UNCLASSIFIED

AD NUMBER
AD463556
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited. Document partially illegible.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; MAY 1965. Other requests shall be referred to Air Force Aeronautical Systems Division, Wright-Patterson AFB, OH 45433. Document partially illegible. This document contains export-controlled technical data.**
AUTHORITY
AFAPL ltr dtd 12 Apr 1972

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 463556

DEFENSE DOCUMENTATION CENTER
FOR
SCIENTIFIC AND TECHNICAL INFORMATION
CAMERON STATION ALEXANDRIA, VIRGINIA

DEPARTMENT OF DEFENSE

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY: DDC
AS AD No. 463556

463556

AVAILABLE COPY WILL NOT PERMIT
FULLY LEGIBLE REPRODUCTION.
REPRODUCTION WILL BE MADE IF
REQUESTED BY USERS OF DDC.

DDC
RECEIVED
JUN 1 1965
DDC-IRA E

AVAILABLE COPY WILL NOT PERMIT
FULLY LEGIBLE REPRODUCTION.
REPRODUCTION WILL BE MADE IF
REQUESTED BY USERS OF DDC.

7

LITHIUM ANODE LIMITED CYCLE BATTERY INVESTIGATION

Quarterly Technical Progress
Report No. 1
15 May 1965
Contract No. AF 33(615)-2455
Task 817304-20

Electrochemistry

Materials Sciences Laboratory

Lockheed Missiles & Space Company

Palo Alto, California

Prepared by:

H. F. Bauman, Staff Scientist
J. E. Chilton, Research Scientist
Materials Sciences Laboratory
Electrochemistry

Approved by:

G. B. Adams, Senior Member
Materials Sciences Laboratory
Electrochemistry

FOREWORD

The work described in this report was accomplished in the Electrochemistry group, Materials Sciences Laboratory, Lockheed Missiles & Space Company, Palo Alto, California, for the Aeronautical Systems Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(615)-2455, Task 817304-20. Mr. W.S. Bishop of the AF Aero Propulsion Laboratory is project engineer for the project. This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

AVAILABLE COPY WILL NOT PERMIT
FULLY LEGIBLE REPRODUCTION.
REPRODUCTION WILL BE MADE IF
REQUESTED BY USERS OF DDC.

LITHIUM ANODE LIMITED CYCLE BATTERY INVESTIGATION

Quarterly Technical Progress
Report No. 1
15 May 1965
Contract No. AF 33(615)-2455
Task 817304-20

Electrochemistry
Materials Sciences Laboratory
Lockheed Missiles & Space Company
Palo Alto, California

Prepared by:

H. F. Bauman, Staff Scientist
J. E. Chilton, Research Scientist
Materials Sciences Laboratory
Electrochemistry

Approved by:

G. B. Adams, Senior Member
Materials Sciences Laboratory
Electrochemistry

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Defense Documentation Center (DDC) (formerly ASTIA), Cameron Station, Bldg. 5, 5010 Duke Street, Alexandria, Virginia, 22314.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., for sale to the general public.

Copies of this report should not be returned to the Research and Technology Division, Wright-Patterson Air Force Base, Ohio, unless return is required by security considerations, contractual obligations, or notice on a specific document.

Foreign announcement and distribution of this report is not authorized.

The distribution of this report is limited because it contains technology identifiable with items on the Strategic Embargo Lists excluded from export or re-export under U.S. Export Control Act of 1949 (63STAT.7), as amended (50 USC APP 2020.2031), as implemented by AFR 400-10.

FOREWORD

The work described in this report was accomplished in the Electrochemistry group, Materials Sciences Laboratory, Lockheed Missiles & Space Company, Palo Alto, California, for the Aeronautical Systems Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(615)-2455, Task 817304-20. Mr. W.S. Bishop of the AF Aero Propulsion Laboratory is project engineer for the project. This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

ABSTRACT

This investigation of the lithium-cupric fluoride and lithium-cobaltic trifluoride electrochemical systems has as its goal the development of technology sufficient to build 1500 a-hr batteries with high (300 whr/lb) energy to weight figures.

Selected glass fiber filter paper appears to have suitable characteristics of resistance, absorption and retention to be useful in these batteries.

Polarographic and cell tests of cobaltic trifluoride cathodes indicate that the major electrical energy producing reaction is probably that of cobaltous ion to cobalt metal. The cobaltic ion reacts with cobalt metal to form the cobaltous ion. These reactions result in a plateau of about 2.7 watts rather than the theoretical 3.5 volts.

The cupric fluoride cathode appears at this time to be reduced to copper metal without intermediate voltage plateau. The problems associated with the cupric fluoride cathode are those of obtaining a proper electrode matrix for efficient electrochemical reduction.

TABLE OF CONTENTS

Section I

INTRODUCTION

This experimental investigation on high-energy battery development has the objective of development of a cell capable of meeting a specific space flight application. Cells with lithium anodes and cupric fluoride or cobalt fluoride cathodes are to be investigated on this program. Significant goals are a battery discharging between 22 and 30 volts within a temperature range of 30 to 100° F and delivery 300 watt hours/pound. A recharge and additional discharge are required from the battery.

Presently available primary batteries will deliver about 100 watt hours/pound during discharges suitable for space applications. This is about 50% of the theoretical energy available from this system (Ago-Zn). The theoretical energy of the Li-CuF_2 couple is 746 watt hour/pound and of the Li-CoF_3 couple 970 watt hours/pound. Achievement of the goals of this project would triple the useful flight time of space vehicle using a primary battery power system, or allow the equivalent increase in instrument load weight.

Section II

SUMMARY

A variety of materials of possible use as separators for nonaqueous electrochemical cells have been characterized by resistance, absorption, and retention values. Glass fiber paper is available which has a combination of desirable characteristics.

Polarographic and cell tests of the CoF_3 electrode indicate that the major electrochemical reaction is probably the reduction of Co^{++} to cobalt metal. The Co^{+++} reacts with the metal to form Co^{++}. This accounts for the lower plateau voltage under load than expected by the 3.5 volt open circuit voltage and the open circuit voltage of 2.6 obtained when a discharge is interrupted.

The reaction at the CuF_2 cathode has not been entirely characterized; however, the consistent open circuit after discharge of over three volts and the detection of copper in the discharged cathode indicate the reduction of cupric fluoride to copper as the major step.

Section III

EXPERIMENTAL WORK AND DISCUSSION

3.1 SEPARATOR STUDY

The separator is an electrochemical cell serving the dual purpose of keeping the two electrodes separated while simultaneously allowing penetration by the electrolyte so that an ionic conducting path may exist between the electrodes. The mechanical separation between the cells must be sufficient to prevent shorting; the ionic conducting path should be of as low a resistance as possible. The resistance of the separator increases with the thickness and decreases as the porosity becomes greater, porosity here being considered as that area of the separator that allows ionic conduction. In cells where the electrolyte does not directly enter the electrode reactions, the thinnest separator with the maximum porosity will give the lowest resistance and have the lowest power loss during discharge.

The separator resistance was measured in a fixture with the flooded separator held between two silver-faced pistons in a teflon tube. The dry and wet thickness of the separator was also measured in this fixture with the aid of a surface plate and a dial indicator. Because of the large faces and close spacing of the electrodes in the fixture, a capacitative element was introduced into the measurement. The series capacitance C_s and dissipation factor D are measured with an AC bridge. From these data, the resistance R per circular inch of the material is calculated by the following formula:

$$R = \frac{D}{2\pi C_s}$$

A sodium hexafluorophosphate solution (0.8 moles/liter) in propylene carbonate (PC) was used for electrolyte in this test. It was prepared from commercial solvent without dehydration and had a resistance of $7 \times 10^{-3}\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

Two other characteristics of separators are important for cells that are to operate in space vehicles. These are the absorption of electrolyte by the separator and its retention during acceleration. Sufficient absorption and retention will maintain electrolyte between the electrodes so that normal discharge will continue during the environmental conditions encountered in such applications. The methods for measuring these characteristics are similar to those suggested for separators for alkaline silver oxide-zinc batteries.[1]

---

[1] J.E. Cooper and A. Fleischer, eds., Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries, AF Aero Propulsion Laboratory, n.d.

The absorption is measured by immersing the sample in electrolyte and soaking, wiping off, and weighing. The weight of the absorbed electrolyte (difference between wet and dry separator weight) divided by the dry separator weight is given as the absorption figure.

The retention was measured by placing the separator sample, supported by a screen in a fixture (Figure 1), and placing it in a centrifuge. The fixture was rotated at a speed to subject it to an acceleration 25 times gravity and maintained at that speed for two minutes. The sample was then removed from the fixture and weighed and the retention represented as a percentage of the absorbed electrolyte retained after centrifugation.

The resistance, absorption, and retention measured for a variety of separator materials are given in Table I. Absorption and retention are similar to those measured with aqueous electrolytes although the higher absorption values were measured with separators for aqueous electrolytes. The glass fiber felts still appear to have the best combination of favorable characteristics for use in nonaqueous cells.

3.2 COBALT TRIFLUORIDE (CoF_3) CATHODE STUDY

3.2.1 Polarographic Study

The study of reactions of cathodic materials such as CoF_3 and CuF_2 is of interest in establishing the reaction path, the reversibility of electrode reactions, and reactant-electrolyte interactions. A polarographic study of the reduction of cobalt and copper salts was conducted by the use of a Sargent Model XV Recording Polarograph with a rotating platinum microelectrode for the working electrode. The reference electrode was constructed from a silver screen which was suspended in one chamber of an H cell and connected to the other chamber containing the Pg microelectrode by a tube with a glass frit. After introduction of the electrolytes into the H cell, oxygen was removed from the working electrode chamber by bubbling argon through the system and a slow stream of oxygen was used during the polarographic run to prevent resolution of oxygen or water. An oxygen reduction peak was found at -0.33 volt for the IM $NaPF_6$-dimethyl sulfoxide electrolyte used in these studies which was removed by argon bubbling.

The studies were performed with dimethyl sulfoxide (DMSO) systems since it is superior to propylene carbonate as a solvent for ionic salts. Solutions of CoF_3 and $CoCl_2$ were prepared. The CoF_3 as received was a brown powder which formed a pink solution in DMSO although of very low solubility. The $CoCl_2$ hydrate was reacted with thionyl chloride to form a dark blue powder. A 0.03 M solution in DMSO was of a deep blue color.

The solubility of $CoCl_2$ was determined by titration of chloride ion by the modified Volhard technique. CoF_3 also reacts with potassium iodide to form iodine; however, none was found in soluble form and the pink color found in CoF_3-DMSO solution is due to Co^{+2}-water impurity. Addition of water to $CoCl_2$-DMSO solution changed the solution color from blue to pink. Addition of LiF powder to CoF_3-DMSO solution did not increase the solubility of the Co species indicating no stable fluoride ion

Table 1 Characteristics of Separator Material

Material	Identi-fication	Thickness		Resistance (ohm/in.^{2})	Absorption	Retention (%)
		Dry (in.)	Wet (in.)			
Membrane Filter	6424	.027	.027	7.3	6.10	100
Membrane Filter	6429	.027	.029	8.8	5.33	80
Glass Fiber Paper	Type G	.040	.039	7.3	6.06	85
Glass Fiber Paper	Type E	.020	.019	3.0	8.70	98
Glass Fiber Paper	Type A	.025	.024	3.8	4.03	95
Glass Fiber Paper	231	.011	.011	2.5	7.43	90
Glass Fiber Paper	221	.003	.003	13.	4.03	54
Glass Fiber Paper	122	.005	.005	3.3	2.22	56
Polyolefin Film, Porous	H1250	.032	.032	6.9	1.03	78
Polyolefin Film, Porous	14PN	.010	.011	1.8	2.09	99
Polycarbonate Film	-	.006	.006	21.5	.093	53
Polycarbonate Film	-	.002	.002	4.1	.140	85
Cellulosic Gauze	478	.006	.006	10.7	1.12	98
Cellulosic Nonwoven	R2201	.005	.004	4.73	10.1	60
Polyester Nonwoven	EM345	.004	.004	7.7	.018	55
Polyester Nonwoven	EM346	.005	.005	17.	.080	54
Polyester Nonwoven	EM343	.004	.004	20.4	.440	95
Polyolefin Nonwoven	SM91	.006	.006	14.4	1.62	94
Polyolefin Nonwoven	EM476	.004	.004	4.4	.993	98
Cellulosic Paper	705-C	.003	.003	3.9	.037	100
Acrylic Paper	922D	.007	.007	6.0	.205	99
Acrylic Paper	922B	.010	.010	7.2	.375	99
Cellulosic Film	300	.001	.001	122.	.100	58
Cellulosic Film	600	.001	.001	202.	.183	68

complex compound formation in the system. The dimethyl sulfoxide used in solution preparation was vacuum distilled and had a specific conductivity of $5 \times 10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$. The base electrolyte was formed by addition of $NaPF_6$ obtained from Ozark-Mahoning to DMSO forming a 1M solution. The final electrolyte contained traces of water from either the $NaPF_6$ or absorbed during make-up. The results of the polarographic tests are summarized in Table II.

Table II Polarographic Test Data

Cell: Ag, Ag^+ | $NaPF_6$-DMSO | Platinum Microelectrode

Material	E 1/2 Half wave potential	n electrons/mole reaction	Waves
CoF_3	None obtained	–	–
$CoCl_2$	0.02	2	One, diffusion current id proportional to concentration

The number of electrons per mole of reaction was calculated from the polarographic voltage-current curves by the following expression for a reversible wave:

$$E_{i=3/4\ id} - E_{i=1/4\ id} = \frac{0.056}{n}$$

No waves were obtained with the CoF_3 system since it was not soluble in either the DMSO or LiF-DMSO solutions. A reversible reduction wave was obtained for $CoCl_2$ indicating reaction to form cobalt metal. An aqueous Ag, Ag^+ | Co, Co^{+2} cell would have a voltage of 1.07 volts at unit activity. The nonaqueous $CoCl_2$-DMSO solution contains cobalt-chloro complex ions which would yield a potential differing from aqueous systems. Although $CoCl_2$ would be an excellent cathode material, the solubility of $CoCl_2$ in DMSO would preclude its use in nonreserve type cells.

3.2.2 Lithium-Cobalt Trifluoride Cell Tests

A cell composed of lithium metal and cobalt trifluoride has been of interest to the high energy density nonaqueous battery program because of its high values of theoretical energy density 940watt hour per pound and high theoretical cell voltage, 3.5 volts. These values were obtained by assuming the reaction to be production of cobalt metal and lithium fluoride. A summary of possible reactions of the cobalt fluorides with lithium is presented in Table III.

Table III Reactions of Lithium and Cobalt Fluorides

Reaction	Standard Free Energy Change	Theoretical Energy Density	Theoretical Cell Voltage
1) $3Li + CoF_3 = 3LiF + Co$	-244.1	940	3.54
2) $2Li + CoF_2 = 2LiF + Co$	-131.0	620	2.84
3) $Li + CoF_3 = LiF + CoF_2$	-113.1	484	4.90
4) $Co + 2CoF_3 = 3CoF_2$	- 95.2	214	2.06

Cobalt trifluoride has been found to be essentially insoluble in propylene carbonate solutions of $NaPF_6$ and PC solutions saturated with LiF. Tests of solubility of CoF_3 in both nitromethane and in dimethyl sulfoxide indicate that Co^{+3} solubility is below the detection point by reaction with potassium iodide. The analytical procedure for the determination of CoF_3 is based on the following reaction:

$$2CoF_3 + 3KI = 2CoF_2 + KI_3 + 2KF$$

The iodine which is formed is determined conveniently by titration with standard sodium thiosulphate with a soluble starch endpoint. Experimental cells have been formed with lithium anodes prepared by rolling lithium metal onto nickel or silver screen, and with CoF_3 cathodes pasted on silver or nickel expanded metal with acetylene black or cobalt metal powder for electronic conduction. The pasting has been done with either toluene or with propylene carbonate without use of a binder. Cells were formed with two lithium electrodes placed around a single cobalt fluoride electrode and with glass fiber mat separators around each electrode. A reference electrode composed of lithium formed on metal screen was inserted between the lithium and CoF_3 electrodes. The cells were placed in a polyethylene container, the electrolyte added, 1 molar propylene carbonate-$NaPF_6$ solution, and the cells compressed with plastic blocks. The runs were conducted in an argon atmosphere dry box in order to minimize the inclusion of water. The results of the cells tests are summarized in Table IV.

Each cell contained electrodes prepared with 90% CoF_3 + 10% acetylene black, except for cell 131 which was prepared with 66% CoF_3 + 33% Co powder. Electrodes used in cells 129 through 131 were pasted with a dried toluene vehicle, vacuum dried at 100° C to remove toluene, and finally heated over argon at 200° C. Electrodes used in cells 136 and 137 were prepared with vacuum distilled propylene carbonate as the vehicle for pasting and used in the cell without drying. The efficiency of the cathodes was calculated from the ratio of the AH capacity obtained above 2 volts to the amount of the CoF_3 in the electrode expressed in ampere hours for two equivalents per mole

Table IV Lithium-Cobalt Trifluoride Cell Tests

Cell No.	OCV	Current (ma)	Area (cm)	Initial V*	Capacity to 2 V	Efficiency (%)
129	2.8	6	40	2.6	0.003 AH	0.3
130	3.5	6	40	3.3	0.006 (drop to 2 V plateau)	1.5
131	3.4	6	40	3.3	0 (immediate drop to 1.3 V plateau)	0
136	–	6	58	2.6	0.008	8
137	–	6	58	2.6	0.012	12

---

*Reference to cathode.

reaction. The final OCV of cells after run was initially 1.0 volts and rose to 2.6 V after 72 hour stand. For purposes of the efficiency calculations it was assumed that the cells spontaneously reacted CoF_3 with formed Co to make CoF_2 and electrochemically reacted the CoF_2 to form the final Co metal product. In all cases except 131, in which no test was made, the existence of cobalt metal as an end product was demonstrated by the presence of magnetic black solid material which was separated from the electrodes after the run.

Analysis of extra electrodes prepared with those which were run in the cells indicated that loss of CoF_3 occurred during the forming and drying operations. CoF_3 is reactive with traces of water, forming the CoF_2, HF, and oxygen. The initial open circuit voltages of 3.5 volts measured indicate that reaction 1 could occur. However, on passage of current and formation of cobalt metal, the cell potentials fall to 2.4 volts or less and after run rise to 2.6 volts, a value close to that which would be expected from reaction 2. This sequence of cell potentials could be due to the spontaneous reaction of CoF_3 with Co as outlined by reaction 4 and the following electrochemical reaction of CoF_2 to form more cobalt metal as a final product. The fact that no observation of cells with 4.9 volts has been made indicates that reaction 3, the electrochemical reaction of lithium and CoF_3 to form CoF_2 does not occur. These studies have been conducted with cells run at constant current and observations of the cobalt trifluoride electrode voltage versus lithium reference have been made as a function of time.

3.3 CUPRIC FLUORIDE CATHODE STUDY

3.3.1 Polarographic Study

By the techniques discussed in section 3.2.1 a polarographic study was made of CuF_2 and $CuCl_2$. The CuF_2 was used as received and was a grey-white powder which formed a light blue-green solution in DMSO and had a concentration of 0.07 M when saturated. The $CuCl_2$ was prepared as a golden brown powder by reaction of the hydrate with thioryl chloride. Its solution in DMSO was yellow-green and contained 0.15 M of the salt when saturated.

The concentration of soluble copper species was determined by reaction with potassium iodide and titration of the resulting iodine with standard sodium thiosulfate solution.

A summary of polarization data obtained with these solutions is shown on Table V.

Table V Polarographic Test Data

Cell: Ag, Ag^+ | $NaPF_6$-DMSO | Pt Microelectrode

Material	E 1/2 Half wave potential	n electrons/mole reaction	Waves
CuF_2	0.24	1	One, id proportional to concentration
$CuCl_2$	0.05, 0.45	1, 1	Two, id proportional to concentration

Two polarographic waves were noted in the reduction of $CuCl_2$ to form copper metal (visually observed on the platinum). Each wave was reversible with a single electron transfer. Aqueous cells with copper ions -Ag, Ag^+ | Cu^{+2}, Cu^o and Ag, Ag^+ | Cu^{+1}, Cu^o yield theoretical voltages of 0.46 and 0.28 volts respectively which are close to the values measured for half wave potential for the $CuCl_2$-DMSO system 0.45 and 0.05 volts respectively. Two waves may be obtained for $CuCl_2$ systems if CuCl is a stable compound and does not disproportionate. The following reactions are not thermodynamically feasible:

$$2CuCl_c \rightarrow CuCl_{2c} + Cu^o \qquad \Delta F = +15 \text{ kcal/mole}$$

$$2CuCl_c \rightarrow Cu^{+2}_{aq} + 2Cl^-_{aq} + Cu^o \qquad \Delta F = +10 \text{ kcal/mole}$$

Only one polarographic wave was obtained from the polarographic reduction of CuF_2 to form (visible) copper metal. If the reduction were reversible with one electron exchanged per mole of reaction, then cuprous fluoride would be formed and by spontaneous disproportionation be converted into CuF_2 and copper metal. This reaction of cuprous fluoride is feasible with the following reactions:

$$2CuF_c \rightarrow CuF_{2_c} + Cu^o \qquad \Delta F = -7 \text{ kcal/mole}$$

$$2Cu^+ \rightarrow Cu^{+2} + Cu^o \qquad \Delta F = -8 \text{ kcal/mole}$$

and CuF_2 in DMSO could react similarly.

If the single wave noted for CuF_2 reduction is considered to be an irreversible wave, the following voltage-current dependent equation is applicable:

$$E_{i=3/4\ id} - E_{i=1/4\ id} = \frac{0.054}{\alpha n}$$

where α is the electron transfer coefficient (usually 0.5). An αn value of 1 would indicate an n value of 2 for an α value of 0.5 and the reduction of CuF_2 in DMSO to form copper metal would be represented as irreversible. Irreversible polarographic waves are obtained when the rates of the forward (cathodic) and reverse reactions are appreciably different, the reverse rate being very small.

Which mechanism is operable for CuF_2 reduction is not apparent from polarographic data which have been taken. If CuF_2 were reversibly reduced to CuF with subsequent reaction to form Cu^0 and CuF_2, then CuF_2 would be a preferred electrode material since a cell using CuF_2 would have a single discharge potential.

A study of polarization obtained with solid electrodes is necessary to determine if reversible reduction occurs with cathodic materials which are insoluble in selected electrolyte.

3.3.2 Cupric Fluoride Electrode Cell Studies

Cathode mixtures have been prepared with 60-40 and 70-30 cupric fluoride to silver flake ratio. In addition, a 70-28 ratio mixture was prepared with 2% acetylene black added. All were prepared from screened CuF_2 and ball milled for 16 hours except for the last mix which was ball milled for 4 hours. A paste was prepared with dried toluene and the ball milled mix, pasted on copper expanded mesh, and then dried at 100° C for 30 minutes and 200° C for 60 minutes in flowing argon.

The electrodes as prepared showed poor adhesion but were tested in polyethylene bag type cells as shown on Figure 4. Inconsistent results were obtained and the test will be repeated. The bag type cells were assembled in polyethylene bags and hot roll sealed with polypropylene wax. This design has not been completely proven but shows promise of a much simplified cell assembly for test cells.

One cause of inconsistent results may be uneven heating in the electrode container because of the argon flow as well as uneven heat concentrations by the heating elements. The heating zone of the furnace was enlarged to entirely cover the electrode container. The electrode container itself is an Inconel pot with a removable "O" ring sealed cover which has a removable water cooling coil to protect the "O" ring from elevated temperatures. The container is of a size to allow it to be passed into the dry box for loading and unloading. The equipment used for cathode baking is shown on Figure 2.

3.4 LITHIUM ELECTRODE STUDIES

A test fixture, shown on Figure 3, was prepared for the evaluation of lithium anodes as well as prepared cathodes that allowed the use of reference electrodes with both cell electrodes. It consisted of a polypropylene block with cavities on both sides to hold electrodes and connected by a substantial electrolyte chamber. Both shoulders holding the electrodes in place were drilled at 45 deg for Lugin capillaries connecting to reference electrode chambers. This block cell was assembled in the dry box with appropriate electrodes and placed in a commercial Pyrex fitting which was closed by an "O" ring gasketed teflon plate holding feed through electrical connections. This assembly could then be removed from the dry box for test.

Lithium wire was used as the reference electrode. Sheet lithium rolled on expanded silver mesh was used for preliminary runs with a PC-$NaPF_6$ electrolyte. In the first tests, slightly higher polarization values were measured than had been previously recorded.[2] This could be the result of the film on the lithium caused by higher water content than normal in the assembly dry box, or by water in the electrolyte. Subsequent runs will include reruns with the PC-$NaPF_6$ electrolyte as well as with other solvent solute combinations.

---

[2] AF33(657)-11709 Final Report 1964

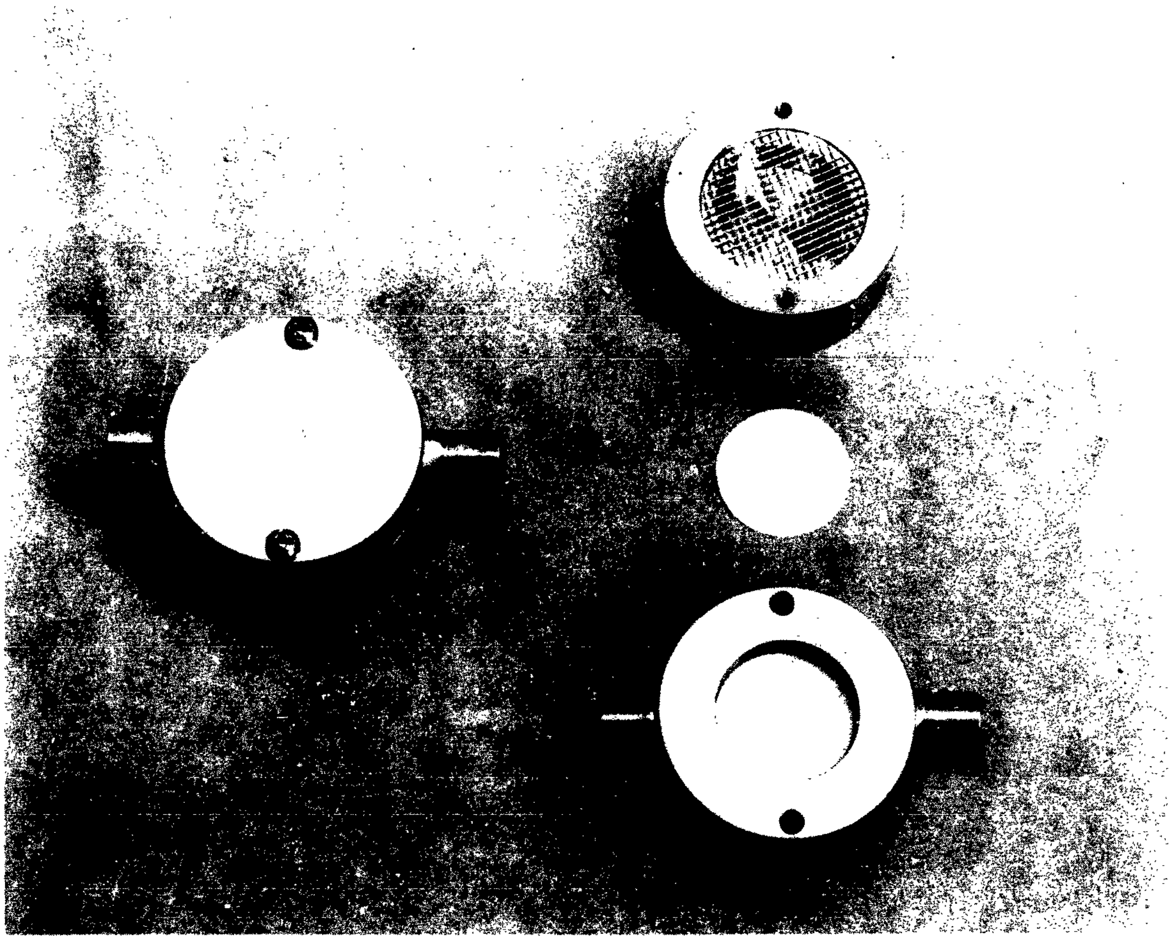

Fig. 1 Electrolyte Retention Fixture

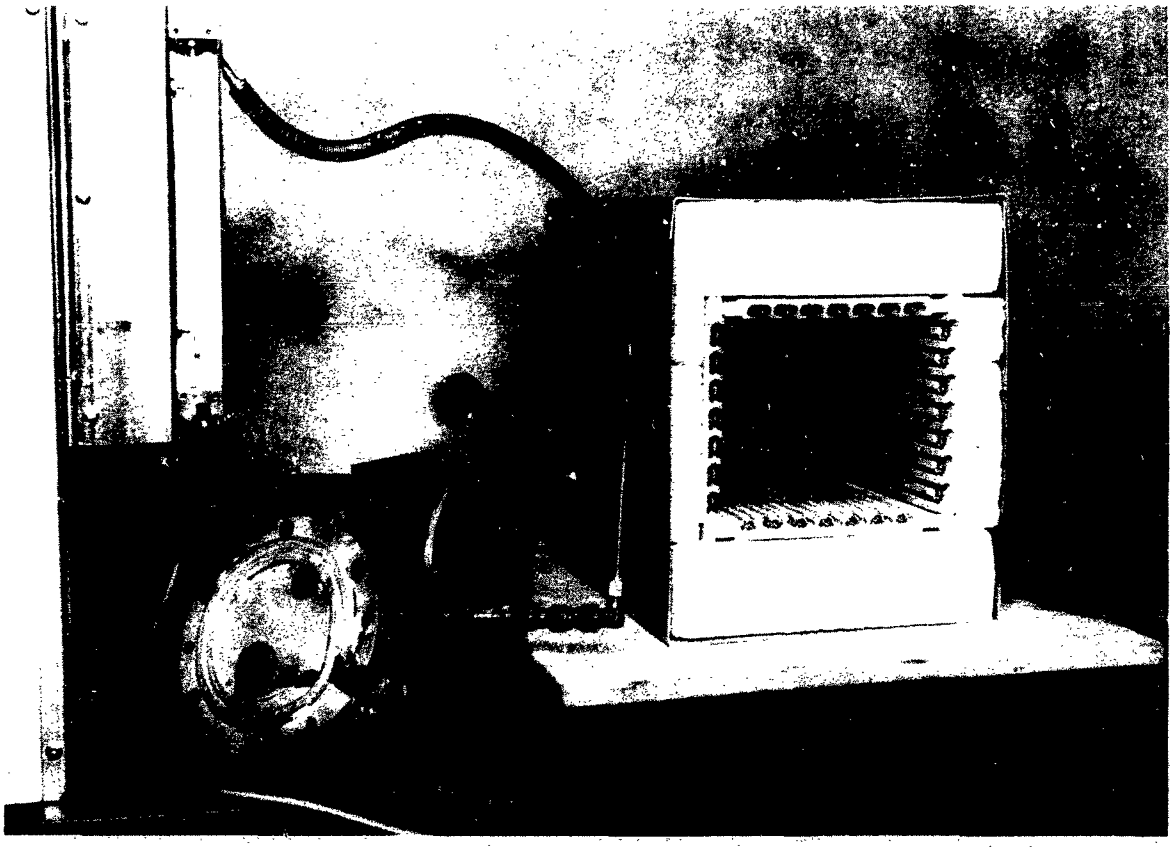

Fig. 2 Cathode Preparation Container and Oven

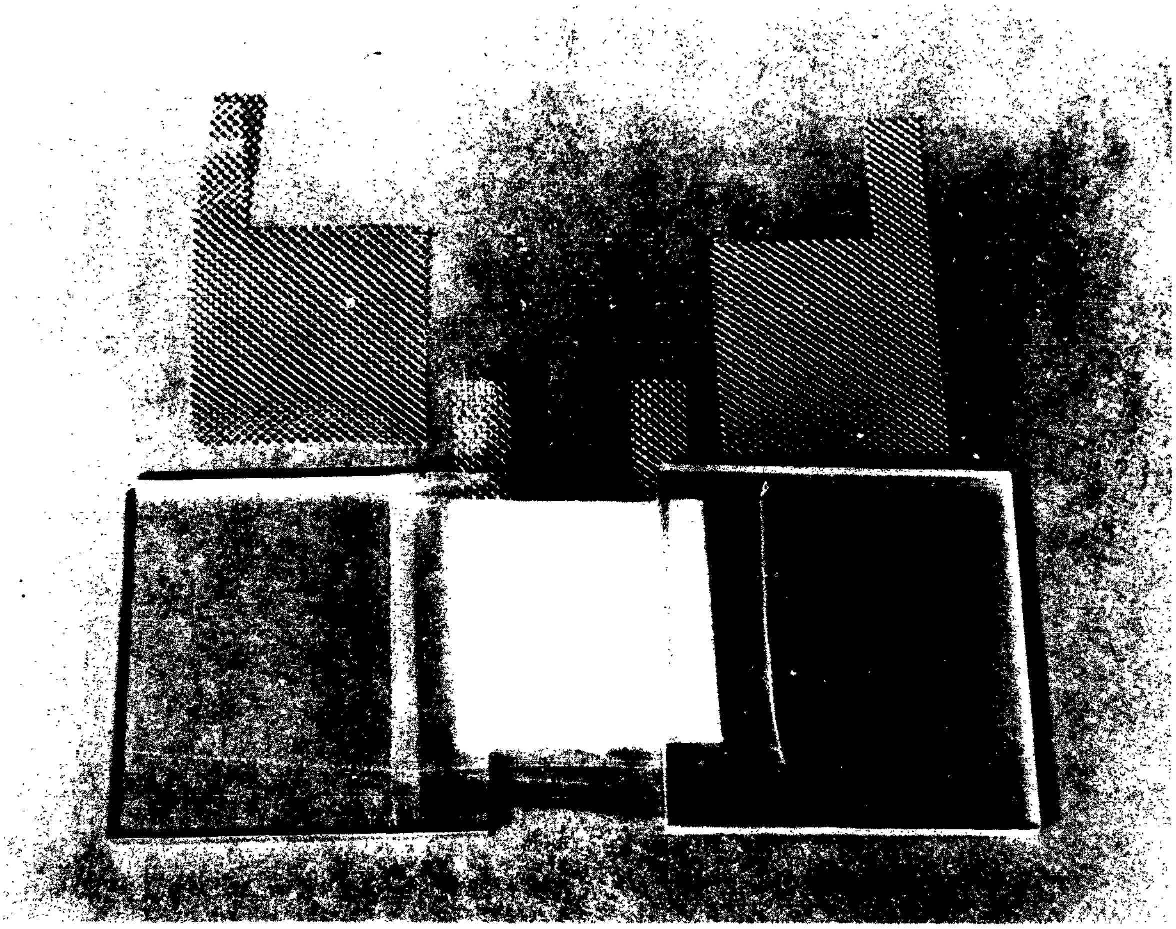

Fig. 4 Bag Type Test Cell

Section IV

FUTURE WORK

Work next quarter will include the following studies:

1. Further study of the CoF_3 cathode to determine utilization and reduction of polarization.
2. Study of the CuF_2 cathode to better determine its reaction and increase its efficiency.
3. Study of lithium dispersion electrodes and the effect of etching on the anode.
4. Preparation and study of electrolytes prepared from butyrolactone, dimethyl-sulfoxide, and diethyl carbonate with complex fluorine salts. The goal of this study is reduced resistance of the electrolyte while retaining other necessary qualities for cell use.