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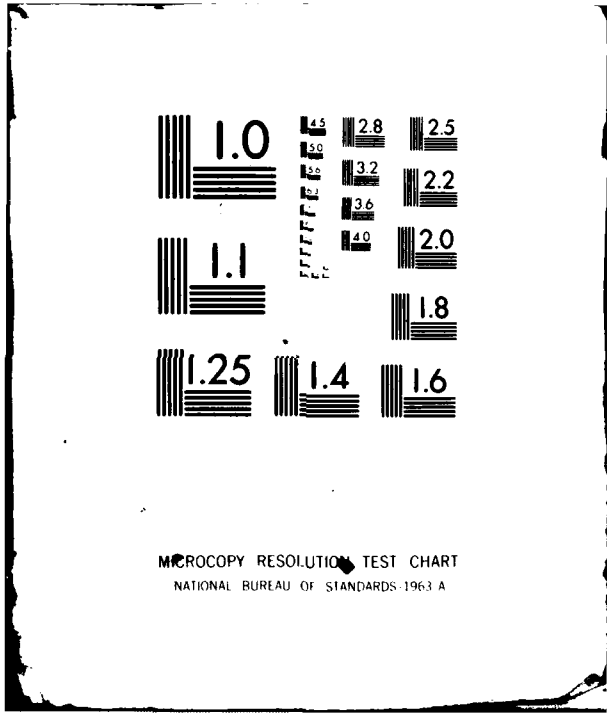
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HIGH RATE LITHIUM-THIONYL CHLORIDE BATTERY DEVELOPMENT FOR UNDE--ETC(U)
AUG 78 W C MERZ, C R WALK N66001-77-C-0284

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**HIGH RATE LITHIUM-THIONYL CHLORIDE BATTERY DEVELOPMENT
FOR UNDERSEA WEAPON PROPULSION APPLICATIONS**

Contract No. N66001-77-C-0284

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FINAL REPORT

September 1, 1977 to June 30, 1978

Revised 23 August 1978

Submitted to

**NAVAL OCEAN SYSTEMS CENTER
San Diego, California**

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Honeywell

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FOR UNDERSEA WEAPON PROPULSION APPLICATIONS**
Revised

by

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W. C./Merz
C. R./Walk

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Contract No. N66001-77-C-0284^{42V}

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ABSTRACT

This report describes the experimental results obtained in the development of a high rate lithium, thionyl chloride battery system. Initially, cell optimization studies were conducted with so-called neutral electrolyte, i. e., thionyl chloride containing equimolar quantities of LiCl and AlCl₃.

During the program, GTE Laboratories published a report which described the superiority of acid electrolyte, i. e., thionyl chloride containing only AlCl₃, for high rate applications. We independently verified their findings and devoted the remainder of the contractual effort to acid electrolyte optimization studies.

This report is divided into four sections, Section I - Cell Performance in Neutral Electrolyte, Section II - Cell Performance in Acid Electrolyte, Section III - Discussions of Battery Characteristics and Section IV - Active Battery Considerations.

Essentially all of the data reported in Sections I and II were obtained by constant current discharge of prismatic cells with lateral dimensions of 0.5 inch wide by 1.0 inch in height. The cells were contained in sealed Pyrex tubes under an argon atmosphere.

The technical goal of operating a cell at a discharge rate of 72 mA/cm² above 2.7 volts for a period of 8 minutes was achieved during this study. The use of acid electrolyte coupled with an elevated temperature of 165°F resulted in run times in excess of 12 minutes at the 72 mA/cm² rate.

Section I - Evaluation of Cell Performance in Neutral Electrolyte

At the inception of the program, our current density capability in the Li/SOCl₂ system was about 30 mA/cm². Since the goal current density was 72 mA/cm², we investigated several cell construction variables that might affect rate capability. When a particular variable proved to be significant, additional experiments were conducted to optimize the condition with respect to run time at a given current density.

A separator evaluation established that the best cell performance was obtained with 5 mil glass mat containing no binder. Cells without separation or with one mil Celgard polarized immediately below 2.7 volts. A pure boron nitride paper had poor mechanical integrity and was not tested.

Current density experiments provided reproducible runs in the eight minute range at 52 mA/cm² but less than two minutes at 72 mA/cm². Therefore, the remaining optimization studies in this section utilized 52 mA/cm².

Capacity continued to increase as the Teflon binder content of the cathodes was lowered. Ratios of 90/10 or 95 Shawinigan Acetylene Black (SAB)/5% Teflon appeared optimum.

Cathodes of 90 SAB/10 Teflon provided maximum run time at a density of 0.5 g/cc as opposed to lower or higher densities.

Peak run time was achieved at an electrolyte molarity of 1.8M LiAlCl₄.

Imposing an atmosphere of \approx 150 psig argon over flooded electrolyte cells had no beneficial effect on run time.

Thick cathodes ran only slightly longer than thin cathodes. Since thick cathodes would necessitate higher current densities, this approach was abandoned.

Cells discharged at +75 and +120°F yielded scattered run times. Several high temperature runs exceeded RT times while several others fell short. The data could not be correlated.

Cells completely immersed in electrolyte produced run times equivalent to cells in which only the separator maintained electrolyte contact and cell parts were wetted by capillary action. Thus, excess electrolyte was not conducive to increased performance.

In an effort to identify substrates which were structurally stronger than SAB/Teflon, bonded carbon fiber, porous silver and porous nickel cathodes were discharged in test cells. All polarized immediately below 2.7 volts at 52 mA/cm².

Optimum cell construction conditions were:

- 1) 90/10 or 95/5 SAB/Teflon
- 2) Cathode density of 0.5 g/cc
- 3) 5 mil glass mat separator
- 4) Electrolyte of 1.8M LiAlCl₄

Cells constructed according to these conditions would reliably run for 8 minutes at 52 mA/cm².

Section II - Evaluation of Cell Performance in Acid Electrolyte

Preliminary tests of this electrolyte established that it rapidly corroded the polypropylene cell tension clips that had been used in all neutral electrolyte cell tests.

Substitution of Teflon covered wire twist locks resulted in cell run times of 5 minutes at 72 mA/cm² and +75°F.

It was recognized that many of the conclusions derived from neutral electrolyte systems were not necessarily valid in acid electrolyte systems. Therefore, most of cell construction variables and discharge conditions were re-evaluated in acid electrolyte.

As before, argon pressure of 150 psig superimposed on the electrolyte had no effect on performance.

Thicker cathodes were much more efficient in 2.3M AlCl₃ than in 1.8M LiAlCl₄. However, the increase in efficiency was insufficient to compensate for the required increase in current density.

As before, capillary fed cells performed as well as totally immersed cells.

Acid electrolyte cells were found to be very temperature sensitive. Cells discharged at 72 mA/cm^2 ran 5 minutes at $+75^\circ$, 9 minutes at $+120^\circ$ and 12 minutes at $+165^\circ\text{F}$. Thus, battery performance would benefit from elevated discharge temperatures.

Increased electrolyte molarity delivered a modest increase in run time but resulted in somewhat lower load voltage plateaus.

As before, carbon fiber, porous silver and porous nickel cathodes polarized below 2.7 volts under load. Rensselaer Polytechnic Institute deposited carbon on nickel foil and porous nickel substrates by chemical vapor deposition. The substrates were warped and embrittled by the procedure. All specimens failed immediately under load.

Air cell cathodes (activated carbon/teflon) and porous carbon cathodes supplied by NOSC also failed under load.

Cathodes prepared by cold molding 70 SAB/30 w/o graphite discharged only 9 minutes at $+165^\circ\text{F}$ and 72 mA/cm^2 versus 12 minutes for 95 SAB/5 Teflon.

A ten mil cathode was prepared by hot rolling 80 SAB/20 Teflon with paraffin lubricant. After leaching out the wax, the resultant cathode was strong and flexible. This cathode ran 3 minutes at $+75^\circ\text{F}$ and 72 mA/cm^2 .

Fiber Materials Inc. prepared cathodes by painting a suspension of SAB on glassy carbon paper. A 20 mil thick cathode ran 4 minutes and a 10 mil thick cathode ran 2.9 minutes at $+75^\circ\text{F}$ and 72 mA/cm^2 .

The hot rolling technique and the FMI approach both produce strong cathodes which could be used in scale-up tests. However, their volumetric efficiencies are in need of improvement.

Cells were discharged with electrode contact maintained by wire twist-locks (baseline) and high compression maintained by a spring clip. The virtually identical runs indicated that high compression will not extend performance.

Attempts were made to evaluate bipolar cell performance. Several four plate (2 anode/2 cathode) cells were fabricated. Even though the cells were activated with only the separator tips immersed in electrolyte, capillary action filled the open areas between the oversized glass slides. This resulted in excessive inter-cell leak paths which depressed the open circuit by approximately one volt. In spite of this, one bipolar cell ran 4.1 minutes at 72 mA/cm^2 and $+75^\circ\text{F}$ versus 5.1 minutes for a single cell.

The effect of cold temperature on reserve mode electrolyte delivery time was investigated. Electrolyte viscosity versus temperature over the interval $+9$ to $+46^\circ\text{F}$ ranged from 1.4 to 0.5 centistokes which should result in rapid electrolyte delivery. No salting out was observed over the specified temperature interval.

In order to properly assess the true capability of this promising system, techniques should be devised to fabricate strong, volumetrically efficient cathodes.

Such cathodes will permit construction of scaled-up bipolar cells for the evaluation of intercell leakage measurements and the determination of discharge temperature profiles.

Section III - Discussion of Battery Characteristics

Per the contract Honeywell is required to discuss conceptual battery designs for underwater weapon propulsion and critical characteristics of those batteries including safety, disposal, storage limitations, technical risk areas, activation time, waste heat and cooling requirements and the effect of depth and pressure. Section III is devoted to the discussions of these areas.

Section IV - Active Battery Considerations

A primary active battery instead of a reserve battery would offer significant weight and volume advantage for underwater weapons propulsion if it could operate after many years of random storage. These considerations are discussed in this section.

SECTION I
EVALUATION OF CELL PERFORMANCE IN NEUTRAL
(LiCl·AlCl₃·SOCl₂) ELECTROLYTE

1.0 INTRODUCTION

1.1 Objectives

Lithium/thionyl chloride batteries deliver energy densities of 18 Wh/in³ and 300 Wh/lb. High rate configurations at the start of this contract work were capable of current densities of 30 mA/cm². However, during storage the film of lithium chloride on the anode continues to thicken. While this film growth has negligible effects on the low rate capability or the capacity, high rate performance is seriously impaired.

One way to maintain the high rate capability of this system during storage is to construct the battery in the reserve mode.

Our experience has shown that the cathode in this system is the limiting electrode. Furthermore, the cathode is extremely rate sensitive, i. e., the higher the rate the lower the cathodic volumetric efficiency. For example, in the G3013C Life Support Cell developed for WPAFB, we achieve 25 mAh/0.025 cm³ of cathode when the current density is 3.3 mA/cm². The same cell delivers only 14 mAh/0.025 cm³ at 28 mA/cm².

The design considerations as set forth by NOSC necessitated that the system operate at a current density of 72 mA/cm² for 8 minutes above 2.7 volts. The physical envelope and performance specifications provided by NOSC for a typical Li battery for undersea weapon propulsion is attached as Exhibit I. A preliminary design concept was also provided by NOSC which is attached as Exhibit II. Additional design studies by Honeywell indicated that the cathode thickness should be increased to 9 - 10 mils. This was considered possible by decreasing the thicknesses of other cell parts. Thus, each square centimeter of cathode would contain 0.0254 cm³. The

required capacity is $(72 \text{ mA})(8/60) = 9.6 \text{ mAh/cm}^2$. Because of system voltage requirements and space limitations, Honeywell was in agreement that bipolar (pile type) module construction was required with individual module capability of 50 amps at 60 volts for 8 minutes.

Accordingly, the objectives of this contract were:

- 1) To achieve current densities of 72 mA/cm^2 for 8 minutes above 2.7 volts.
- 2) To demonstrate the feasibility of a high rate bipolar Li/SOCl₂ battery.

Both of the above objectives were met during the performance of this contract.

1.2 Technical Approach

Honeywell's proposed technical approach was to first evaluate and optimize the cathode, anode, neutral electrolyte and separator in 0.5 in^2 laboratory cells for high rate discharge of the Li/SOCl₂ battery system. Larger cells were proposed (maximum size allowed by safety policy at Honeywell Power Sources Center) if the laboratory cell data showed promise to gain additional intercell leakage, electrode sealing and activation data. Based on these data the contract final report was to contain discussions of hazards identified, battery disposal techniques, estimated activation times, estimated waste heat and cooling requirements as well as expected storage limitations of a conceptual battery design.

It became clear as the data were generated in laboratory cells that the cathode limited cell performance. Even though considerable improvements in cathode performance were made the goal of 72 mA/cm^2 could not be achieved and at the request of the NOSC technical representatives pursuit of additional parametric data, as planned on the electrochemical system and as identified in Honeywell's proposal, was abandoned to search for active components (particularly a cathode) having improved discharge rate capabilities. As a result of this work a cell capability was developed

which could operate at 72 mA/cm² of electrode surface area above 2.7 volts for more than the goal time of 8 minutes. The improvements resulted mainly from operation of an improved cathode structure in an acid thionyl chloride electrolyte solution.

The effort required to improve the cell current handling capabilities to an acceptable level and to obtain the necessary parametric data on these cells prohibited the planned scale-up and activation concept work. The required discussions related to the battery design, hazards, disposal techniques, storage limitations, activation time, heat and cooling requirements are, however, still discussed in Section **III** of this report.

1.2.1 Test Chambers and Cells

The test chambers used in this program are shown in Figure 1. Prismatic cells measuring 0.5 inches wide x 1.0 inch high were sandwiched between glass slides with compression applied by polypropylene clips or wire twist-locks.

An exploded view of a two plate cell is depicted in Figure 2 with parts drawn to actual size. The cells were fabricated in a dry room where the relative humidity is maintained below 2%. After the cell tabs were spot welded to the fixture leads the fixtures were sealed and transferred to a controlled atmosphere (argon) glove box for the addition of electrolyte. Except in cases of elevated temperature runs (where a one hour equilibration soak time was employed) cells were discharged within 5-10 minutes after activation. Despite their small size, we found that these cells had reproducible performance characteristics and were reliable for the assessment of cell improvements.

With the exception of cell tests described in the special cathode experiments, all cells contained molded Shawinigan Acetylene Black (SAB) cathodes with a teflon binder.

1.2.2 Anode Requirements

The density of lithium is 0.534 g/cc. The weight of lithium per sq cm/mil is $0.534 \text{ g/cm}^3 \times 0.00254 \text{ cm}^3 = 1.35 \times 10^{-3} \text{ g}$. The capacity of lithium is 26.8 Ah/eq $\div 6.94 = 3.85 \text{ Ah/g}$. Therefore, the capacity of lithium expressed in sq cm/mil is $3.85 \text{ Ah/g} \times 1.35 \times 10^{-3} \text{ g} = 5.19 \times 10^{-3} \text{ Ah/cm}^2/\text{mil}$.

At a current of 0.072 A for 8 minutes, each cm^2 of plate must deliver:

$$\frac{0.072 \text{ A} \times 8 \text{ min}}{60 \text{ min/hr}} = 9.6 \times 10^{-3} \text{ Ah/cm}^2.$$

The theoretical lithium thickness required is:

$$\frac{9.6 \times 10^{-3} \text{ Ah/cm}^2}{5/19 \times 10^{-3} \text{ Ah/cm}^2/\text{mil}} = 1.85 \text{ mils.}$$

In the tests described below, our main concern was cathode capacity. It was desirable to identify the particular combination of cell design features that would result in the longest possible run time. Two mil anodes would limit the run time to 8 minutes and would obscure truly significant cell improvements. Therefore, all cells employed 7.5 mil lithium anodes.

2.0 EXPERIMENTAL PROCEDURE

2.1 Separator Evaluation

In order to achieve the highest possible energy density and rate capability in primary cells, it is desirable that the volume and weight of inert components such as separators be kept to a minimum. The corrosive qualities of thionyl chloride and the reactivity of lithium impose serious constraints upon the choice of separator materials. For example, fully halogenated plastics such as Teflon are compatible with thionyl chloride electrolyte. However, we have found that Teflon in intimate contact with lithium is electrochemically reduced to carbon and lithium fluoride. Therefore, a cell with Teflon separators would not possess the dry storage capability that this application requires.

Three separator materials and an alternative approach were investigated under this program. They are discussed below:

- 1) Glass Mat - this material is commonly used in Li/SOCl_2 batteries. It is available in thicknesses down to 5 mils without binder. Sheets thinner than this contain binders which react with SOCl_2 .

- 2) Celgard - this is a microporous polypropylene separator manufactured by Celanese Corporation. It is available in one mil thick sheets. Even though polypropylene is attacked by SOCl_2 , it was felt that this material might suffice in view of the 8 minute requirement.
- 3) Boron Nitride - this material is available in 2 mil thick sheets without binder.
- 4) No Separator - lithium and thionyl chloride would be thermodynamically unstable were it not for the film of lithium chloride which forms upon the lithium surface. We wished to determine whether this film would provide adequate electrode separation. The basis for this work is U.S. Patent 3,891,457.

2.2 Results

With 5 mil glass mat separator, at a current density of 52 mA/cm^2 , the cell operated 5.6 minutes with a ten mil cathode at room temperature. The boron nitride paper was too fragile to use in cell fabrication. Under identical conditions, cells with Celgard separator or no separator polarized immediately below 2.7 volts. Unless indicated, all subsequent tests utilized 5 mil glass mat separators.

2.3 Current Density

A series of cathode-limited cells containing 5 mil glass mat separator, ten mil SAB/PTFE cathodes and $\text{LiAlCl}_4 \cdot \text{SOCl}_2$ electrolyte were discharged at current densities of 52 and 72 mA/cm^2 . It was apparent that the design current density of 72 mA/cm^2 was well beyond the capability of these cells since the maximum discharge time achieved was two and one half minutes with widely scattered results. On the other hand, cells consistently delivered discharge times in the 7-9 minute range at 52 mA/cm^2 .

2.4 Discussion

It was assumed that any cell modification that resulted in a significant improvement at 52 mA/cm² would also prove beneficial at 72 mA/cm². Therefore, neutral electrolyte cell tests, unless otherwise noted, were conducted at the more reproducible current density of 52 mA/cm².

2.5 Cathode Formulation

The standard cathode used in Li/SOCl₂ cells at HPSC consists of cold-pressed 80% Shawinigan Acetylene Black (SAB)/20% Teflon. Acetylene blacks possess a unique property that provides for the efficient reduction of thionyl chloride. Teflon is an inert, non-conductive binder and excessive amounts would be expected to adversely affect the performance of the cathode with respect to current handling capability, load voltage and volumetric efficiency. Therefore, SAB/Teflon cathodes were cold pressed in formulations of 80/20, 90/10 and 95/5 weight percent ratios. The cell tests of the various formulations are shown below.

<u>Run</u>	<u>Mix</u>	<u>C. D.</u>	<u>Time to 2.7V, Min.</u>
1	80/20	52 mA/cm ²	5.6
8	90/10	52 mA/cm ²	8.3
12	95/5	52 mA/cm ²	8.0
13	95/5	72 mA/cm ²	1.8

2.6 Results

The results showed significant improvement with lower binder levels and also demonstrated that 8 minutes at 72 mA/cm² could not be achieved simply by altering mix composition. Formulations below 95/5 were not attempted because cathode fragility was noticeably increasing with decreased binder levels.

Several attempts were made to prepare 8 and 6 mil cathodes of all three formulations. In all cases they proved to be too fragile to permit cell construction.

While the ten mil cold-pressed cathodes were strong enough for $0.5 \times 10''$ cells, it was recognized that fabrication in large diameters would be difficult or impossible. However, it was obvious that other cell parameters needed improvement to meet the goal. Therefore, we elected to use this cathode to develop further cell improvements and continued a parallel search for better and stronger cathode substrates.

2.7 Cathode Density

The cathode density would be expected to affect cell performance in two conflicting ways. Higher densities imply lower resistance but less void space and hence, lower capacity. With lower densities the converse should hold.

We attempted to vary the density of 95/5 cathodes but found that regardless of forming pressure, they had a rather constant density of 0.45 g/cc. With 90/10 formulation we successfully prepared ten mil cathodes with densities of 0.4, 0.5 and 0.6 g/cc. The discharge results are shown below.

<u>Run</u>	<u>Density</u>	<u>C. D.</u>	<u>Time to 2.7V, Min.</u>
7	0.4 g/cc	52 mA/cm ²	5.8
8	0.5 g/cc	52 mA/cm ²	8.3
9	0.6 g/cc	52 mA/cm ²	7.0

2.8 Results

The results indicated the optimum density to be at or near 0.5 g/cc with respect to both load voltage and capacity.

2.9 Electrolyte Molarity

The conductivity of $\text{LiAlCl}_4 \cdot \text{SOCl}_2$ rises with increasing molarity and reaches a conductivity maximum of 20 millimhos $\times \text{cm}^{-1}$ at 1.8 molar. Ten mil cathodes were discharged in 1.0, 1.5, 1.8 and 2.0M electrolytes. The results are shown below.

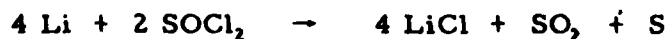
<u>Run</u>	<u>Electrolyte</u>	<u>C. D.</u>	<u>Time to 2.7V, Min.</u>
10	1.0M	52 mA/cm ²	7.2
11	1.0M	72 mA/cm ²	0.9
12	1.5M	52 mA/cm ²	8.0
13	1.5M	72 mA/cm ²	1.8
14	1.8M	52 mA/cm ²	8.8
15	1.8M	72 mA/cm ²	2.5
20	2.0M	52 mA/cm ²	3.7

2.10 Results

These results showed a definite trend of increased run time up to 1.8 molar. However, the two molar electrolyte resulted in a shorter run time. Since the plot of conductance versus concentration plateaus at 1.8 molar, this may be a result of increased viscosity without a corresponding increase in conductivity.

2.11 Pressure

The generally accepted discharge reaction in the Li/SOCl_2 system is:



Generation of SO_2 during discharge could conceivably lead to gas bubble formation in the cathode and thus increase polarization. If pressure over the electrolyte exceeds the vapor pressure of SO_2 ($\approx 3 \text{ Atm}$) bubble formation should be prevented.

Several tests were conducted in which 10 Atm of argon were introduced over the cells while companion cells were run at 1 Atm.

2.12 Results

The results were scattered and it was concluded that pressure was affecting the cells in an unforeseen way. Since, however, none of the ten Atm runs exceed the best one Atm runs, it was concluded that the cell pressurization technique was without merit.

2.13 Cathode Thickness

Thicker unit cells could be used for the intended application if they are capable of operating at higher current densities. In order to establish the role of cathode thickness on cell performance, we discharged cells with ten and twenty mil thick cathodes.

2.14 Results

The twenty mil cathode (100% thicker) only provided a 9% increase in run time at 52 mA/cm². Since thicker cathodes would of necessity operate at higher current densities (because of fewer plates in the available space), it seemed apparent that thicker cathodes were not a viable solution to the problem at hand.

2.15 Temperature

In an effort to determine the effect of temperature on cell performance, a series of cells were discharged at +75 and +120°F. The cells were soaked for one hour at their respective temperatures and then discharged at the same temperatures.

2.16 Results

The data were quite scattered and it was concluded that the one hour open circuit soak period might be detrimental to performance.

2.17 Electrolyte Volume

The reserve electrolyte chamber volume requirements are governed by the cell needs. The question addressed here was "Will a cell run more efficiently if fresh electrolyte is available to replenish that used in the discharge reaction?" Should this be the case, both the weight and volume of the electrolyte reserve chamber would increase.

Cells were constructed and activated with either 1 ml of electrolyte (wick) or 8 ml of electrolyte (flooded). The wick cells were suspended with only the glass mat separator extending into the electrolyte. All cell parts of the flooded cells were completely immersed.

2.18 Results

The run times of these cells fell within the average reproducibility range of identical pairs. It was concluded that excess electrolyte is not beneficial to run times.

2.19 Special Cathodes

In a parallel effort to identify cathode substrates with high rate capability which could be fabricated in the required size, Fiberform (1) cathodes 11 mils thick, reticulated silver foam (2) 16 mils thick, and porous nickel (3) 30 mils thick were tested in cells.

(1) Fiber Materials Inc., Biddeford, ME.

(2) Foamental, Inc., Willoughby, Ohio.

(3) Yardney Electric Corp., Pawcatuck, CO.

2.20 Results

All three materials polarized immediately below 2.7 volts at 52 mA/cm². Although all of these candidate cathode substrates had the mechanical properties desired for large cell construction, none of them proved to be efficient reduction sites for thionyl chloride. Additional ad hoc experiments were conducted in attempts to impregnate reticulated metal foams with SAB. When the pore size of the metal foam was large enough to obtain a reasonable SAB loading, the SAB content sifted out during handling. Impregnation of metal foams with smaller pore sizes that tended to retain the acetylene black resulted in low SAB loadings. Therefore, none of these composite cathodes were tested in cells.

3.0 SUMMARY AND CONCLUSIONS

None of the cell design changes resulted in goal performance of 72 mA/cm² for 8 minutes. Optimum performance was achieved under the conditions shown below:

- 1) Five mil thick glass mat separators
- 2) Cathode formulation of either 90/10 or 95 SAB/5 PTFE
- 3) Cathode cold pressed to 0.45 - 0.50 g/cc density
- 4) Electrolyte of 1.8M LiAlCl₄·SOCl₂.

Under the conditions described above, cells would operate in the eight minute range at current densities of 52 mA/cm² but less than two minutes at 72 mA/cm². It seemed obvious that significant improvement was required to meet the goal.

SECTION II

EVALUATION OF CELL PERFORMANCE IN ACID ($\text{AlCl}_3 \cdot \text{SOCl}_2$) ELECTROLYTE

1.0 INTRODUCTION

1.1 Objective

After completing the work described to this point, we received a report titled "Inorganic Electrolytes" by M. Domeniconi et al, which described work carried out by GTE for ONR under Contract No. N00014-76-C-0524. In this report, the authors describe tests conducted with cells having 15 cm² lithium anodes, glass mat separators and 25 cm² carbon-Teflon cathode cathodes 37 mils thick. With 1.8M $\text{LiAlCl}_4 \cdot \text{SOCl}_2$ (neutral) electrolyte, the cell polarized immediately to below 2.7 volts at 70 mA/cm. However, with 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ (acidic) electrolyte, the cell ran 14 minutes to 2.7 volts.

Accordingly, our objective was to re-evaluate many of the cell construction variables and discharge conditions in acid electrolyte.

1.2 Technical Approach

A series of runs were initiated with our cells using 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ electrolyte. The first few runs at 72 mA/cm² provided discharge times ranging from two to five minutes at +75°F. Inspection of the cells revealed that the polypropylene cell clamps used to maintain electrode contact were being rapidly attacked by the acidic electrolyte. Even though these clamps maintained resiliency for days in neutral electrolyte, they were visibly deteriorating within minutes in acidic electrolyte.

After the clamps were replaced with Teflon coated wire twist locks, reproducibility improved dramatically. At 72 mA/cm², cells consistently ran 5 minutes to 2.7 volts at 75°F. For purposes of comparison, in 1.8M neutral electrolyte cells ran a maximum 2.5 minutes at this current density. Furthermore, the acid electrolyte tended to plateau in the 2.9 - 3.0 volt range during discharge while the neutral electrolyte voltage decayed uniformly during discharge at 72 mA/cm².

2.0 EXPERIMENTAL PROCEDURE

2.1 Pressure

Cells with ten mil cold pressed cathodes were activated with 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ (flooded). After sealing the fixtures, one cell was pressurized with additional argon to 150 lbs gage.

2.2 Results

Figure 3 shows the almost identical discharge curves of both cells. Apparently, sulfur dioxide formed during discharge is absorbed by the electrolyte in both neutral and acid electrolytes.

2.3 Cathode Thickness

Cells were prepared with both ten mil and 40 mil cold pressed cathodes. After activation with 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$, they were discharged at 72 mA/cm².

2.4 Results and Discussion

As shown in Figure 4, the thick cell operated 11 minutes versus 5.2 minutes for the thin cell. This is in direct contrast to the neutral electrolyte studies in which ten and twenty mil cathodes ran 5.6 and 6.1 minutes respectively at 52 mA/cm².

Note, however, that the mid-point voltages of both cells in Figure 4 lie between 2.85 and 2.90 volts. This indicates that both cathodes are equally polarized. As discussed in Section I-2.13, thicker cells necessitate higher current densities. A forty mil cathode would be required to operate at ≈ 200 mA/cm². The similarity of the mid-point voltages indicated that a forty mil cathode would be unable to sustain a potential of 2.7 volts at the required current density.

2.5 Electrolyte Volume

Flooded and wick cells were constructed and activated under conditions described in Section I-2.9.

2.6 Results

Figure 5 shows the voltage-time discharge curves for the cells at 72 mA/cm². Note that the run times are virtually identical and that the major portion of the discharge curve of the wick cell is above 3.0 volts. As in the case of neutral electrolyte cells, there is no apparent need for excess reserve electrolyte storage capacity with acid electrolyte cells.

2.7 Temperature

Cells were constructed, activated with 2.3M AlCl₃·SOCl₂, soaked for one hour at +75, +120 or +165°F and then discharged at 72 mA/cm² at their respective temperatures.

2.8 Results and Discussion

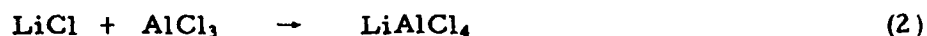
Figure 6 shows the voltage-time curves for the cells. In contrast to the neutral electrolyte studies, we found that elevated discharge temperatures produced higher discharge plateaus and significantly longer run times. Thus, elevated discharge temperatures, which could conceivably be achieved by thermostated coolant, should result in dramatic improvement in cell performance.

In neutral electrolyte cells, lithium chloride is deposited quantitatively in the cathode interstices. Cogley, et al (4) have shown that each equivalent of lithium

(4) Cogley, P. R., Turchan, M. J., "Lithium-Inorganic Electrolyte Batteries," Newton, MA. Research & Development Tech. Report, ECOM-0030-2, May 1974.

anode consumed during discharge produces one equivalent of LiCl in the cathode. The low solubility of LiCl in neutral electrolyte probably accounts for the lack of temperature response in Section I-2.15.

In acid electrolyte however, LiCl can react with the electrolyte to form soluble LiAlCl₄:



This reaction removes the LiCl by solubilization and, in effect, rejuvenates the cathode. One would expect the rate of Eq. 2 to be highly temperature dependent and this would account for the results obtained.

If this assumption is correct, it also follows that cathode limited cells with acid electrolyte should yield higher energy densities than identical cells with neutral electrolyte.

2.9 Electrolyte Molarity

Dominiconi, et al, reported discharge data for 1.8M AlCl₃ and 2.3M AlCl₃ electrolytes which showed significant improvement in cell performance at the higher molarity. Their data showed continuous improvement with increasing molarity but terminated at 2.3 molar. Therefore, we prepared and tested electrolytes in incremental increases of 0.5 molar up to 4.3 molar.

2.10 Results

<u>M, AlCl₃·SOCl₂</u>	<u>Time, Min. to 2.7V</u>
2.3	5.1
2.8	5.1
3.3	5.1
3.8	6.0
4.3	6.0

The discharge curves for 2.8 and 4.3 molar electrolytes are shown in Figure 7. Note that the longer run time of the 4.3 molar cell was achieved at the expense of lower load voltage.

Since the higher molarities only delivered a 17% increase in run time and more baseline data existed for 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$, the remaining cell tests utilized this electrolyte.

2.11 Special Cathodes

A subcontract was let to RPI (5) during the early phase to investigate the ramifications of depositing carbon on metal substrates by chemical vapor deposition (CVD). This technique involves heating of the metal substrate at very low torr and then introducing methane at low rate. The high temperature dissociates the methane and deposits carbon on the metal substrate. Type 304 stainless steel, nickel foil and porous nickel plaque (Yardney) were used as substrates. Dr. R. J. Diefendorf and his assistant, T. R. Jachlewski, performed the experimental work. The results of their efforts are detailed in their report which is included as Exhibit III.

RPI provided samples from all of the experiments in order that we could determine their utility as cathodes. Visual inspection of the samples revealed that the high temperatures required for CVD had seriously warped and embrittled all of the specimens.

2.12 Results

Nevertheless, six specimens that had coherent carbon deposits were tested in 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ at 72 mA/cm². All tests resulted in instantaneous polarization below 2.7 volts. Evidently the type of carbon produced by CVD is unsuitable for the reduction of SOCl_2 .

(5) Rensselaer Polytechnic Institute, Troy, N. Y.

Yardney also supplied a sample of Teflon bonded, activated carbon on Ni grid which is used in air cells. This cathode was 18 mils thick and ran 1.9 minutes to 2.7 volts.

Two samples of porous carbon (6) were supplied by NOSC. The first sample, 21 mils thick, polarized immediately to below 2.7 volts at 72 mA/cm². The second sample, 10 mils thick, had been graphitized to increase conductivity. At +165°F, a flooded cell ran 0.3 minutes while a wick cell ran 0.7 minutes.

An 80/20, SAB/Teflon hot-rolled cathode was prepared by mixing Teflonated SAB with paraffin wax and milling above the melting point of the wax. When the desired thickness is achieved, the paraffin is leached out in hot tetrachloroethane (TCE). The residual TCE is removed by vacuum drying. These cathodes are strong, flexible and can be produced in thicknesses below 6 mils. This cathode ran 3.0 minutes at +75°F versus 5.1 minutes for the best cold pressed SAB cathode. If lower Teflon levels and improved manufacturing techniques could improve the performance of this material, it would be a prime candidate for scale-up tests.

In order to increase the conductivity of the cathode, 6 mil thick nickel expanded metal grids were spot welded to 1 mil thick nickel foil rectangles measuring 0.5 x 1.0 inches. Rather than 35 mg of 95/5, SAB/Teflon, 30 mg of mix were used to allow for the volume occupied by the grid. After cold pressing to 11 mils, the cathodes were assembled into cells, one with the standard 5 mil glass mat separator and one with 3 mil glass mat supplied by Manning (7). This mat contains an acrylic binder which eventually decomposes in neutral electrolyte.

At +75°F and 72 mA/cm², the cell with standard separator ran 4.0 minutes. The voltage plateau was no higher than in cells without grid which indicated that the conductivity of compressed SAB is sufficient. The shorter run time is probably a result of the lower SAB content.

(6) Manufactured by POCO Graphite, Inc., Decator, Texas.

(7) Manniglas 1200, 0.003" thick - Manufactured by Manning Paper Co., Troy, N. Y.

The cell with 3 mil glass mat ran only 3 minutes. It is not known whether the one minute reduction was a result of reduced thickness, binder degradation or higher resistivity.

In many solid oxidant cells, graphite serves as the electronically conductive medium and also doubles as a binder. For example, strong, conductive cathodes of 90 V_2O_5 /10 w/o Graphite can be molded at a few thousand pounds of pressure. If this technique proved applicable to SAB cathodes, the non-conductive binder Teflon could be replaced by graphite. Since the amount of graphite required to form cohesive structures varies with the other component, a few ad hoc pelletizing experiments were carried out with KS-5 (8) and SAB. In this case, a 70 SAB/30 KS-5 blend proved to be moldable at 4000 psi. Cathodes 15 mils thick were prepared by molding 70 mgms of mix. When discharged at 72 mA/cm^2 at $+165^\circ\text{F}$, these cathodes ran 9 minutes versus 12 minutes for 95 SAB/5 Teflon ten mil cathodes. The voltage plateaus were similar and on the basis of SAB loading, the graphite bonded cathodes should have run 16 minutes. Since these cathodes offered no advantages in performance or mechanical integrity, no further effort was expended in this area.

In a telephone conversation with Mr. Herbert Deitrich of FMI, it was pointed out that acetylene blacks appear to be unmatched in reduction efficiency, i. e., as cathodic substrates. FMI immediately initiated a series of experiments to obtain cohesive deposits of SAB on KB-10 which is 15 mil thick vitrified carbon paper. Their initial attempts involved painting a SAB suspension in an organic vehicle, which contained a binder, onto the substrate. After evaporation of the vehicle, the product was heated to 900°C under nitrogen to decompose the binder. The finished product measured $4 \times 4 \times 0.015$ inches and possessed good mechanical integrity. Cells containing these cathodes averaged 2.5 minutes at $+75^\circ\text{F}$ and 72 mA/cm^2 .

(8) A 99.9% pure synthetic graphite with an average particle size of 5μ manufactured by Joseph Dixon Crucible Company.

In further discussions with FMI it was pointed out that the high temperature treatment might be adversely affecting the structural properties of the SAB. They then prepared a suspension of SAB in a mixture of toluene and iso-propyl alcohol without binder. This was applied to KB-10 paper and air-dried at temperatures below 100°C. Two different SAB loadings resulted in 20 mil and ten mil thick specimens. At +75°F and 72 mA/cm², the cells ran 4.0 and 2.9 minutes respectively. This is approaching the 5 minute capability of ten mil cold pressed cathodes at similar conditions. The SAB adheres remarkably well to the KB-10. Extensive immersion in boiling water dislodged only a fraction of the SAB. According to FMI, thinner, more open grades of vitreous carbon paper would permit higher loading of SAB. Unfortunately, they were unable to obtain these grades in time to evaluate them under this contract. In retrospect, it seems likely that a thin, expanded metal screen might also be impregnated by this technique.

2.13 Cell Compression

The Teflon covered wire twist-locks which were used to assemble the acid electrolyte cells have no resiliency. If a cell undergoes negative volume change during discharge, the twist-locks would not be expected to ensure intimate electrode/separator contact and this could adversely affect performance. Therefore, a 10 mil cold pressed cathode was assembled into a cell and approximately 9 lbs/in² of compression was supplied to the cell by a spring binder clip pressing on the glass slides.

2.14 Results

At +75°F and 72 mA/cm², this cell ran 5.0 minutes versus 5.1 minutes for a cell with twist-locks. This indicates that cell assembly measures that ensure intimate electrode to separator contact will result in adequate cell performance.

2.15 Inter-Cell Leakage

If reserve bipolar cell construction and activation schemes can provide absolute isolation of the electrolyte between adjacent cells, then the absence of intercell

leakage paths should result in stack performance equal to single cell performance. In practice, absolute isolation is often impractical or impossible to achieve. In these instances, excess capacity is usually incorporated into each cell in order that the pile may deliver the required watt-hours in spite of intercell leakage currents. The magnitude of intercell leakage that will be encountered appears to be governed by the efficiency of cell isolation (sealing techniques), by the conductivity of the electrolyte (inherent in the system), by the path lengths of bridged electrolyte (through the electrolyte feed paths) and by the number of plates per stack (higher voltages result in higher leak rates).

In order to assess the magnitude of the intercell leakage problem in Li/SOCl₂ cells, several bipolar (2 anode/2 cathode) cells were constructed and discharged. In spite of the fact that they were wick cells, it was observed that capillary action caused the electrolyte to fill the voids between the glass plates. Thus, these cells had intercell leakage paths through the electrolyte film for most of their perimeters.

2.16 Results and Discussion

Figure 8 shows the discharge curves of a cell that was discharged at room temperature after a 10.5 minute open circuit stand and a cell that was discharged at +165°F after a 12.5 minute soak. Both cells had open circuit values which were approximately one volt below theoretical. This indicates that the leakage current between cells was of sufficient magnitude to depress the open circuit to the recorded value. The room temperature cell ran 4.1 minutes versus 5.1 minutes for a single cell at that temperature while the +165°F cell ran only 1.9 minutes versus twelve minutes for a single cell. The severe capacity loss of the latter cell may have been a result of the longer open circuit stand and an acceleration of intercell leakage at the higher temperature.

After discharge, both cells recovered to open circuit values of about 3.5 volts, i. e., those typical of single cells. Inspection of the cells revealed that the number

two bi-metal anode in each pile contained no lithium. Since the anodes in these cells consisted of 7.5 mil thick lithium (about four times theoretical) it seems apparent that thinner anodes would have resulted in shorter run times.

It is probable that the small size of these cells and the complete lack of intercell isolation were highly significant factors in these tests.

Consider that each cell measuring 0.5 x 1.0 inch had a linear leak path of 6 inches/sq inch of electrode. For the intended application, cells 12 inches in diameter with a center feed tube of about one inch diameter are required. Cells of this size with no peripheral sealing would have only 0.36 inch of linear leak path/sq inch of electrode area. Cells with peripheral seals would have only 0.026 inch of leak path/sq inch of electrode area. Thus, intercell leakage would be expected to diminish with increased cell size and improved sealing techniques.

2.17 Electrolyte Viscosity

In reserve mode configurations, the activation time of the battery can be adversely affected during cold temperature operation. Electrolytes which become viscous or salt out at low temperatures impede proper activation. Viscosity versus temperature was measured for 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ over the temperature range of +9 to +46°F.

2.18 Results

The temperature-viscosity curve is shown in Figure 9. At 32°F the electrolyte is about as fluid as water at room temperature and the slope of the curve does not increase drastically at lower temperatures. No salting out occurred and it is assumed that this electrolyte would be functional over a fairly wide temperature range.

3.0 SUMMARY, CONSLUSIONS AND RECOMMENDATIONS

The use of acid electrolyte effected the most dramatic improvement in cell performance. Whereas a cell with 1.8M $\text{LiAlCl}_4 \cdot \text{SOCl}_2$ ran only 1.8 minutes at $+75^\circ\text{F}$ and 72 mA/cm^2 , a cell with 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ electrolyte ran 5.1 minutes under the same conditions. Furthermore, the capacity of acid electrolyte cells was found to increase at higher discharge temperatures. At 72 mA/cm^2 , twelve minutes of operation were obtained under the conditions described below:

- 1) Five mil thick glass mat separator
- 2) Cathode formulation of 95 SAB/5 PTFE
- 3) Cathode cold-pressed to 0.45 - 0.50 g/cc density
- 4) Electrolyte of 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$
- 5) Discharge temperature of $+165^\circ\text{F}$

Thus, the Li/SOCl_2 system has demonstrated the rate capability to meet the intended application. Further investigation is recommended in the problem areas listed below:

- 1) Cathodes - improved techniques must be developed to manufacture strong, thin cathodes that equal or surpass cold pressed SAB/PTFE performance.
- 2) Intercell Leakage - using improved cathodes, the severity of intercell leakage should be investigated. If required, cell isolation sealing techniques should be developed.

- 3) Heat - the ΔT during discharge of cell stacks should be measured to obtain temperature profiles.
- 4) Separators - the search should be continued for thinner, stronger alternatives to 5 mil glass mat.

Successful resolution of problems one and two combined with the data from three should prove invaluable in any future scale-up efforts.

SECTION III

DISCUSSION OF BATTERY CHARACTERISTICS

1.0 INTRODUCTION

A concept of a battery for under water propulsion (see Exhibit 2) was provided by NOSC as part of the contract document for the work being reported herein. As a contractual requirement for this final report the design and critical aspects of a battery for undersea weapon propulsion is to be discussed and modified as required using as the basis the data generated under this contract and Honeywell's experience in the design and construction of the Li/SOCl₂ power sources. Our considerations in these areas are discussed in Section III - 2.0 through 9.0.

2.0 CONCEPTUAL DESIGN OF THE BATTERY SECTION- ITS CELL MODULES AND AUXILIARY EQUIPMENT

The NOSC preliminary battery design concept as shown in exhibit 2 served as the basic concept throughout our work with the following exceptions.

Single Cell

- 10 mil cathodes were found necessary to deliver the required run times at 72 mA/cm² (the NOSC design shows 6 mil cathodes).
- 3 mil separators were used instead of 2 mil separators as shown.
- 1 mil of Ni metal was used for the cathode substrate instead of the 4 mil Al with a Ni flash.
- 3 mil of Li are deemed necessary to allow for losses due to intercell leakage, film formations during storage and inefficient utilization near the end of discharge. The NOSC concept shows 2 mil of Li which is the theoretical amount required.

The above results in an overall cell thickness increase of 3 mils.

The Cell Module

Honeywell agrees completely with the NOSC concept for the cell module which consists of 22 single cells connected in parallel to provide 60 V at 50 amps. We feel, however, that 509 cc of electrolyte solution is required instead of 350 cc as shown for the NOSC concept. This is based on laboratory experimental cells discharged at 72 mA/cm². If improvements in cell reaction efficiency can be made, the amount of solution required would approach the 350 cc value.

The electrolyte solution now considered best as discussed in Section II is 2.3 to 4.3M AlCl₃ in SOCl₂ instead of 1.8M LiAlCl₄ + 13% S₂Cl₂ in SOCl₂.

The concept of a bladder between each cell is good except that a suitable material to use as an acceptable bladder is difficult to find as the acid electrolyte attacks all plastics except highly fluorinated hydrocarbons (which will have sealing problems). Stainless steel bellows were considered but because of the small thickness and large diameter required, electrolyte transfer efficiency would be poor. In addition, a reliable method of activation would be difficult to develop. If this concept could be developed the collapsed bladder would provide the space for circulating water for module cooling.

Honeywell has more than 20 years experience via designing reserve activation concepts for high rate ammonia cells. The approach used in those cells is adaptable to this cell and therefore design concepts have been generated using a single reservoir to activate 40 modules of 22 cells each. The best battery design is shown in Figures 10 and 11. The activation concept is shown in Figure 12. It involves a stainless steel bellows that contains the electrolyte solutions. A pressure is applied in back of the bellows (usually from stored freon gas) to serve as the force that will collapse the bellows on activation when a diaphragm on the battery is ruptured. This can be accomplished manually, by pyrotechnics or pneumatically. Activation across the

top of the cell stack as shown will initially provide heat through intercell leakage to get the battery to an ideal operating temperature and after complete activation intercell leakage will be eliminated without expensive, complicated valving. Activation through the center of the cell stack is possible but presently is considered to be excessively complicated.

Designs have been generated (based on the above concept) for batteries utilizing cells capable of 72 mA/cm^2 (present Honeywell capability) to 250 mA/cm^2 (optimistic estimate of what may be possible from the Li/SOCl_2 electrochemistry). Design data based on these two extremes are shown below.

Cathode thicknesses assumed for both designs is 10 mils. This is because as the understanding is gained to reach 250 mA/cm^2 , the discharge reaction efficiency will be increased in a like manner. The anode thickness used for the 250 mA/cm^2 design was 7 mils while 3 mils was used for the 72 mA/cm^2 design. All other parameters were the same for both designs. It is Honeywell present thinking that with the appropriate development effort the true length and weight will fall somewhere in the middle of the weight range of 104 to 238 pounds and length range of 13 to 36 inches.

Design #1 (Assume 72 mA/cm² current handling capability)

40 Modules (5 series stacks of 8 in parallel)

- 60V and 57A each module
- 3420 watts and 456 watt hours each module
- 300V and 456A each battery
- 136.8 KWatts and 17.2 KWatt hours each battery

Weight Analysis

- Battery*	=	115#
- Electrolyte	=	75# (20 liters)
- Electrolyte container **	=	48# (12" OD x 14" L)
- Total	=	238#

Length Analysis

- Battery	=	22 inches
- Electrolyte container	=	14 inches
- Total	=	36 inches

Energy Analysis

- Whr/#	=	72
- Whr/in ³	=	4.2

Power Analysis

- W/#	=	573
- W/in ³	=	33.6

* Includes case, terminal plate, buss bars and plastic barriers between modules.

** End plates designed to contain \approx 100 psi without deforming.

Battery Design #2 (Assume 250 mA/cm² current handling capability)

15 Modules (5 series stacks of 3 in parallel)

- 60V and 133A each module
- 9000 watts and 1200 watt hours each module
- 300V and 400A each battery
- 120 KWatts and 16 KWatt hours each battery

Weight Analysis

- Battery * = 48#
- Electrolyte = 28# (7.7 liters)
- Electrolyte Container ** = 28# (12 inches OD x 5" long)
- Total = 104#

Length Analysis

- Battery = 8 inches
- Electrolyte container = 5 inches
- Total = 13 inches

Energy Analysis

- Whr/# = 154
- Whr/in³ = 10

Power Analysis

- W/# = 1100
- W/in³ = 72

* Includes case, terminal plates, buss bars and plastic barriers between modules.

** End plates designed to contain 100 psi without distorting.

3.0 IDENTIFICATION AND DISCUSSION OF HAZARDS

The major hazard associated with Li/SOCl₂ cells is that Li metal (the anode) and sulfur (a discharge reaction product) when hot (> 170°C in the dry state) can explode. In excess electrolyte explosions due to the presence of sulfur do not occur below 360°C. Methods found useful in eliminating the sulfur/Li reaction in cells are as follows:

- 1) Anode limited cell designs
- 2) Additives to batteries that dissolve sulfur
- 3) Proper heat rejection and cooling
- 4) Warm cells (≈ 55°C) containing excess electrolyte for ≈ 24 hours to react the sulfur that has formed
- 5) Use of a pressure vent

A completely different mode known to cause explosion is forcing cells into electrode polarity reversal. This mode of explosion is not fully understood but could involve plating of Li metal into the positive electrode of the cell. The condition can occur in batteries containing cells connected in series such as is the case for the battery proposed here for under water weapon propulsion.

The use of diodes or any other means of preventing cell reversal is recommended for batteries such as proposed here, at least until the problem is better defined. Some of the solutions suggested above, such as use of a pressure vent, may be useful in minimizing the hazard associated with cell reversal.

4.0 CONCEPTS FOR BATTERY DISPOSAL

The current practice used by Honeywell in disposing of large Li/SOCl₂ cells is as follows:

- 1) Remotely connect discharged cells thru a predetermined bleed resistor until the open circuit voltage of the cell is 0.0 volt.
- 2) Remotely heat the cell at temperatures of about 50°C to eliminate sulfur (by-product of discharge reaction) via the reaction $2 \text{SOCl}_2 + 3\text{S} \rightarrow \text{SO}_2 + 2 \text{S}_2\text{Cl}_2$.
- 3) Remotely puncture the cell.
- 4) Remotely immerse cell in medium such as water.

It should be noted that the above disposal technique applies only if the following design conditions exist:

- 1) An anode-limited cell design
- 2) Cell is electrolyte-flooded and contains enough SOCl₂ to react with the theoretical amount of sulfur generated during discharge.

If used in an underwater weapon such as a torpedo, the above disposal technique may not be practical. If not, it should be possible to eject the used battery from the weapon and allow it to be destroyed by chemical attack of the sea water. There are no strategic materials in the battery and the chemicals or their reaction products should not be a significant ocean contaminant.

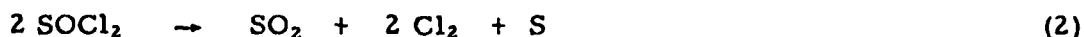
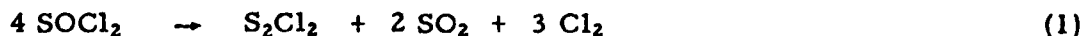
5.0 EXPECTED STORAGE LIMITATIONS

The battery is to be stored in the reserve mode. Therefore, two issues need to be addressed:

- 1) Compatibility of the material of construction used for the electrolyte reservoir, and
- 2) Decomposition of the solution over the storage period and effects thereof.

The AlCl_3 in SOCl_2 solution to be used in the battery is acidic and hence very corrosive in nature. Both components of the solution are extremely reactive. The solution will attack many plastics and several metals and alloys. The choice of the material of construction is limited to stainless steel which has excellent resistance to chemical attack as long as there is no water in the solution. Water is undesirable in the battery and strict precautions must be taken to keep the water content to a minimum (≈ 50 ppm). Therefore, an electrolyte reservoir made from stainless steel can effectively contain the reactive electrolyte over the anticipated storage period (10 years).

Decomposition of the thionyl chloride over the long storage period is conceivable. Two different mechanisms are possible:



Thermodynamic considerations show that reaction (1) is more likely to occur than reaction (2). But, even reaction (1) will not proceed spontaneously at temperatures below 580°C . The effect of AlCl_3 , well known for its catalytic properties, on the decomposition of SOCl_2 are not known yet. However, in view of the high spontaneous

reaction temperature, it appears unlikely that decomposition of SOCl_2 will be significant over the storage period at the anticipated storage temperatures up to $+162^\circ\text{F}$. Thus, no problem is foreseen. Nevertheless, it is recommended that the storage characteristics of the $\text{AlCl}_3 \cdot \text{SOCl}_2$ solution be established over a 10 year period via periodic analysis of the stored solution for qualitative and quantitative determination of the expected decomposition products.

6.0 IDENTIFICATION OF TECHNICAL RISK AREAS

The technical risk areas that can be identified at this time are as follows:

- 1) Safety
- 2) Intercell leakage
- 3) Activation
- 4) Heat rejection

1. Safety

The reactions which have resulted in hazards in the past are rapidly being understood and it is Honeywell's opinion that lack of safety is not an inherent phenomena associated with the electrochemistry involved. Design solutions such as anode limited cells, electrolyte flooded cells and additives to remove sulfur as it is formed are already showing promise in making Li/SOCl_2 cells safe. Honeywell, however, although optimistic about the safety of these cells cannot yet say the problem has been solved.

2. Intercell Leakage

If a bipolar electrode design is used to build the high rate batteries, there will be intercell leakage. The extent of the leakage is not yet fully known but present

indications are that it will be small. If serious intercell leakage must be solved, the problem could be difficult to solve because of the limited materials that can be used with the very reactive thionyl chloride. Honeywell has dealt with severe intercell leakage in ammonia batteries for years and is optimistic about design solutions to this potential problem.

3. Activation

The activation concept shown in the design of Section III - 2.0 is practical and has been developed fully. With this approach activation in less than 6 seconds is realistic. Metering of the proper amount of solution to each cell is more of a problem. If individual reservoirs must be attached to each cell because of cooling requirements development of the activation system could be the major risk area.

4. Heat Rejection

Preliminary indications are that some heat must be rejected from the battery. If the amount to be rejected is enough that large quantities of water must be circulated, the battery weight and length could become excessive and therefore not be competitive with other forms of undersea weapon propulsion.

7.0 ESTIMATED ACTIVATION TIME

This activation time is based on test data obtained on the NSWC battery development program (Contract No. N60921-75-C-0078). These data show that 250 cc of electrolyte can be delivered in 30 seconds thru manifold tubing which has a total cross sectional area of $7.85 \times 10^{-3} \text{ in}^2$.

The flow rate (R_1) associated with the above test work is as follows:

$$R_1 = 250 \text{ cc}/30 \text{ seconds} = 8.33 \text{ cc/sec}$$

Based on transferring 22,000 cc of electrolyte, the flow rate required in the propulsion (R_2) battery design in order to activate in 5 seconds has been computed as follows:

$$R_2 = 22,000 \text{ cc}/5 \text{ seconds} = 4400 \text{ cc/sec}$$

Assuming that the electrolyte driving pressure is constant at 15 psi as it was in the above NSW test work, the cross sectional area (A_2) required to achieve a flow rate R_2 is equal to:

$$A_2 = \frac{R_2}{R_1} \times \text{Cross sectional area associated with } R_1.$$

$$A_2 = \frac{4400 \text{ cc/sec}}{8.33 \text{ cc/sec}} \times 7.85 \times 10^{-3} \text{ in}^2.$$

$$A_2 = 4.15 \text{ in}^2 \text{ or } 2.3 \text{ inch ID tubing.}$$

It should be pointed out that the above analysis is very conservative, i. e., the area required may be significantly less than that computed above. The reasoning behind this is that for the test data presented, the manifold tubing diameter was very small and no attempt was made in the above analysis to correct for the wall friction associated with the flow in these small diameter (0.050 inch) tubes.

8.0 ESTIMATED WASTE HEAT AND COOLING REQUIREMENTS

Significant heat generation is foreseen during two stages (1) activation and (2) discharge.

Heat will be generated during activation because of the chemical reaction between Li and SOCl_2 leading to the formation of LiCl. The reaction is spontaneous and highly exothermic. With neutral solutions (that contain LiAlCl_4 as the electrolyte) such a reaction slows down very quickly because the LiCl forms a protective film on Li.

With an acidic solution (containing AlCl_3 as the electrolyte), as in this battery, some of the LiCl formed on activation is dissolved by the Lewis acid AlCl_3 , forming LiAlCl_4 . As a consequence, the protective film is stripped and the reaction between Li and SOCl_2 will continue to be rapid for a longer time. The implication is that much more heat will be generated during activation with the acid electrolyte than with a neutral electrolyte. Preliminary experiments with small test cells, performed under an internal Honeywell program, have shown that heat generation during activation with acid electrolyte to be about $5 \text{ cal/cm}^2 \text{ Li}$. Since, the reaction generating the heat is chemical, normalization on the basis of lithium area is considered to be accurate.

A single module of the battery has an anode area of approximately 15400 cm^2 . Thus, the heat of activation can be projected to be 77 Kcal per module. If this heat is not removed, the temperature of the module with an estimated average specific heat of $0.2 \text{ cal/g } ^\circ\text{C}$ will rise about 200°C or well above the melting point of Li . Thus, considerable amount of heat will need to be removed. It must be pointed out that this heat is generated quite rapidly, over a 10 second period. On that basis the required cooling rate will be 32 KW (7.65 Kcal/sec). Other ways of reducing this heat, besides cooling, must be found. Two possible approaches are:

- 1) Adding an optimum quantity of LiCl to the solution such that the LiCl film is not stripped rapidly while at the same time permitting the high discharge rate; and
- 2) Introducing the electrolyte cold, perhaps using sea water to cool it in the reservoir.

During discharge, heat is generated due to the irreversibilities in the discharge process. These irreversibilities, like ohmic losses, electrode polarization, etc., increase with increasing current. The result is that the electric work done by the battery is accompanied by heat. The voltage drop in the cell (open circuit voltage -

operating cell voltage) is a measure of such irreversibilities. The heat generated in a single cell discharging at I amperes with a voltage drop of ΔV volts is $I \cdot \Delta V$ watts. With the acid electrolyte, an open circuit voltage of 4.0V is attained on activation. A single cell of the battery is required to operate at 2.7V and 50 amperes. Therefore heat generation in a single module, containing 22 cells is estimated to be $(22 \times (4 - 2.7) \times 50)$ 1430 watts. Total heat generation in the 40 module battery is projected to be 57.2 KW. The battery is required to operate for 8 minutes during which time 6.56×10^6 cal will be generated. If none of this heat is removed, the temperature of the battery (190 lbs, 0.2 cal/g °C) will rise 380°C. Such a temperature rise cannot be tolerated. Hence considerable cooling is required.

There is one difference between the heat generation during activation and discharge. The activation heat is generated at the anode, which is a good conductor of heat and has a high specific heat, both of which are desirable and help cooling. The heat during discharge is mostly generated inside the carbon cathode which has a very low specific heat and poor thermal conductivity, both of which hinder cooling.

Another source of heat generation is the intercell leakage, inevitable in a bipolar cell. There is no data available on how much intercell leakage would occur. Hence the resulting heat generated cannot be quantified. The intercell leakage can be minimized, however, and the consequent heat generation can be made insignificant compared to the heat generated during activation and discharge.

9.0 DEPTH AND PRESSURE EFFECTS ON CELL PERFORMANCE

Experiments carried out during the course of this contract indicate that pressure will have little beneficial or detrimental effect on battery performance if the cells are tightly built into the battery.

SECTION IV

ACTIVE BATTERY CONSIDERATIONS

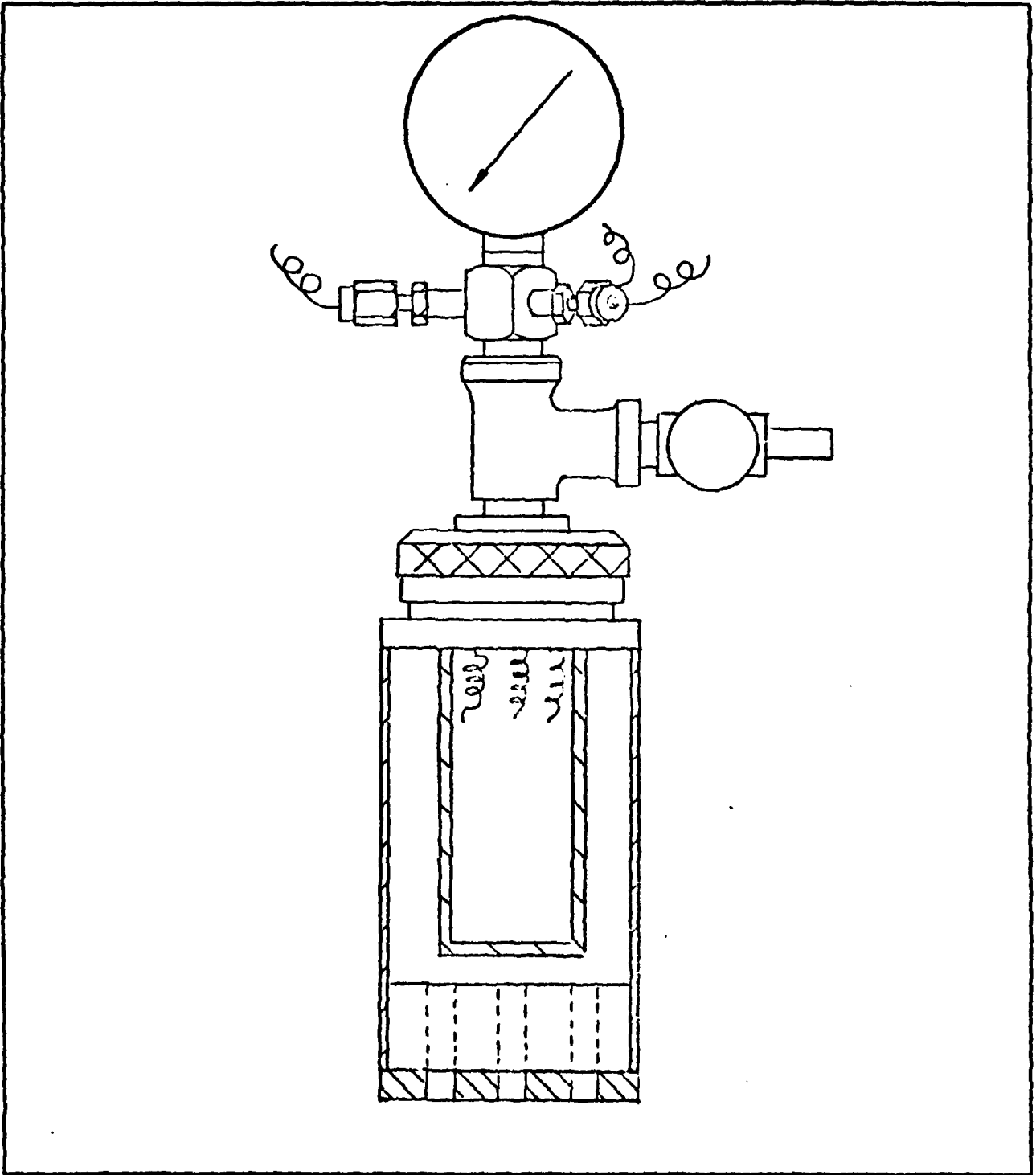
The battery as presently conceived for underwater weapon propulsion is of the primary reserve type because the electrodes of the battery are not compatible during extended periods of storage when in contact with the electrolyte solution. Therefore, the electrolyte solution is stored apart from the electrodes until time of use. If the components could be stored together (in the active mode) the battery weight and volume would be nearly cut in half.

With today's Li/SOCl₂ technology the major problem centers around the material added to the thionyl chloride to produce conductive solutions (either LiAlCl₄ or AlCl₃). When LiAlCl₄ is used a LiCl film growth forms on the anode (Li) of the cell during storage which limits the current handling capability of the battery. When AlCl₃ (acid) is used the Li electrode is consumed in just a few days. The storage of Li in pure thionyl chloride (free of ionizable halides) appears to be stable for very long periods of time, even at 75°C.

During the course of this contractual effort and while discussing the concept of active batteries for underwater weapon propulsion with the NOSC technical monitor, Mr. Merz of Honeywell conceived the idea of placing the pure thionyl chloride (electrolyte solvent) in the cells and in contact with the electrodes. (A stable situation as discussed above.) The battery in this condition is not capable of delivering current because ions are not available in the solution to transport the current from one electrode to the other. However, by substituting a gaseous acid for the AlCl₃ (solid) presently being used a means could be developed for adding the gas when power is needed from the battery.

By storing only the gas outside the battery in a small cylinder considerable space and weight savings could be achieved. Mr. Merz suggested the use of a gas such as BCl₃ (boron trichloride) for this purpose. The idea has not yet been evaluated but if feasibility can be demonstrated, Honeywell will apply for a patent, identifying that

78-142

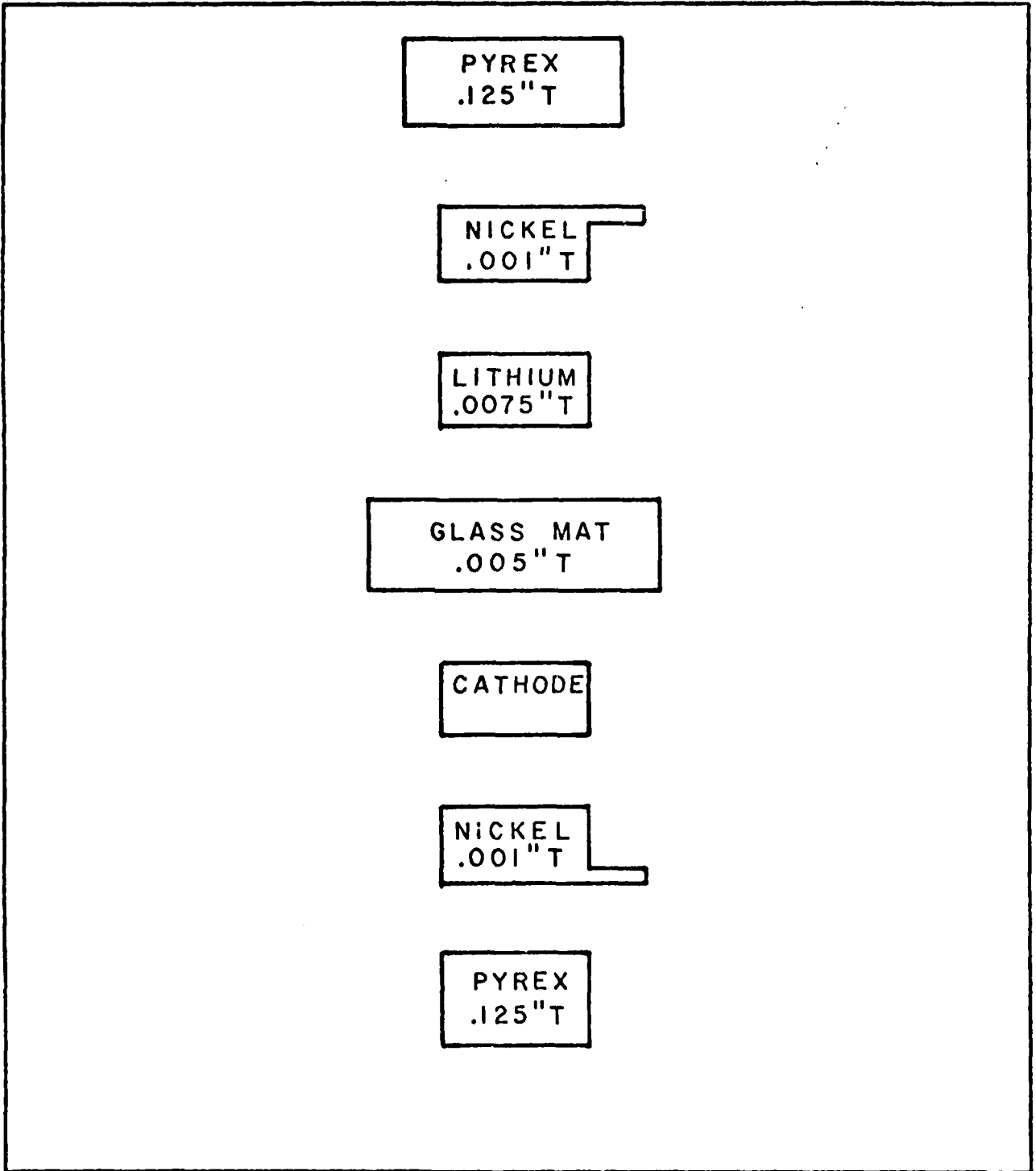


FORM FM-100

TEST CHAMBER

FIGURE 1

78-143

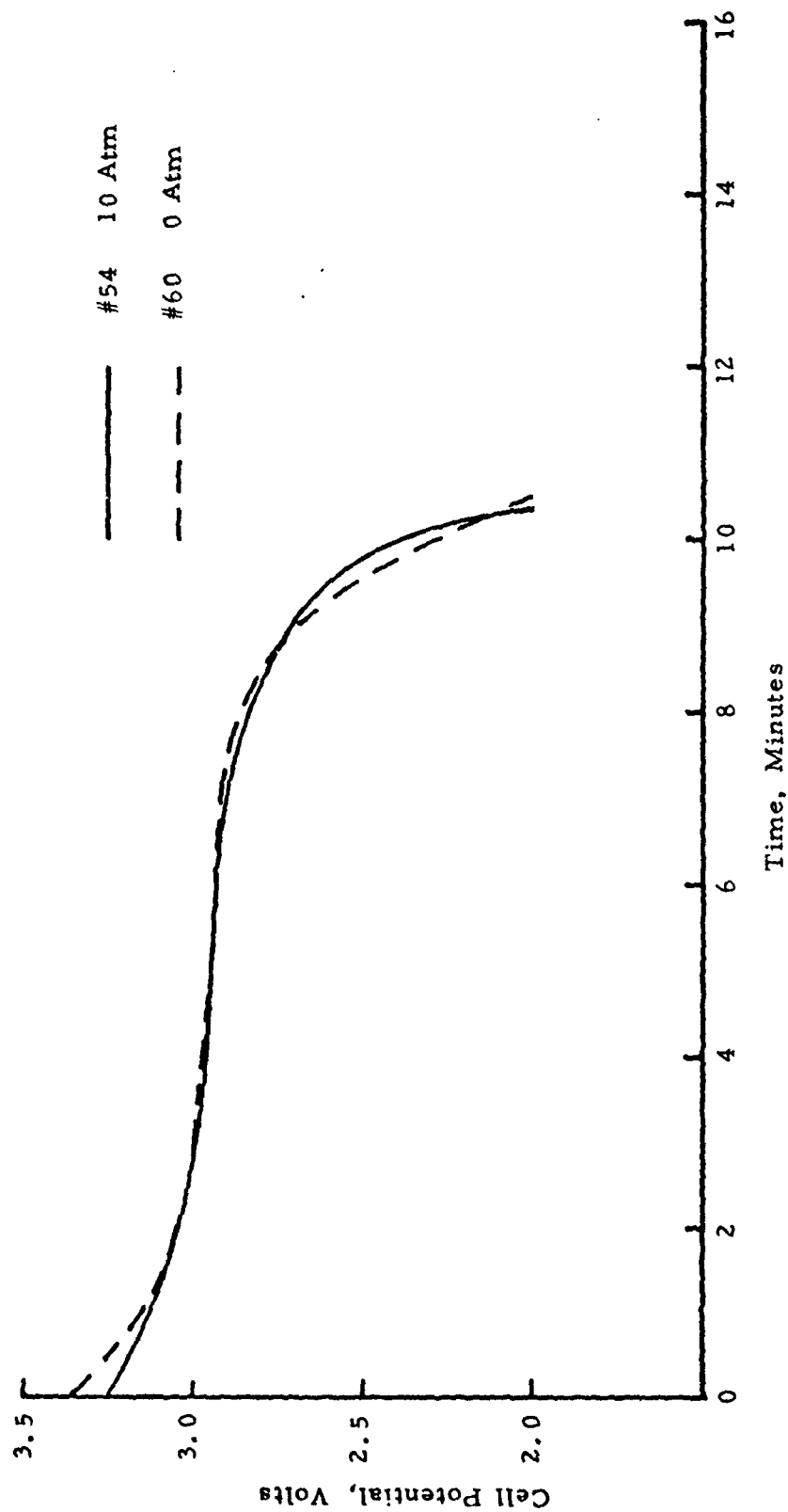


FORM FM-100

CELL COMPONENTS - EXPLODED VIEW

FIGURE 2

Electrolyte: 2.3M $\text{AlCl}_3 \cdot \text{SOCl}_2$ (flooded) Cathodes: Cold pressed, 95/5 mix, 10 mils
 Current Density: 72 mA/cm² Anodes: Lithium, 7.5 mils
 Electrode Area: 0.5 in² Separator: Glass fiber mat, 5 mils
 Temperature: +120°F Grids: Nickel foil, 1 mil
 Gauge Pressure: 0 or 10 Atm



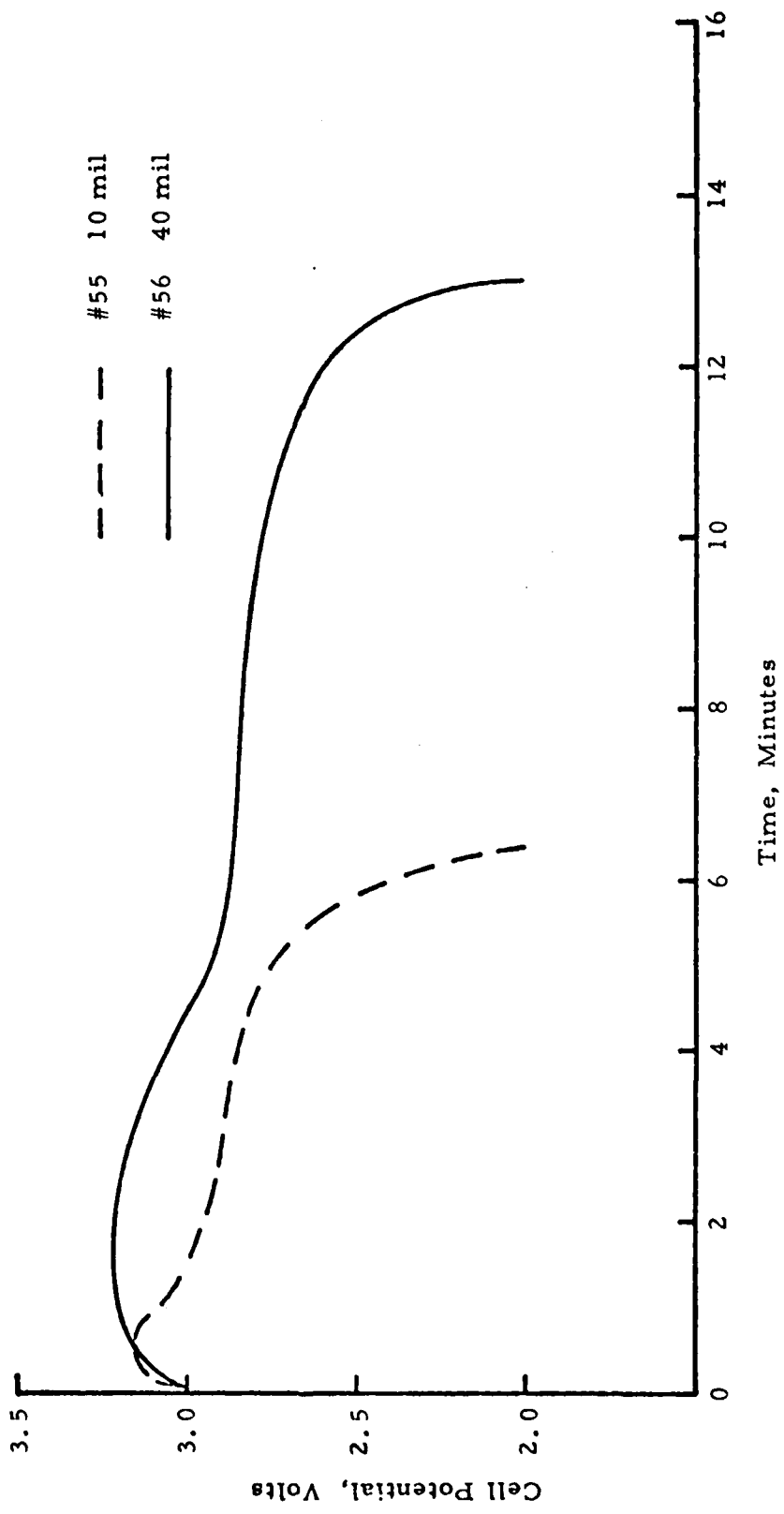
FORM FM-101

THE EFFECT OF PRESSURE ON CELL PERFORMANCE

FIGURE 3

76-158

Electrolyte: 2.3M $AlCl_3 \cdot SOCl_2$ (flooded) Cathodes: Cold pressed, 95/5 mix, 10 or 40 mils
Current Density: 72 mA/cm² Anodes: Lithium, 7.5 mils
Electrode Area: 0.5 in² Separator: Glass fiber mat, 5 mils
Temperature: +75°F Grids: Nickel foil, 1 mil
Gauge Pressure: 0 Atm



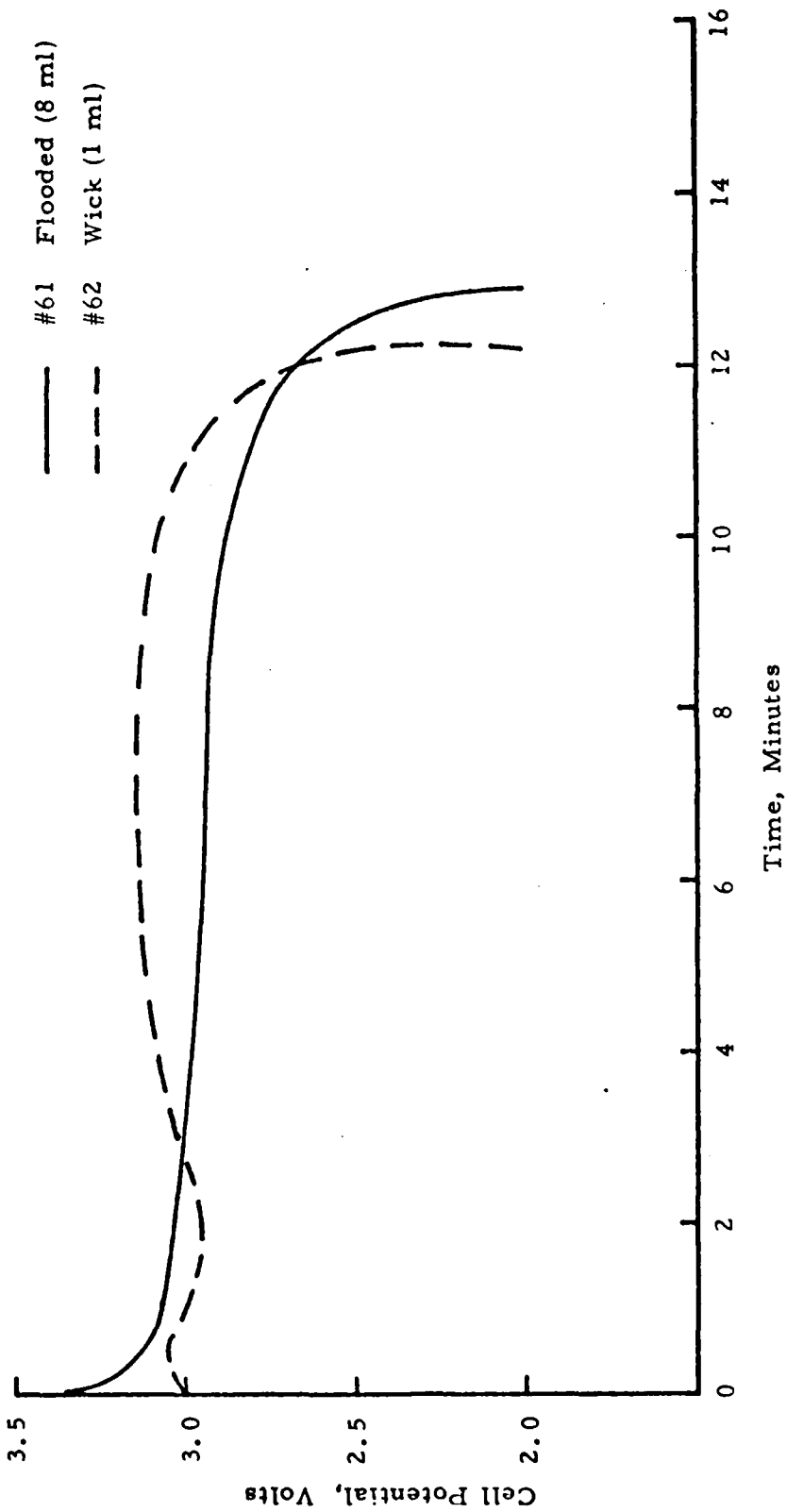
FORM FM-101

THE EFFECT OF CATHODE THICKNESS ON CELL PERFORMANCE

FIGURE 4

Electrolyte: 2.3M $AlCl_3 \cdot SOCl_2$
Current Density: 72 mA/cm²
Electrode Area: 0.5 in²
Temperature: +165°F
Gauge Pressure: 0 Atm

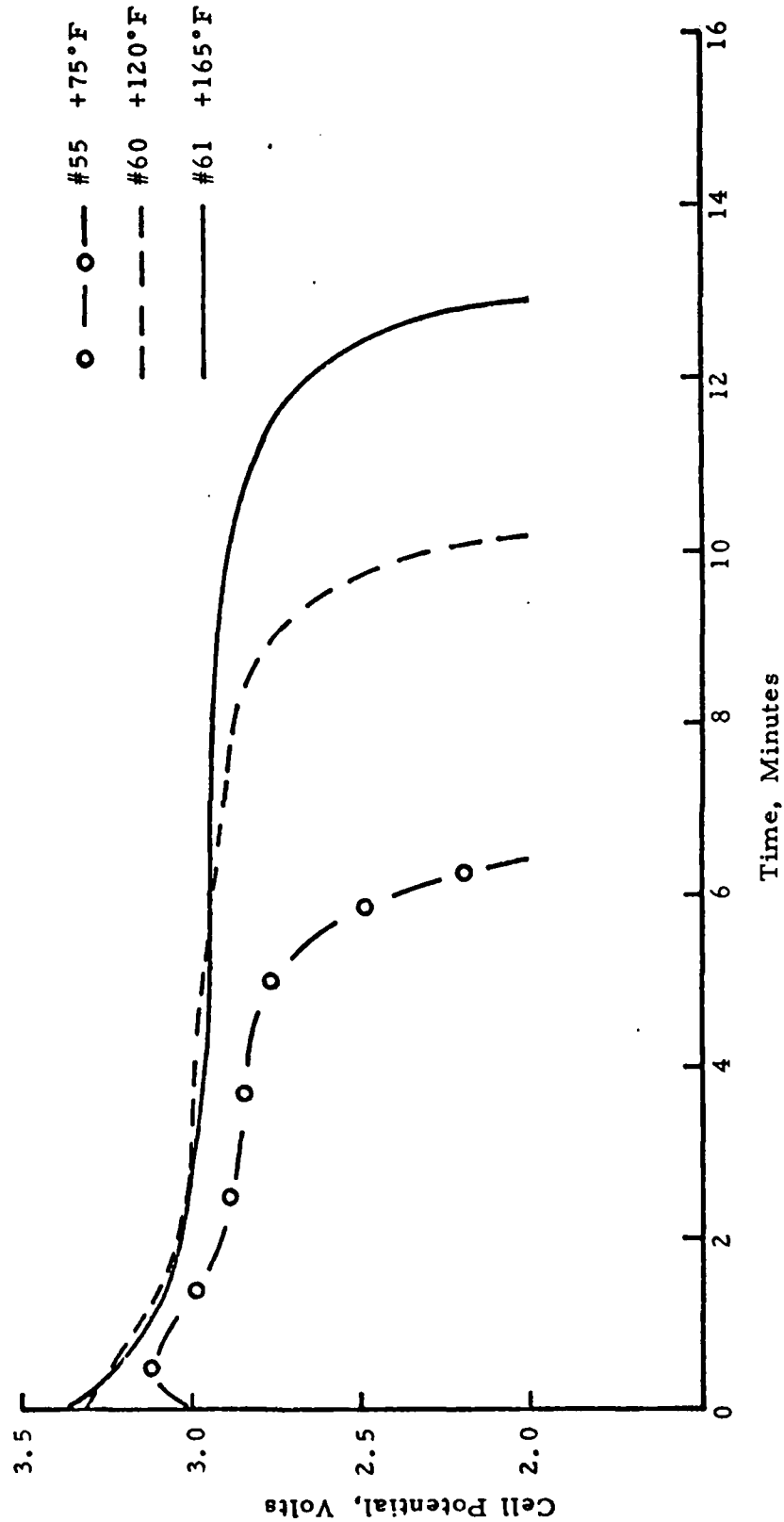
Cathodes: Cold pressed 95/5 mix, 10 mils
Anodes: Lithium, 7.5 mils
Separator: Glass fiber mat, 5 mils
Grids: Nickel foil, 1 mil



THE EFFECT OF ELECTROLYTE VOLUME ON CELL PERFORMANCE

FIGURE 5

Electrolyte: 2.3M AlCl₃·SOCl₂ (flooded) Cathodes: Cold pressed 95/5 mix, 10 mils
Current Density: 72 mA/cm² Anodes: Lithium, 7.5 mils
Electrode Area: 0.5 in² Separator: Glass fiber mat, 5 mils
Temperature: +75°F, +120°F, +165°F Grids: Nickel foil, 1 mil
Gauge Pressure: 0 Atm



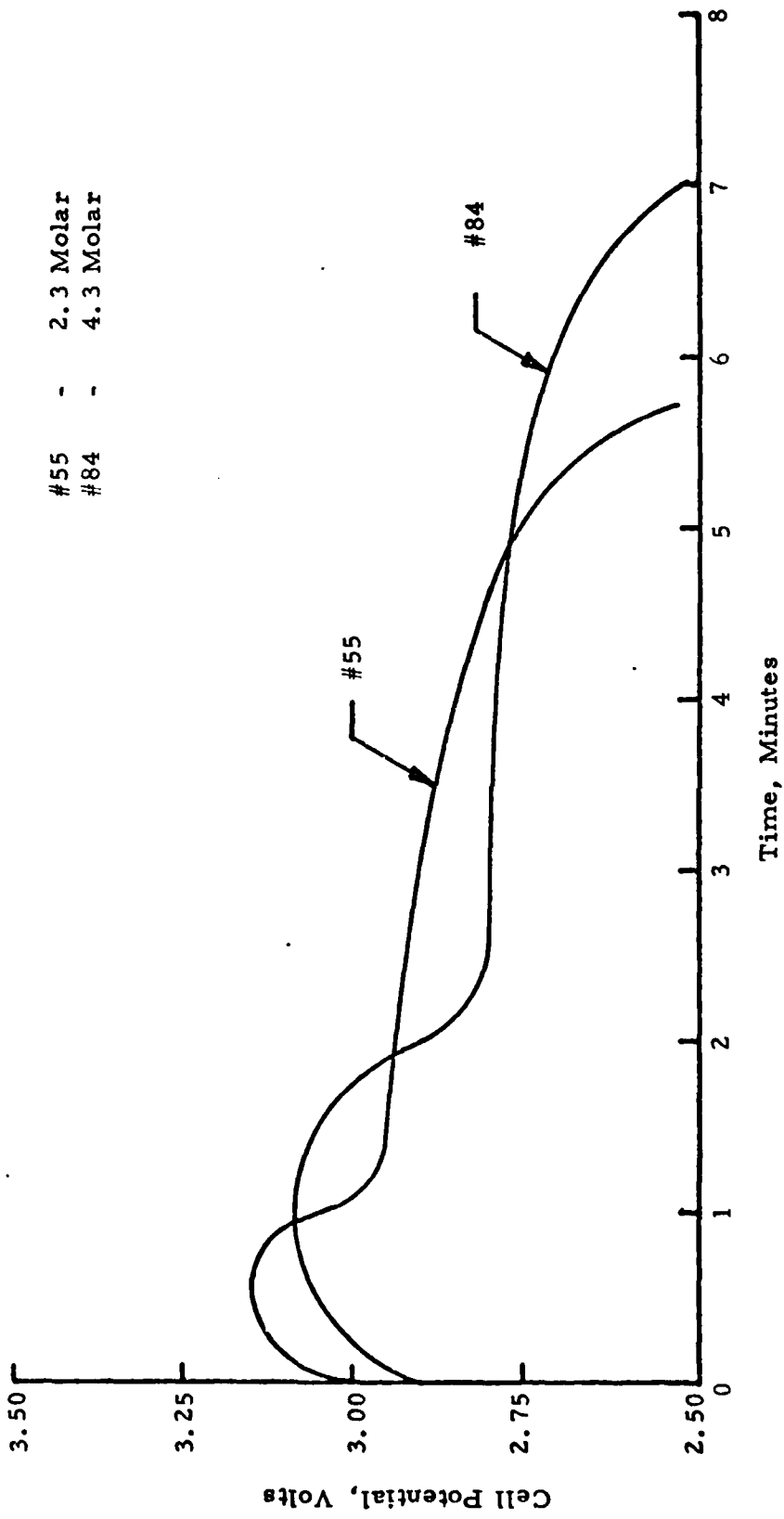
THE EFFECT OF TEMPERATURE ON CELL PERFORMANCE

FIGURE 6

78-145

Electrolyte: XM $AlCl_3 \cdot SOCl_2$
 Cathodes: Cold Pressed, 95/5 mix, 10 mils
 Current Density: 72 mA/cm²
 Anodes: Lithium, 7.5 mils
 Electrode Area: 0.5 in²
 Separator: Glass fiber mat, 5 mils
 Temperature: +75°F
 Grids: Nickel foil, 1 mil
 Gauge Pressure: 0 Atm.

#55	-	2.3 Molar
#84	-	4.3 Molar



FORM FM-107

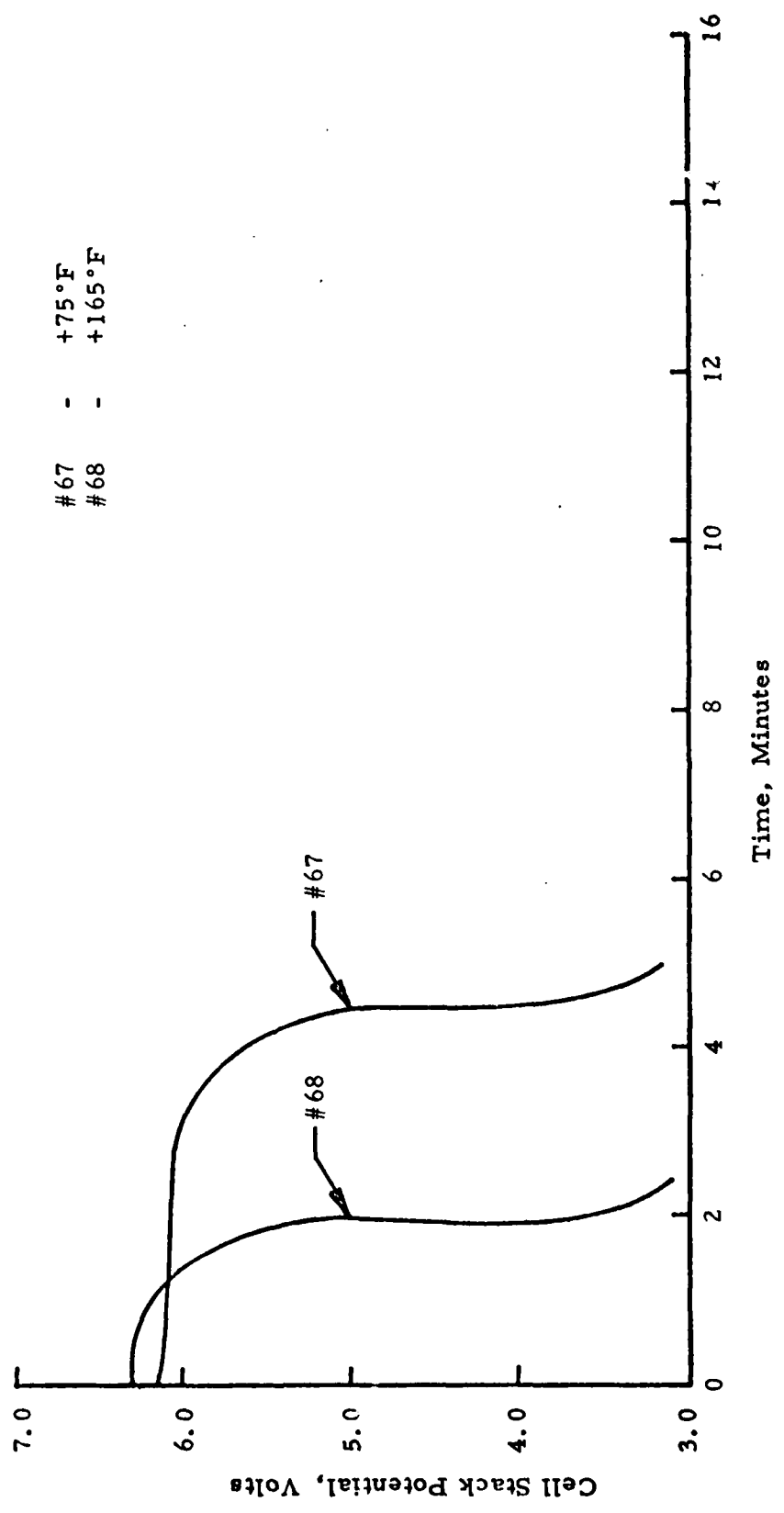
THE EFFECT OF ELECTROLYTE MOLARITY ON CELL PERFORMANCE

FIGURE 7

78-146

Electrolyte: 2.3M $AlCl_3 \cdot SOCl_2$ (1 ml, wick)
 Cathodes: Cold pressed 95/5 mix, 10 mils
 Current Density: 72 mA/cm²
 Anodes: Lithium, 7.5 mils
 Electrode Area: 0.5 in²
 Separator: Glass fiber mat, 5 mils
 Temperature: +75°F, +165°F
 Grids: Nickel foil, 1 mil
 Gauge Pressure: 0 Atm.

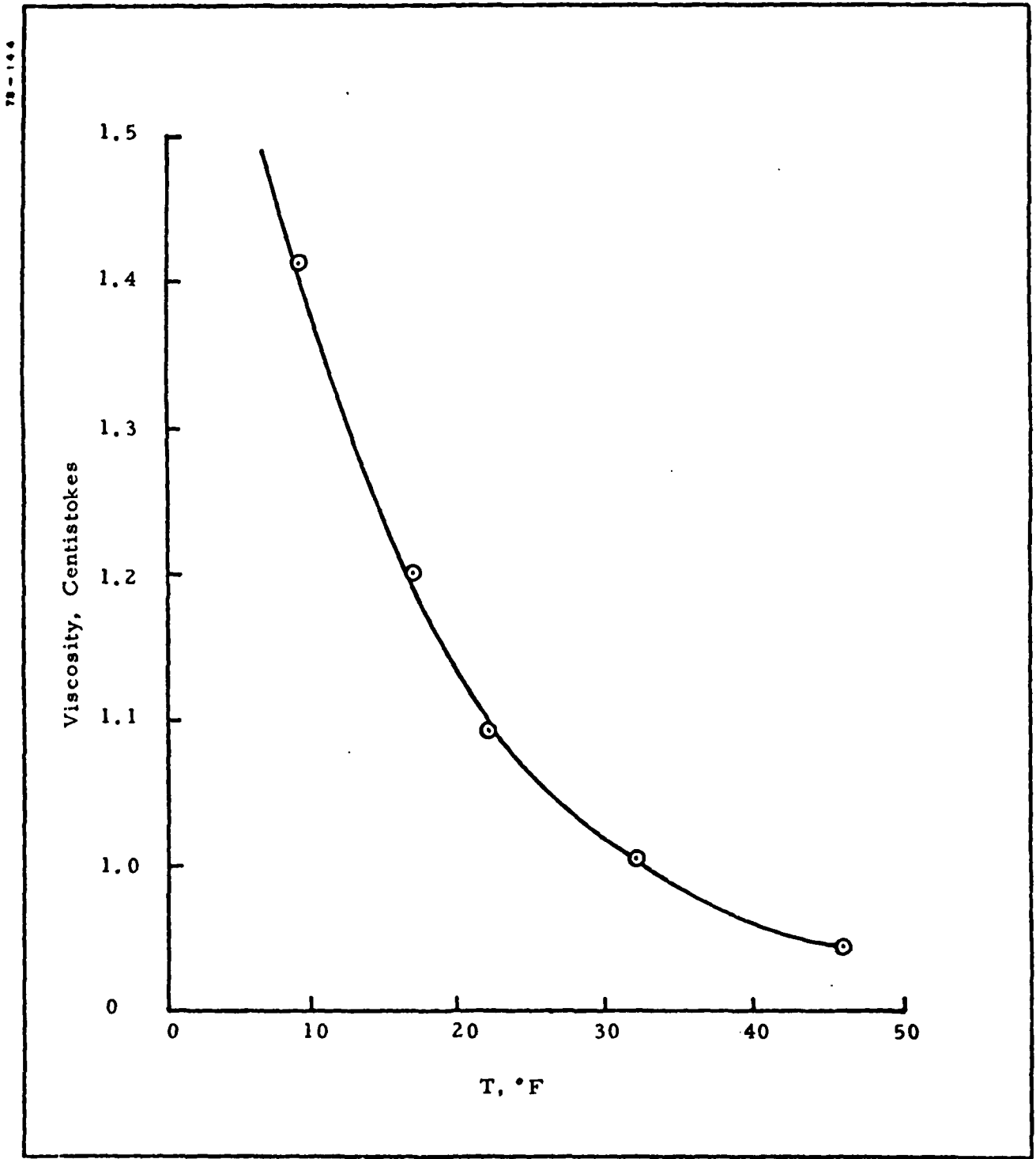
#67 - +75°F
 #68 - +165°F



FORM FM-101

THE EFFECT, TIME, TEMPERATURE AND INTERCELL LEAKAGE ON BIPOLAR CELLS

FIGURE 8

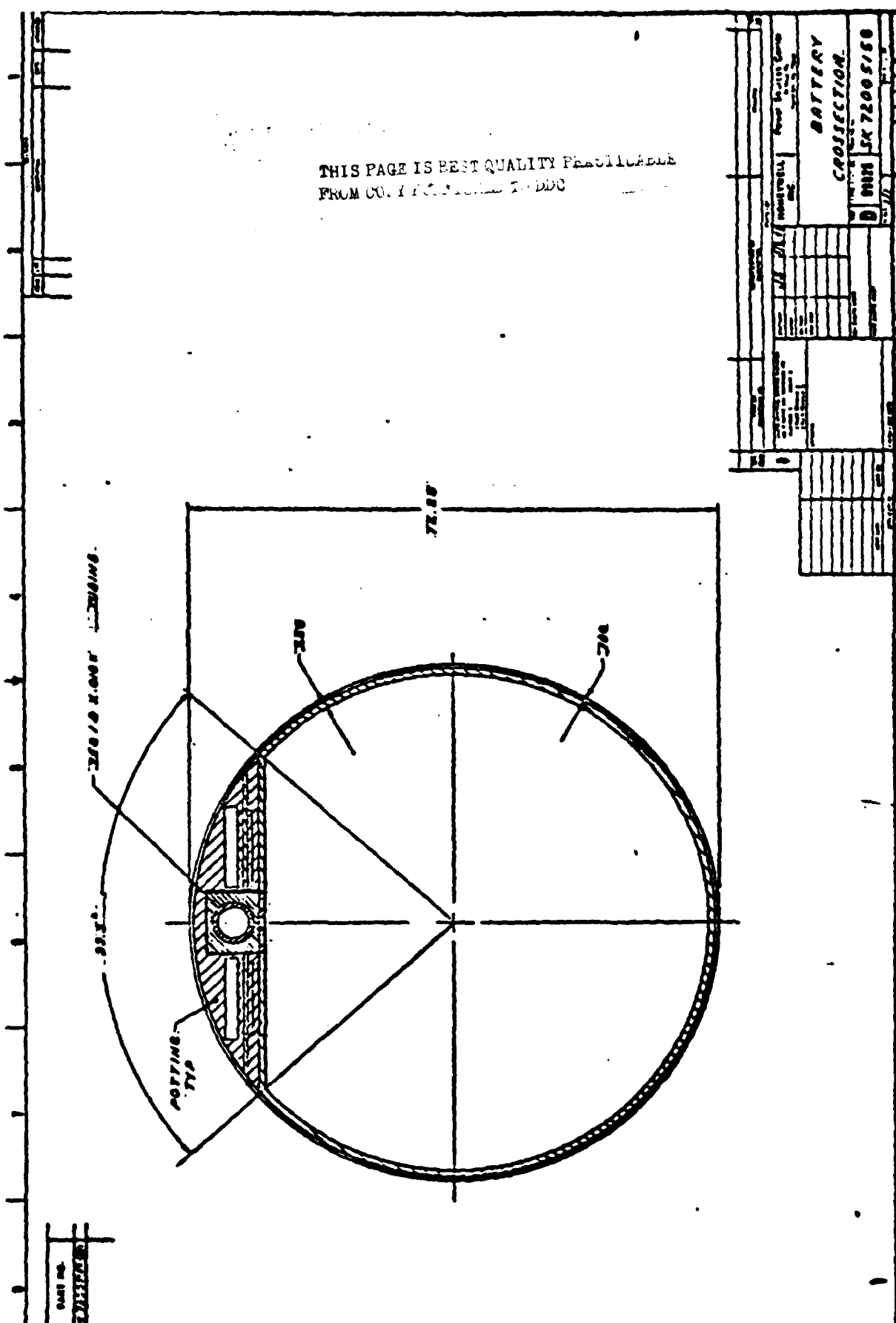


FORM FM-100

VISCOSITY OF 2.3M $AlCl_3 \cdot SOCl_2$ VS. TEMPERATURE

FIGURE 9

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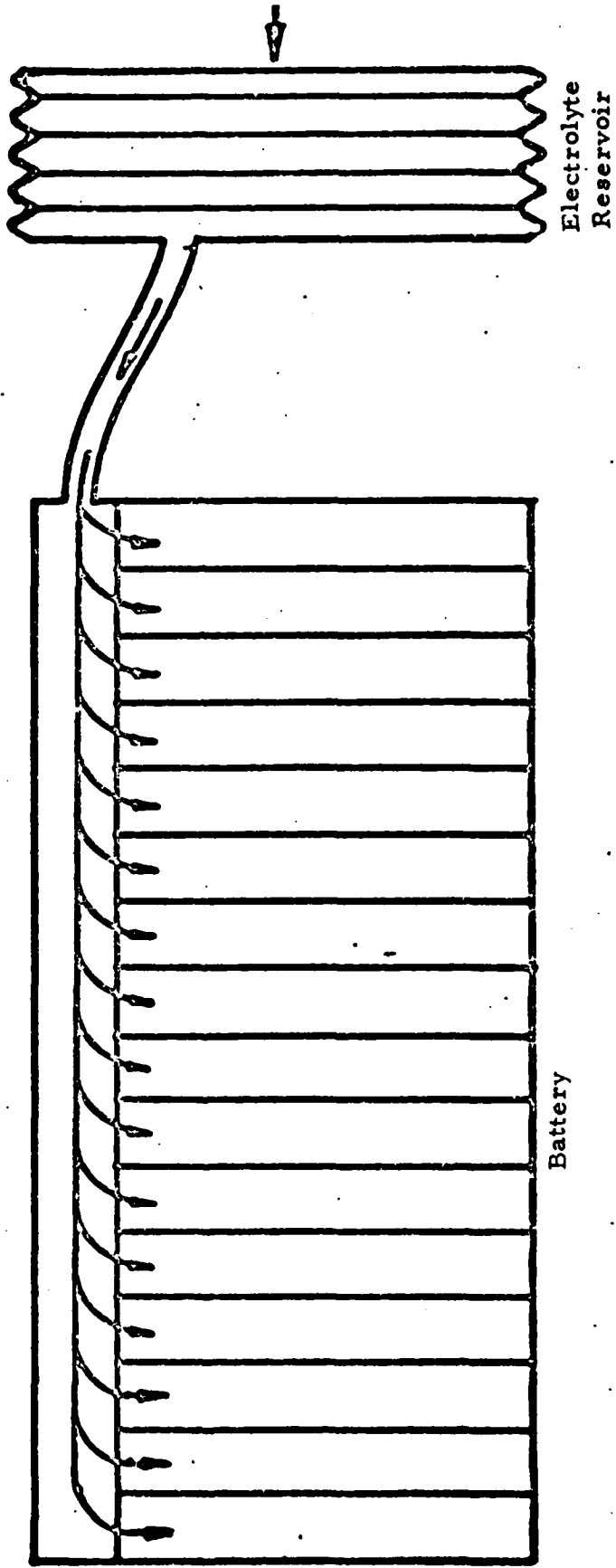


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BATTERY
COLLECTION
DMM JK 7205150

... ..

DATE 10/1/50
BY 11111111



HONEYWELL Li/SOCl₂ PROPULSION BATTERY ACTIVATION CONCEPT
FIGURE 12

ACKNOWLEDGMENT

We would like to acknowledge the extensive cooperation extended by Mr. Herbert Dietrich of Fiber Materials Inc in providing cathode specimens.

Yardney Electric Company was also generous in supplying samples of their active carbon air cathodes and porous nickel plaques.

Finally, the meticulous efforts of Jon S. Gore, were invaluable in the areas of cell construction, cell discharges and data collation.

PHYSICAL ENVELOPE AND PERFORMANCE SPECIFICATION FOR A TYPICAL
LITHIUM BATTERY FOR UNDERSEA WEAPON PROPULSION

Battery type	-	Reserve electrolyte
Battery dimensions:		
Max OD	-	12.75 inches (32.38 cm)
Max length	-	26.0 inches (66.0 cm)
Performance specifications:		
Power	-	120 KW
Energy	-	16 KWh
Power density	-	> 1095 W/kg
	-	> 2.39 W/cm ³
Energy density	-	> 146 Wh/kg
	-	> 0.32 Wh/cm ³
Operating temperature	-	27°C
Operating depth	-	2000 ft (610 meters) max.
Self noise	-	Low
Radiated noise	-	Low
Safety	-	Non-explosive
Storage	-	Uncontrolled 10 years at 70°C
Noise	-	Low self and radiated noise
Other considerations provided were:		
Space for routing electrical cables longitudinally thru battery section		
	-	2 square inches (12.9 cm ²)
Seawater for cooling:		
Supply head	-	50 psi (3.45 x 10 ⁵ pascal)
Flow rate	-	100 g/sec (6.31 liters/sec)

NOSC DESIGN CONCEPT OF A LITHIUM BATTERY FOR
UNDERSEA WEAPON PROPULSION

The first design was a battery consisting of 114 cylindrical, reserve electrolyte, pressure compensated cells. Each cell was designed to deliver 400 amperes at 2.6 volts. Cell dimensions were 2-1/2 inches in diameter and 6.42 inches long. Total battery length was 38.52 inches for a cell performance of 76 mA per square centimeter of electrode surface. (An alternative battery performance at 100 mA/cm² of electrode surface was 32.52 inches.) The battery was seawater activated, that is, hydrostatic pressure forced the electrolyte into the volume of active elements. The water also cooled the discharging cell.

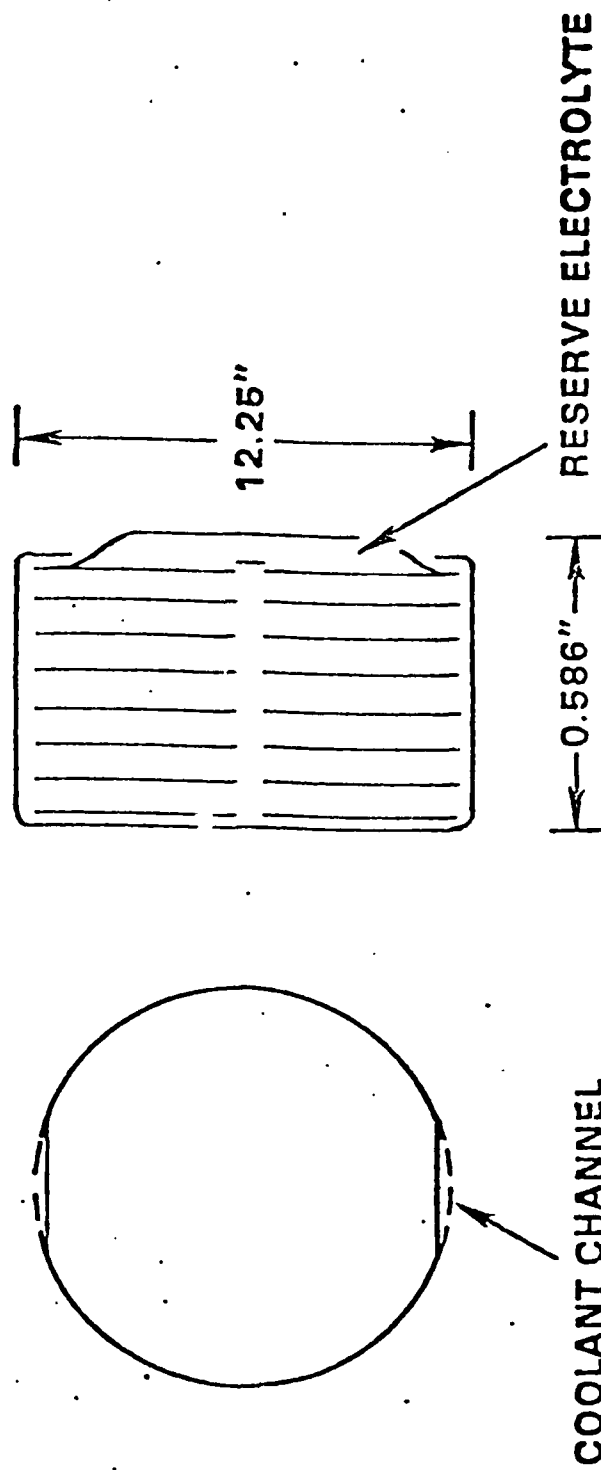
In an effort to shorten the torpedo battery length, NOSC designed a bipolar lithium cell. Each bipolar module delivers 50 amps at 60 volts or 71.2 mA per square centimeter of electrode surface. Each torpedo battery pack is composed of 40 modules with a total battery pack length of 23.5 inches. Figure E-1 shows the bipolar concept and Figure 2 illustrates a 12-3/4 inch diameter advanced torpedo layout for the propulsion system.

The individual module has the following design characteristics:

Electrical output - 60 volts/50 amps/3000 watts/400 watt-hours
Cell performance - 2.7 volts/71.2 mA/cm²
Cells/module - 22 bipolar cells
Cell area - 702 cm²
Anodes - 0.002 inches of lithium
Cathodes - 0.006 inches of carbon (81% porous)
Electrode base material - 0.004 inches of aluminum with nickel flash
Separators - 0.002 inches of fiberglass (74% porous)
Heads - 0.031 inches of aluminum with nickel flash
Bladder - 0.010 inches of nickel

FIGURE E-1

IMPROVED CELL CONFIGURATION FOR TORPEDO APPLICATIONS



PILE TYPE CONSTRUCTION OF 22 BIPOLAR CELLS
PROVIDING 60 VOLTS AT 50 A

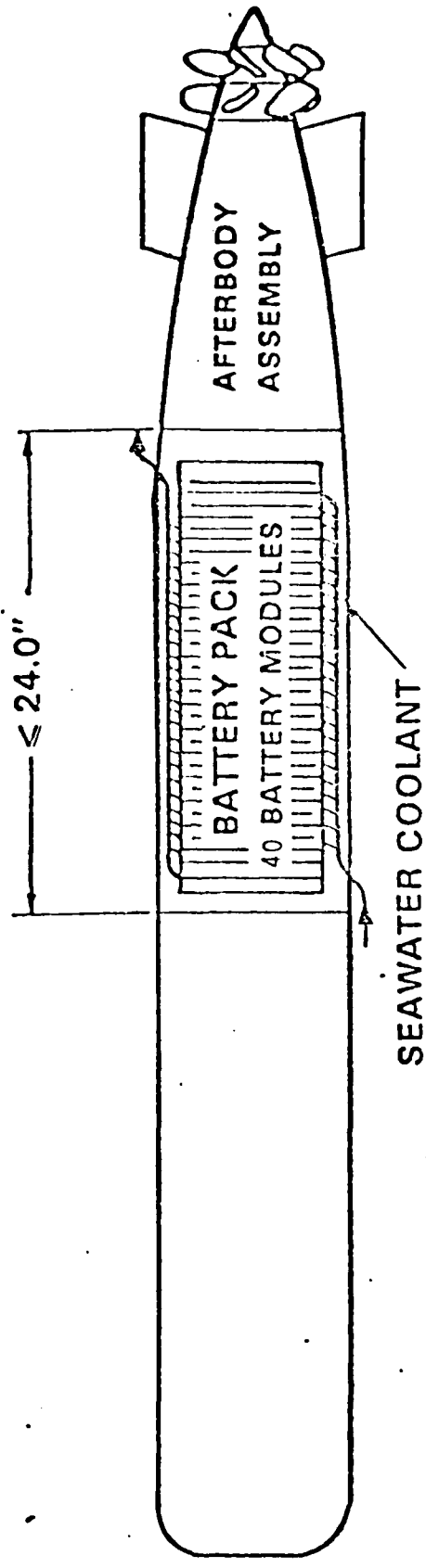


FIGURE E-2
TORPEDO LAYOUT FOR PROPULSION SYSTEM

-
-
Electrolyte - 350 cc (SOCl_2 + 1.8M LiAlCl_4 + 13% S_2Cl_2)
-
Dielectric coating - 0.002 inches of teflon
-
Total weight - 4.3 lbs/module
-
Total heat rejection - 1462 watts at 1 volt drop

-
The entire battery for an advanced propulsion system has the following design characteristics:
-

-
Electrical output - 300 volts/400 amps/120 kw/16 kWh
-
Number of modules - 40 modules (8 in parallel/5 in series)
-
Total heat rejection - 58.5 kw
-
Total module weight - 171 pounds
-
Battery section diameter - 12.75 inches OD
-
Battery length - 24 inches
-
Shell weight - 23 pounds
-
Bus weight - 7 pounds
-
Cooling water weight - 40 pounds
-
Total weights - 241 pounds
-
Battery section volume - 3063 in³
-
Wet condition energy - 66.4 Wh/lb, 5.22 Wh/in³
-
Wet condition power - 498 W/lb, 39 W/in³

-
The lithium advanced torpedo propulsion system also has many safety features:

-
Reserve electrolyte - Maximum safety when remotely activated
-
Lithium limited - No lithium at end of life
-
Many small modules - Limited energy/modules
-
Expendable battery - At sea disposal
-
Electrolyte additive (S_2Cl_2) - Non-explosive modules
-
Parallel/series modules - Averages performance variations
-
Pressure equalized - No high pressure build-up
-
-

-
- Other advantageous considerations are:

- Self noise - Battery has no source of noise

- Payload - Battery section is less than 30 inches long thereby providing maximum payload

- Safety - Reserve electrolyte configuration provides maximum safety

- Cost - Estimated to be \$2000 per battery; requires no precious metals for recycling

- Response time - Simultaneous activation of all cells provides fast startup

- Radiated noise - Battery is silent

- Wake - None

- Vehicle recovery weight - Lithium batteries are the lightest weight energy source

- Reliability - Simplicity of all design should result in high reliability

- Variable speed - Battery efficiency is very high at reduced loads, thereby providing infinitely variable speed capability and sustained low speed endurance

Report #1

CARBON DEPOSITIONS ON CARBON AND NICKEL SUBSTRATES

Submitted to

Honeywell Incorporated

N66001-77-C-0284

Dr. R. J. Diefendorf
Principal Investigator

T. R. Jachlewski
Research Assistant

Rensselaer Polytechnic Institute
Materials Engineering Department
Troy, New York 12181

January, 1978

Three runs were made in this primary investigation. These three runs placed an emphasis on the nickel substrates, and secondarily on the carbon substrates, due to ease of working with the nickel materials. The final run made use of results gained in the first two runs to improve adhesion.

The parameters of each run were:

100% CH₄ gas flow
2.0 torr pressure
1100°C temperature
50 hours run time
1000 SCCM flow rate

These parameters indicate a maximum gas concentration of methane for chemical vapor deposition (CVD) of carbon to occur. The temperature and pressure are in a region where a more amorphous and voluminous carbon deposit should occur without melting the nickel substrate. A growth cone deposit is observed in some photographs; this type of deposit is more dense and probably not as desirable. The flow rate (standard CC per minute) also aids an amorphous, somewhat porous deposit.

Chopped Fiber and Shawinigan

Chopped fiber and shawinigan(soot) appears to have no mechanical strength. Some stability is necessary for battery use, so as a main substrate this combination was not pursued. In order to develop a porous carbon deposit 150-200 μ thick, these materials were then applied to the nickel substrate surfaces. The CVD of carbon was intended to cement the composite structure together to form a coherent, adhesive deposit.

In each run four nickel pieces were used, in the first run the plain nickel sheet and in the second run the nickel plaque. In each run a set of four samples were evaluated. These were: 1) a plain nickel surface, 2) nickel surface with soot (shawinigan), 3) a soot and carbon fiber coating on the nickel surface, 4) a coating of fibers on the nickel surface.

Nickel Substrates

The photographs included show the nickel sheet and nickel plaque substrates and the CVD of carbon on the surface. These carbon deposits appear to have excellent adhesion to the nickel surfaces as well as good impregnation into the sintered nickel powder in the plaque. The deposit is 5-6 microns thick which represents an approximately 0.1 micron per hour deposition rate. This rate is as expected at the temperature used. Along with an extremely strong adherence, no spalling or fracture of the CVD of carbon deposited was observed. This could have occurred due to the mismatch in coefficient of thermal expansion between nickel and carbon upon cool-down. A composite structure is clearly necessary to develop the 150-200 μ porous carbon surface.

Further observations on the plain nickel sheet and nickel plaque showed negligible warping or buckling of the nickel samples during firing. The samples used were of course small, the only damages incurred were primarily mechanical from specimen preparation.

Further sintering and shrinkage which might occur during the firing of the nickel plaque was difficult to estimate. This should be included in any size considerations where the plaque material is used.

Composite Nickel, Chopped Fiber and Shawinigan Substrates

The three other specimens in each run were composites of carbon substrates on the nickel surfaces. The first was a simple soot coating. An actual substrate of soot (perhaps pressed) would have been too fragile. The soot was placed dry, directly in contact with the plain nickel sheet in the first run. As seen in the photograph, the adherence of selective soot particles to the nickel surface was good. In the second run an attempt at a uniform layer was made. Soot particles were suspended in acetone and the surface of the nickel plaque washed with the mixture. When the acetone vaporized a coating of carbon was left. When fired, this coating appears to have been too dense. It formed a separate layer which spalled off, as can be seen from the samples sent to Honeywell. In the future a roughened nickel surface should be used as a substrate to improve adhesion. Then a deposit of porous carbon of proper thickness may best be obtained by depositing a soot layer on nickel substrate. The nickel plaque has sufficient roughness but the nickel sheet would require some roughening to hold the powder.

Both type of nickel surfaces were used with chopped carbon fiber and a mixture of chopped carbon fiber and soot coatings. The plain fibers were too voluminous and did not adhere well to the surface or within itself as a bundle. While chopped fibers did not work, a carbon fiber weave as a porous carbon substrate would probably have worked well. Cost and fragility would probably exclude this alternative, however.

The soot and chopped fiber mixtures produced results similar to the plain soot coatings described above. All formed spalled but mechanically sound layers when applied as a dense uniform layer.

Third Run

Four samples were included in this test. These were two nickel plaque substrates, one with a rough (soot) layer rubbed over the surface. Soot with a PVA (polyvinyl alcohol) binder in water was the other coating. Nickel sheet was the main substrate for a second soot and PVA coating, another sheet was a soot and light oil coating.

These carbon layers were cemented together by the CVD of carbon process to produce a coherent, porous carbon layer on the nickel substrate.

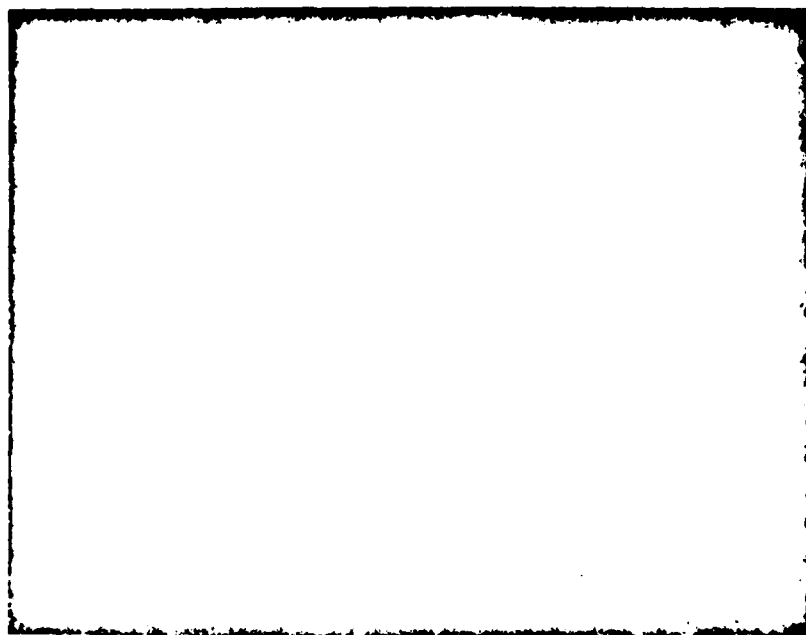
In all cases some adhesion was achieved, although not acceptable because some spalling occurred. The carbon layer was flaky and tended to fall off. The only exception was a soot layer rubbed over the surface of the nickel plaque. After the CVD of carbon, this layer seemed best in uniform adhesion but was too thin and difficult to control.

Final Runs

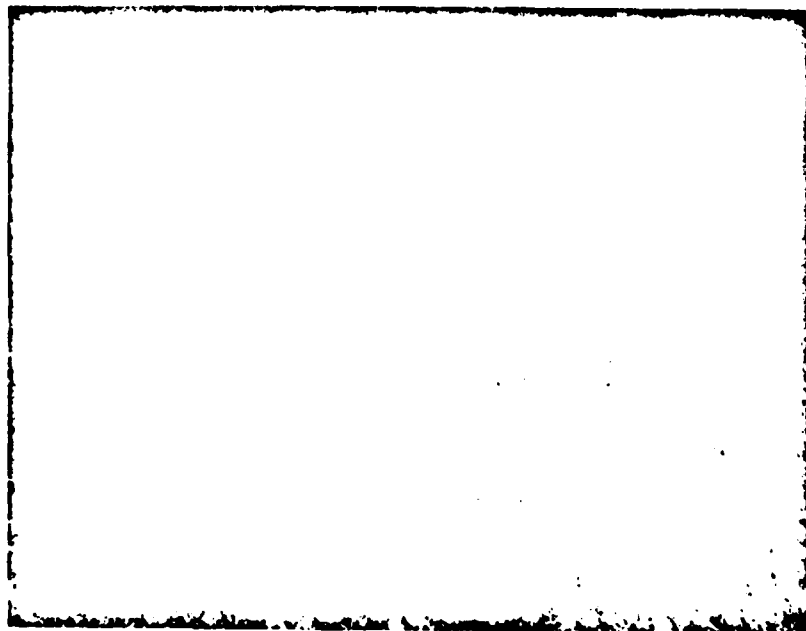
As a final series of experiments, a measure of success was obtained using pitches as the carbon coating.

The nickel sheet was processed to obtain an approximately 1.0 μ thick CVD of carbon layer. This was done to assure a good carbon nickel bond, (and was found necessary). Run parameters were the same as before except run time was reduced to ten hours.

Ashland-240 pitch was then placed on the substrate.

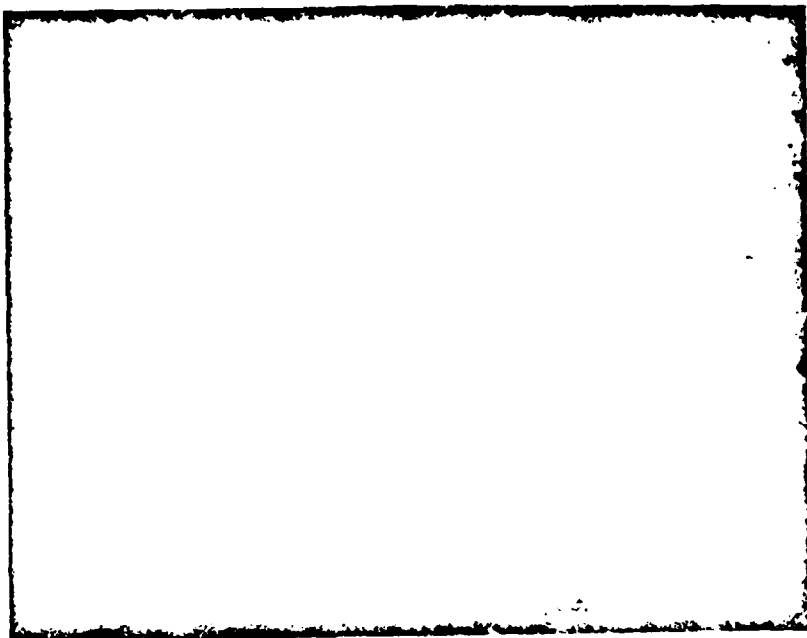


(a)

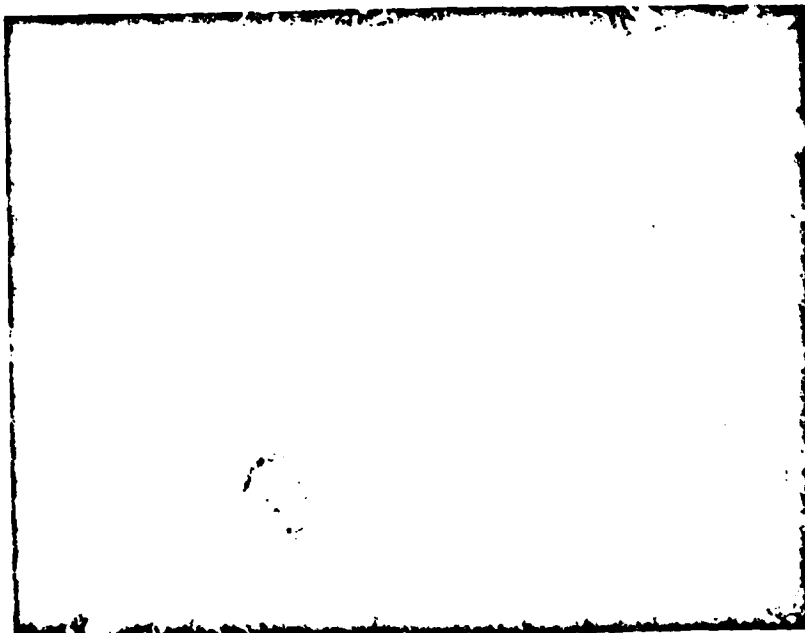


(b)

Nickel plaque specimen edge;
a) without, b) with CVD of carbon.
500X



(a)



(b)

Nickel plaque, a) without, b) with CVD carbon. 500X.



(a)

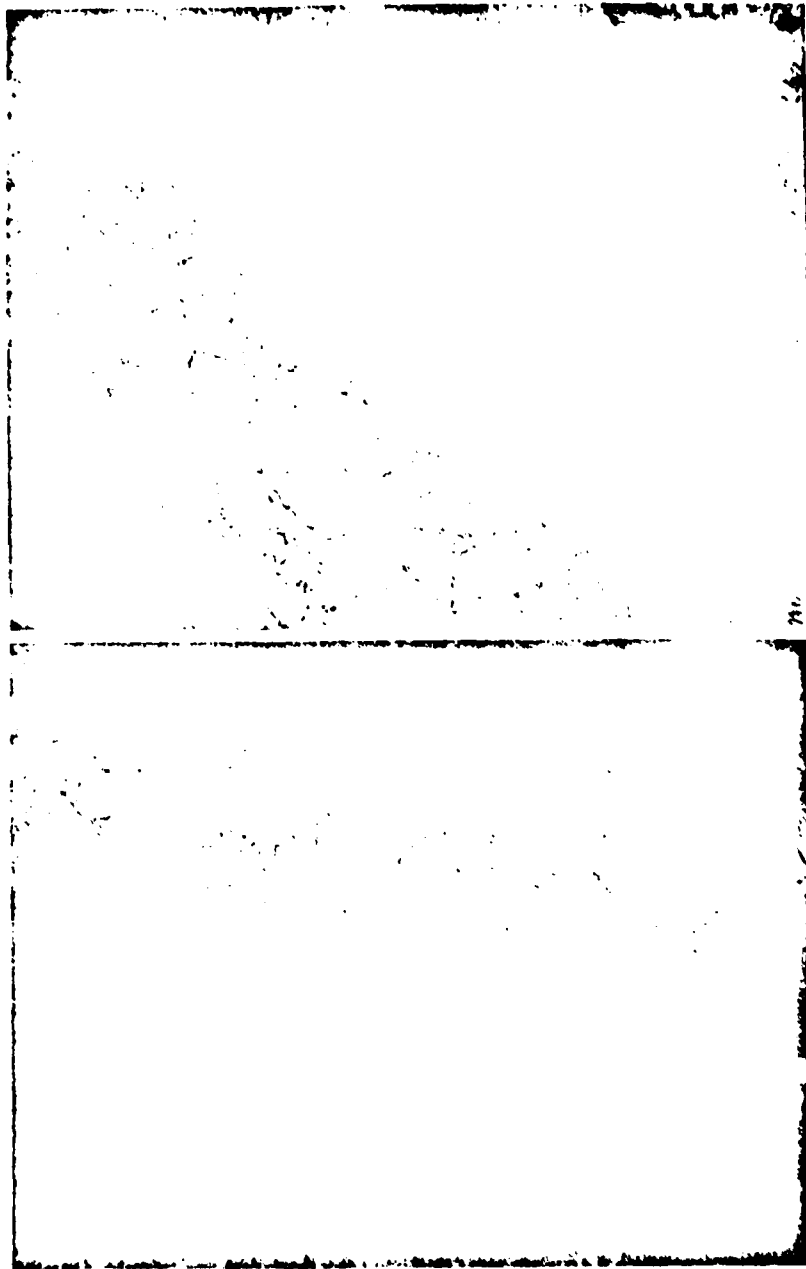


(b)

Nickel plaque; a) without, b) with CVD of carbon.
500X

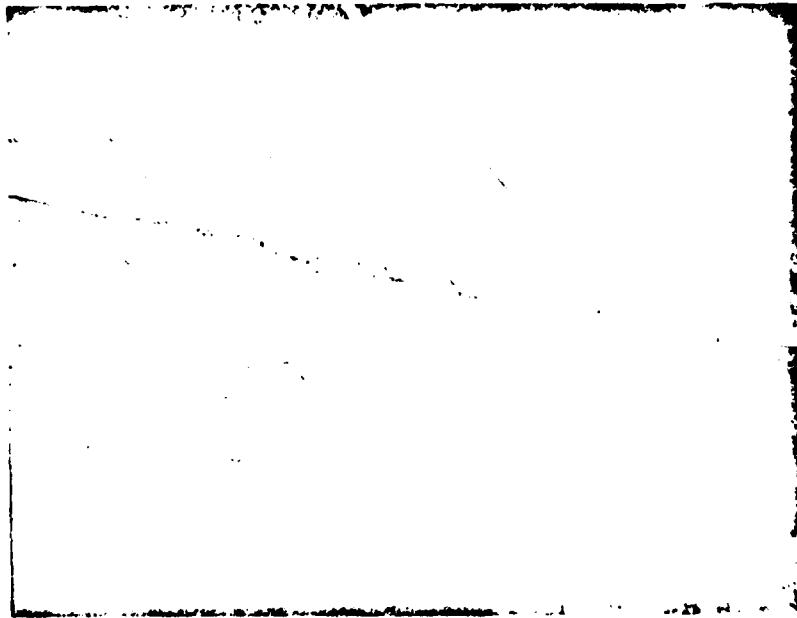
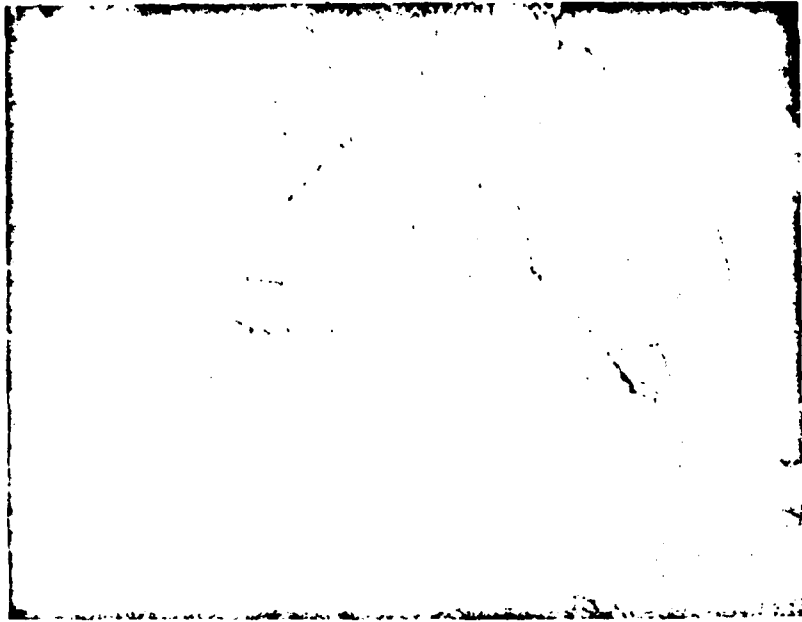


Plain nickel sheet with CVD of carbon. 500X



Adherence of soot particals to surface
of plain nickel sheet.

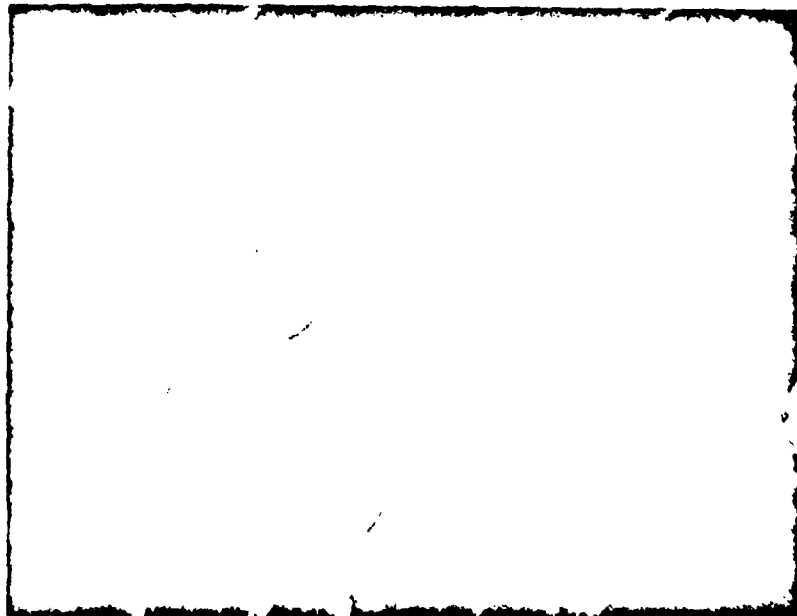
500X



Fibers and soot particals showing interaction
of CVD of carbon
500X



(a)



(b)

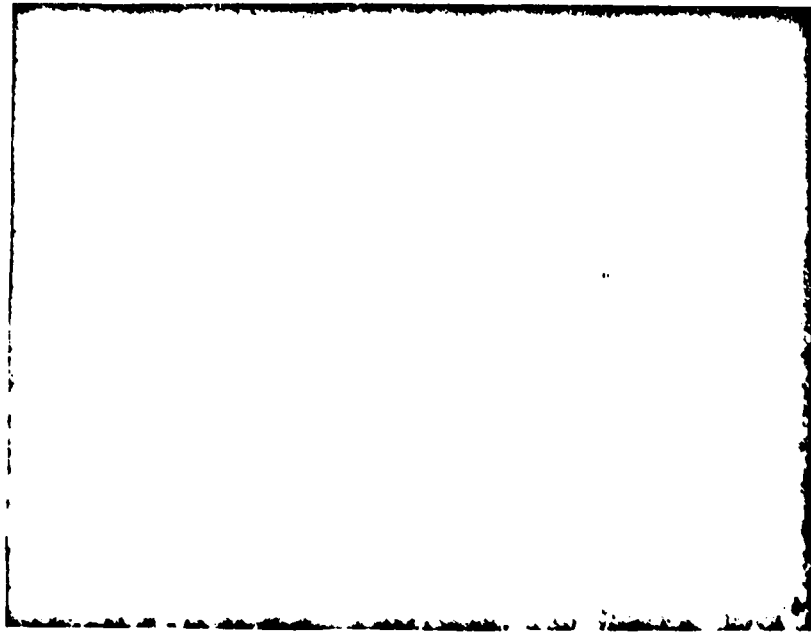
Scanning Electron Micrographs of CVD
of carbon on plain nickel sheet
a) 500X, b) 2000X,



Nickel sheet with soot, PVA, and water coating,
after standard run. 500X.



Nickel plaque with soot, PVA, and water coating.
Standard run. 500X.



Nickel plaque with soot rubbed smooth over
its surface. Standard run. 500X.

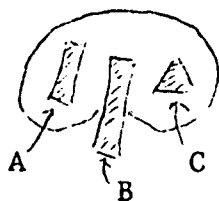


Nickel sheet with soot and oil coating, after
standard run. 500X.

Metallographic Specimens

- Deposit and soot on metal - the plain nickel sheet from Run #1 and the soot on its surface. (From #1 sheet soot sample.)
- Fibers and fibers and soot - the non-adherent fibers and fiber and shawinigan observed from its self-adhesion. (From sample marked #1 sheet fibers, and #1 sheet soot and fibers.)
- Deposit on metal - first run, plain nickel sheet with CVD coating. (From #1 sheet plain.)

#2 Soot



(From #2 plaque soot) nickel plaque and its deposit.

A) unused plaque sample, (B and C) CVD of carbon on plaque (transverse and longitudinal).

Specimen Identification

Box #1

Nickel sheet - first run, plain nickel sheet used as main substrate.

Sheet plain - the plain nickel sheet used as a substrate with CVD of carbon on its surface.

Sheet soot - a plain nickel sheet boat was made and shawinigan lumped on its surface. This type of combination did not spall off, but is difficult to make as a uniform layer.

Sheet fibers - plain nickel sheet and a voluminous fiber bundle which did not adhere to the surface.

Sheet soot and fibers - plain nickel sheet and a soot and fiber mixture lumped on its surface. The fibers prevented adherence as well as the above simple shawinigan application.

Box #2

Plaque - the second run using the nickel plaque as a main substrate.

Plaque (plain) - the nickel plaque and CVD of carbon on its surface.

Plaque soot - nickel plaque used as a surface and shawinigan washed across its surface (in acetone) to form a uniform layer. This layer, as can be seen tended to spall off.

Plaque soot and fibers - the nickel plaque and a shawinigan and chopped fibers in acetone washed across its surface. Again as above, the spalling on the surface can be seen.

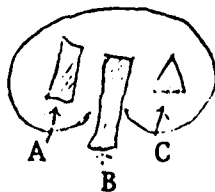
Plaque fibers - chopped fibers in acetone washed across its surface to form a carbon layer. When the acetone dried the residue was insufficient to hold the fibers.

Plaque (plain) - nickel plaque without any attempted coating.

A) unused plaque for comparison

B) plaque with CVD of carbon on surface transverse cut

C) plaque with CVD of carbon on surface longitudinal cut.



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