness)	0.0025 in.	
Total		0.125 in.
Can inside height		1.87 in.
Height required by insulators, cover, and crimp		0.25 in.
Component thickness variation (total)		0.12 in.
Available height for unit cells (by difference)		1.5 in.
Number of unit cells allowable in can 1.5/0.125		12
Total electrode area for 12 unit cells (12 × 2.7)		32.4 in.^{2}

TABLE VII. (CONCLUDED)

Current from cell at 2.83 mA/in.^2 (500 load on test cell)		92 mA
Current density at 20 mA rate		0.62 mA/in.^2
Ahr capacity of cell (estimated)		9.2 Ahr
Whr capacity of cell (estimated with 2.5 V average)		23 Whr
Unit cell weight		
Anode grid (1/2 thickness)	0.61 g	
Anode	0.52 g	
Separator	0.012 g	
Cathode	5.35 g	
Cathode grid (1/2 thickness)	0.61 g	
Total		7.10 g
Weight of 12 unit cells		85.2 g
Can		35.5 g
Cover		18.0
Insulators		3.0
Contact tube and other hardware (est.)		16.0
Electrolyte (estimated)		40.0
Total estimated weight of battery		197.7
Estimated Ahr capacity of battery		9.2 Ahr
Estimated Whr of battery		23.0 Whr
Estimated energy density of battery		53 Whr/lb
Equivalent explosive power of battery (est.)		32 g of C-4

SECTION III

BATTERY FABRICATION AND TEST

1. BATTERY FABRICATION

a. Preparation of Components

(1) Anode

Lithium metal, which was the selected anode material, was purchased in strip form 0.020 inch by 4 inches by 30 feet. The material was received in coils enclosed in a soldered metal can with an enclosed argon atmosphere. These cans were opened in the glove box and were punched to size in a Delrin (polyacetal resin) die. A plastic die set was used for punching to minimize the welding that occurs when lithium is worked with metal tools. The die was held in a standard die set that was operated in a horizontal position in the glove box to allow better visual control of the operation and for the removal of the punched disk. The die had spring-loaded sections that allowed both the anode perimeter and the central hole to be punched on the same stroke. The anodes were punched in groups of 12, sufficient for one battery, and held on simple fixtures consisting of a post and a base. These fixtures allowed ready access during assembly, and the grouping of parts for one battery controlled the number of components entering a single battery. Anodes were generally punched as needed for battery assembly but were, on occasion, stored in foil bags in the glove box.

(2) Cathode

The cathodes for the battery are prepared from 80 percent by weight of vanadium pentoxide (V_2O_5) and 20 percent of graphite. The vanadium pentoxide, selected as the result of comparative cell discharge tests, was reagent grade material purchased from Matheson Coleman and Bell, while the graphite was Dixon Grade 200-43 purchased from Joseph Dixon Crucible Company. These materials were weighed as received into a Twin Shell Blender in approximately 600-g lots. After 2 hours of blending, the cathode material was stored or used immediately for the tabletting of the cathodes. Tabletting was accomplished in a four-piece die consisting of a base, the outside barrel (which sized the perimeter), a removable center core, and the top piston (which was bored to receive the center core). A charge of 7.7 g was weighed into the die, the charge was leveled, and the top piston was placed in position. The die was then placed into a hydraulic press where the cathode was compressed under a total pressure of 15,000 pounds. The cathode was removed from the die and placed on a stacking fixture similar to that used for the anodes except that the post was only slightly undersize of the central hole in the cathode. The center post of the fixture could then be used to guide the vacuum cup used to pick up the cathode during battery assembly. The stacking fixtures with enough cathodes (12) for one battery were dried at 185°F for at least 24 hours before being assembled into batteries. Experiments were made in which the cathode stacks were dried for 24 hours at 221°F in a vacuum.

(3) Electrolyte

The electrolyte used in the MEB battery is 80 percent by volume of nitromethane and 20 percent by volume of ethylene carbonate, with two moles of lithium perchlorate ($LiClO_4$) and 0.5 mole of aluminum chloride ($AlCl3$) added per liter of mixed solvent. Reagent grade nitromethane and technical grade ethylene carbonate were used to prepare the solvent. The ethylene carbonate was melted and measured, and the required amount of nitromethane was added. The material was then passed in a stoppered bottle into the glove box where a freshly prepared molecular sieve was added. Linde 4A molecular sieve was used for drying and it was activated by vacuum drying for 24 hours at 608°F.

After the initial drying, the solvent was decanted and dried the second time, again with freshly activated molecular sieve. Lithium perchlorate, which had been vacuum dried for 24 to 48 hours at temperatures to 329°F, was added to the mixed solvent followed by aluminum chloride. Heat developed with the addition of aluminum chloride, which resulted in some darkening of the electrolyte. This was eliminated by freezing the electrolyte before addition of the salt. Freezing reduced the rate at which the salt dissolved, and thus the rate of the exothermic reaction, and also cooled the reaction. In this case, the electrolyte was water white as prepared but darkened with about a week's storage at room temperature. The electrolyte was stored with clean aluminum foil immersed in the electrolyte to react with any acid that might be formed by the reaction of the aluminum chloride with any water in the electrolyte. This hydrolysis reaction can be considered as

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

and the reaction with aluminum as

$$3HCl + Al \rightarrow AlCl_3 + 3/2H_2$$

Electrolyte prepared by this technique would normally have less than 200 ppm water content.

Additional drying of the electrolyte involved an additional treatment with lithiated molecular sieve. The lithiated molecular sieve was prepared by soaking Linde 4A molecular sieve in 20 percent lithium chloride. This substituted lithium ions for the sodium ions in the molecular sieve. The material was then washed and dehydrated by vacuum drying as previously mentioned. Electrolyte with less than 50 ppm of water could be prepared with this additional step.

(4) Separator

The separators used in the MEB were of glass fiber and nonwoven polypropylene material. The Whatman GF/A glass fiber filter paper and the Kendal Mills polypropylene nonwoven fabric were cut individually with the same steel cookie cutter-type die used in an arbor press. The separators were then stacked on an aluminum fixture in the correct order and with the appropriate number for a battery assembly. These separator stacks were dried a minimum of 48 hours at 185°F and were stored at that temperature until placed in the glove box for battery assembly. The glass paper was fragile mechanically but was selected because it could undergo the drying cycle without shrinking. Other glass fiber material with a binder shrank appreciably during the drying cycle.

(5) Machined and Fabricated Parts

Plastic parts used in the battery assembly were used as-received, without additional preparation. The electrode grids were punched with the appropriate die from nickel-expanded metal and then were degreased in trichlorethylene solvent and dried. The center post was cleaned similarly after machining, and the positive electrode lead was spot welded to the post. Inside the top rim the battery cans were treated with acid flux and then tinned with 60-40 tin lead solder and the excess solder wiped off while it was molten. The cans were washed immediately with hot water and then scrubbed with alkaline cleaning solution to remove traces of flux and free acid, which would result in additional corrosion of the can.

The battery top was a more complex subassembly, which consisted of four parts assembled with silver solder. The parts were soldered in a series of steps using Easy Flo 45.032 in wire preforms and Easy Flo flux (Handy & Harmon Company). The assembly was then sandblasted to remove flux and scale, and the top was flattened and positions squared with the detonator tube in a jig placed in a hydraulic press. The perimeter of the top was fluxed with acid flux, tinned, and washed as was the battery can.

b. Battery Assembly

(1) Metal Assembly

As batteries were assembled, it was recognized that some changes were necessary in the mechanical design from that presented in the R&D Design Evaluation Report of February 1972. These changes were incorporated in the assembled battery as a means of giving more latitude to the battery assembly, to simplify assembly, and as a more economical means of component preparation.

It was found during the initial assembly of batteries that if there was any interference between the cathode and the cathode insulating ring, the material was chipped from the cathode and this material acted as an immediate short from the can to the cathode or was a potential source of trouble after the battery was filled. In the subsequent assemblies, the cathode insulator was slit diagonally so that,although it encircled the cathode completely, it could expand to the full diameter of the battery can, using up the space that was allowed for tolerance between the can and the cathode insulator. This modification appeared successful in removing a major cause of cathode crumbling during assembly. Similarly, it was found that the top insulator, which was fabricated with the equivalent of the cathode insulator as part of the complete component, caused cathode crumbling when it was inserted because of the problem in centering this component in the assembly. The top was modified to remove the cathode ring as part of that component, and a separate half-height ring (to enclose a single cathode disk) was made as a separate part. The top insulator was modified slightly to allow transposition of the cathode feedthrough hole and the opening for the fill hole.

Because of breakage at the point of welding to the center electrode when a single cathode lead was used in the assembly, a five-strand lead of 0.005- or 0.010-inch nickel wire was substituted. This added a measure of safety as continuity could be maintained even if a single lead wire did break. As mentioned previously, a top was used that was fabricated from four pieces rather than the single drawn item in the original design. This step was taken simply as a means of economy as the cost of making single-piece tops for 50 batteries would be prohibitive under terms of the present contract.

(2) Assembly Conditions for the Battery

It was implicit in the assembly of the battery that all possible moisture be excluded so that deleterious reactions implemented by the presence of water would be minimized. For this reason, all components of the battery that could carry adsorbed moisture were dried as explained previously, and all assembly was carried out in a glove box in a dry argon atmosphere. The glove box was vacuum tight and filled with argon, which had been passed over titanium chips held at 1112°F. At this temperature, titanium will react to make nonvolatile solids with oxygen, nitrogen, or water vapor. The atmosphere of the glove box was circulated through molecular sieve columns to remove water and through hot titanium chips to scavenge other impurities in the gas. Under these conditions, the moisture content of the glove box could be kept below 50 ppm of water. The cathodes, separators, electrode grids, and anode and cathode spacers were passed into the glove box on fixtures containing the required number for a single battery assembly. The anodes that were die cut in the box were stacked similarly on a fixture. Assembly was accomplished with tweezers or, in the case of the cathodes, with a tool with a porous face to which the cathode could be held by vacuum until positioned within the battery. When the cell stack was placed within the battery can, the top insulator was positioned and the cell was then pressed into place. The can was crimped over the top in four places, using a crimping die operated with a small arbor press. The battery was then sealed using rosin core solder and an electric soldering iron.

Filling of the battery with electrolyte was accomplished using a two-position valve, which allowed evacuation of the battery in one position and connecting to a filling syringe containing electrolyte in the other position. The syringe piston was allowed to operate freely and about 33 ml of solution was added to the battery under these conditions. A fill plug with a Viton O-ring seal was then used to fill seal the fill hole. The batteries weighed approximately 220 g after filling.

2. BATTERY TEST RESULTS

a. Electrical Tests

(1) Battery Discharge Tests

The primary parameters to be evaluated by the electrical discharge test of the batteries are the long-time discharge properties of the battery when discharged at low rate, the high-rate discharge capability, and the ability to deliver pulse loads with reasonably good voltage regulation. The effect of high and low temperatures on these parameters was also to be evaluated. A program was set up to discharge duplicate batteries in each position to minimize the number of batteries required, and with the general rule that the batteries would perform at high rate best at the higher temperatures when battery impedance was lower. At lower temperatures parasitic chemical reactions would be minimized and would favor the low rate discharges where stand time would be a factor in the life of the cell. The test program that was mutually acceptable to the contractor and the program sponsor is given on Table VIII.

TABLE VIII. DISCHARGE TEST SCHEDULE FOR MULTIFUNCTIONAL EXPLOSIVE BATTERY

Drain Rate Temperature (°F)	Drain				
	4 mA	20 mA	80 mA	400 mA	4/100 mA(a)
165	2 cells	2		2	
70	2	2, 2(b), 2(c)	2	2	2
-10	2	2			2
-40					2

(a) 4 mA for 58 minutes followed by 100 mA for 2 minutes and repeat.

(b) After 30 days of wet stand.

(c) After 60 days of wet stand.

All batteries discharged on this program were discharged at a constant current. A constant-current discharge fixes one of the electrical parameters for more ready comparison between discharges and also makes power and efficiency calculations simpler. In the case of pulse loads, a cam timer was used to switch the control resistor of the power supply, and the constant current mode was applied during the pulses. The batteries were frequently discharged in series and, with the constant current regulator, a battery reaching the end of its discharge before other batteries in the series string could be forced into reversal. Battery reversal is dangerous as it eventually causes shorting and heating of the battery and may result in case rupture and fire. Reversal was prevented on these discharges by connecting a germanium diode (1N-91) across the battery terminals so that the diode presented a high resistance during normal discharge but would conduct when a reversed potential of 0.3 to 4 V appeared across the battery terminals. Therefore, the reverse potential across the battery would not exceed the conduction potential of the diode. Four enclosures maintained at fixed temperatures were used to hold the batteries during discharge. A forced convection oven was used at 165°F, a forced convection enclosure at 70°F, and two low temperature boxes for the -10 and -40°F discharges.

Current and potential of the batteries during discharge were recorded on a digital data acquisition system with recordings made every 2 hours. In the case of the shorter discharges of the 400-mA rate, values were recorded every 20 minutes.

The discharge curves for battery discharge at a constant current of 4 mA are shown on Figure 14. It is evident that at the low rate, the discharge life is limited at 165°F. It was subsequently found that the electrolyte when stored at 160°F in glass bottles would gel in less than 30 days. Gellation would drastically reduce the electrolyte conductivity as well as reduce the diffusion rate of the electrode reaction products. These results would be most apparent on the longer discharge tests at low current. This is because the rate of parasitic reactions in the battery is increased with temperature. This discharge time at -10° and 70°F are similar, although there is some depression of the voltage during the -10°F discharge because of the lower temperature.

The effect of high temperature is also evident on those batteries discharged at a constant current of 20 mA, as shown on Figure 15. Again, the discharge was longer at -10°F than at 70°F, with the discharge voltage being lower at the lower temperature.

At the 400-mA rate, the batteries discharged at 160°F were superior to those discharged at 70°F (Figure 16). This is predictable as the total discharge time is short enough that the parasitic reactions are of lesser importance, and the lower battery resistance at the higher temperature encourages the high rate discharge.

A comparison of the coulombic capacity of batteries discharged at the same temperature but at different rates is shown on Figures 17, 18, and 19. On these figures the horizontal ordinate is graduated directly in Ahr so that direct comparisons may be made between the different rates. It can be seen on these figures that poorer coulombic efficiency is realized at the 4-mA rate than at higher rate, even at -10°F. Therefore, it appears that the wet-stand capability of the battery is limiting its useful life. From these discharge curves, optimum discharge conditions are in the -10 to 70° F range at currents of 20 to 80 mA.

Batteries were discharged at a 4-mA nominal constant current, with 2 minutes, 100 mA pulses imposed regularly once an hour. This corresponds to a 7.2-mA average discharge rate. Two batteries were started at -40, -10, and 70° F. The pulse at -40° F could not be sustained after 50 hours of discharge and the temperature was raised to -30°F; additional discharge life was obtained at this temperature. The electrolyte begins freezing at about -30°F, and this region of operation will show a large change in electrolyte resistance with temperature that, in turn, makes the battery sensitive to temperature and load changes. Slightly less than 200 hours of high-current pulse life was obtained with cells at 70°F. The discharge curve shown in Figure 20 has been smoothed and does not show potential fluctuations recorded during discharge. Such fluctuations, including that of Figure 18, can be explained by accumulations of gas between the electrodes, which block off the electrode surface and increase the electrode current density significantly at high rate discharge. These gas bubbles eventually reach the central area of the battery where they accumulate and free electrode area for additional discharge. Gas can be generated in the cell by the reaction between the lithium anode and water in the electrolyte. Water in the cell components such as the cathode or separators will be scavenged by the electrolyte and will reach the anode by diffusion. Such fluctuations were not evident during the 4-mA portion of the discharge shown in Figure 21, probably because the current density is so low in this case that electrode blocking has little effect on the potential. Again, the best discharge results were at -10°F, and 5.8 Ahr of capacity was obtained from a discharge at that temperature.

Two batteries which were discharged at 70°F on this test were unable to maintain voltage during the pulses after about 200 hours as shown on Figure 20 although a total of about 600 hours was obtained at the lower rate. These batteries initially had an internal resistance similar to the other cells on this test. It appears that the high rate discharge capability of the battery is compromised by aging which would have a greater effect at 70°F than at lower temperatures.

The shape of the voltage curve during application of the high-current pulse is of interest and is shown in Figures 22 and 23. At -40°F, there is a steady decline to the point where the diode conducts; at both -30 and -10°F the voltage drops abruptly when the

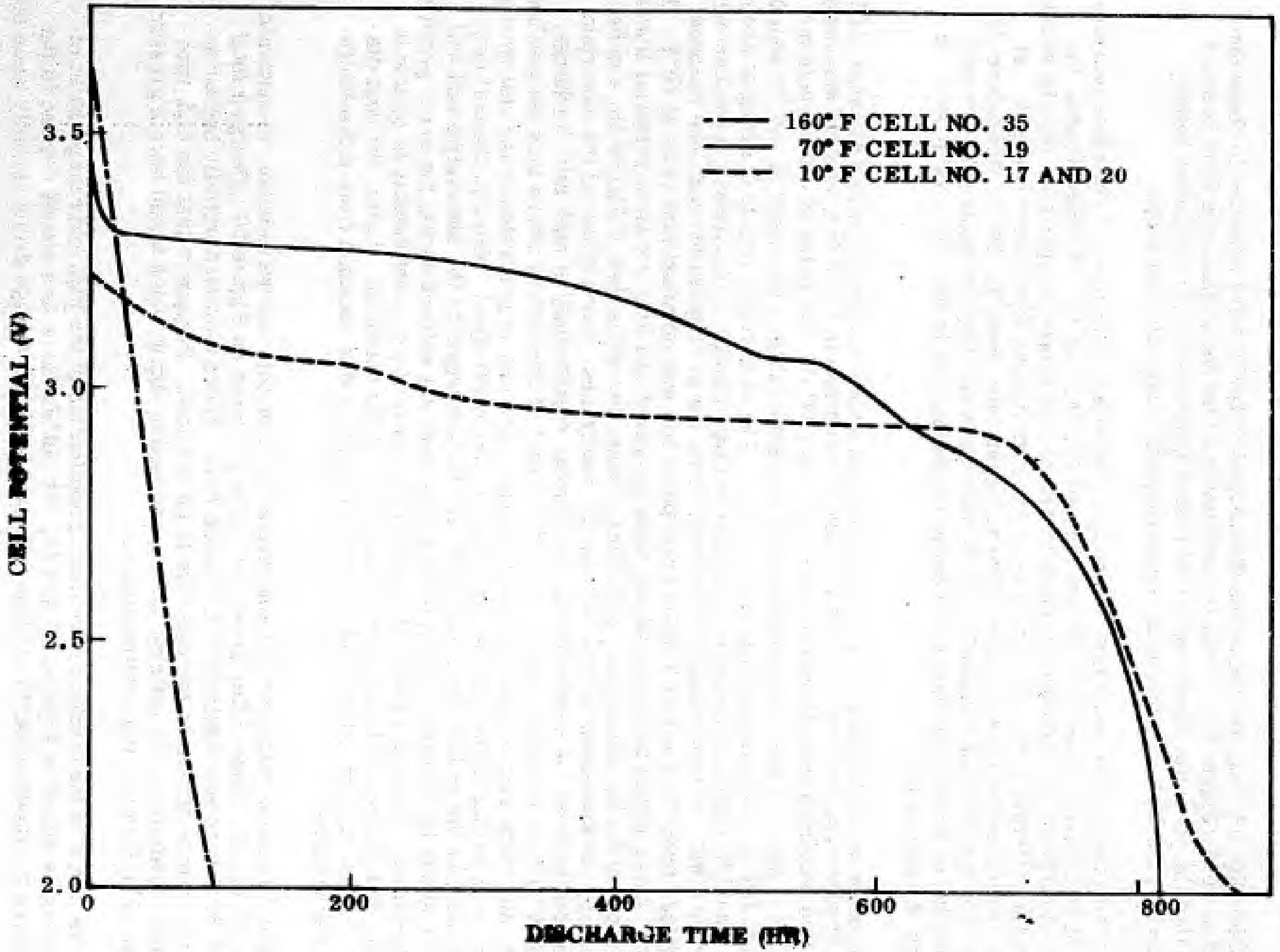


Figure 14. Discharge of MEB Batteries at 4-mA Constant Current

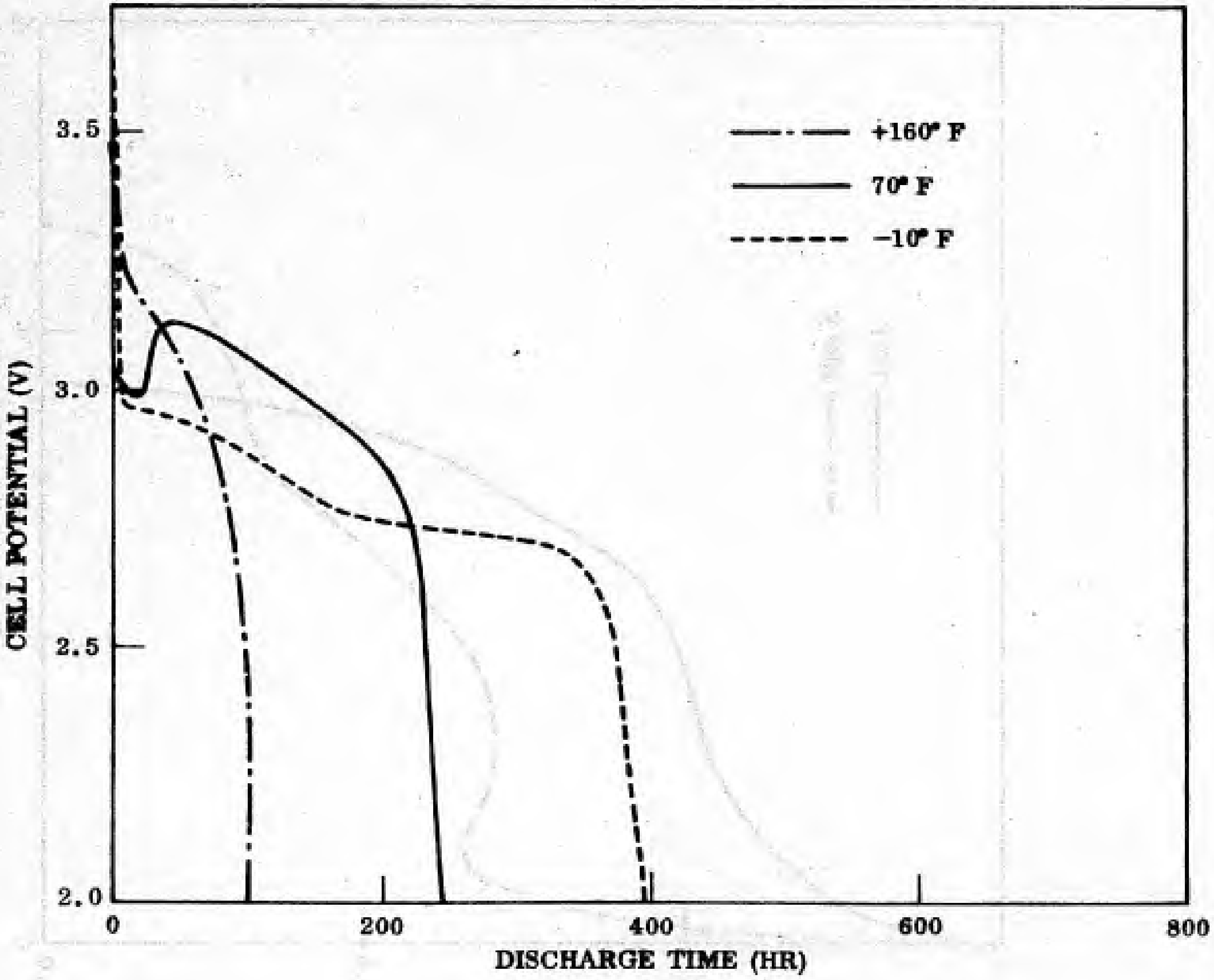


Figure 15. Discharge of MEB Batteries at 20–mA Constant Current

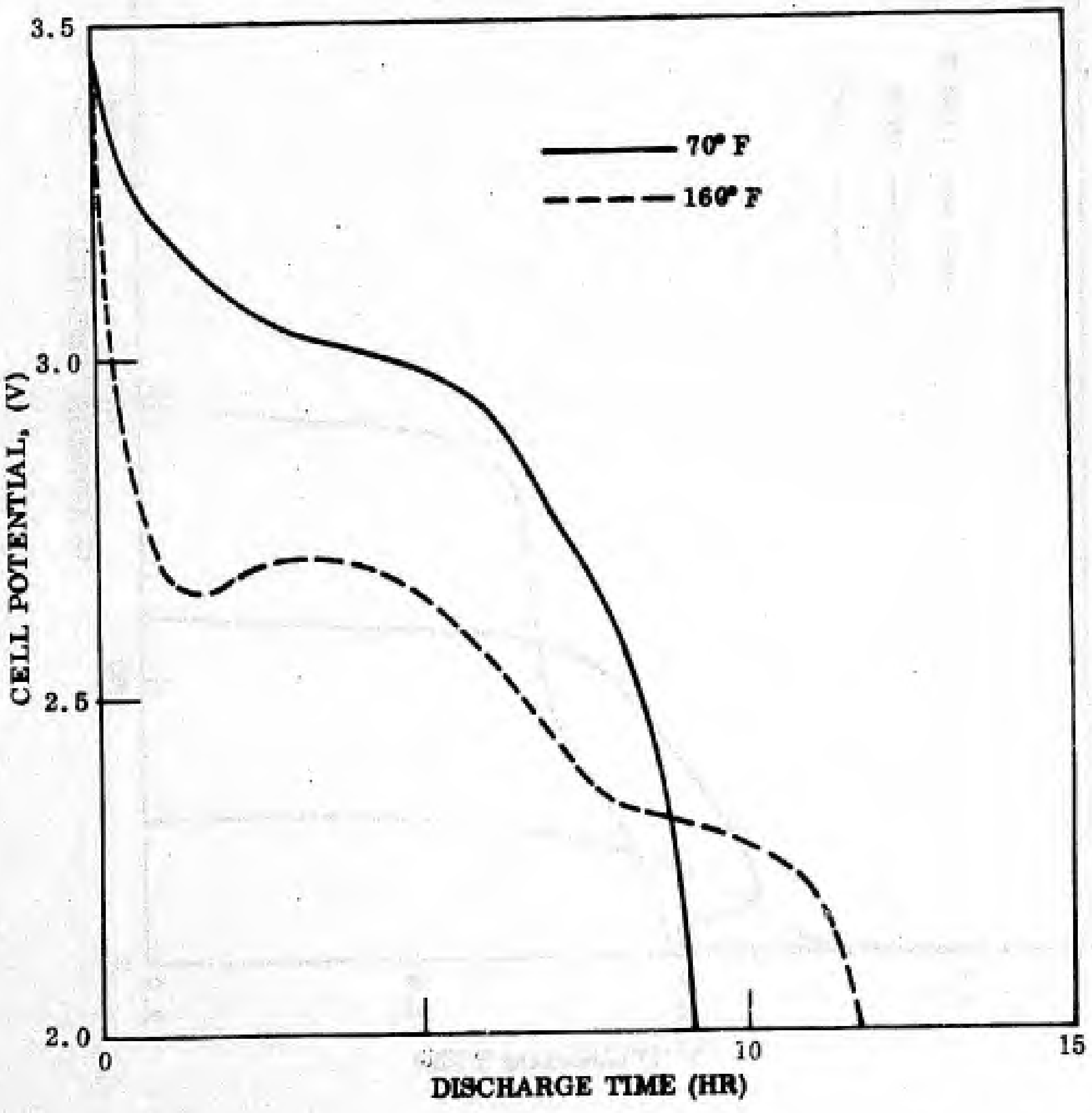


Figure 16. Discharge of MEB Batteries at 400-mA Constant Current

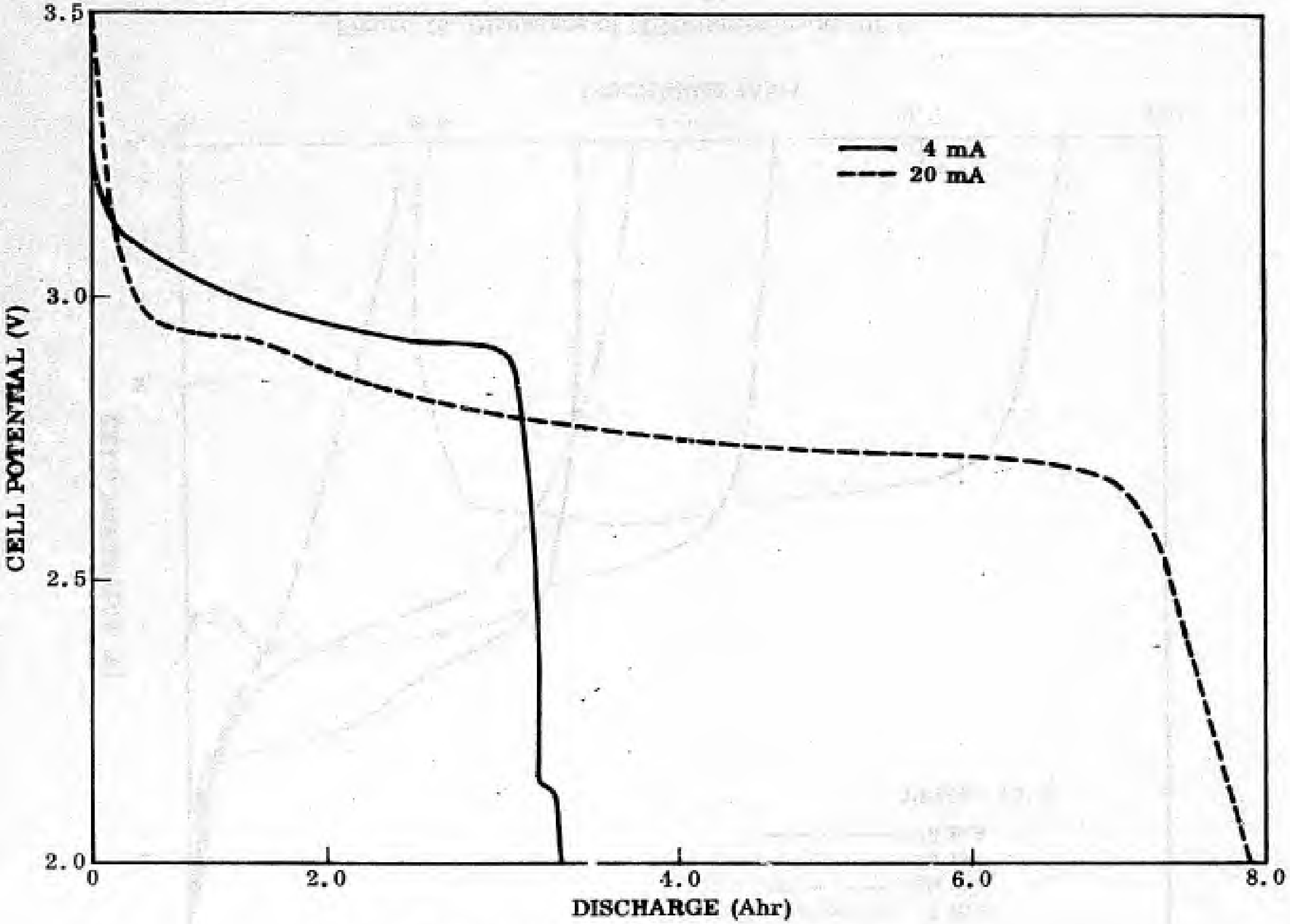


Figure 17. Discharge of MEB Batteries at -10° F

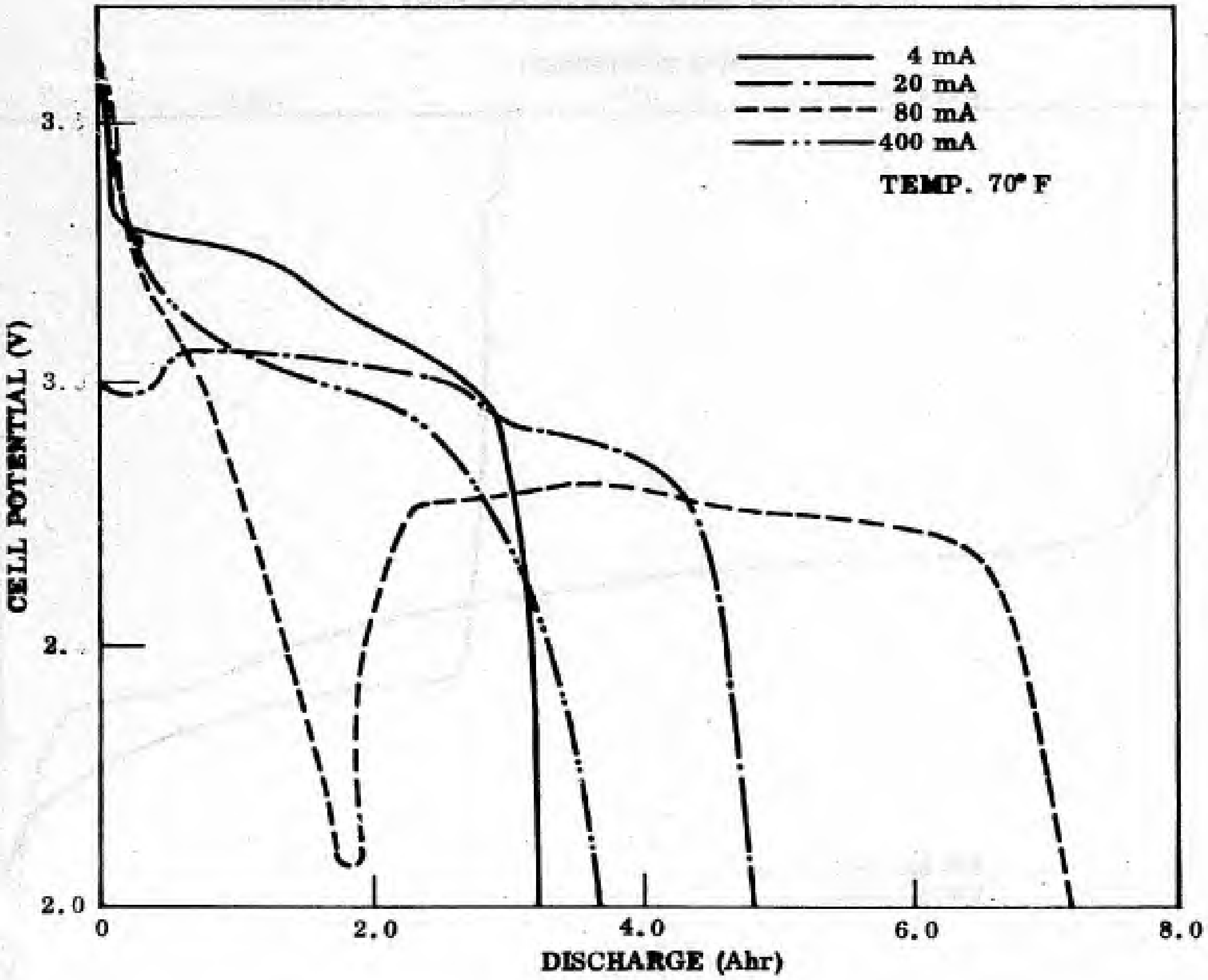


Figure 18. Discharge of MEB Batteries at 70° F

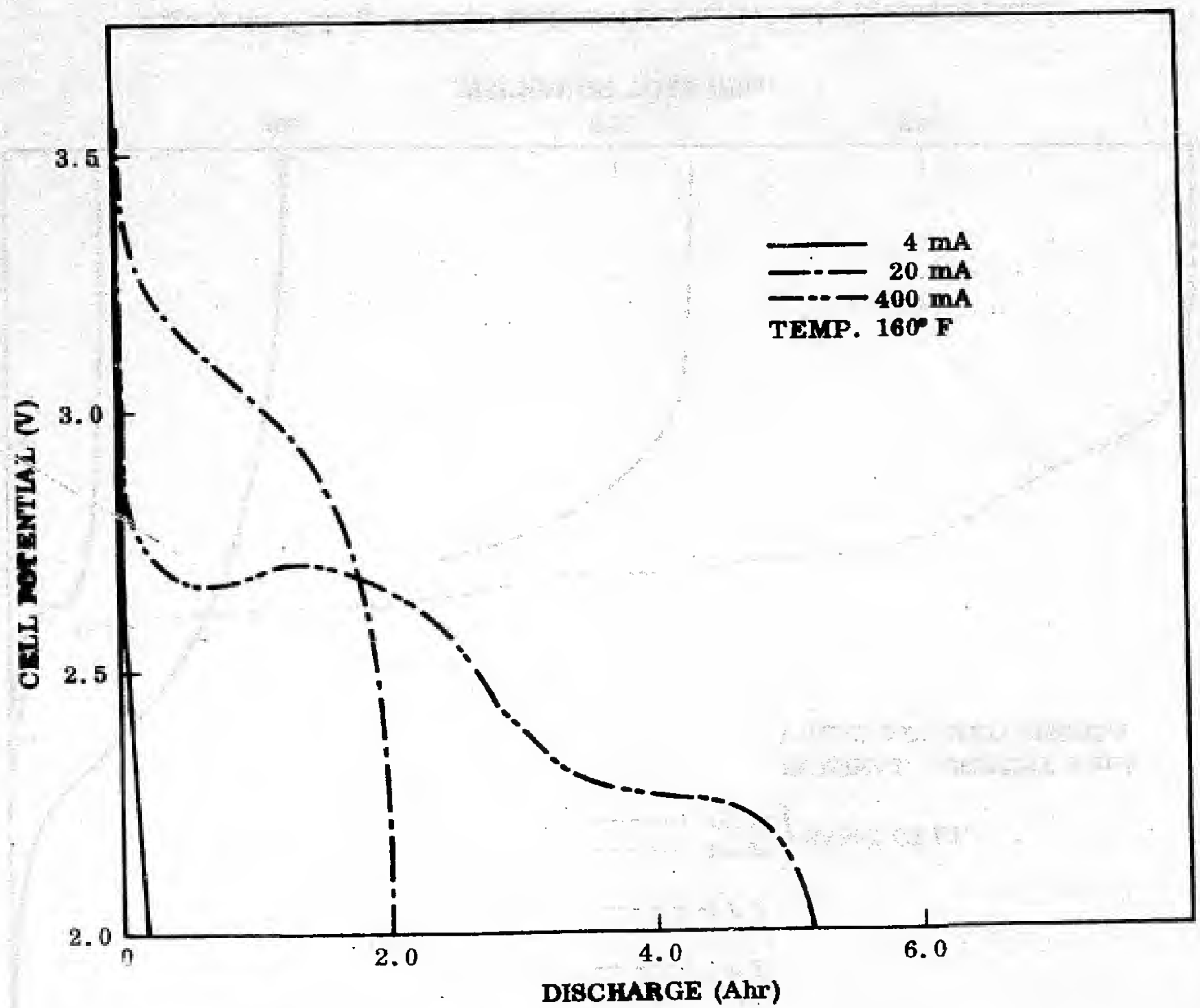


Figure 19. Discharge of MEB Batteries at 160° F

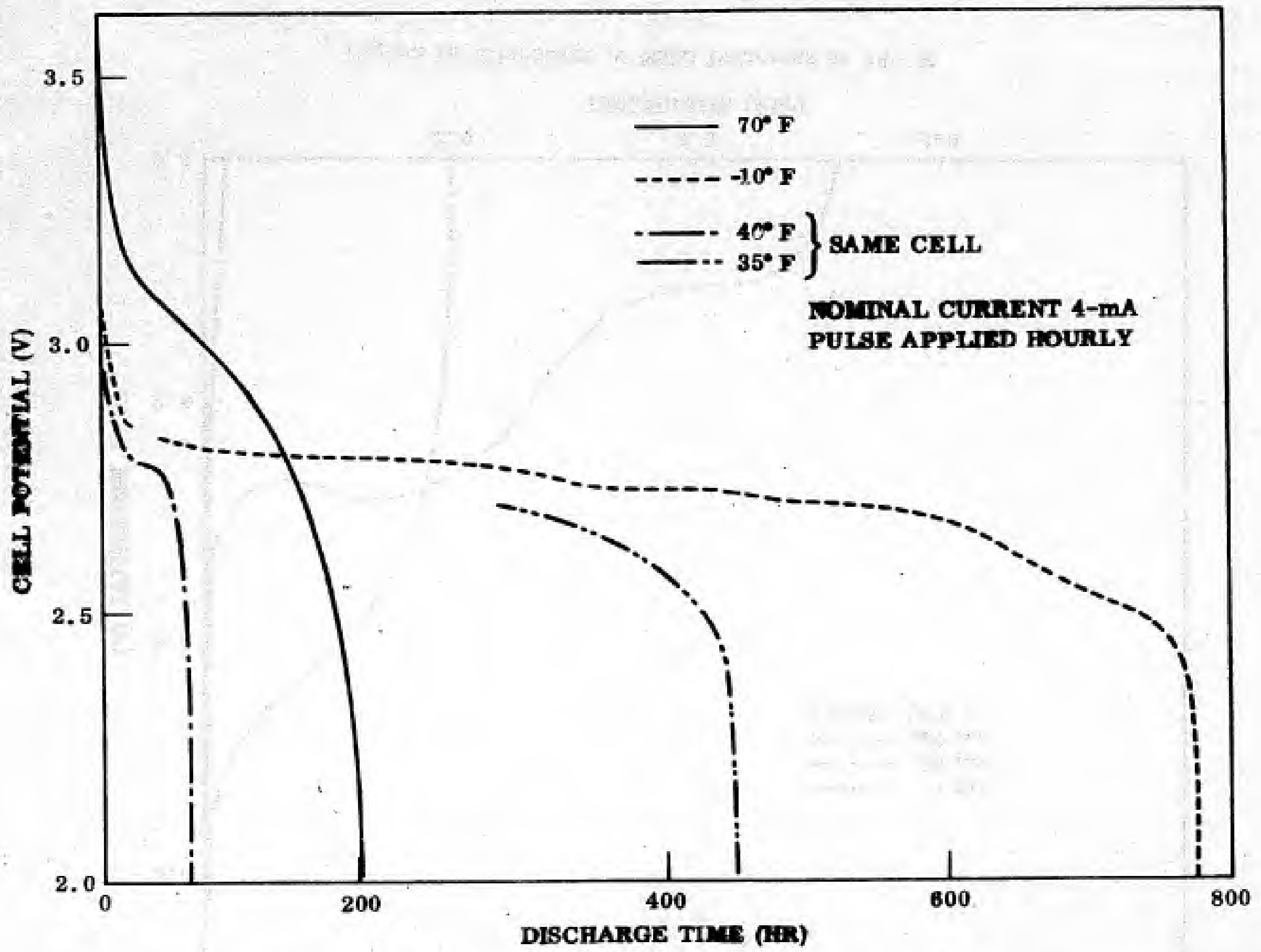


Figure 20. Voltage of MEB Batteries During 100 mA, 2-minute Pulse

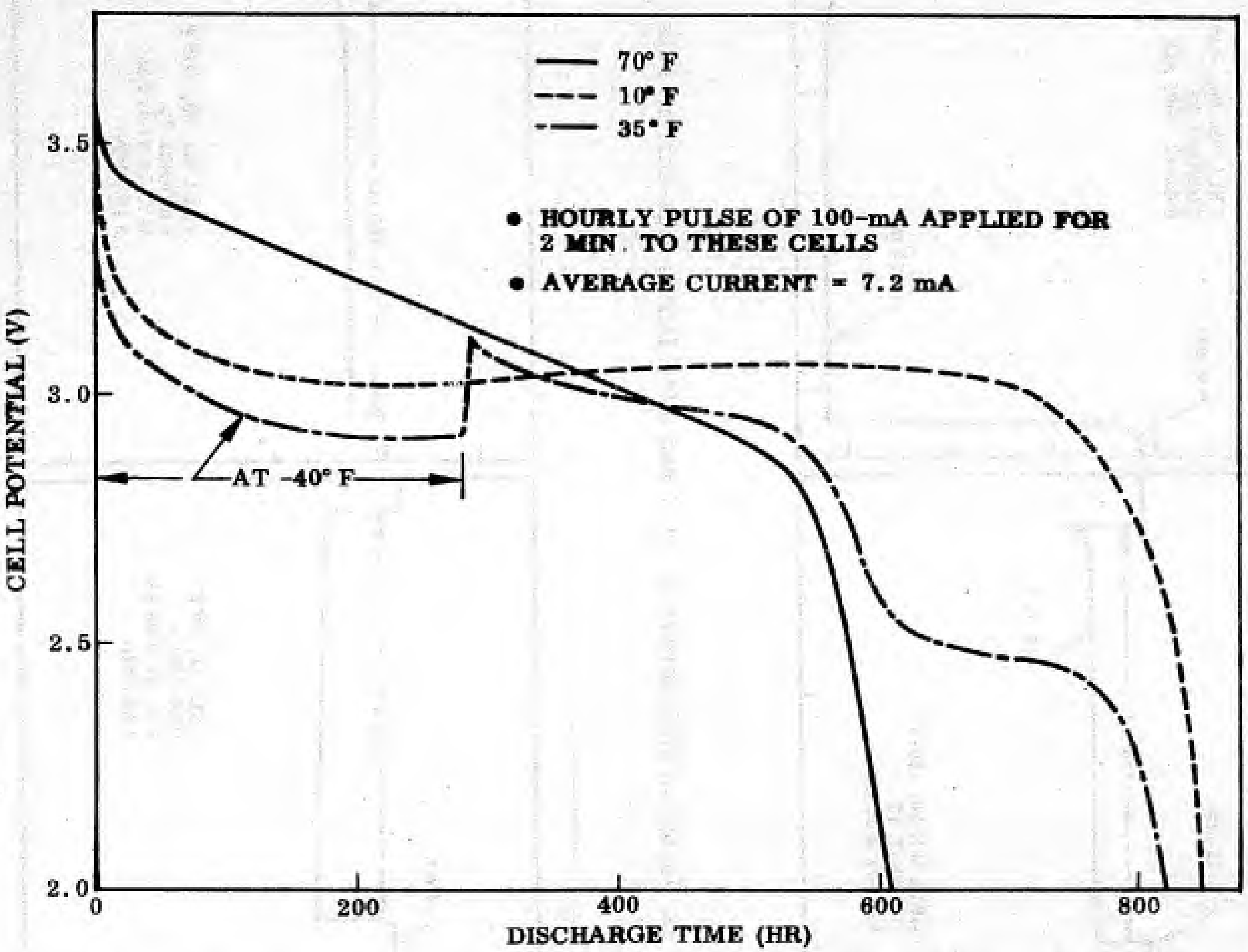


Figure 21. Voltage of MEB Batteries During Nominal 4-mA Discharge

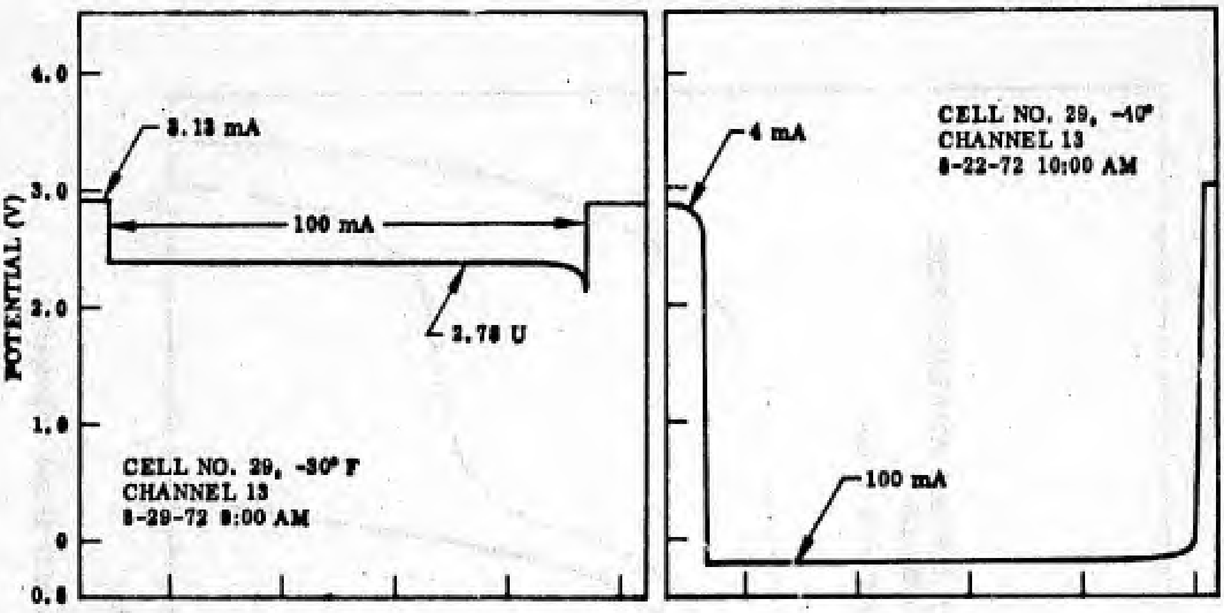


Figure 22. Voltage of MEB Battery at -30° F and -40° F During High-Current Pulse

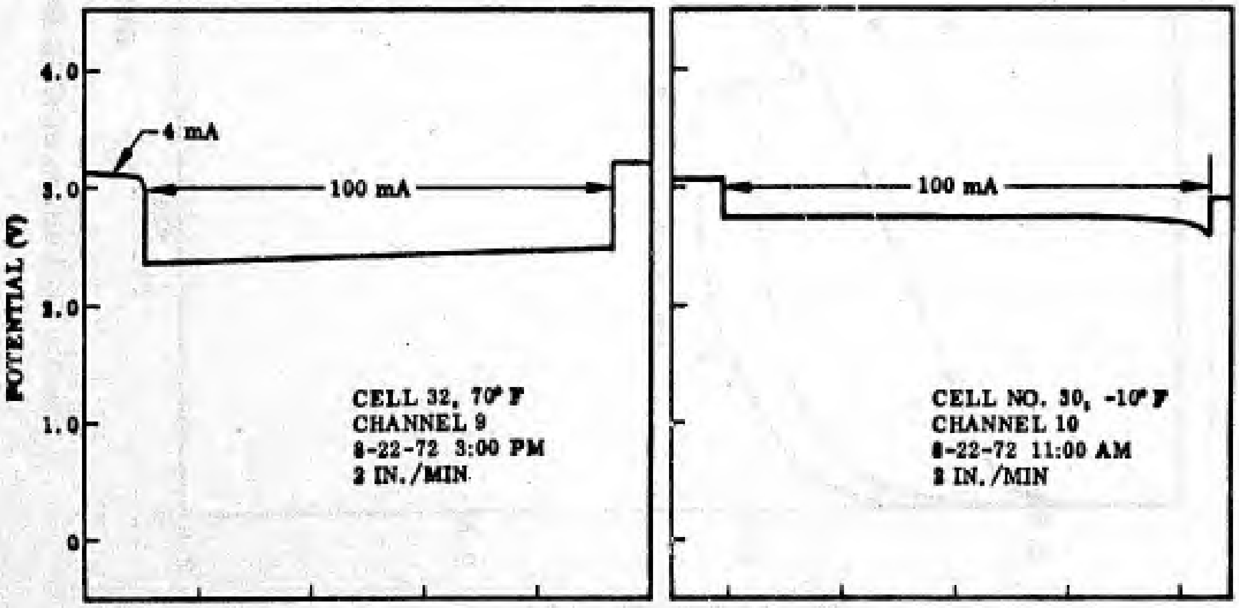


Figure 23. Voltage of MEB Batteries at -10° F and 70° F During High-Current Pulse

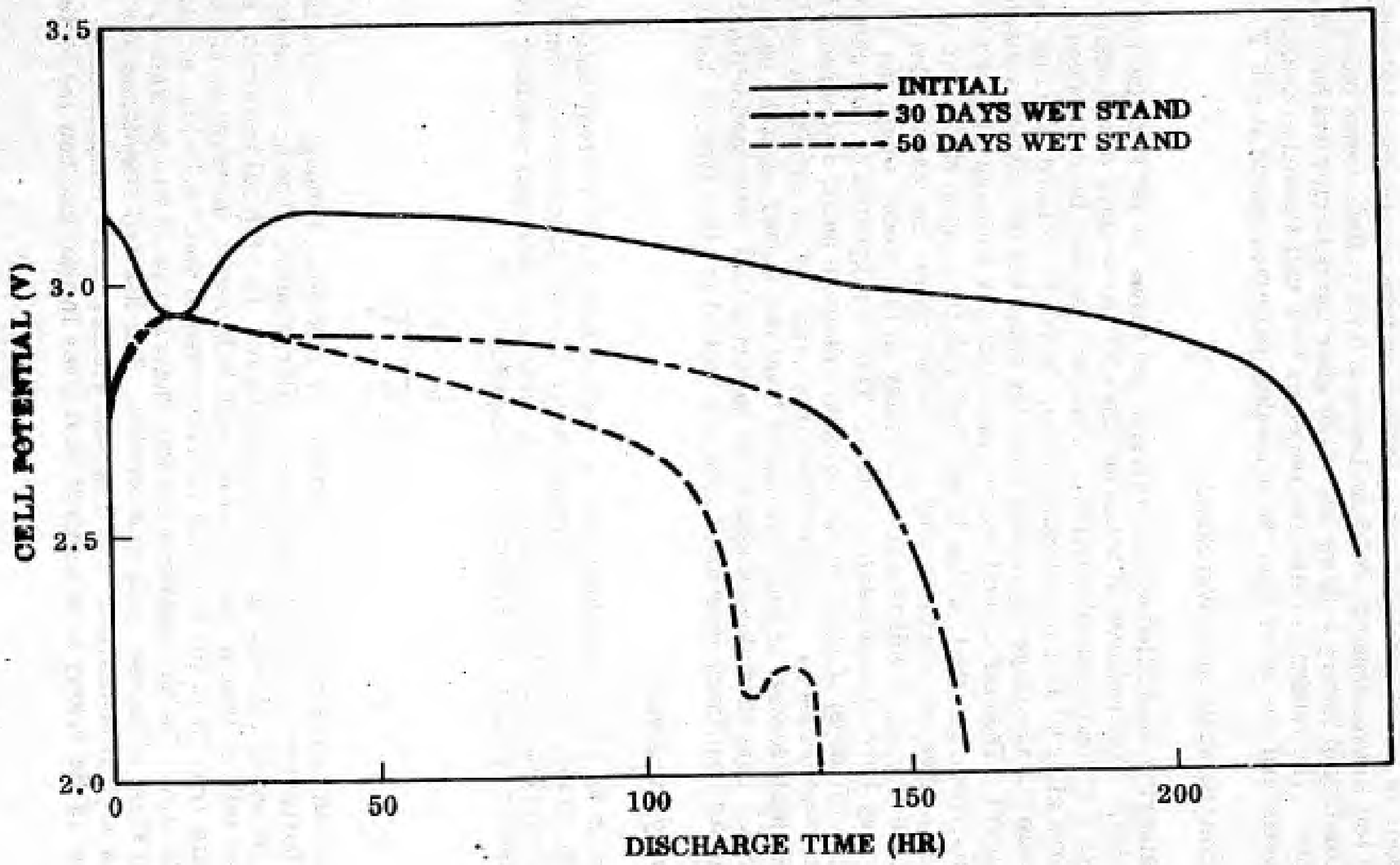


Figure 24. Discharge of MEB Battery at 20-mA Constant Current After Wet Stand

load is applied and then recovers to a voltage level, but this is not evident at 70°F. This effect is probably related to the cathode as both the anode and electrolyte would be expected to experience gradual decline to a level voltage under pulse conditions. The recording of battery voltage was made after the batteries had been discharged for 140 hours. The voltage of batteries tested at 70°F had started to decline during pulses at this point and was lower than the equivalent batteries tested at -10°F.

(2) Discharge Tests After Wet Stand

Batteries were filled with electrolyte and stored at 70°F to find the effects of aging on cell life. The discharge of batteries after 30 and 60 days of wet stand is compared on Figure 24 with that obtained initially. It can be seen that there is about a 50 percent loss of capacity after 60 days of wet-stand time. It will be noticed also that not only is the initial under-load voltage depressed after the stand but the batteries discharge at a lower voltage level. The open circuit voltage also declines with age as shown on Figure 25. The open circuit potential, which is reached with time, is 3.38 to 3.40 V. In addition, the ac resistance, as measured with a 1000-Hz bridge, increased from 0.20 to 12. The aging process likely develops a film, possibly on the anode, which has a high resistance but also may have some protective effect. This is suggested by the capacity left after 1440 hours (60 days) of aging on open circuit, whereas under discharge a life of only 800 hours was obtained at very low discharge rates. Film formation is also suggested by the gradual increase in potential until a level is reached when the battery is placed under load. This effect did not appear on batteries that were aged without electrolyte where the ac resistance after activation was typical for this type of battery.

(3) Battery Impedance

Both an ac and dc technique may be used to determine the resistance of a battery. A 1000-Hz bridge may be used to measure the ac resistance as mentioned previously. A direct-current method is to measure the change in potential resulting from a current change and to calculate the resistance using Ohm's law.

$$R = \frac{E_1 - E_2}{I_2 - I_1}$$

Different values are obtained with the two methods, although comparisons made between batteries by either method give similar results. The dc resistance also changes somewhat, depending on the load change. For typical batteries, the dc resistance will be from 0.5 to 0.8 ohm with light loads, increase to 1.0 to 1.5 ohms at currents from 30 to 100 mA, and then decrease to about 0.5 ohm at currents from 100 to 300 mA. The ac resistance for the equivalent cells will be from 0.5 to 0.25 ohm, and this, of course, is at open circuit. The internal resistance of a battery increases as it is discharged, and it is also greater at low temperatures. The resistance of the battery is of interest as it gives insight into how the battery will react to loads.

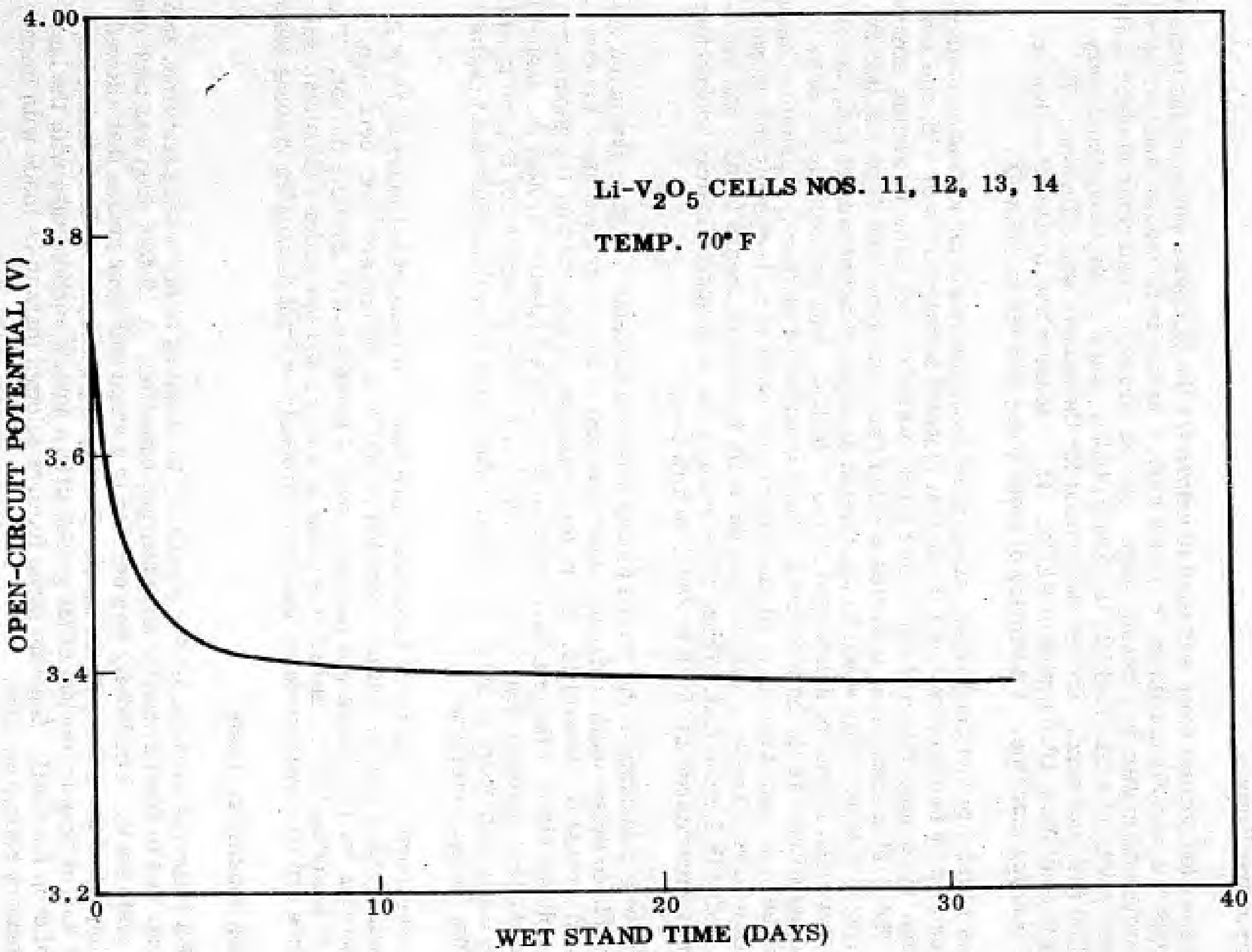


Figure 25. Open Circuit Voltage of MEB Batteries on Stand

b. Explosive and Sensitivity Tests

(1) Explosive Tests

A modified Trauzl block was used to determine the explosive power of the battery. The block was of 6061 aluminum, 8 inches high, 6 inches in diameter, and was bored 2-1/4 inches diameter by 5 inches deep. The battery with a detonator in place in the detonator cavity was inserted into the Trauzl block, and the hole above the battery was filled with wet sand. The detonator used for these tests was a Dupont E-78 detonator containing 13.5 grains of PETN. The detonator was fired with a Dupont CD-31 blasting machine. A summary of these tests is given in Table IX.

The reliability and comparison value of the test results for the explosion tests was compromised by two factors – cell leakage at elevated temperatures or with age and the geometric configuration of the Trauzl block, which did not allow maximum expansion. The O-ring seal on the batteries probably allowed some loss of electrolyte by vapor transmission. This would be aggravated at elevated temperatures and, in some cases, batteries stored or discharged at 160°F leaked. Nitromethane is the most volatile constituent in the battery and is also the explosive element. When nitromethane evaporated, the explosive power of the battery was reduced and probably the character of the explosion. The oven used to heat the cells for test in Blocks 5 and 6 had overheated to 200°F for the test. These cells were in the oven approximately twenty-four hours at temperatures of 160°F to 200°F before test.

The wall thickness of the Trauzl blocks had been calculated to give expansion values comparable to those obtained during electrolyte tests, with allowance made for the increased amount of electrolyte. From test evidence, it appears that the geometry of the cell blocks allowed the explosive force to be expended upward through the sand-filled hole rather than in expansion of the aluminum block. The expansion of the cavity after the C-4 test would seem to indicate a faster shock wave from that RDX-based explosive than from the nitromethane.

Loud reports indicative of detonation were heard on tests of batteries at 70°F in both undischarged and discharged condition at -65°F in the undischarged condition. The batteries for the discharged test were over 4 months old at the time of test. The batteries tested at 160°F, and after storage at 160°F, had low order explosions, and the smoke and fire were evidence that there probably was not detonation in these tests.

(2) Drop Sensitivity Tests

MEB batteries were tested for sensitivity to dropping at three temperatures, two positions, and in discharged and undischarged condition. A 40-foot drop was used onto a steel plate anvil. The battery was carried in a strap with four guides that allowed direct impact of the battery on the anvil. The battery position was fixed during the first 35 feet of drop by contact of the guides with a square vertical tube with the last 5 feet of drop free-fall. Separate strap fixtures allowed tests to be made with impact on the battery bottom or side.

The results of the drop sensitivity tests are shown on Table X. There were no instances of detonation on any of these drop tests. The solder seal of the battery broke in some cases, but in only one test was there leakage and heating.

TABLE IX. EXPLOSIVE TEST OF MEB BATTERY

Block No.	Condition of Cell	Test Temperature (°F)	Volume Expansion (ml)	Remarks
5	Undischarged	160	3	Low report
6	Undischarged	160	6	Low report
1	Undischarged	70	20	Sharp report
2	Undischarged	70	45	Sharp report
8	Undischarged	-65	41	Loud report Some smoke
9	Undischarged	-65	14	Loud report Some smoke
3	Discharged	70	0	Loud report Some smoke
4	Discharged	70	8	Loud report Some smoke
11	Undischarged, 30 days of wet stand at 160°F	70	3	Low report Burning
12	Undischarged, 30 days of wet stand at 160°F	70	8	Low report Burning and fire
10	30 g of C-4 in cavity	70	168	

(3) Heat Sensitivity Tests

Heat sensitivity tests were conducted to determine the reaction of a battery as its temperature was steadily increased. Two batteries were tested at one time. Both were supported on an insulating brick and separated by a second brick. Quartz-tube radiant heaters on each of two sides of the batteries were used as heat sources. The heat output was controlled by a variable autotransformer in the lamp circuit. The test components were mounted in a reflective foil-lined box, and the test was conducted in a mesh-covered explosion-proof shed. The temperature of the batteries was monitored by a potentiometer which measured the output of thermocouples placed in the detonator cavity of the batteries. The temperature in the batteries was controlled manually by adjusting the input to the lamps so that the temperature increase was approximately 100°F/hour. Two discharged and two undischarged batteries were used for this test. Three of the batteries acted similarly. At temperatures of about 330°F an exothermic reaction appeared to start within the battery as the measured temperature increased at a much greater rate than had been found with the heat lamps. At temperatures from 330° to 430°F, the battery tops were blown off with a sound resembling a compressed-gas release. The expelled contents of the battery (including lithium) burned, and there were open flames in the battery case.

The fourth battery, which was undischarged, emitted acrid fumes at 400°F and some smoke at 415 to 420°F, but there was no obvious battery damage. This test was terminated at 420°F because the end of the work shift had been reached, and no test personnel were available to continue the test. The measured temperature of the two batteries under test at the same time differed by as much as 50°F, although their situation in the heat flux was similar. Either the heat absorption rate of batteries differ, or the exothermic processes start at lower temperatures but do not reach a critical rate until higher temperatures are reached. The reaction of batteries on this test was similar to those occurring in two laboratory accidents. In both cases, temperature in an oven increased because of controller malfunction and, at some unmeasured temperature, a battery blew the top of its case and burned. In one accident, the reaction of one battery initiated the reaction in a group of batteries. All these batteries had been discharged previously.

The reaction of these batteries to heat is to be expected as even when discharged they still contain appreciable amounts of oxidizing material such as the vanadium pentoxide and lithium perchlorate and reducing material such as the lithium and the electrolyte solvents. The dominating reaction in a heated cell was not determined.

TABLE X. DROP SENSITIVITY TESTS OF MULTIFUNCTIONAL EXPLOSIVE BATTERY

Battery Condition	Battery Temperature (°F)	Battery Impact Position	Remarks
Undischarged	160	Side	Dent, possible seal rupture
Undischarged	160	Bottom	No dent or rupture
Undischarged	70	Side	Badly deformed, seal rupture, leakage, heating
Undischarged	70	Bottom	No rupture
Undischarged	-65	Side	Very slight dent, no rupture
Undischarged	-65	Bottom	Very slight dent, no rupture
Discharged	160	Side	Dent and seal rupture
Discharged	160	Bottom	Slight dent
Discharged	70	Side	Solder seal cracked
Discharged	70	Bottom	Seal cracked on whole perimeter
Undischarged, aged 30 days at 160°F	70	Side	Slight dent, seal rupture
Undischarged, aged 30 days at 160°F	70	Bottom	Slight dent, real rupture

SECTION IV

SUMMARY

1. ACCOMPLISHMENTS

MEB batteries delivered over 25 Whr/lb when discharged over a temperature range of -30 to 160°F. The best operating temperatures tested were at -10 and 70°F, and energy density values of over 40 Whr/lb were obtained at these temperatures. Continuous constant current discharges of 20 to 80 mA gave the best energy values at those temperatures. The batteries responded well to extended pulse loads in tests from -30 to 70°F.

The ampere hour capacity and energy density estimated on Table VII were not obtained. The values on the table were extrapolated from the best single electrode cell tests. The batteries tested had twelve electrodes in parallel and the average utilization was less than that obtained with a single electrode. This was probably the result of uneven contact with the electrode grid or insufficient wetting with electrolyte.

There were no detonations of batteries during any of the safety tests. Damage on 40-foot drop tests was limited to denting and slight leakage. When heated sufficiently, the batteries will burn and break the case seal as will other high-energy density batteries. The explosive power of the battery was not completely explored because of the insensitivity of the test vehicle. Electrolyte tests show that it has approximately 130 percent of the explosive power of TNT.

2. PROBLEM AREAS

A problem area was found in the present MEB battery design in that its shelf life is limited,and this condition is severely aggravated by storage or operation at 160°F. Two causes of the poor shelf life have been identified – gas generation within the battery and instability of the electrolyte at elevated temperatures. The instability in this case is different from that encountered during the original program where the trouble was the reaction between nitromethane and lithium perchlorate. The first problem is probably related to water in the completed battery and the direct reaction of this water with the lithium anode to produce hydrogen. The second problem is characterized by almost complete gelling of the electrolyte when stored at 160°F without contact with the battery components. Darkening of the electrolyte occurs at room temperature,but there have been no other indications of further reaction after 6 months of storage. The reaction is probably related to the ethylene carbonate in the electrolyte, although this hypothesis has not been proved. This problem could be avoided in a reserve-type battery by impregnating the battery separators with the electrolyte salts and storing only the solvent system, which has good stability by itself, in the battery reservoir.

3. FUTURE DEVELOPMENT

Future development of the MEB should consider both an immediate program to extend and establish the limits of electrolyte stability and a longer range program in which a complete battery with reservoir and activation system would be considered and related to a munition program.

An electrolyte program should include a brief study of solvents to replace ethylene carbonate, an identification of reaction participants, and establishment of temperature limitations for solvent and electrolyte systems.

A battery integration program should consider battery sizes and configuration suitable for a given munition, identification of usable detonators of a smaller physical size, integration of reservoir and activation mechanisms into a complete battery, and optimization of the electrochemical system for specific electrical and operational requirements.

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13. ABSTRACT

This report covers work on an explosive battery whose feasibility was established during an earlier program. On the present program, the lithium vanadium pentoxide couple with a nitromethane-ethylene carbonate lithium perchlorate-aluminum chloride electrolyte was selected for battery fabrication and evaluation. Batteries were discharged at rates from 4 to 400 mA and at temperatures from -40° to 160°F. Energy densities of over 40 Whr/lb were obtained with discharges at -10° and 70°F. Batteries survived drop tests without significant damage. Detonation was demonstrated over a temperature range of -60 to 160°F, but the test fixture did not allow complete evaluation. High temperature storage results in electrolyte gelling, but this could be prevented in reserve cells by storing the solvent system in a reservoir and having the electrolyte salts present in the separator.

14 KEY WORDS	LINK A		LINK B		LINK C	
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