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NEW CATHODE-ANODE COUPLES USING NONAQUEOUS ELECTROLYTE

QUARTERLY TECHNICAL PROGRESS REPORT NO. 2



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NEW CATHODE-ANODE COUPLES USING NONAQUEOUS ELECTROLYTE

QUARTERLY TECHNICAL PROGRESS REPORT NO. 2

**Electrochemistry Laboratory
Material Sciences Laboratories
Lockheed Missiles & Space Company
Palo Alto, California**

WORK CARRIED OUT UNDER CONTRACT NO. AF 33(616)-7957

PROJECT NO. 8173, TASK NO. 817304-10

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FOREWORD

This report was prepared by the Electrochemistry group, Materials Sciences Laboratory, Lockheed Missiles & Space Co., Palo Alto, California, for the Aeronautical Systems Division, U. S. Air Force, Wright-Patterson AFB, Ohio, under Contract No. AF 33(616)-7957, Task No. 817304-10. The project is under the guidance of Mr. W. S. Bishop of the Flight Accessories Laboratory, who is project engineer.

The work covered by this report was done under Air Force Contract, but this report is being published and distributed prior to Air Force review. This publication, therefore, does not constitute approval by the Air Force of findings or conclusions contained herein. It is published for exchange and stimulation of ideas.

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Section 1
INTRODUCTION

Improved batteries for flight in satellites may be obtained by using cells composed of new cathode-anode couples with nonaqueous electrolytes that have specific energy values and long cycle life. This work is concerned with the study of a lithium-silver chloride cell with theoretical values of 240 w-hr/lb and 3.0 v open-circuit cell voltage. In order to increase the output of the cell, studies of cell materials, methods of fabrication, and improved electrolytes are being made. Previous work performed under this contract and an outline of the basic program have been summarized in Quarterly Report 1, dated January 1963.

The present report describes the work completed during the first quarter of 1963 and includes the results of charge-discharge tests of single cells, investigation of anode and cathode processes, and preliminary design of larger cells.

Section 2 WORK DISCUSSION

2.1 CATHODE STUDIES

Further studies were carried out in order to determine the greatest amount of silver chloride that would be useful on the cathode. It should be possible to determine in this manner the optimum composition and thickness for the electrodes that would be used in the final prototypes. In order to properly make these determinations, it was necessary to carry out further experiments with various silver-chloride and graphite concentrations and to study the effects of varying the thickness of the electrodes under consideration.

2.1.1 Silver-Chloride Concentration

Cathodes were fabricated keeping the ratio of graphite to silver constant while varying the silver-chloride concentration. (The silver-chloride content ranged from 18.6 percent to 31.3 percent by weight of the cathode mix.)

Previous studies indicated that with higher silver-chloride concentrations, current efficiency decreased. In the present studies, thin electrodes were used (0.12g/cm^2). With these electrodes, no apparent relationship was found between silver-chloride concentration and percent utilization. The average utilization was 42.5 percent with 20 percent voltage variation and 65.1 percent utilization for an end voltage of less than 0.5 v. Polarization experiments were conducted with these cells. Figure 2-1 shows experiment results for two cells of very different silver-chloride concentrations, second cycle. Note that cell polarization can be explained in terms of cell resistance (IR drop) up to a current density of nearly 30 ma/cm^2 . Because of the small amount of active material used, the experiment was not continued to higher current densities.

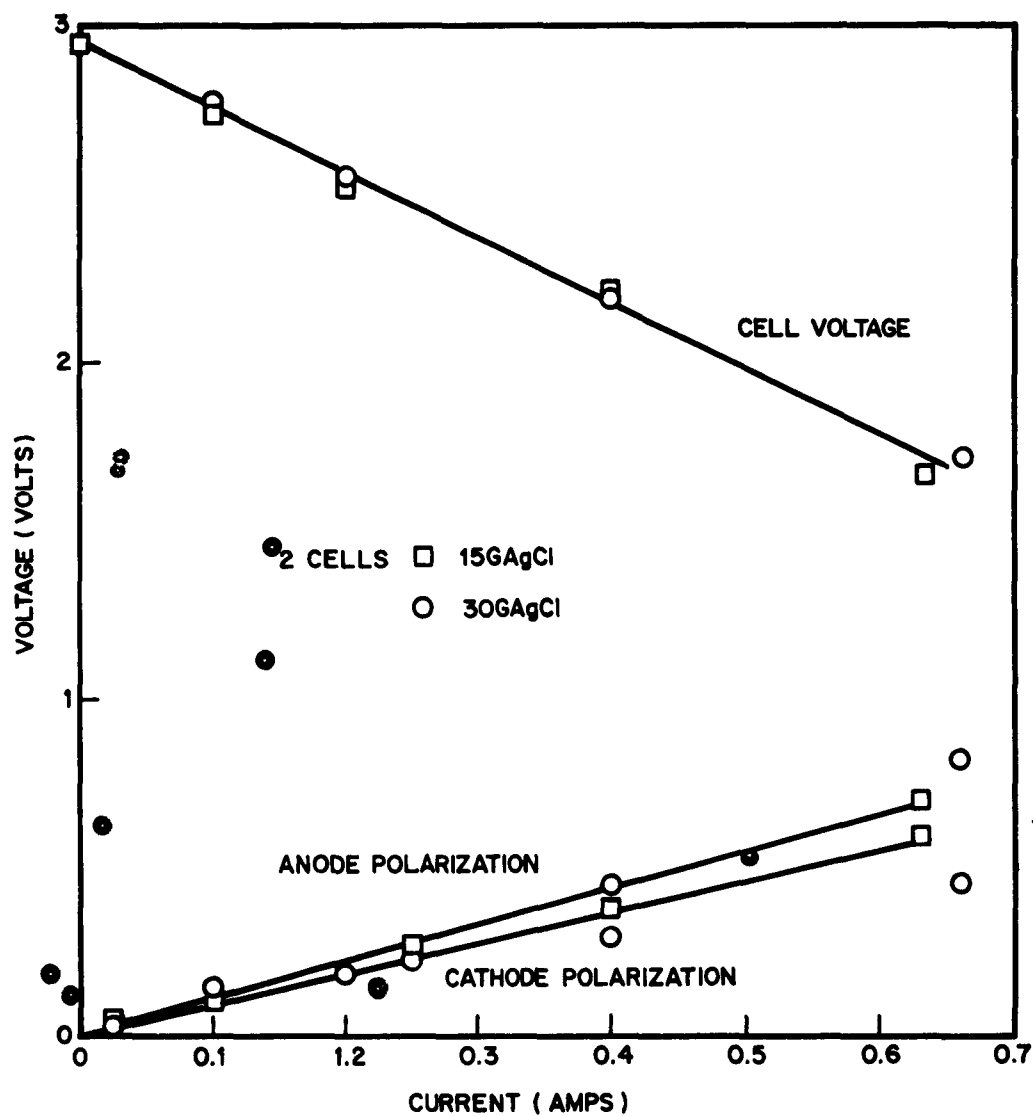


Fig. 2-1 Discharge Characteristics for a Lithium-Silver Chloride Cell

2.1.2 Graphite Concentration

Graphite is used in the cathode as an expander and a light-weight electronic conductor. Investigations were directed primarily at the first discharges. Electrodes were prepared that contained from 11 percent to 38 percent graphite (by volume) of the raw materials. These electrodes were thin (0.12 g/cm^2). The ratio of silver-chloride to silver was held constant, so that as the amount of graphite was increased, the amount of silver-chloride decreased.

The first discharges indicated that the availability of the silver-chloride was approximately the same in all cases. The extent of discharge, compared to that calculated, indicated yields of 40 percent for a 20 percent voltage drop to about 75 percent for an end voltage less than 0.5 v. Polarization measurements showed no differences in the cathode for the third discharge cycle. Another type of experiment was carried out to determine how well these cells would perform under typical conditions. They were charged at 5 ma/cm^2 for 35 min with the voltage limited to 4.5 v and discharged at 5 ma/cm^2 until the voltage dropped 30 percent (15 percent voltage regulation). Three cycles were run at two of the graphite concentrations with no appreciable differences. The resulting current efficiencies were found to range between 70 and 80 percent.

2.1.3 Addition of Silver Metal

It was thought that the addition of metallic silver with large particle size compared to the AgO powder might produce a more open structure that would allow greater utilization of silver-chloride in thick electrodes. The mix used was 25 parts silver-chloride, 25 parts silver oxide and 50 parts silver metal, all by weight. Three types of metal were used: (1) precipitated powder -150 + 200; (2) spherical silver; and (3) flake silver. Figure 2-2 represents the data obtained as compared to electrodes of the following composition: (4) 30 parts silver-chloride, 60 parts silver oxide, 10 parts graphite; (5) 30 parts silver-chloride and 60 parts silver oxide. The figure shows that the addition of graphite is preferable.

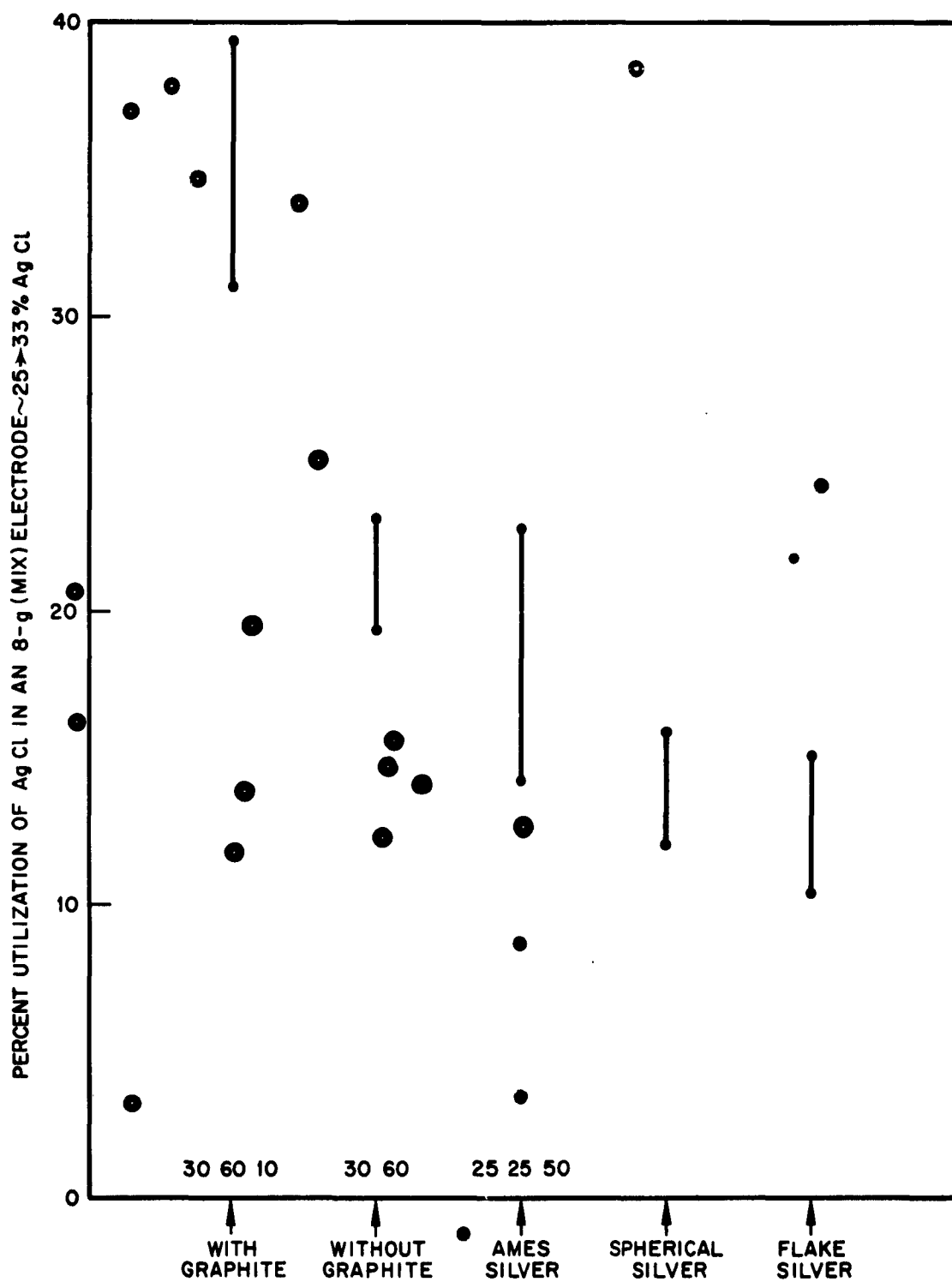


Fig. 2-2 Utilization of AgCl in Various Electrodes

2.1.4 Cathode Thickness

Using the previous information as a basis, it was decided to study the effect of electrode thickness upon utilization of silver-chloride in the cathode. The mixes used were Nos. 4 and 5, mentioned above. It had been found that with thin electrodes, these mixes gave good utilization; and that with somewhat thicker electrodes, the graphite was preferable to silver metal. Figure 2-3 is a plot of the amount of silver-chloride consumed as a function of the amount present in the electrodes themselves. The dotted line indicates 50 percent utilization or 100 percent if both sides of the cathode were to be used. The lower ends of the vertical lines indicate the utilization for a 20 percent drop in voltage; the upper end indicates utilization for an end voltage below 0.5 v. Note that addition of graphite results in greater utilization of silver-chloride. The technique used on each electrode is important; that is, graphite opens the structure, and proper pasting technique will give a less dense cathode.

The preceding study indicates that to date, the cathodes were prepared from the mix using silver-chloride, silver oxide, and graphite. Figure 2-3 indicates that the cathode should contain between 1 and 2 gm of silver-chloride ($1/4$ to $1/2$ gm/in²) for maximum available active material per unit area and weight. This presupposes a technique equivalent to the best used to date. The electrolyte used in all of the preceding experiments was the standard electrolyte.

2.1.5 Effect of Electrolyte on AgCl Utilization for First Discharges

In general, the cathodes used were the 30-60-10 mix with 0.44 gm silver-chloride per in². From Fig. 2-3 the percent utilization with standard electrolyte is in the neighborhood of 25 percent. Using an electrolyte consisting of 100 ml propylene carbonate, 3-gm aluminum chloride, and 8-gm lithium perchlorate, utilization to a 20 percent drop is about 20 percent and 35 percent to an end voltage below 0.5 v. If the electrolyte consists of 100-ml propylene carbonate, 6-gm aluminum chloride, and 8-gm lithium chloride, the percent utilization climbs to 47 percent and 55 percent. With an electrolyte consisting of 100-ml nitromethane, 20-gm aluminum

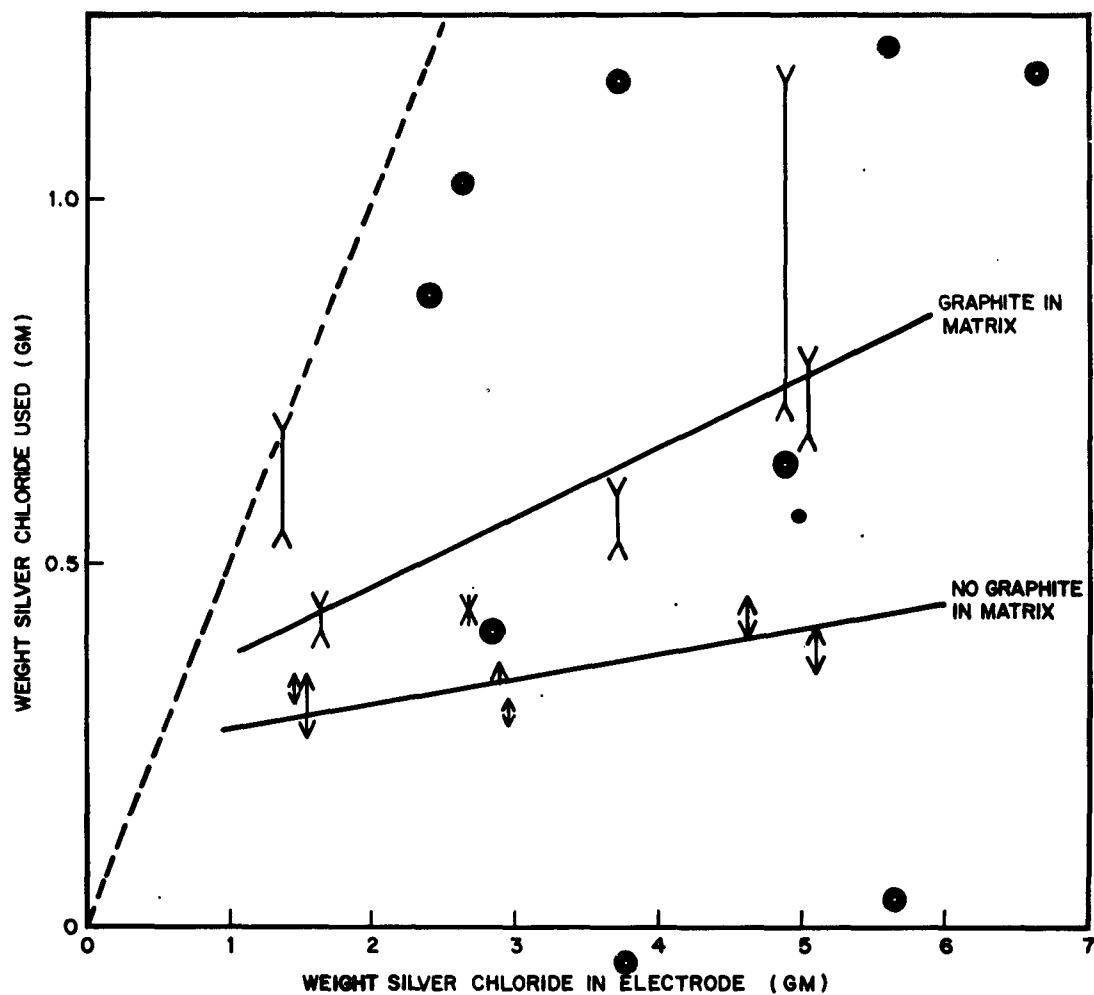


Fig. 2-3 Silver-Chloride Concentration Effect on Utilization

chloride, and 6-gm lithium chloride, the corresponding utilization figures are 35 percent and 70 percent. In the last two cases, electrodes were run that contained more silver-chloride (increased thickness). The second used an electrode containing 25 percent more silver-chloride, and the third (nitromethane solvent) used an electrode containing twice the amount of silver-chloride. In both of these cases, no reduction in the percent utilization of silver-chloride was found. Indeed, both had higher percentages than any of the corresponding cathodes of lesser thickness. This study emphasizes the fact that the electrolyte, as well as the electrode, must be considered when determining the extent of utilization possible.

2.1.6 Anodic Oxidation of Silver in Nonaqueous Solution

The anodic oxidation of silver was studied in both the propylene carbonate (PC) and nitromethane (NM) systems and the results are summarized in Table 2-1.

Table 2-1
ANODIC OXIDATION OF SILVER IN SELECTED SYSTEMS

	Solution			Current Efficiency (Percent)	Adhesion	Remarks
	LiClO ₄	AlCl ₃	LiCl			
PC* 100 ml	8	0	0	0	—	Soluble AgClO ₄ Formation
*Propylene Carbonate	8	1	0	—	poor	AgCl deposit in solution
	8	2	0	—	fair	
**Nitromethane	8	3	0	100	good	pale-white color
	8	10	0	100	good	
	4	10	2.7	100	good	
	0	10	5.4	100	good	
NM** 100 ml	8	0	0	0	—	soluble AgClO ₄ formation
	0	3	0	100	good	dark-gray color
	8	3	0	100	good	dark-gray color

The LiClO_4 propylene carbonate and LiClO_4 nitromethane solutions produced soluble AgClO_4 as the silver oxidation product and, because of the soluble cathode material, these solutions containing LiClO_4 alone cannot be used in a secondary battery. By addition of AlCl_3 to the LiClO_4 solutions, the silver oxidation forms silver-chloride with good adherence in the 3 gm AlCl_3 or more concentrated systems. AgCl produced in the PC system is white or light-gray in color while AgCl produced from the NM systems is dark-gray or purplish in color. Measurement of the amount of AgCl produced when the deposit was adherent was done by determining the weight gain of the silver anode. This measurement was complicated by solvent adsorption even after washing the deposit with acetone and water. In all cases, the theoretical amount of silver was oxidized as noted by measuring the total weight loss of the silver anode after dissolving the AgCl deposit in an ammonia solution.

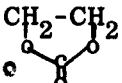
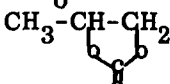
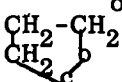
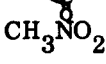
2.2 ANODE STUDIES

Irreversibility of cycled cells and increase in anode polarization after long periods of charge-discharge cycling indicate need for a study of processes occurring at the lithium anode and, in particular, the lithium electrodeposition process.

2.2.1 Lithium Deposition From Mixed Solvents

The deposition of lithium metal on silver cathodes from selected nonaqueous solutions was studied in order to ascertain current efficiency for deposition and the form and adherence of the lithium particles obtained. Using the standard propylene carbonate electrolyte, the electrochemical reversibility of the lithium deposition reaction has been shown to be 100 percent, but the adherence of the metal particles has been poor. Loose metal particles not electrically in contact with an anode structure cannot be used in the cell reaction because utilization of the particles during discharge will be poor and electrochemical efficiency will be low. Thus, a study was made of the effect of change in solvent composition on the adherence of the lithium. The physical properties and chemical structure of several solvents are listed in Table 2-2.

Table 2-2
SOLVENT PROPERTIES (25° C)

Solvent	Melting Point ° C	Boiling Point ° C	Dielectric Constant	Viscosity C. P.	Density	Formula
Ethylene Carbonate	36	248	89 ^{40°}	1.9 ^{40°}	1.32 ^{40°}	
Propylent Carbonate	-49	242	64	2.5	1.19	
Butyrolactone	-43	204	39	1.7	1.12	
Nitromethane	-29	101	36	0.6	1.13	
Water	0	100	78	1.0	0.99	HOH

The solvents listed have long liquid ranges and high dielectric constants, as indicated in comparison with water. Solutions were made with propylene carbonate and other organic solvents in a 50 volume percent ratio and 10-gm AlCl_3 with 3-gm LiCl added per 100-ml of solution. Lithium deposition was studied in pyrex containers under argon gas with 1/4 in. diameter lithium rod anodes. The amount of lithium produced was determined by reaction of lithium with water and measurement of the hydrogen gas produced. Since some of the cyclic carbonate solvents decompose and produce CO_2 , a 6-Molar NaOH solution was used for hydrogen production with adsorption of any CO_2 produced. The current efficiency for lithium production, the nature of the deposit, and the solution conductivity are listed for mixed solvents in Table 2-3. Addition of water to propylene carbonate decreases the current efficiency for lithium production, but the other solutions have high efficiency. The most adherent deposit of lithium was obtained with the PC-nitromethane mixture that also had the highest electrical conductivity.

Table 2-3
LITHIUM DEPOSITION FROM MIXED SOLVENTS

Solution*	Volume (Percent)	Current Efficiency**	Lithium Deposit	Solution Conductivity $\text{ohm}^{-1}\text{cm}^{-1}$
Propylene Carbonate + Ethylene Carbonate	50	100	Dark-gray, poor adherence	6.2×10^{-3}
+ Nitromethane	50	100	Light-gray, den- dritic, good ad- herence	13.3
+ Butyrolactone	50	100	Gray, poor ad- herence	7.2
+ Water	1	65	Gray-white, fair adherence	—
Propylene Carbonate	100	100	Dark-gray, poor adherence	6.7

* Solvent 100 cc, 10-gm AlCl_3 3 gm LiCl

**Current density 13 ma/cm^2

2.2.2 Lithium Deposition From Nitromethane Solutions

Using the same experimental setup, lithium deposition was also studied in nitro-methane solutions with AlCl_3 and LiCl . As shown in Table 2-4, the production of lithium from these solutions was not efficient at lower AlCl_3 - LiCl concentrations. By increasing the AlCl_3 - LiCl concentration, the current efficiency for lithium production is increased, and the metallic character of the lithium deposit is substantially improved.

Table 2-4
LITHIUM DEPOSITION FROM NITROMETHANE SOLUTION

AlCl ₃ -LiCl Concentration gm/100 ml	Current* Efficiency (Percent)	Remarks
10-3	80-80	Light-gray, dendritic growth Adherent
20-6	80-100	Adherent
40-15	70-93	Adherent
40-15	90-100	Vacuum treated, then run under fresh argon gas

*Current Density ma/cm² 13-32

2.2.3 Effect of Addition Agents on Lithium Deposition

Aqueous plating solutions may use addition agents to obtain a shiny or brilliant deposit or to produce a smoother or smaller or grained deposit. The effect of possible agents on the lithium structure in nonaqueous solutions was studied. The common addition agents used may contain water or may have reactive groups such as alcohols or acids, and these would affect the efficiency of the nonaqueous plating solutions. Nonreactive chemicals containing polar groups have been tested for their effect on the dendritic lithium deposits. Some results on the effect of chemical additives in the electrolyte (0.5 percent) on other nature of the lithium deposit were presented in the previous quarterly report, and further results are given in Table 2-5. Improved adherence of the lithium particles was noted with the addition of Rhodamine B sodium salt, a dye material.

The effect of LiClO₄ addition on the lithium deposit from both propylene carbonate PC and nitromethane NM solutions was determined and is summarized in Table 2-6. The lithium deposit was the most metallic in appearance of any solution yet tested in the PC-LiClO₄ solution, and addition of AlCl₃ to the system decreased the metallic character and adherence of the lithium. The deposit was very poor in the LiClO₄-NM solutions, and the lithium was extremely reactive chemically.

Table 2-5

EFFECT OF ORGANIC ADDITIVES ON LITHIUM DEPOSITION
 (Solution A - Propylene Carbonate 100 ml - AlCl_3 10 gm - LiCl 3 gm)

Solution	Current Efficiency (Percent)	Remarks
A	90	dark-gray, poorly adherent
+ Rhodamine B, Sodium Salt	100	gray, fair adherence
+ 4 Azobenzenesulfonic Acid, Sodium Salt	100	dark-gray, poor adherence
+ Cholestane	100	dark-gray, poor adherence

Table 2-6

LITHIUM DEPOSITION FROM SYSTEMS WITH LiClO_4 ADDITION

Solution				Current Efficiency (Percent)	Remarks	Electrical Conductivity $\text{ohm}^{-1}\text{cm}^{-1} \times 10^3$
	LiClO_4	AlCl_3	LiCl			
PC*						
100 ml	8	0	0	100	Light-gray, very adherent	4.9
	8	10	0	100	Dark-gray, poorly adherent	4.0
	8	3	0	100	Dark-gray, adherent	—
	8	2	0	100	Dark-gray, fairly adherent	—
NM**						
100 ml	8	0	0	30	Black, adherent	—
	8	3	0	30	Black, adherent	—
	0	20	6	100	Gray, adherent	31.4

* Propylene carbonate

**Nitromethane

2.2.4 Effect of Pressure on the Lithium Anode

The general appearance of the lithium anodes has been mossy. It is known that in plating zinc, for instances, that the plate is firmer when formed under pressure. It seemed worthwhile, therefore, to attempt to run cells with the anode under pressure. Leaf springs were formed from chlorinated polyether plastic. When immersed in the standard electrolyte for several days, this material neither softened nor swelled. Several force constants were used, with forces varying from 7 to 220 gm/cm². It was found that the force was not evenly distributed over the electrode surface even though 0.18-in. thick polyethylene plates were placed between the spring and the electrodes under test. Thus, the results obtained were variable: The pressure helped to produce a more compact deposit. The electrode surfaces were quite dry (the electrolyte was apparently squeezed out). For long-term runs, polarization studies indicated that the anode had failed. This result was found even when great care was taken to prevent overcharging. At the present time there appears to be no good reason for the use of spring loading in the cells. When more uniform cells can be made and cell cycling is more predictable, it will be worthwhile to study these pressure effects more thoroughly.

2.3 LiCl CONDUCTANCE IN PROPYLENE CARBONATE SOLUTIONS

A saturate solution of lithium chloride in propylene carbonate (0.06 Molar) was prepared, aliquots were taken and diluted to the desired volume, and the resistance of these solutions measured. Calculation of the solute conductance indicates that lithium chloride is associated to a rather large extent except in very dilute solutions.* This is different from the results obtained for mixtures of lithium chloride and aluminum chloride in propylene carbonate, where the results show that the solute is 86 to 94 percent ionized.

*The equivalent conductance at infinite dilution, Λ_0 , is estimated to be 21 ohm⁻¹ equivalent⁻¹cm².

Sealing and filling of aluminum cans present some problems. With the drawn cans, it is intended that the cell assembly be connected to terminals already in place on the cover. The cover must be sealed to the case in an inert atmosphere and by a method that will not harm the lithium anode or other components. The cell must then be filled, also in an inert atmosphere, with electrolyte and sealed.

Initially, cells will be made with a plastic plug-type cover with an "o" ring seal; that is, this polypropylene cover can be inserted into the can with the "o" ring forming a seal. Screws inserted through the can sides into the top outside the seal will provide mechanical sealing. Soldering, welding, or crimping will also be investigated as means of sealing aluminum cases.

A design with thin electrodes (each 20 to 25 mil thick) and separators (8 to 10 mil thickness) would allow 5 amp-hr capacity in presently-available aluminum cans.

Present separators consist of 16-mil thick glass fiber mat with 23 ohm/cm^2 resistance with the standard electrolyte. Use of the 8-mil thick glass fiber mat will be tested, using cell-cycling tests, to determine whether this separator thickness provides adequate separation of anode and cathode structures.

2.4 CYCLING TESTS

2.4.1 Charge-Discharge Cycling Apparatus

A revised circuit for the charge-discharge control unit is shown in Fig. 2-4. Modification from the original circuit (Quarterly Technical Progress Report No. 1, 15 December 1962, Contract No. AF 33(616)-7957) includes changes in the input to the constant-current circuit, switching of both sides of the recorder input to achieve isolation, and switching of additional power circuits to prevent bias-battery discharge and partial operating voltage on control relays. Photographs of the completed cell charge-discharge cycling apparatus, front and rear views, are shown in Figs. 2-5 and 2-6, respectively. Design and construction of a discharge panel to handle 5 amp-hr cells and batteries is near completion. This includes a 5-amp charging supply and similar controls.

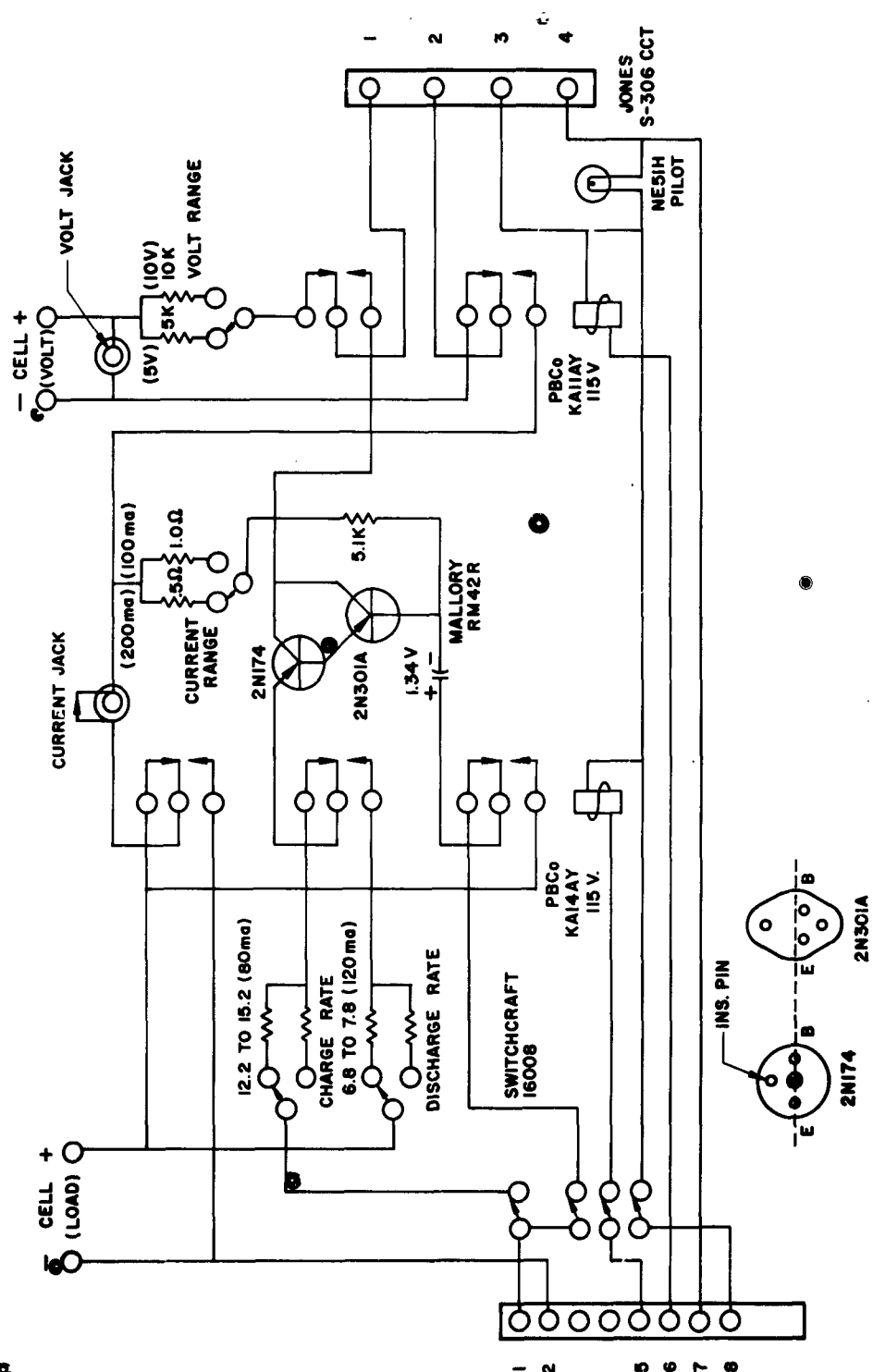


Fig. 2-4 Charge-Discharge Circuit, Modification A

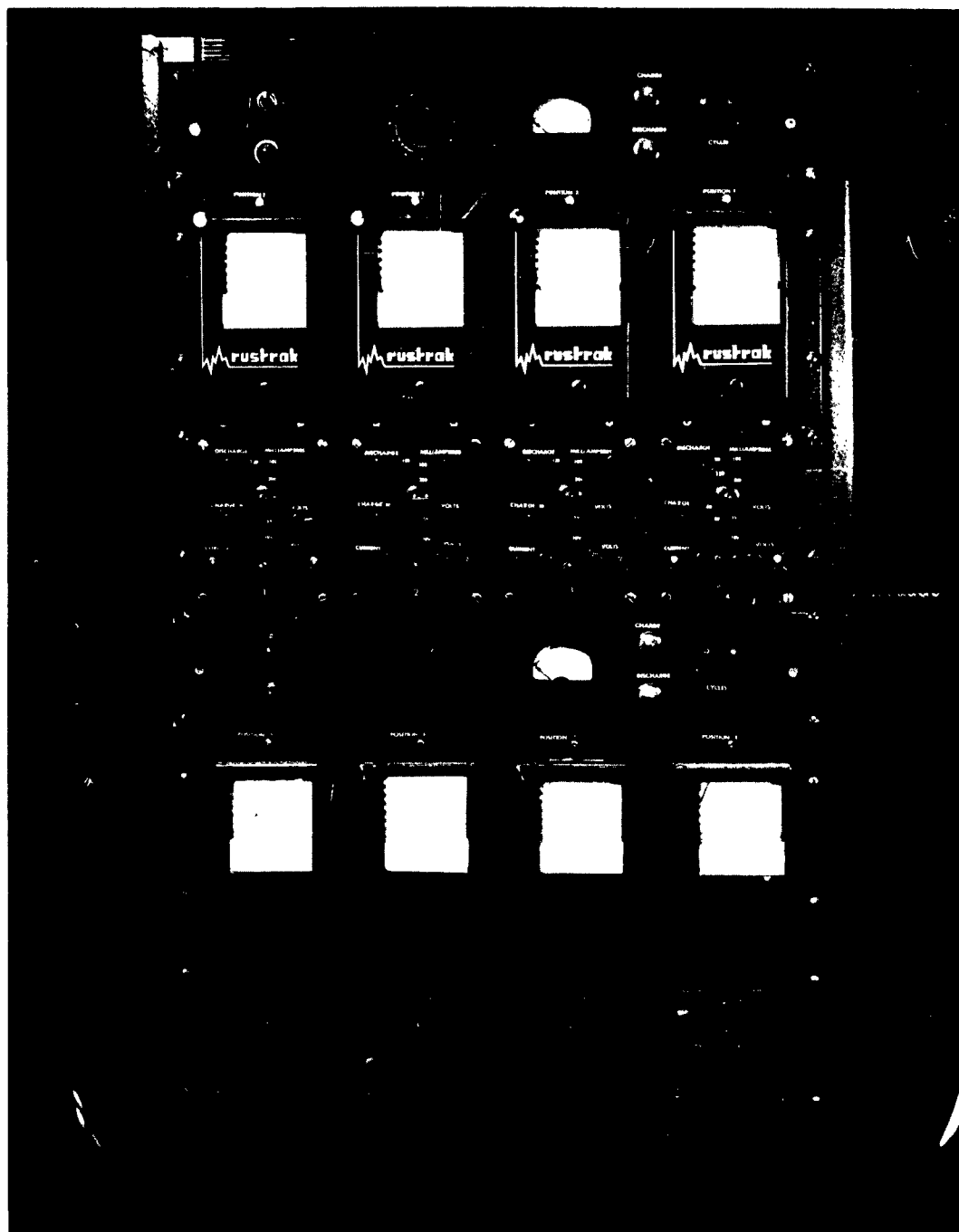


Fig. 2-5 Constant Current Charge-Discharge Cycling Apparatus, Front View

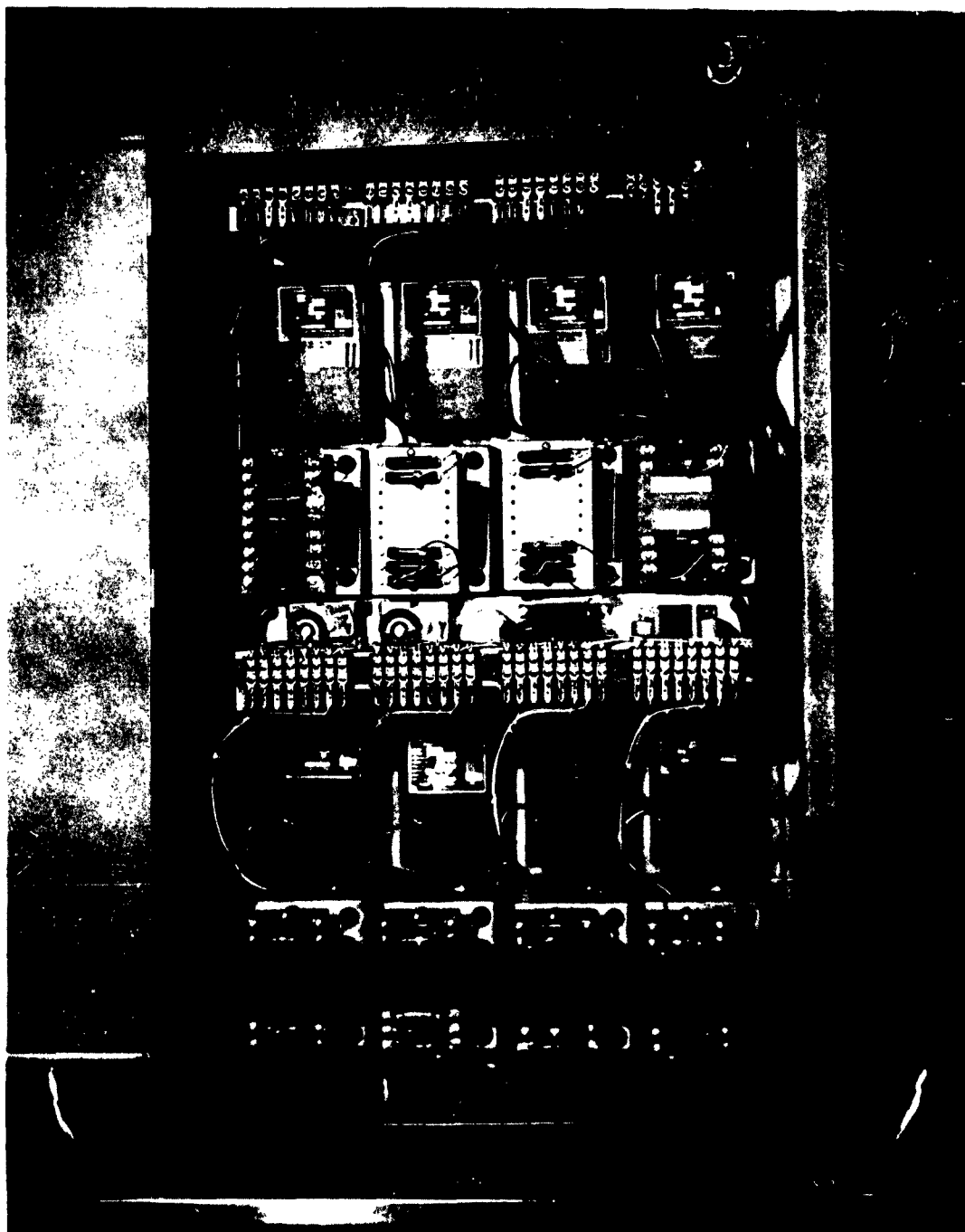


Fig. 2-6 Constant Current Charge-Discharge Apparatus, Rear View

In addition to the metering of battery current and voltage, recorders will be used for noting the voltage of individual cells in the battery.

2.4.2 Cell Cycling Results

Several types of cells were cycled, with 90-min cycle length and 35-min discharges. Most of the cells run during the past quarter were run on a constant current charge-discharge apparatus.* The electrode face area for the cells of configuration 1-1-1 (one anode - one cathode - one cell) is on the order of 23.5 cm^2 . When the cathodes are initially in a charged condition, the cells are discharged to a voltage below 0.5 v prior to cycling. Table 2-7 gives the key to symbols used for the various components. Table 2-8 gives results of the cycling experiments. Charge-discharge cycling of the cells was done in order to evaluate several aspects of the cells and/or the apparatus. Particular details that were studied are presented in various paragraphs in this report.

2.5 BACKGROUND WORK ON 5 AMP-HR CELLS

The 5 amp-hr cells are intended to exhibit some optimization of material and components developed during preceding work. The split plastic cases used for test cells are convenient to assemble but contribute a major portion of the volume and weight of the test cells. Isolated aluminum strips placed in test cells show no sign of corrosion following cell cycling, and aluminum appears to be a good cell-case material. Drawn aluminum cans (Type 1100, per QQ-A-561c) commercially available, were procured. These cans are approximately 1 in. $\times$ 2 in. $\times$ 4 in. and, although not the ideal shape, should satisfy preliminary requirements. It was felt that the cost of drawing dies could not be justified at this stage of development.

*A charge-discharge curve obtained with a Li, PC-AlCl₃-LiCl, AgCl-Ag cell is shown in Fig. 2-7. The current during charge remains constant until the cell charging voltage becomes limited by the apparatus input voltage. Current during discharge remains constant until the discharge voltage falls below the control-transistor bias voltage. The optimum shape for a charge-discharge curve, with the current remaining constant during the cycling, is shown in Fig. 2-8. This shape was constructed from data obtained using an Li-AgCl-Ag cell and a nitromethane-AlCl₃-LiCl electrolyte.

Table 2-7
ELECTRODE PREPARATION

Designation	Ingredients	Treatment
st •	propylene carbonate aluminum chloride lithium chloride	combine at low temperature (less than 0° C)
st ² ●	as above with lithium perchlorate instead of lithium chloride	as above
CH ₃ NO ₂	nitromethane aluminum/chloride lithium chloride	as above
N	lithium	silver-plated nickel screen dipped into molten lithium
U	glass fiber filter paper	flame-sealed edges
F	silver powder graphite	sintered in H ₂ atmosphere
H ¹	silver oxide, silver chloride 1 percent, polyvinyl alcohol- water	paste on F/S Ex-met. (silver), dry for an hour at 85° C
H ²	H ¹ + graphite	as above
H ⁴	H ¹ + precipitated silver	as above
H ⁵	H ¹ + spherical silver	as above
H ⁶	H ¹ + flake silver	as above

Table 2-8
AVERAGED CELL CYCLING RESULTS

Electrolyte	Anode	Cathode	Separator	Configuration Anode-Cathode Cells	No. of Cells run	No. of cycles	Percent Efficiency	Initial R ohm	AR (Initial- Final) ohm	Voltage volt		Current ma	
										Charge I - F I*	Discharge I - F	Charge I - F	Discharge I - F
Std.	N	H ¹	U	1-1-1	5	28	89	7	+3.5	2.8 - 4.2	2.5 - 1.2	80 - 80	120 - 96
Std.	N	H ²	U	1-1-1	32	44	84	5.25	+1	2.9 - 4.3	2.4 - 1.2	80 - 60	116 - 100
**Std.	N	F	U	1-2-1	1	44	86	3.1Ω	final	2.7 - 3.4	2.7 - 2.1	80 - 80	120 - 120
Std ²	N	H ²	U	1-1-1	7	46	84	4.0	-1.5	3.2 - 4.2	2.4 - 1.4	90 - 65	130 - 80
CH ₃ NO ₂	N	H ²	U	1-1-1	4	26	78	2.6	+1.2	3.0 - 3.3	2.4 - 2.3	84 - 84	120 - 120
Std.	N	H ⁴	U	1-1-1	2	45	82	8.0	-5.4	2.9 - 4.3	2.0 - 1.2	80 - 48	116 - 92
Std.	N	H ⁵	U	1-1-1	2	50	78	12.0	-8.0	2.9 - 4.4	2.4 - 1.2	76 - 72	120 - 88
Std.	N	H ⁶	U	1-1-1	3	30	85	16.0	-11.6	2.9 - 3.4	3.1 - 1.8	76 - 40	124 - 72

* I = Initial

F = Final

** Cell made 8/6/62; cycles run 2/25/63

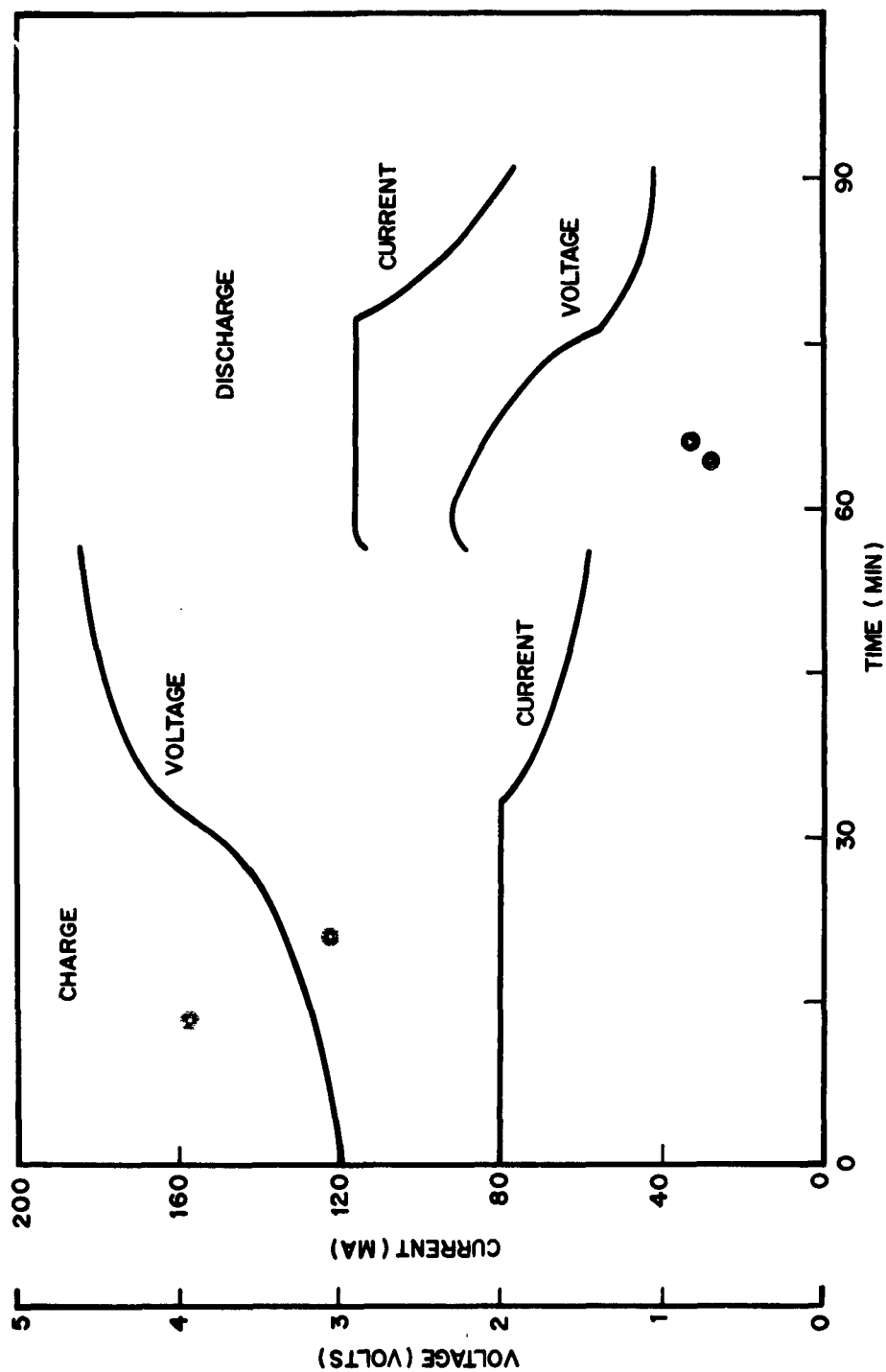


Fig. 2-7 Charge-Discharge Cycling Curves Obtained with Li-AgCl-Propylene-Carbonate System

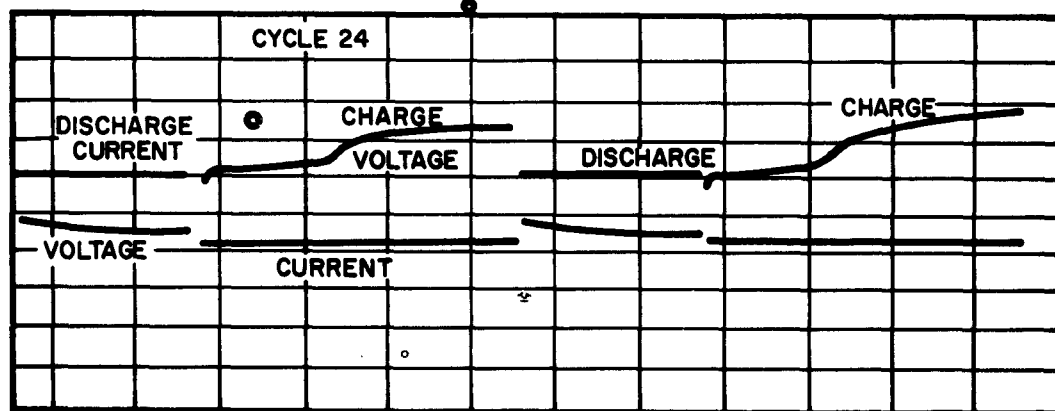
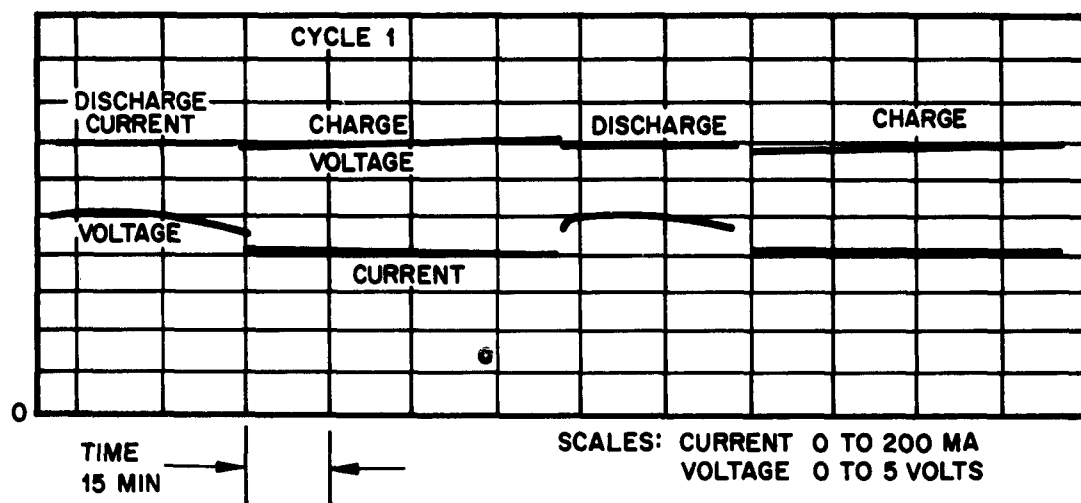


Fig. 2-8 Charge-Discharge Curves Obtained with Li-AgCl Nitromethane System

2.6 CELL ASSEMBLY DRY BOX

A commercial dry box was obtained and modified for use in assembling cells, filling with electrolyte, and conducting experiments. Argon was plumbed to allow filling the internal balloon box, and vacuum entrance chamber. A balloon is used in this dry box to force the original atmosphere out of the box, then argon is used to collapse it. Argon is used to fill the balloon; thus, if there is a small leak in the balloon, the exchange will be less efficient, but the atmosphere would not be contaminated. The balloon fitting and collapsing techniques are then repeated several times. The entrance chamber is evacuated and filled with argon to purify its atmosphere before opening the inner door.

The filling procedure is as follows:

1. Open valve to the interior of the dry box
2. Fill balloon with Argon
3. Close valve to the interior of the dry box
4. Allow balloon to vent to the atmosphere
5. Fill box with Argon
6. Close balloon vent

The degree of purity of the atmosphere in the dry box was followed by analyzing samples of the atmosphere with a gas chromatograph. It was found that with a single exchange there was a 96 percent replacement of the initial atmosphere. Under optimum operating conditions, this figure can be improved considerably; in this test, a vacuum oven was placed within the dry box, thus leaving a nonreplaceable volume. In an actual trial, the partial volume of air had been reduced to 0.06 percent of the original after three filling and balloon-collapsing cycles. With optimum replacement, this value would be improved by a factor of ten.

Section 3
TRAVEL

On January 24, 1963 a trip was made to Wright Patterson Air Force Base, Ohio, to discuss the project effort and direction. Deliverable items were given to Wayne S. Bishop, the project engineer. The following items were included:

1. Two polypropylene cell cases filled with helium and sealed with neoprene gaskets
2. Two completed cells with glass fiber separators, each filled with a single dipped lithium anode, 2 in. $\times$ 2 in., a single pasted cathode 3-gm mix - 30-gm AgCl, 60-gm Ag powder, and 10-gm graphite flake with 1 percent PV Acetate, and propylene carbonate solution of 100 ml, AlCl_3 10 gm, and LiCl 3 gm
3. Two pieces glass separator
4. Two pasted cathodes and two sintered cathodes on silver screen

Cells that will be delivered at the end of the contract were required to be of 5 amp-hr capacity, based on a one-hour rate, with the voltage regulation of ± 10 percent from 3.0 to 25 volts.

Section 4 SUMMARY

In Li-AgCl cells with thin electrodes ($0.12 \text{ gm cathode mix/cm}^2$), no relationship is found between AgCl concentration ranging from 18.6 percent to 31.3 percent weight, and the utilization, which was an average of 42.5 percent for 20 percent voltage variation. At current densities up to 30 ma/cm^2 , the cell polarization is resistive in character. Variation of graphite content of cathode mix from 11 to 38 percent by volume in thin electrodes had no effect on utilization of AgCl that was 40 percent for 20 percent voltage variation.

However, with thick electrodes ($0.44 \text{ gm cathode mix/cm}^2$), graphite in the mix increased the AgCl utilization. The graphite may aid formation of an open or porous structure with Ag and AgCl powder. Utilization of AgCl on initial discharge was measured with cells using the standard $\text{PC} - \text{AlCl}_3 - \text{LiCl}$ electrolyte. Using different electrolytes, such as $\text{PC} - \text{LiClO}_4 - \text{AlCl}_3$ or $\text{NM} - \text{AlCl}_3 - \text{LiCl}$, utilization is considerably increased with thick electrodes. Utilization for the latter solution was 35 percent to 20 percent voltage variation. The effect of pressure on the lithium anode during cell cycling was studied, using plastic leaf springs, with forces to 220 gm/cm^2 for a 24-cm^2 area. No systematic improvement in cell performance was noted. After cycling tests with electrodes under pressure, the electrode surfaces were dry.

The anodic oxidation of silver was studied in nonaqueous systems. With LiClO_4 containing solutions, an adequate amount of AlCl_3 is necessary to form insoluble AgCl on the cathode surface, or else a soluble AgCl_4 salt is formed. In all cases, 100 percent current efficiency for AgCl formation was observed.

The deposition of lithium metal was studied in various systems, and the most metallic deposits were obtained from the LiClO_4 -PC solutions; the lithium obtained is

light-gray in color with metallic sheen and is very adherent. Mixtures of PC and NM with AlCl_3 -LiCl electrolyte, and NM solutions with AlCl_3 and LiCl salts produced an improved lithium deposit over that obtained from the standard PC solution. Water addition to the PC- AlCl_3 -LiCl solution drastically reduced the efficiency of lithium deposition. Improvement of the lithium deposit was noted with the use in the standard electrolyte of an organic addition agent Rhodamine B sodium salt. Lithium formed by deposition from LiClO_4 -NM solutions was very reactive and was produced at low current efficiency. In dilute PC-LiCl solutions, LiCl is largely associated as noted by determining the equivalent conductivity of the solution as a function of the LiCl concentration. Cell-cycling tests run with the constant current charge-discharge apparatus indicated generally high efficiency for most of the runs; however, overcharging the cells was noted during the tests, leading to increased destruction of the silver cathode and an increased cell resistance. Best voltage regulation was obtained with cells using nitromethane electrolyte, and these cells had lower cell resistances than cells using standard PC electrolyte. In cells operated with an electrolyte containing LiClO_4 , it was found that a soluble silver species had migrated through the separators during cycling. Apparently an inadequate amount of chloride ion was available for silver chloride formation at the cathode structure because of local depletion.

Preliminary calculations for design of 5 amp-hr cells have been made, and it has been determined that with careful fabrication of thin electrodes, these cells can be housed in 4 in. $\times$ 2 in. $\times$ 1 in. aluminum cases.

Section 5
PROGRAM FOR THIRD QUARTER

Improved lithium adherence and silver-chloride insolubility have been noted for tests run in certain $\text{PC-LiClO}_4\text{-AlCl}_3$ and $\text{NM-AlCl}_3\text{-LiCl}$ systems. Further studies of these solutions with the lithium-silver chloride cells will be conducted using charge-discharge cell testing. To eliminate effects of traces of water and oxygen on cell performance, assembly of cells and electrolyte filling will be done in the recently completed dry-box facility. Further studies of mixed electrolyte systems with lithium-silver chloride cells also will be made. Testing of thin (8 mil) glass fiber mat separator material will be done in cycled cells to determine if the thin separator material is adequate to prevent anode-to-cathode shorting. Testing of other separator materials for electrolyte compatibility and for resistance in solution will continue. Battery cycling apparatus has been assembled for testing assemblies of five cells and for determining the effects of overcharge and reverse charging on individual lithium-silver chloride cells. Production and testing of 5 amp-hr Li-AgCl cells will begin, using 4 in. $\times$ 2 in. $\times$ 1 in. aluminum cases that have polyethylene top closures. Fabrication and methods of sealing all-aluminum cell cases also will be investigated.

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