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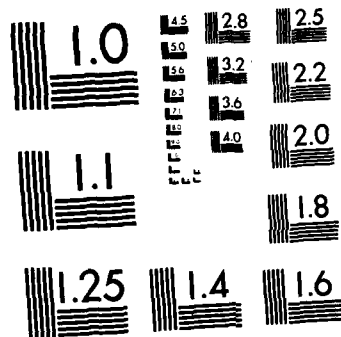
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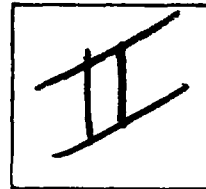


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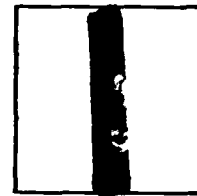
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DTIC ACCESSION NUMBER



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INVENTORY

Rept. No. AFWAL-TR-81-2044

DOCUMENT IDENTIFICATION

Final, Sept. 77-Nov '80

Contract F33615-77-C-3147

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ADVANCED THERMAL BATTERIES

NATIONAL UNION ELECTRIC CORPORATION
ADVANCE SCIENCE DIVISION
1201 E. BELL STREET
BLOOMINGTON, ILLINOIS 61701

JUNE 1981

FINAL REPORT FOR PERIOD SEPTEMBER 1977 - NOVEMBER 1980

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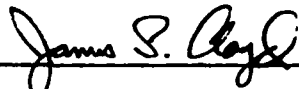
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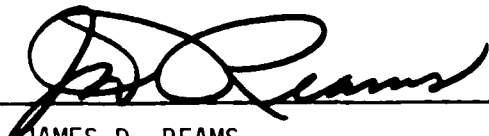


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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-81-2044	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ADVANCED THERMAL BATTERIES		5. TYPE OF REPORT & PERIOD COVERED Final Report Sept. 77 - Nov. 80
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) David M. Ryan		8. CONTRACT OR GRANT NUMBER(s) F33615-77-C-3147
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Union Electric Corporation Advance Science Division Bloomington, Illinois 61701		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62203F31452285
11. CONTROLLING OFFICE NAME AND ADDRESS Aero Propulsion Laboratory (AFWAL/POOC-1) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, Ohio 45433		12. REPORT DATE June 1981
		13. NUMBER OF PAGES 296
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Work done under Air Force Contract No. F33615-77-C-3147 with The Eureka Company		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Thermal Battery, Lithium-Aluminum Anode, Tetrachloroaluminate, electrolytes, CuCl ₂ catholyte, MoCl ₅ catholyte, Low Temperature Activation, Low Operating Temperature, Acid - Base Properties		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The feasibility of building thermal batteries with cells composed of an anode of LiAl alloy, a cathode with a heavy metal chloride, and a tetrachloroaluminate alkali metal salt electrolyte has been demonstrated. During the further investigation of this system some interesting problems have developed and had to be studied. The phenomenon originally referred to as the particle size growth		

problem developed into a major storage life problem. As a result, MoCl_5 was abandoned and CuCl_2 was used as a substitute cathode material.

Alternate component materials investigated included alternate anode materials, alternate electrolytes and electrolyte binders. Alternate cathode active materials and cathode complimentary materials such as heavy metal chlorides, heavy chlorides, heavy metal oxides, sulfur, graphites, sulfurous compounds, and binders were given various trials. This research produced an optimum cell composed of an anode mixture of 35 w/o Mg and 65 w/o LiAl alloy, an anolyte of basic LiAlCl_4 , and a catholyte of CuCl_2 , with slightly acidic NaAlCl_4 as a electrolyte.

A final battery design was built and tested. The final design was intended to develop a relatively long active life. To achieve this a system of heat sinks and thermal buffers were employed. The principal function of the thermal buffers was to reduce the activation high voltage spike which could greatly impair useful life. Weight and volume were sacrificed to achieve a longer useful life. Significant advantages of this battery include a low internal operating temperature and a low skin temperature.

SUMMARY

The appearance of a commercial source of tetrachloroaluminate salts eased one of the major problem areas of this program. These materials, manufactured by Alcoa Aluminum have proven to be entirely satisfactory for thermal battery use and as a result electrolyte fabrication has become easier, faster, more reproducible and safer. The three most significant areas of interest for these materials are acidity, iron content and moisture. Alcoa is capable of controlling these parameters satisfactorily. After these materials have been used to make electrolyte powder the acidity can be spot checked using FeCl_3 as a color type indicator. Moisture can be measured with a Differential Scanning Calorimeter. The relative amounts of Na (or other alkali metal) and Al can be measured by standard analytical chemical procedures.

The phenomenon originally referred to as the particle size growth problem mushroomed into a serious storage problem. MoCl_5 forms volatile products in the catholyte. These materials quickly distribute throughout the interior of a battery and the battery quickly autodischarges. The only remedy for this problem was to eliminate the MoCl_5 in the catholyte and use CuCl_2 as a substitute. The necessity of this action caused a 20 percent reduction in voltage and a consequent reduction of energy density and packing density.

Antiflow agents for the molten electrolyte were also studied. The optimum electrolyte antiflow agent for this electrolyte has been Cab-O-Sil. It was found that the cell performance did not vary significantly if the amount of Cab-O-Sil was within the range of 10 ^{w/o} to 13 ^{w/o}. LiAlCl_4 electrolytes appeared to require two or three percent more Cab-O-Sil than NaAlCl_4 electrolytes. Other binders experimented with were kaolin, amorphous silica, and magnesia. MgO

did not wet NaAlCl_4 but did wet LiAlCl_4 . The use of kaolin has the advantage of not needing to be fused into the salts in order to function but had the disadvantage of producing slightly higher internal resistance and lower energy density. The cells made with amorphous silica did not display cold voltage as did all of the other cells.

A few alternate electrolytes were given trials. These experiments included the use of NaAlCl_4 , basic, very acidic, and slightly acidic; LiAlCl_4 , basic, and slightly acidic; LiCl and KCl ; and all of the previously mentioned materials prepared with different degrees of purity. Acidic LiAlCl_4 was found to be entirely unsuitable for this application. In general, mixtures of KCl and LiCl were abandoned because they required such a relatively high operating temperature. The optimum cell was made with an alkaline LiAlCl_4 anolyte and a slightly acidic NaAlCl_4 catholyte.

Included in the alternate materials trials were experiments with alternate cathode active materials. Alternate cathode chlorides studied were WCl_6 , FeCl_3 , CuCl_2 , CrCl_3 and MoCl_5 . MoCl_5 and WCl_6 were abandoned due to a storage problem caused by volatility of cathode electrolyte products. FeCl_3 was abandoned because it was noxious, difficult material to work with and a possible storage problem. CrCl_3 was abandoned because it only functioned well at relatively high operating temperatures. Alternate cathode materials, not chlorides, were considered as a separate class of materials. These included various heavy metal oxides and sulfur compounds. All of the oxides were unsuitable for this system. The sulfurous materials such as FeS_2 , TiS_2 , and TiS_3 all turned out to be relatively high temperature cathode materials and were abandoned for this reason. Carbon monofluoride was also found unsuitable for this system. A final alternate cathode material was elemental sulfur. Sulfur did make some

excellent cells but the activated cells had to be charged. Sulfur was not pursued because the magnitude of the work involved in the study would have been sufficient to constitute an entirely new project and was considered beyond the scope of this program. Sulfur should be considered a good cathode material for this electrolyte system.

In addition to alternate cathode active materials other cathode complimentary materials studies were done. Alternate graphites were tested but none were found superior to the Fisher graphite used throughout most of this program. The process of fusing the catholyte materials together was abandoned when the MoCl_5 catholyte was found to be volatile. The process was never tried with CuCl_2 . The use of additional binders in the catholyte was tried and proved to be unnecessary. Another cathode (and anolyte) process experimented with was the mixture of the electrolyte salts, binder, and active materials with a Freon slurry in a commercial blender. The process did provide excellent materials but these did not perform significantly better than conventionally mixed materials and so the process was not routinely used. The physical properties of the materials such as particle size distribution, homogeneity and bulk density were superior to conventionally prepared materials and the process could be considered for large commercial operations.

Anode experiments involved the use of alternate lithium alloys and additives mixed with the alloy granules. When attempting to use alloys with high concentrations of lithium (i.e., 40 m/i LiAl or 56 m/o LiSi) the high voltage activation spike phenomenon was aggravated. It was found that the cells were cathode limited so that high concentrations of lithium were not necessary. The spike was somewhat controlled by diluting the anode with some inactive material

such as electrolyte or granulated magnesium. Anode which contained granulated magnesium also had superior mechanical and handling properties. Cells with pure LiAl anodes are brittle and difficult to shear but cells made with magnesium included could be sheared easily. The optimum cell design included an anode which was 35 ^{w/o} Mg and 65 ^{w/o} LiAl alloy (28 ^{m/o} Li).

Two heat sources were used, Zr/BaCrO₄ and Fe/KCl₄. Initially experiments with Fe/KClO₄ were unsuccessful because the heat disk did not always ignite but this was later remedied by inserting a 0.004" disk of asbestos on each side of the heat disk. The iron heat disks have superior heat sink properties and were included in the final design. The iron heat disks have the disadvantage of heavy weight which seriously diminishes energy density.

Component fabrication and reproducibility problems dissappeared as experience with the materials grew. The cell making problems disappeared when the cathode was changed to CuCl₂ and the anode was changed to 35% and 65% LiAl. The cells did have to be compacted at relatively low pressures and whenever pellets of anolyte were prepared the anolyte had a tendency to adhere to the steel dies. Another process found to be very beneficial was the calcining of Cab-O-Sil for 16 hours at 500°C prior to anolyte mixing and to vacuum desiccate the graphite prior to catholyte mixing. It was found that if the finished cells were vacuum desiccated they did not have as severe a spike but usually had less capacity.

Batteries were built and tested for two major reasons, to test components and to characterize the final system and design. Early in the program it was discovered that cells made with MoCl₅ catholyte could not be stored in a battery. CuCl₂ type cells could be stored if care was taken to protect the LiAl anode from exposure. Because the AlCl₄⁻ anolytes are 10,000 times more conductive in the uninitiated state than the conventional thermal electrolyte, KCl/LiCl eutectic,

no thermal battery made with AlCl_4^- electrolytes is going to have as great a shelf life as a more conventional thermal battery. However, the shelf life of AlCl_4^- batteries can be quite significant if great care is taken to insure dry fabrication conditions and the battery is not stored hard wired into a closed circuit during final application.

The final battery design sacrificed volume and weight (i.e. sacrificed packing density and energy density) to include an extensive heat sink/thermal buffer system. This system involved the use of the Fe/KClO_4 heat disks with massive metal heat sink/thermal buffers. The purpose of this system was to decrease the activation spike by buffering the initial thermal shock and thereby increase the useful lifetimes. It was believed that useful lifetimes had a higher priority over battery weight, volume or activation time. This design did indeed lead to the longest useful lifetimes but the battery was too large and the activation was too slow. Many of the early test batteries, not of the final design, had greater energy and packing densities.

The final design was characterized (see Section XXI, this report). It was found that the battery could function equally well across the entire test temperature range of from -55°C to $+75^\circ\text{C}$. The battery can also withstand typical vibration and acceleration specifications. The skin temperature of this final design battery is about 200°C less than a conventional thermal battery (the skin temperature of most cold tests increased 50°C and most hot tests increased 75°C). Energy density can be significantly increased by using the Zr/BaCrO_4 instead of the Fe/KClO_4 heat source and by using salt heat sinks instead of steel heat sinks. If the activation high voltage spike can ever be completely removed from the system without the use of the heat sink/thermal buffer sign the activation times can be made more competitive with conventional systems.

The most expensive material in the battery is the LiAl anode. If an inexpensive source of LiAl alloy is discovered, this system could be quite cost competitive with existing systems. The cost is presently no greater than existing systems.

PREFACE

This report describes development of technology for an advanced thermal battery to be used for ordnance applications. This effort began with electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories. The next effort was a battery engineering feasibility study completed by the Eureka Advance Science Corporation under Contract F33615-77-C-2080. This effort demonstrated that a thermal battery with a LiAl alloy anode, a NaAlCl_4 anolyte, and a catholyte made primarily with MoCl_5 was at least feasible. However, the work under the above contract was extremely limited in scope due to both time and funding limitations and, as a result several very promising applications and techniques were not investigated. This new effort, Contract F33615-77-C-3147, provides for further exploratory development and optimization of an advanced thermal battery system.

The submitted date for this report was February 1981, covering effort completed during the interval 15 September 1978 thru 15 November, 1980.

The cognizant Air Force project officer was Mr. James S. Cloyd, AFWAL/POOC-1, Wright-Patterson Air Force Base, Ohio. The technical support rendered by Mr. R. A. Marsh, W. S. Bishop, and Dr. Joseph Malloy of the project offices organization was very beneficial and greatly appreciated. The consultation and technical support of Lt Col Lowell King, Major John Erbacher, Capt Chuck Hussey, Capt Larry Vaughn and Lt John Nardi of the Air Force Academy was outstanding and a major contribution to the program. Sandia Laboratories, particularly Don Bush and Rod Quinn, have made significant contributions of thermal battery experience and expertise. Dr. Roger Bunting, of Illinois State

University, has made considerable contributions to the solution of the MoCl_5 storage problem. Of particular assistance were Mr. L. C. Bricker and Mr. James Walker of the Advance Science Division of National Union Electric Corporation.

This is the final report including all three years of work.

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SECTION I

INTRODUCTION

It has previously been demonstrated that an advanced thermal battery based on the $\text{LiAl}/\text{NaAlCl}_4/\text{MoCl}_5$ electrochemical system was feasible (Contract #F33615-76-C-2080). The work done under the above feasibility contract was extremely limited in scope due to both time and funding limitations and as a result, several promising materials applications and design/fabrications techniques were not investigated. This most recent effort (Contract #F33615-77-C-3147) provides for further characterizations, development, and optimization of an advanced thermal battery system along with testing of sufficient cells and batteries to establish reliable performance predictions over the range of interest.

This work had a general and specific objective. The general objective was to develop technology for an advanced, long life, compact, lightweight thermal battery for missile and air delivered ordnance applications. This effort was built upon electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories and engineering research and development done by the Advance Science Division to demonstrate the feasibility of using such a system for thermal battery application. The most critical problems such as activation voltage spike; availability of sufficient high purity electrolyte; pellet building and fabrication; etc., were to be eliminated or at least controlled. Alternate materials were to be investigated to optimize the cell/battery performance. These investigations were to include use of alternate alloys or surface preparation techniques to insure rapid and predictable activation; alternate electrolyte formulations; studies of other cathode reactants such as CuCl_2 , FeS_2 , or other applicable materials; and use of more efficient thermal materials.

The specific objective of the program was to design and develop a battery which would meet the requirements outlined below. The voltage of the battery should be 28 volts nominal. The battery should be capable of carrying a 2 amp current across a resistive load for as long as possible. The activation time is less than one second. The electrical noise maximum is $\frac{1}{2}$ volt peak to peak. The battery should not ideally exceed 1 pound. The battery must function at both -65°F and at 165°F . The skin temperature should not exceed 200°F . The battery must also be capable of withstanding other normal thermal battery environments such as storage requirements; vibration, shock, spin, etc.; and other usual thermal battery requirements.

This report is the final report of this work. It includes the first year of work which was originally reported in December 1978 in:

"Advanced Thermal Batteries"
AFAPL-TR-78-114
Air Force Aero Propulsion Laboratory
Air Force Wright Aeronautical Laboratories
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

Also included in this report is the second year of work which was originally reported in March 1980 in:

"Advanced Thermal Batteries"
AFAPL-TR-80-2017
Air Force Aero Propulsion Laboratory
Air Force Wright Aeronautical Laboratories
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

SECTION II

A COMMERCIAL SOURCE OF NaAlCl_4

NaAlCl_4 is a difficult material to prepare. The salts are hygroscopic and volatile. Their vapors are corrosive and poisonous. The Alcoa Aluminum Company has developed a new method of producing AlCl_3 and has become a source of pure NaAlCl_4 . It was the purpose of this experiment to evaluate this material for thermal battery use.

The first sample from Alcoa was received in August, 1977. The second sample was received in September, 1977. The earlier sample was somewhat yellow in color but the second sample was quite white. The material was received in the form of 50 to 100 gram chunks mixed with smaller chips.

When the first sample was received it was tested by a differential scanning calorimeter (DSC). The DSC showed a large endotherm peaking at 167°C . The melting point was at 159°C . The sample was further heated to nearly 290°C and then allowed to cool. The sample froze at 97°C . The sample was reheated and the melting point was at 157°C .

A sample of this material was then mixed with 10 w/o Cab-O-Sil, sealed in a glass container, and heated one hour in an oven at 220°C . When cooled, ground and sieved, this mixture was called Anolyte #102. Another anolyte was made identically like this and it was labeled Anolyte #104. The DSC spectrum of Anolyte #104 yielded a melting point of 152°C . The sample was cooled and reheated. The new melting point was 151°C .

Anolyte #102 was mixed with graphite and MoCl_5 to make a catholyte. The catholyte formula was:

25.43 w/o Anolyte #102

56.50 w/o MoCl_5

18.08 w/o Graphite

This was labeled Catholyte #103. The DSC spectrum of Catholyte #103 provided a melting point of 151°C. This sample was allowed to cool and was then reheated. The new melting point was 147°C.

A second catholyte (Catholyte #101) was made identically like Catholyte #103 except that Anolyte #104 was used instead of Anolyte #102. The melting point of Catholyte #101 was 149°C as measured with the DSC.

A single cell test was performed with cells made from Anolyte #104 and Catholyte #103. The anode was 20 ^W/o LiAl alloy. The cell formula was:

Anode: 0.277 gm 20 ^W/o LiAl alloy

Anolyte: 0.935 gm Anolyte #104

Catholyte: 1.039 gm Catholyte #103

The platen temperature was 200°C and the test load was 25 ohms.

Single Cell #101

Peak Voltage (V_p) = 2.34v

Peak Current (I_p) = 93.6 ma

Current Density (i_p) = 18.5 ^{ma}/cm²

Life to 80% Peak (T_{80}) = 960 sec.

Energy Density (E/m) = 21.0 ^{Wh}/kg

This cell has the longest 80% lifetime of any single cell test yet reported (for earlier single cell test results see AFAPL-TR-77-12)¹. This long life can be primarily attributed to the absence of a high voltage spike.

A single cell test was also performed upon a cell made with Anolyte #102 and Catholyte #101. In every other respect this single cell test was identical to Single Cell #101.

1. Reference. D. M. Ryan, and L. C. Bricker, "High Energy Density Pelletized Aluminum Chlorine Thermal Batteries", AFAPL-TR-77-12, April, 1977

Single Cell #102

$$V_p = 2.33v$$

$$I_p = 93.2 \text{ ma}$$

$$t_{80} = 960 \text{ sec.}$$

$$E/m = 20.86 \text{ Wh/kg}$$

$$i_p = 18.4 \text{ ma/cm}^2$$

This single cell showed no spike at all.

It is felt that these tests indicate clearly that the Alcoa NaAlCl_4 can make excellent electrolyte for use in this system and can indeed be considered a commercial source of NaAlCl_4 .

A second sample of NaAlCl_4 was received from Alcoa in September, 1977. This sample was whiter than the somewhat yellowish first sample. Some of this material was used to make a test anolyte. A test anolyte is composed of 10 w/o Cab-O-Sil and 90 w/o NaAlCl_4 . This was labeled Anolyte #1002. The DSC spectrum showed a peak at 436°K (163°C) and another broad exotherm at 628°K (355°C). A second sample was tested and both the endotherm (163°C) and the exotherm (347°C , 2nd sample) were reproduced. The melting points measured by the DSC were 151°C and 150°C respectively.

Anolyte #1002 was used to make a test catholyte, Catholyte #1001. A test catholyte is composed of:

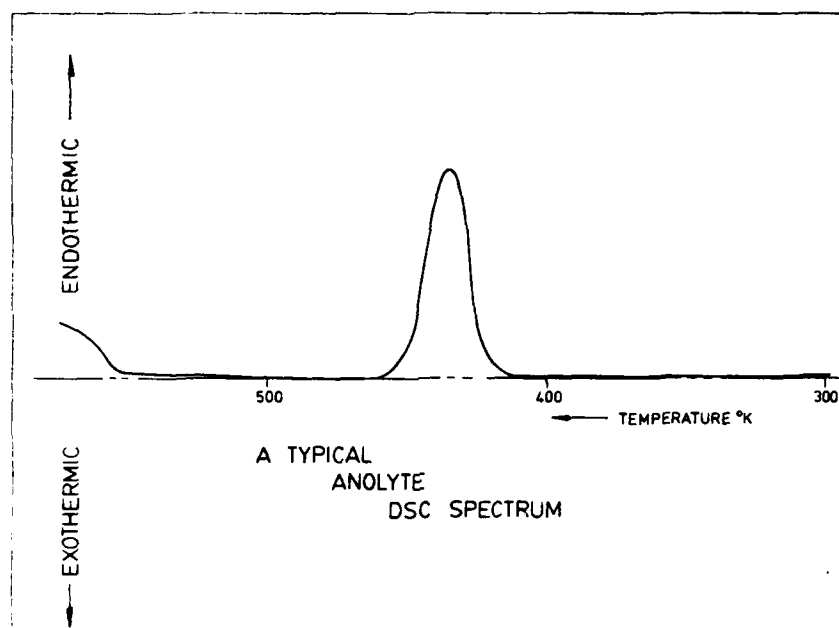
<u>Test Catholyte</u>	25.4 w/o test anolyte
	56.4 w/o MoCl_5
	18.1 w/o graphite

The DSC spectrum of Catholyte #1001 showed an endotherm at 379°K (106°C) and an endotherm at 432°K (159°C) and a confusion of peaks and valleys which start about 470°K (197°C). A second sample was run and the two endotherms were well

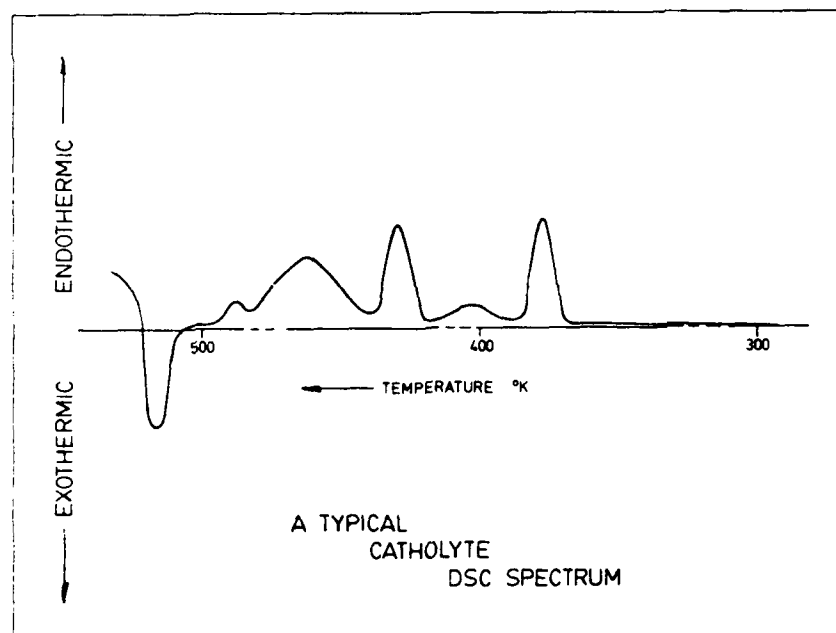
reproduced (2nd sample, 105°C & 159°C). Heating of the second sample was stopped at about 200°C and the material was allowed to cool. When the cooled sample was reheated only one endotherm was noticed (159°C). The endotherm at 105°C did not reappear upon the second heating of the sample. It is interesting to note that the area of the second 159°C endotherm was approximately equal to the sum of the areas of the original two endotherms at 105°C and 159°C. If the endotherm at 159°C corresponds to the fusion of NaAlCl_4 then the melting point of this material was about 152°C and was lowered to 148°C upon reheating. The catholyte appears to react with the aluminum sample pan at about 195°C and this corresponds to the peaks and valleys noted at the hot end of the spectrum. This area is not very reproducible. Figures 1a & 1b are typical anolyte and catholyte DSC spectra.

CONCLUSION:

The NaAlCl_4 prepared by Alcoa Aluminum for this project is entirely suitable for thermal battery use. The three major parameters of interest are acidity, iron content and moisture content. Alcoa is capable of controlling all of these parameters.



a. A Typical Anolyte DSC Spectrum



b. A Typical Catholyte DSC Spectrum

Figure 1. DSC Fingerprint Spectra

SECTION III

NaAlCl₄ ANALYSIS

The physical/chemical properties of NaAlCl₄ depend upon the ratio of sodium and aluminum in the material. Three of the most important properties controlled by composition are conductivity, melting point, and acidity. In addition to these three properties a thermal battery chemist is also interested in moisture contamination. These properties can be monitored by performing two analyses on the NaAlCl₄:

- 1) Differential Scanning Calorimetry (DSC)
- 2) An acid/base analysis

After many DSC spectra were generated for test electrolytes, typical spectra were gradually characterized. A typical DSC spectrum for an anolyte displays two prominent features:

- 1) an endotherm at 162°C, and
- 2) a large endotherm at about 290°C.

The sharp endotherm at 162°C is probably caused by the fusion of the salt. The large endotherm at 290°C is not explained.

A typical DSC spectrum for a catholyte, Figure 1b, displays many more features. The first feature noticed is an endotherm at 105°C. This peak is probably due to the loss of moisture. The next peak is an endotherm at about 156°C. This is probably due to fusion of the NaAlCl₄. The next feature is two endotherms, so broad and close together that they sometimes are hard to resolve. These appear at about 189°C and 214°C respectively. The next feature is a strong exotherm at about 258°C. These last two endotherms and exotherm are reproducible, but often difficult to resolve and identify.

It is interesting to note that the moisture peak has been present in each of the catholytes and absent in each of the anolytes. Upon referring to some DSC spectra made on catholytes that had been prepared six months previously, it is noticed that these catholytes did not show a moisture peak. Despite the contemporary appearance of a moisture peak in the catholytes there appears to be no immediate or obvious effect upon performance of either cells or batteries. The absence of moisture in the anolytes suggest that the source of the moisture in the catholytes is either the MoCl_5 or the graphite.

While the source of moisture in the catholyte is not clear this observation does indicate that a DSC can be used to detect moisture contamination. Accordingly, a DSC spectrum was generated for an anolyte sample. The anolyte was then exposed to room air and resampled. This was repeated every ten minutes for the first hour. The last sample was taken after overnight exposure to moist air (chemistry laboratory ambient air).

The dry sample had a clear peak at 164°C (See Figure 2). Upon repeated exposure to the moist room air this peak was found to diminish and a new peak began to appear at the temperature range from 131°C to 142°C , increasing in amplitude as the 164°C peak diminished. As the exposure was repeated, the initial 164°C peak and the 137°C peak moved closer together and broadened until it was nearly impossible to resolve the two peaks. Also, after prolonged exposure another peak appeared at about 97°C and then the only two features that remained were the peaks at 97°C and a broad peak at about 151°C .

Another interesting, but not always repeatable, feature of these spectra was the appearance of an exotherm which sometimes followed the broad endotherm at about 160°C . Figure 2 is an illustration of the above described spectra.

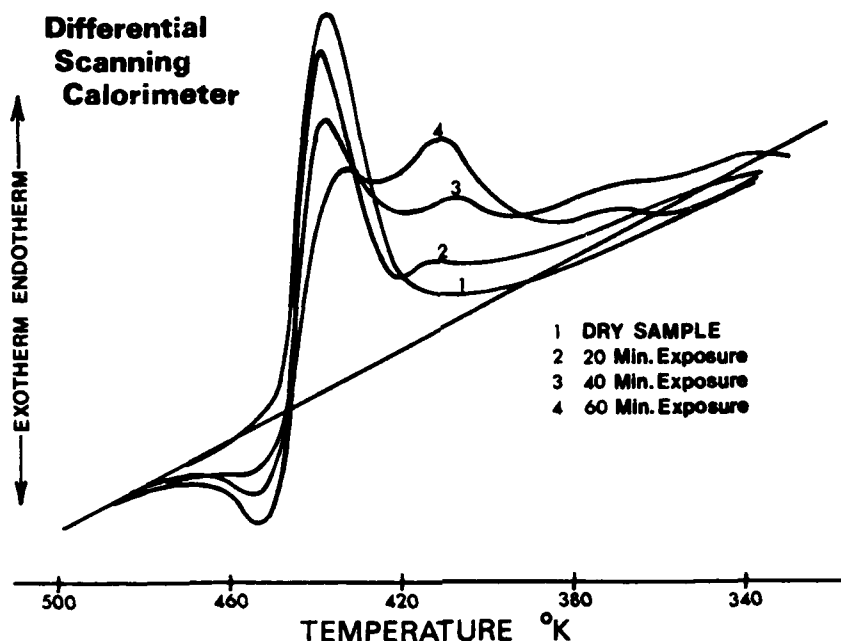


Figure 2. Differential Scanning Calorimetry Used To Monitor Moisture In Anolytes

It appears that the absence of hydrolysis products can be monitored by measurement of the relative heights of the peaks at the 160°C range and the 136°C range. For "total" hydrolysis of the sample (*i.e.*, exposed overnight), the sample became more endothermic by a factor of 2.8 over the total range 47°C to 327°C.

The most inexpensive, easiest way to monitor the acidity or alkalinity of the NaAlCl_4 would be by addition of a colored "indicator" to the melt. FeCl_3 was tested as a possible acid-base color indicator. Two clean 20 ml. coors crucibles were placed on a hot plate in an argon box. A few grams of NaCl saturated NaAlCl_4 were placed in one crucible and a few grams of NaAlCl_4 (69 ^m/o AlCl_3) were placed in the other crucible. The temperature was raised until both materials were molten. The molten salts were clear, dark gray liquids. About

10 or 20 mg of FeCl_3 was sprinkled into each crucible. In the basic sample the liquid immediately turned yellow-green, then brown. After about one minute the FeCl_3 crystals had completely dissolved and the solution was dark yellow-green. There was a trace of white smoke over the crucible that disappeared after the FeCl_3 was completely dissolved. The reaction in the acidic melt was similar except that the crystals did not dissolve.

The experiment was repeated. The second time the temperature was brought up slowly and the FeCl_3 crystals were added just a few minutes after the NaAlCl_4 melted. The acidic mix happened to melt first. Again when the FeCl_3 crystals were added they did not appear to dissolve but the melt turned light yellow-green. There was no smoke. When the basic salt melted and the FeCl_3 crystals were added they immediately dissolved and the solution turned dark yellow-green. There was no smoke.

The solubility of FeCl_3 in the basic mix and insolubility in the acidic mix is the inexpensive, fast and easy acid-base indicator that has been desired.

The only impurity which appears to be important in the Alcoa NaAlCl_4 is iron. Alcoa claims the iron content of their NaAlCl_4 is about 10 ppm. Therefore, it is concluded that if the supplier will certify the iron content of the NaAlCl_4 they supply and the level is maintained at about 10 ppm, the only additional analytical procedures necessary to control this material is a DSC spectrum and an indication of acidity or alkalinity.

CONCLUSION:

There are three major analytical concerns about the tetrachloroaluminates; acidity, moisture contamination, and iron content. Acidity can be controlled by Alcoa and easily monitored by measuring the relative concentrations of Al and Na. A quick qualitative acid/base indicator is FeCl_3 added to the molten sample. The iron content can be controlled by Alcoa and monitored by regular techniques employing atomic absorption spectrophotometric equipment. Moisture contamination can be monitored with a "fingerprint" technique utilizing DSC equipment.

SECTION IV

MoCl_5 CATHOLYTE PARTICLE SIZE GROWTH

The thermal cells made for this program were made by filling a cylindrical cavity with electrolyte powders, passing a straight edge across the top of the cavity to make an even upper surface, and compressing the powders to make a round pellet. However, some difficulty occurred while making cells with catholytes made with NaAlCl_4 and MoCl_5 . The upper layer could not be struck off to form a smooth surface because of the presence of some unusually large particles which caused deep furrows to form as the straight edge moved across the top of the cell making cavity. It was noticed that these large particles were not initially present in the catholyte but appeared after storage. It appeared that the catholyte particles were growing larger. It was believed that, since the electrolyte materials were so hygroscopic, some produce of hydrolysis was probably slowly forming. Therefore, an experiment was performed to investigate the effects of storing MoCl_5 catholytes in atmospheres which contain various amounts of moisture.

Four catholyte samples were stored in four respectively different atmospheres and were periodically examined with a microscope. The catholyte was a regular test MoCl_5 catholyte. Two gram samples of catholyte were placed in a three inch length of 1/2" square section glass tubing. The first sample was stored in ambient chemical laboratory air which had a nominal relative humidity of greater than 50%. The second sample was stored in dry room air which maintained a nominal relative humidity of about 2 1/2%. The third sample was placed in the sample tube while in an argon box and was sealed so it contained an atmosphere in dry argon.

The fourth sample was similar to #3 except that 25% of the argon was pumped out of the sample tube, refilled with O_2 and then sealed. The atmosphere in the above sample #4 was 20% O_2 and 80% argon.

The samples were inspected and photographed periodically. The intervals of inspection were:

<u>Inspection</u>	<u>Elapsed Storage Time</u>
1st	None
2nd	1 Hour
3rd	2 Hours
4th	3 Hours
5th	4 Hours
6th	19 Hours
7th	24 Hours
8th	45 Hours
9th	70 Hours
10th	118 Hours
11th	163 Hours

The sample that reacted quickest to the presence of moisture was the sample exposed to moist air. The first evidence of reaction occurred after three hours exposure. After about 24 hours a profuse growth of yellowish-white needle crystals had grown, either on the catholyte surface or, above the surface on the walls of the glass sample tube. The sample exposed to dry room air reacted similarly except that the first changes were not noticed until after about 19 hours of exposure. There were even some small white crystals starting to form in the two sealed samples but these were just barely visible after even 163 hours of elapsed time.

In addition to the profuse growth of large needle crystals there were also some small salmon pink crystals noticed. These appeared in all four samples and were not necessarily hydration products.

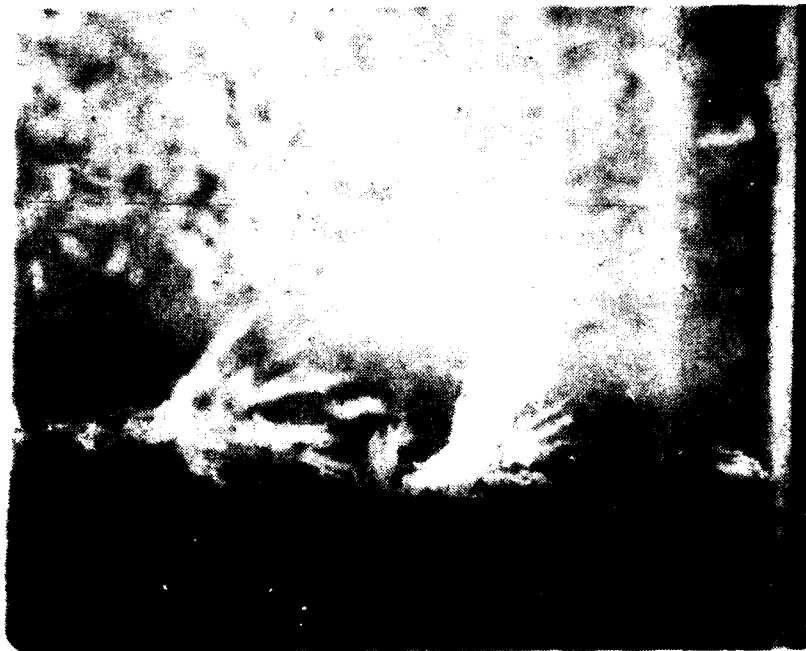


Figure 3. Yellowish White Crystals in $\frac{1}{2}$ " Square Section Sample Tube

In addition to this experiment some practical observations can be made. One day an attempt was made to make cells even though the dry rooms were wet (above 3.5% R.H.). The project had to be stopped because a noxious red vapor formed above the catholyte as the cells were being made. Also, after only about 30 minutes small yellowish crystals were noticed forming in the jar of catholyte. The catholyte was obviously reacting to the moisture.

On another occasion a small glass jar with a plastic screw type lid was used to store MoCl_5 cells. This was stored in a dry room next to a jar of CuCl_2 cells. After a couple of weeks the MoCl_5 cells had grown a fine crop of yellow needle crystals on the catholyte layer. After a month the cells bowed badly and cracked. After two months the cells were completely crumbled. During the same time period there was only a slight bowing of the CuCl_2 cells stored in the adjacent jar. After about three months the CuCl_2 cells also cracked and eventually broke. There were never any yellow crystals visible on the CuCl_2 cells.

Another experiment showed that the yellow crystals were related to hydration products with the Mo compounds in the catholyte. A MoO_3 catholyte was prepared by mechanically mixing the three ingredients (MoO_3 , A #1042, and graphite). This catholyte was used with 28 % LiAl and A #1050 with the usual press weight settings of 0.45 gm anode, 1.75 gm anolyte, and 1.9 grams catholyte, to prepare the first MoO_3 cells. The cells averaged 0.081 inches thick. These cells were tested on the single cell tester. The performance of these cells will be discussed in a later section of this report.

A second set of cells were made with an acidic anolyte. When these cells were tested they emitted a white or yellowish "smoke". This "smoke" was not noticed with the previous set of cells made with basic anolyte.

The cells were allowed to cool in the dry box and were then removed and examined post-mortem. The anolyte layers were all yellow or slightly green. As the cells were being examined they turned a little deeper blue. There appeared to be very little difference in the coloring characteristics of either the acidic or the basic anolytes.

It was decided to try to make the catholyte a little more concentrated with respect to the MoO_3 . Also it was decided to leave the graphite out of the catholyte. This is reasonable considering that graphite is not used with V_2O_5 in conventional cells and there was no evidence that graphite was needed with cathodic oxide species. It is interesting to note that these cells were flat and not bowed. It can only be concluded that the graphite relieves stress in the catholyte layer which causes the cell to bow with the catholyte forming a concave surface.

When these cells were tested they produced yellow smoke from about the time peak voltage was reached to a time about 15 or 20 seconds later.

These cells were also examined post-mortem. Once again the catholyte was yellow-green or bluish colored. In addition to this some cracks were noted in the cells and there appeared to be a black material which flowed out of (or into) these cracks. It was speculated that the bluish-green color in the anolyte might indicate the presence of Ni^{++} . Some of the colored anolyte was dissolved in water and tested with dimethylglyoxime for the presence of nickel. The test was completely negative. The sample was then salted with a very small crystal of NiCl_2 and the test was immediately positive. The anolyte was then spot tested for molybdenum and was immediately positive. The conclusion is the colored material in the anolyte is due to the presence of Mo species and nickel is not present at all.

In addition, the post-mortem examination of cells was accompanied by a post-mortem examination of the cell connectors. It was noticed that the cell connectors were partially covered with thin yellow "fuzzy" crystals. When examined under a X10 microscope some blue rhombohedral crystals were also noticed. These were stored in the dry box overnight and re-examined in the morning. The blue crystals turned reddish-purple during the storage. The cell connector was washed

off with water and there was no visible evidence of etching or corrosion of the nickel surface.

The DSC spectra of these MoO_3 catholytes very closely resemble the spectrum of a slightly moist anolyte. These spectra in no way resemble the usual spectrum of a normal MoCl_5 catholyte.

Some of these cells were tested with no load. These cells activated quickly and formed a spike. Then the potential started to climb very slowly until a second peak had been reached. Then the voltage started to slowly drop in a manner similar to usual cell tests. Some MoCl_5 tests were observed to behave in a similar manner. It was thought that the MoO_3 (or MoCl_5) may have reacted with the electrolyte to produce a more active species. When the concentration of the more active species was high enough it could have produced a second, less immediate, peak voltage.

Since it was believed that the MoO_3 was reacting with the electrolyte it was decided to try to prefuse some catholyte. The plan was to mix together the catholyte ingredients, fuse the ingredients to a relatively homogeneous mass, then grind and sieve the cooled resulting mixture.

Accordingly, 23 grams of rough ground NaAlCl_4 (69 % AlCl_3) was placed in the bottom of a 1000 ml beaker. On top of the salt was sprinkled 50 grams of MoO_3 . These two materials were then well blanketed by 10 grams of Cab-O-Sil. The beaker was on a hot plate in the dry box. The heat was turned on a very slow rate. After just 20 minutes a thick yellow colored area appeared in the Cab-O-Sil layer. After another 20 minutes the entire Cab-O-Sil layer was yellow. After another 10 minutes a band of yellow fuzzy crystals started to condense upon the cooler upper portions of the beaker. A cover which contained a thermometer was placed over the beaker. The temperature read 85°C . The setting on the hot plate was increased slightly. The yellow crystals grew thick and large (about an inch long needle crystals). A blue green layer began to form on the Cab-O-Sil near the bottom of

the beaker. As the temperature approached 130°C the blue coloration increased to encompass almost all of the yellow crystals that were formed. The inside glass of the dry box was rapidly obscured by light blue dust.

It was decided to try to grow some more of the yellow crystals for analysis. To accomplish this a large test tube was about 1/4 filled with the ingredients. The test tube was then placed with the reactants over the hot plate and the upper part of the tube leaning to the side so it would not be heated. As expected a thick crop of yellow crystals formed in the cooler neck of the test tube. These crystals were harvested time after time until a large sample (about 5 grams) had been obtained.

While collecting the yellow crystals some of them fell on the hot plate surface. These crystals were observed to immediately turn deep blue.

In addition to the yellow and bluish crystals previously mentioned some dark yellow, orange platelets were found in the sample generator. These flat platelets were also turned blue green upon storage and none were saved for further observation.

A few of the yellow crystals were dissolved in D.I. water and tested for the presence of Mo and Al. The water solution was quite acidic ($\text{pH} \leq 1$) and the presence of both Mo and Al was indicated. The spot test for Al was quite positive but the color reaction which indicated Mo was not the correct color. In addition to this it was planned to perform these analyses on this material:

- 1) An emission spectrum on the yellow material.
- 2) Generate a DSC spectrum on the yellow material.
- 3) Generate an IR spectrum for the yellow material.
- 4) Generate A D.M.E. polarogram for the yellow material.
- 5) Generate a powder pattern for the yellow material.

- 6) Perform a Redox titration on the yellow material.

A related problem is the presence of some yellow material found in the stored catholyte and cells and while performing single cell tests:

- 7) DSC on C #1119, and C #1121.
- 8) Grind C #1117, C #1119 and C #1121 and rerun the DSC's.

The yellow crystal generator was exposed to dry room air for about 5 days after it was no longer needed. The yellow crystals which had continued to adhere to the inside surface of the generator slowly turned to blue-green-grey platelets.

Some of the yellow crystals were placed in a micro test tube and heated over a bunsen burner flame. The crystals turned green and then blue. Light colored smoke was produced. When the effluent smoke was allowed to pass through the oxidizing region of the bunsen flame the flame turned light yellow-green. The reducing portion of the flame did not change color.

In a micro test tube a few of the yellow crystals were dissolved in a few drops of deionized water. A deep blue-violet solution resulted. A spot test for the presence of Mo turned the test paper dark violet instead of the expected red. A few drops of concentrated NaOH caused the solution to turn green. When the solution was neutral it was colorless with a pale blue precipitate at the bottom of the test tube.

A new solution of yellow crystals was prepared. The pH was measured with indicator papers to be 1.18. Sodium acetate crystals were added until the pH measured 5.0. This buffered solution gave a strong positive test for Al^{+++} . It is not known if Al (III) was responsible for the presence of the wrong color reaction during the Mo spot test.

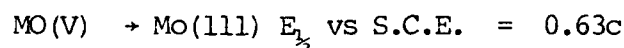
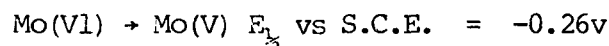
DSC spectra were generated for these yellow crystals. There is a distinct endotherm at about 160°C. An infrared spectrum of the compound in Nujol mull was recorded over the range 4000 to 500 cm^{-1} , but showed no significant absorption bands except those representative of traces of water.

The electronic spectrum of a water solution of the compound gave two very intense charge transfer bands in the UV at 300 and 345 nm. The visible spectrum was not recorded.

The mass spectrum of this compound gave no conclusive evidence of high molecular weight species, but this may be due to the high energy of the ionizing radiation (70 kv) which results in a very short lifetime of the molecular ion when made up of massive atoms such as Mo and Cl. A mass spectrum taken at 10 kv of ionizing radiation should give a peak for the parent ion.

The emission spectrum of the yellow crystals showed strong evidence of Mo with a weak indication of Al.

A polarogram was made of an aqueous solution of the yellow crystals. The solution was 0.51 mg/ml in 0.3 M HCl. A dropping mercury electrode was used vs. a saturated calomel electrode. The scan was run from 0.0 volts to -0.90 volts. Two waves were noted. One wave $E_{1/2} = 0.14\text{v}$, was interfered with by the presence of a large maximum. The second wave was $E_{1/2} = -0.67$. One reference, L. Meites, "Polarographic Techniques", 2nd Edition, 1965, John Wiley & Sons, P. 629, lists:



in 0.3 M HCl

Gelatin was added to suppress the maximum.

At that time it appeared that some volatile Mo compound (and perhaps an Al compound), tended to condense out to form the yellow-white crystals (perhaps H_2MoO_4 or $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$). These crystals could hydrolyze to form blue and green materials (Mo_2O_3 , MoOCl_3 , MoOCl_2 , MoO_2Cl , etc.). The Al may have been present only as AlCl_3 which could hydrolyze to Al_2O_3 . This takes place when MoO_3 reacts with acidic NaAlCl_4 and also appears to be taking place while a MoCl_5 battery is being stored. The yellow crystals were later purified by Dr. Roger Bunting at Illinois State University and were sent to Seiler Research Laboratory at the Air Force Academy. Capt Larry Vaughn reported that the samples sent to the academy were MoO_2Cl_2 . This suggest that the above mentioned mechanism could be correct.

It has been known for a couple years that the MoCl_5 catholytes and cells were not storable under normal dry room conditions. Storage battery tests now indicate that these materials do not store well inside a sealed battery. It now appears that the MoCl_5 materials are not stable enough to provide significant thermal battery shelf life.

To gather more information about this same cell material compatibility samples have been prepared. These samples were testing five major cell materials; LiAl alloy, NaAlCl_4 anolyte, MoCl_5 catholyte, CuCl_2 catholyte, and MoO_3 catholyte.

Cylindrical glass vials with plastic screw cap tops were used to hold the compatibility samples. The vials were about 3 inches tall and 3/4 inch in diameter. The first sample contained only LiAl and anolyte. First, about 1/2 inch of alloy was poured into the vial and then about 1/2 inch of anolyte. The cap was screwed on and taped into place with vinyl electricians tape. The entire operation was done in the dry box.

Samples were prepared with 1/2 inch of 20 ^{w/o} LiAl, 1/2 inch of basic or acidic anolyte, and MoCl₅ catholyte, again either acidic or basic. Some of the samples were exposed to moist air before they were closed but most were maintained in the dry box until closed. Most of the materials were tested by storing in an oven at 160^oF but a few of the samples were maintained at room temperature. One sample with MoCl₅ catholyte was made with the alloy on the top and the catholyte on the bottom so the LiAl could be removed and examined. One MoCl₅ sample was made with the layers of materials separated with disks of quinargo.

Similar samples were prepared for CuCl₂ catholytes and for MoO₃ catholytes (Table #1).

Most of these samples were stored in an oven at 160^oF. After just one day storage all of the MoCl₅ samples showed signs of change. The anolyte began to darken near the catholyte surface. After a few days the color had turned to a brick red which has progressed to nearly the center of the anolyte. After about a week the anolyte was entirely brick red. The reaction was significantly faster in the acidic catholyte than for the basic catholytes. There is no apparent reaction for any of the CuCl₂ samples. There was not any apparent reaction in any of the MoO₃ samples, even the acidic samples.

TABLE 1 SCHEME FOR ORGANIZING COMPATIBILITY SAMPLES

MoO ₃ CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Basic Catholyte	Not Exposed
	BASIC CATHOLYTE	Acidic Catholyte	X
		Basic Catholyte	X
		Acidic Catholyte	Not Exposed
		Basic Catholyte	X
CuCl ₂ CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Basic Catholyte	Not Exposed
	BASIC ANOLYTE	Acidic Catholyte	X
		Basic Catholyte	Not Exposed
		Acidic Catholyte	Exposed
		Basic Catholyte	Not Exposed
MoCl ₅ CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Basic Catholyte	Not Exposed
	BASIC ANOLYTE	Acidic Catholyte	X
		Basic Catholyte	Not Exposed
		Acidic Catholyte	Exposed
		Basic Catholyte	Not Exposed

TABLE 2 SOME EXTRAORDINARY COMPATIBILITY SAMPLES

20 ^{w/o} LiAl & Basic Anolyte
LiSi/Basic Anolyte/Basic MoCl ₅
LiSi/Basic Anolyte/Basic CuCl ₂
LiSi/KCl·LiCl/V ₂ O ₅
28 ^{w/o} LiAl/KCl·LiCl/V ₂ O ₅
Basic MoCl ₅ /Basic Anolyte/LiAl

In every case there was a discoloration of the LiAl alloy. There appears to be no correlation between the cathode material and the degree of anode discoloration. The samples with the most degraded anode layers were the samples exposed to moist air. The anode discoloration appears to be due to exposure to moist air and the anode is compatible with the NaAlCl_4 system.

The LiSi turned black within days after the samples were prepared. It is concluded the 58 % LiSi is more sensitive than 20 % LiAl.

The sample that contained no catholyte still had LiAl that turned light blue which proves that the anode discoloration was not caused by the presence of the catholyte. There was even a slight "bluing" of the anode in the $\text{LiAl/KCl} \cdot \text{LiCl/V}_2\text{O}_5$.

After about 5 weeks the samples had to be removed from the vacuum oven. The MoCl_5 samples leaked and released a deep blue material which coated the inside of the vacuum oven. The oven had to be shut down and cleaned and everything stored in that oven had to be discarded.

A new set of compatibility samples were prepared. These samples were sealed in borosilicate glass tubes.

The first sample was a regular MoCl_5 catholyte, stored with regular anolyte and 28 % LiAl. The 1/4" diameter sample tube was evacuated and filled with argon before the top of the tube was fused shut. The three layers of materials were separated by small fibrefrax pads which were cut slightly larger than the diameter of the sample tube. The sample tubes and fibrefrax separators were dried in a vacuum oven for one hour at 160°F and 30" Hg.

The second sample was regular CuCl_2 catholyte, regular anolyte, and 28 % LiAl. The tube was filled with argon. The third sample was 28 % LiAl and normal anolyte sealed in argon. The 4th, 5th, and 6th samples were sealed

with a vacuum above the sample. Sample #4 was regular MoCl_5 catholyte with regular anolyte and 28 % LiAl . Sample #5 was regular CuCl_2 catholyte with regular anolyte and 28 % LiAl . Sample #6 was 28 % LiAl with production $\text{KCl} \cdot \text{LiCl}$ and production $\text{V}_2\text{O}_5 \cdot \text{LiCl} \cdot \text{KCl}$ catholyte. The last two samples were sealed in an atmosphere of dry O_2 . Sample #7 was regular MoCl_5 catholyte with regular anolyte and 28 % LiAl . Sample #8 was regular CuCl_2 catholyte with regular anolyte and 28 % LiAl .

In all eight samples the fresh, metallic, 28 % LiAl anode material discolored after just one day storage at 160°F . This color change ranged from black to light blue. The only black samples was a fine black ring which formed on the inside of the glass sample tube just above the anode/fibrebrax interface in the MoCl_5 sample sealed under vacuum, sample #4. The other two samples which contained MoCl_5 (sample #1, in argon, and sample #7, in O_2) had broad deep blue rings form around the top $1/8$ " of the anode material but there was no hint of the "black ring" on the glass. The samples which contained CuCl_2 catholytes, V_2O_5 catholyte, or no catholyte at all also displayed discolored anode material. With these latter materials the bluing was moderate to slight. It also appeared that all of the discoloration, regardless of the degree, took place within the first few hours. This seems to indicate that the alloy is reacting with some minor contaminant such as air or moisture which may have been carried into the sample tube with the samples.

A second observation made was that the anolyte slowly turned brick red in all of the MoCl_5 samples but not for any sample without MoCl_5 . It could be concluded that the volatile nature of the MoCl_5 catholyte is relatively independent of the nature of the atmosphere it is stored in.

Some pyrex tubes about 3/8" in diameter were cut about one foot long. One end was sealed in each tube. The tubes were baked for 2 hours at 110°C and were allowed to cool in the interchange of a dry box under vacuum. In tube #1 was placed enough acidic anolyte to fill the tube about 1". The following is a tabulation of the nine samples tested.

TABLE 3 VOLATILITY SAMPLES

#1	Acidic Anolyte
#2	Basic Anolyte
#3	MoO ₃
#4	MoCl ₅
#5	MoO ₃ , Acidic Anolyte, graphite
#6	MoCl ₅ , Basic Anolyte, graphite
#7	MoO ₃ , Basic Anolyte, graphite
#8	WCl ₆
#9	CuCl ₂

After the sample was introduced into the tube, a vacuum was pulled on the tube and it was fused shut. Then the tube was suspended about 3 inches in an oil bath maintained at 165°F. Five samples showed signs of volatility. The two anolyte samples (#1 & #2), the MoO₃ and the CuCl₂ samples showed no signs of volatility. Samples #5 & #7, the MoO₃ catholyte samples, had a few square, dark colored crystals condense onto the cooler upper portions of the sample tube. Sample #4, the MoCl₅ sample produced a large number of square crystals on the collar portion of the tube. However, samples #6 and #8, the

MoCl_5 catholyte and the WCl_6 sample produced profuse growths of needle crystals.

It is the conclusion of these tests that MoCl_5 and WCl_6 are probably too volatile to make a thermal battery with an acceptable storage life using only state-of-the-art thermal battery manufacturing methods. CuCl_2 is quite suitable for a thermal battery with a long shelf life.

SUMMARY:

It had been observed that when a catholyte was exposed to dry room air some of the particles appeared to grow in size. The particle size growth phenomenon was investigated because it might have indicated a storage life problem. The investigation revealed that high valence molybdenum compounds reacted with moisture and the anolyte to form molybdenum oxychlorides and other hydration products. It later became evident that these products were quite volatile and could not be contained in the cathode portion of the cell. Therefore, any thermal batteries made with MoCl_5 catholytes would have very short shelf lives. For this reason MoCl_5 (and later WCl_6) was abandoned and CuCl_2 used as a substitute cathode active material. One of the major consequences of this step was a significant sacrifice of energy density for a significant increase in shelf life.

SECTION V

ANOLYTE CAB-O-SIL CONCENTRATION

Cab-O-Sil is a synthetically prepared siliceous material manufactured and marketed by the Cabot Corporation, Boston, Massachusetts. The thermal battery industry uses this material as a thickening agent to prevent electrolyte flow in activated batteries. As this program began the only percentage of Cab-O-Sil even tried was 10 ^W/o. An experiment was performed to test the effects of using some other percentage and optimizing the percentage of Cab-O-Sil used to immobilize electrolyte powders.

A series of anolytes containing from 7.4 to 15 ^W/o Cab-O-Sil was prepared. These anolytes were used to prepare corresponding catholytes. These materials were tested with a DSC, made into cells and given single cell tests.

The DSC spectra of these anolytes and catholytes show no changes due to the difference in the amount of Cab-O-Sil present in the anolyte.

The single cell test data have been organized into four groups of 7.4 ^W/o Cab-O-Sil, 10 ^W/o Cab-O-Sil, 13 ^W/o Cab-O-Sil and 15 ^W/o Cab-O-Sil. Curves for 80% life versus current density have been generated for these four groups. The curve for the 15% group is lower than for the curves for the other three groups. The curves for the 7.5 ^W/o, 10 ^W/o, and 13 ^W/o have been collected under one envelope. The data points for the 7.4 ^W/o group are scattered worse than the others. The scatter in the 7.4% group is unexplained except that electrolyte flow was noted for some of these cells. There was a large activation high voltage peak which appeared in the 15% group but was not as pronounced for the other three groups.

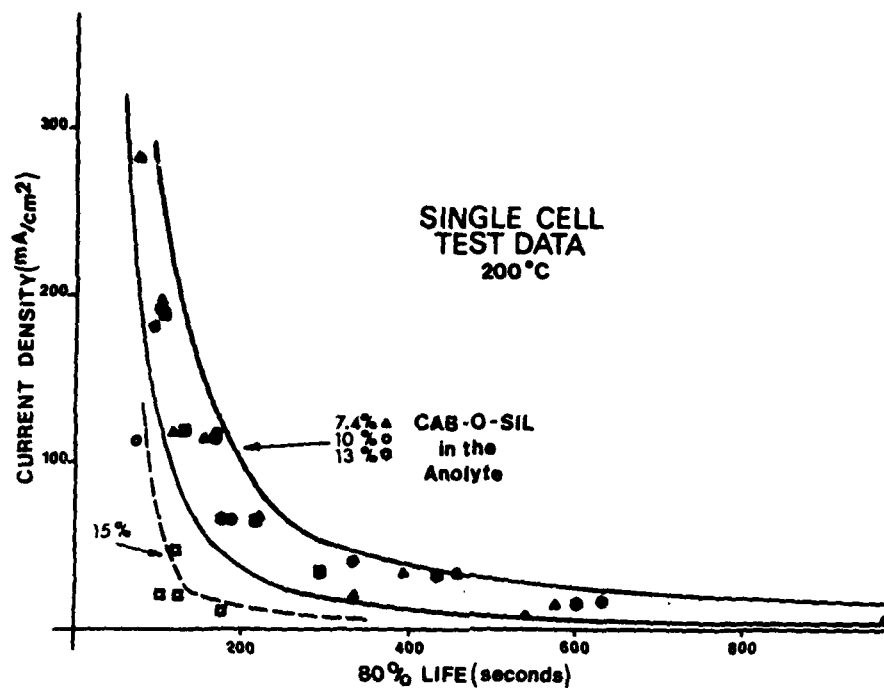


Figure 4. Single Cell Test Results For Cells Made With Various Amounts Of Cab-O-Sil In the Anolyte

Another set of four curves was generated as test temperature versus energy density (Figure 5). The best data were at 10 ^{w/o} and the worst were at 15 ^{w/o}.

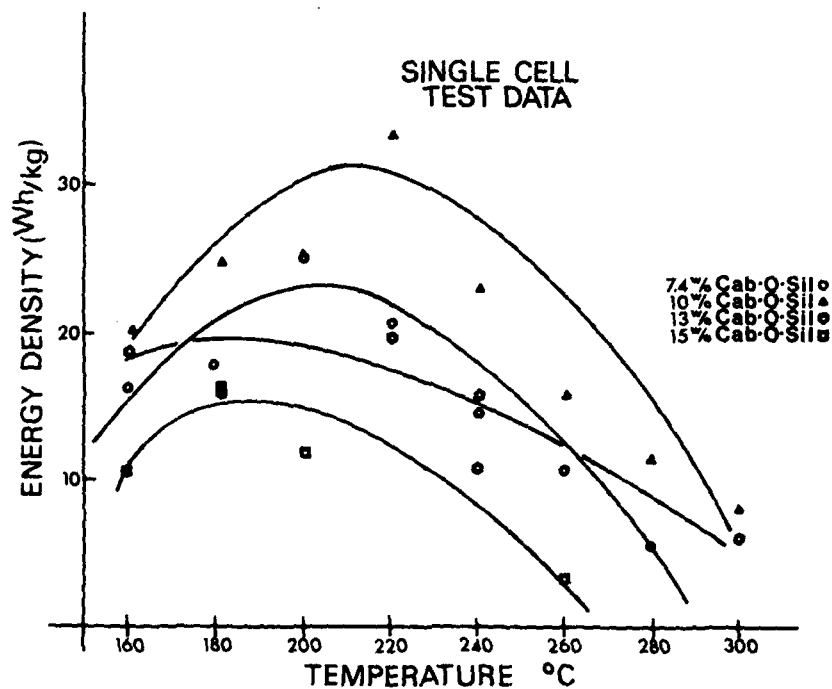


Figure 5. Single Cell Test Data For Cells Made With Various Amounts Of Cab-O-Sil In The Anolyte

An attempt to make anolyte from LiAlCl_4 was successful. By performing experiments similar to those described above it was found that the optimum amount of Cab-O-Sil was 12 % for LiAlCl_4 anolytes.

When an attempt was made to prepare anolyte with acidic LiAlCl_4 the preparation failed because the Cab-O-Sil was not wetted by the molten salt.

CONCLUSION:

This concentration of Cab-O-Sil has very little effect on cell performance within the range of 10 % to 13 % Cab-O-Sil. As the concentration is increased above 13 % to 15 % the tendency to form an activation high voltage spike is increased. Anolyte prepared from NaAlCl_4 was found to flow at a concentration of 7.4 % Cab-O-Sil in a NaAlCl_4 anolyte is 10 % and for a LiAlCl_4 anolyte it is 12 %. Cab-O-Sil functions as an antiflow agent for acidic NaAlCl_4 melts but not for an acidic LiAlCl_4 melt.

SECTION VI

LiCl AS AN ELECTROLYTE ADDITIVE

The normal peak voltage expected from a thermal cell with a LiAl anode and a MoCl_5 catholyte is about 2.4 volts (dependent upon how the cell is loaded for testing). However, in some instances in the first few seconds after initiation the peak voltage may be as high as 3.7 volts (again depending on how the cell is loaded). Because this initial high voltage peak appears as a long, narrow, sharp pointed curve on the strip chart made during single cell testing, this phenomenon has been called "spike" formation. It was believed that perhaps a reaction between lithium and chlorine could produce this high voltage. Therefore it was felt that perhaps the spike formation could be retarded by slowing the lithium reaction. Since Li^+ ions are probably a product of this reaction it was anticipated that adding LiCl to the anolyte would prevent spike formation. It was also felt that adding LiCl would lower the melting point of the electrolyte and, therefore, speed activation.

To test these theories a series of anolytes were prepared which contained different respective amounts of LiCl.

<u>Anolyte Number</u>	<u>% LiCl Contained</u>
A #1016	1 w/o
A #1018	5 w/o
A #1022	10 w/o
A #1024	20 w/o
A #1026	40 w/o

The DSC spectra of these analytes were similar to all of the other analyte spectra. It was noticed that the spectra for the 10 ^{w/o}, 20 ^{w/o}, and 40 ^{w/o} analytes displayed characteristic moisture peaks while the 1 ^{w/o} and 5 ^{w/o} analytes did not. It is interesting to note that there was only very little cold voltage noted for cells made with the 1 ^{w/o} or the 10 ^{w/o} analytes. On the other hand all of the cells made with the 5 ^{w/o}, 20 ^{w/o} analytes did display high cold voltage. There would seem to be a correlation between the observed cold voltage and the presence of a moisture peak in the DSC spectrum. However, the correlation is not perfect or the 5 ^{w/o} cells would not display cold voltage and the 10 ^{w/o} cell would.

Single cell tests were made to test these LiCl containing powders. The purpose of the experiment was to reduce the spike formation but the single cell test results showed just the opposite. The results of these tests are illustrated by Figure 6. Adding LiCl to the anolyte greatly increased the spike, and no batteries were ever made with cells containing LiCl.

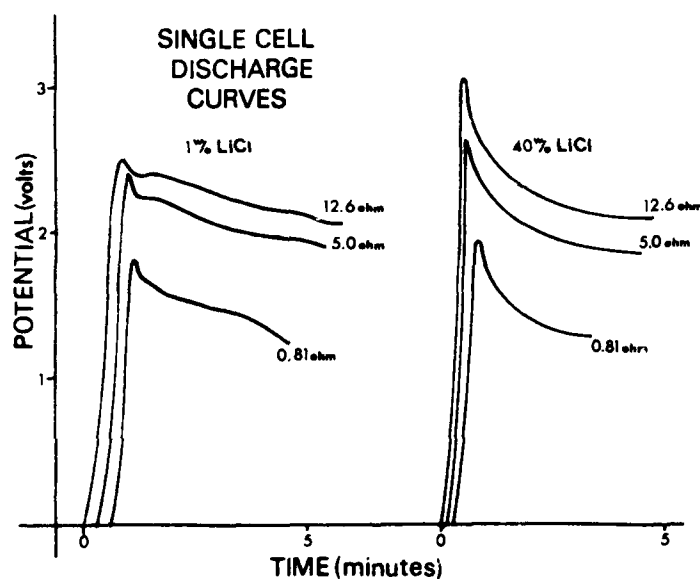


Figure 6. Single Cell Discharge Curves Illustrate The "Spike" Formed By Adding LiCl To The Anolyte

CONCLUSION:

It was believed that an addition of LiCl to the electrolyte would surpress the high voltage spike experienced at cell activation. However, just the opposite was true and the idea was abandoned.

SECTION VII

ALTERNATE BINDERS

At the temperature at which thermal batteries operate the electrolyte is a clear, free flowing liquid. In order to prevent this material from flowing while the battery is functioning, some antiflow agent is included in the electrolyte powders. This material is often referred to as a binder. Florida kaolin ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$) is a naturally occurring mineral which is mined, cleaned and purified. This material has been used as a binder in thermal cells for many years and has just recently been replaced by Cab-O-Sil, a synthetic silica. All of the cells made so far for this project have been made with Cab-O-Sil and now cells have been made with kaolin for comparison of electrical properties performance.

Prior to being used the kaolin was further processed by being baked at 485°C overnight. This was done to remove the water and change the structure to metakaolin ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which has superior binding properties.

One hundred fifty grams of NaAlCl_4 was melted in the dry box. Twenty-five weight percent (50 gm) kaolin was added and stirred in. The molten material took on a pink color. More kaolin was added to bring the weight percentage up to 40 % kaolin. This was necessary to prevent flow of the molten electrolyte. The kaolin was stirred into the open container of molten material with a glass rod. After 40 % kaolin was added the material was cooled and ground until it could pass through a #40 sieve. This anolyte was stored in a jar and labeled A #1034.

A catholyte was prepared with the anolyte and MoCl_5 . This was a test catholyte which contained about 10 % kaolin. This was labeled C #1065.

Test cells were made from these materials. Some cells (#1289 thru #1292) were made with 40 ^w/o LiAl anode. Cell #1293 was made with 28 ^w/o LiAl. Cells #1287 & #1288 were made with Cab-O-Sil catholyte and 40 ^w/o LiAl and were control cells for this test. The results of the tests are shown in Tables 4 and 5.

TABLE 4 SINGLE CELL TEST RESULTS
FOR KAOLIN CONTAINING POWDERS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ³	seconds	seconds	Wh/kg	Wh/kg	ohms	
1288	1.81	204	145	220	32.2	43.7	.81	Cab-O-Sil Catholyte With 40 ^w /o LiAl anode
1287	2.35	43	642	876	37.7	47.5	5	
1292	2.31	42.3	218	638	12.3	29.4	5	170°C 40 ^w /o Kaolin
1290	2.23	40.8	675	970	35.4	46.6	5	180°C 40 ^w /o LiAl
1289	2.26	41.4	498	732	26.0	35.1	5	200°C 10 ^w /o Kaolin in
1291	2.29	41.9	459	637	25.5	32.6	5	220°C the Catholyte
1293	2.31	42.3	391	686	21.5	33.5	5	200°C 28 ^w /o LiAl

TABLE 5 SINGLE CELL TEST RESULTS FOR KAOLIN
CONTAINING CELLS - SPECIFIC RESISTIVITIES

S/N	V _p	i _p	t ₈₀	Load	Temp	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	mA/cm ²	sec.	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1288	1.81	204	145	.81	200	1.31	.955	1.84	-	Cab-O-Sil 40 ^w /o LiAl
1287	2.35	43	642	5	200	.477	.261	.146	1.02	
1292	2.31	42.3	218	5	170	8.20	6.40	5.94	-	Kaolin 40 ^w /o LiAl
1290	2.23	40.8	675	5	180	3.94	-	4.67	2.48	
1289	2.26	41.4	498	5	200	.249	3.11	1.23	6.96	
1291	2.29	41.9	459	5	200	2.67	1.07	1.81	2.47	
1293	2.31	42.3	391	5	200	3.84	7.29	3.58	3.76	Kaolin & 28 ^w /o LiAl

Another alternate material has been received and tested. This is a naturally occurring amorphous silica mined, processed, and marketed by the Illinois Mineral Company, 2035 Washington Ave., Cairo, Illinois, 62914.

Imsil A-25 is a naturally occurring silica which is mined in southern Illinois. The Illinois Mineral Company then processes, refines, and grinds this material. The finished material is quite similar to another naturally occurring material, tripoli. It is similar in appearance to kaolin clay.

An anolyte was prepared by gradually stirring weighed increments of Imsil A-25 into a 1000 ml. beaker of molten NaAlCl_4 until a paste was formed. This required 90 gms of Imsil A-25 into 100 gm of NaAlCl_4 (about 47.4 %). In order to prevent flow only about 8 % Cab-O-Sil is necessary and only about 35 % kaolin is necessary.

A second anolyte was prepared with some specially prepared Imsil A-25. This Imsil was placed in a crucible and baked in a muffle furnace for 1½ hours at 950°C. The cooled Imsil was then mixed gradually into 100 gms of molten NaAlCl_4 . Only 80 gm (44.4 %) were necessary to form a paste.

Catholytes were made from these two anolytes and these electrolytes were tested by DSC and with single cell tests.

A third anolyte was prepared by mixing silica #54, another Illinois Mineral product, into molten NaAlCl_4 . It required 130 gms to immobilize the liquid (56.5 %). The cooled material was hard and glass like. After an attempt to grind this material it was discarded and not further tested.

It is interesting to note that as the Imsil A-25 was stirred into the molten NaAlCl_4 the mix turned light green. The cooled anolyte was a faint gray-green. The DSC spectra of both the anolyte and catholyte were similar to what might be expected of a slightly moist anolyte. This implies that the spectrum of the catholyte was quite unusual.

The single cell tests performed to test these materials were interesting. Table 6 is a tabulation of test results taken at constant temperature and varying load resistance. Table 7 is a tabulation of test results run at constant load and varying temperatures.

TABLE 6 SINGLE CELL TEST RESULTS OF CELLS MADE FROM 28 ^{w/o} LiAl/IMSIL A-25, NaAlCl₄/IMSIL A-25, CuCl₂, GRAPHITE AND TESTED AT CONSTANT TEMPERATURE WITH VARIOUS LOADS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohms	
1357	1.53	173	90	212	13.5	26.9	0.81	200°C
1362	1.61	98.2	292	488	26.1	39.0	1.5	
1363	1.79	54.6	341	879	18.4	40.3	3	
1356	1.89	34.6	433	1145	15.6	35.0	5	
1359	2.08	15.1	265	1372	4.5	18.9	12.6	
1365	1.93	7.1	250	520	1.89	3.43	25	

The test results in Table 6 can be compared to results from earlier cell tests on similar cells (made with Cab-O-Sil instead of Imsil A-25). When this comparison is made it can be seen that the energy densities reported for the Imsil A-25 cells are smaller than for the Cab-O-Sil cells. A little closer observation shows that, for the Cab-O-Sil cells, as the load was increased the current density decreased but the 80% and 70% energy densities increased. That is, the Cab-O-Sil cells worked increasingly better as the current density became less and less. This was certainly not the case for the Imsil A-25 cells. They showed much better performance at high current density than at low current density. This is similar to what has been previously reported for MoCl₅ cells.

There is another feature about these cell tests which does not show in Table 6. These cells displayed a discharge curve similar to a negative log curve very reminiscent of the MoCl_5 spike. The presence of a spike explains the decreased relative performance. As the load approached open circuit the spike became even worse. This is exactly analogous to the MoCl_5 cells.

The results in Table 7 can also be compared to prior reported test results. The earlier cells were made with Cab-O-Sil instead of Imsil A-25. Again it can be seen that the cells made with Imsil A-25 had lower energy densities than the cells made with Cab-O-Sil. Once again a closer investigation shows that this is caused by a spike formation.

It is also interesting to note that when cells were made with kaolin the internal resistance increased dramatically but the cells made with Imsil A-25 had internal resistances of about the same magnitude as expected with Cab-O-Sil cells.

There was no cold voltage displayed for the cells made with Imsil A-25. There was also no cold voltage with cells made previously with kaolin. However, all the cells made now with Cab-O-Sil do display cold voltage.

TABLE 7 SINGLE CELL TEST RESULTS FOR CELLS MADE FROM 28 ^{w/o}
 $\text{LiAl}/\text{IMSIL A-25}$, $\text{NaAlCl}_4/\text{IMSIL A-25}$, CuCl_2 , GRAPHITE AND TESTED
 AT A CONSTANT LOAD AND VARIOUS TEMPERATURES

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	TEMP	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	$^{\circ}\text{C}$	
1360	1.82	33.3	72	638	2.13	44.2	160	5 ohms
1361	1.80	32.9	314	870	10.3	24.0	180	
1356	1.89	34.6	433	1145	15.6	35.0	200	
1366	1.89	34.6	452	890	16.5	28.4	260	
1367	1.89	34.6	111	325	4.45	10.3	320	

Many months later an optimum cell formula was developed for cells prepared with Cab-O-Sil binder. Because the Imsil A-25 had made such good cells it was decided to try it again with the new optimum formula. Table 8 contains the results of tests of cells made with Imsil A-25 and the optimum cell formula. As a result of these tests the Imsil A-25 was abandoned and no longer pursued.

TABLE 8 SINGLE CELL TEST DATA FOR CELLS MADE WITH IMSIL A-25

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT}	R_{INT}	R_{INT}	R_{INT}	LOAD	NOTES
						Peak	t_{90}	t_{80}	t_{70}		
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²		
2002	1.82	33.3	5.02	15.3	21.8	2.05	2.24	2.50	3.20	5	Unfused
2003	1.83	33.5	2.66	6.37	9.17	X	3.12	2.14	2.83	5	
2004	1.72	31.5	1.74	3.91	6.16	X	5.14	5.03	5.38	5	Fused
2005	1.80	13.1	2.14	4.96	7.02	4.49	4.12	X	3.14	12.6	

Another material tested as an antiflow agent was MgO. This material was made into an anolyte with the freon blending process. The freon blending process will be detailed later in this report.

An anolyte was prepared by blending 90 gm of MgO (J.T. Baker Chemical Company, light powder, USP, Food Grade, APD = 2.1 μ) with 110 gm of NaAlCl₄ in a Waring blender with 300 ml. Freon. The MgO had been previously vacuum desiccated and the NaAlCl₄ had been previously ground until it passed thru a #40 sieve. The freon slurry was poured into a porcelain pan. The freon was allowed to evaporate into a fume hood in a dryroom until the cake that formed could be easily crumbled. The crumbled cake was then placed in a vacuum chamber

in the dryroom, at room temperature, overnight. The anolyte was then easily passed thru a #40 sieve. A similar anolyte was prepared with Cab-O-Sil to act as a control for any testing that might be done with the MgO anolyte.

Portions of each of these anolytes were used to prepare CuCl_2 catholytes. The anolytes had not fused at this point. These materials were then used to make cells for testing. The bulk density of these unfused materials was very light and because of this the anolyte and catholyte layers were lighter than usual. For the unfused MgO cells the cell formula was:

UNFUSED MgO ANOLYTE

$$\begin{array}{r} \text{anode} = 0.45 \text{ gm} \pm .1 \\ \text{anolyte} = 1.45 \text{ gm} \pm .1 \\ \text{catholyte} = 1.30 \text{ gm} \pm .1 \\ \hline \text{Total} = 3.20 \text{ gm} \pm .1 \end{array}$$

The cells were approximately 0.060" thick.

When tested the cells flowed badly and displayed considerable noise.

Similar observations were made about the unfused Cab-O-Sil. Their cell formula was:

UNFUSED CAB-O-SIL ANOLYTE

$$\begin{array}{r} \text{anode} = 0.45 \text{ gm} \pm .1 \\ \text{anolyte} = 1.75 \text{ gm} \pm .1 \\ \text{catholyte} = 1.20 \text{ gm} \pm .1 \\ \hline \text{Total} = 3.40 \text{ gm} \pm .1 \end{array}$$

These cells were approximately 0.069" thick. Once again the electrolytes flowed badly during testing. In spite of the severe flow three tests were completed.

Some of the unfused Cab-O-Sil cells were vacuum desiccated for 4 hours. These cells were significantly worse due to an increased spike!!

Then the two anolytes were fused, cooled, reground, and sieved. Again a portion of each anolyte was used to prepare a CuCl_2 catholyte.

The MgO anolyte was heated to 180° for 1 hour, cooled, reground and sieved. There was not real evidence that the MgO had been wetted by the NaAlCl_4 (the powder was still light and fluffy) but there was no evidence that the two materials had separated either. A portion of this material was used to prepare a catholyte and cells were made for testing.

The cell tests were not good. The internal resistance was extremely high. The peak voltage was 0.1 volts. The MgO has been abandoned for use with NaAlCl_4 .

The Cab-O-Sil anolyte was also fused and reground. Again a CuCl_2 catholyte was prepared and cells were made for testing. Except for a very large spike at the 12.6 ohm test the fused anolyte cells were superior to the unfused anolyte cells (see Table 9 for all of these cell tests).

The first attempts to use MgO as an immobilizer failed. The freon blended NaAlCl_4 and MgO would not wet. Some time after that Argonne Labs reported wetting MgO ceramic separators with LiAlCl_4 . Because of this report it was decided to again try MgO as a binder.

Some powdered LiAlCl_4 was slowly heated on a hot plate in the drybox until fusion. MgO was slowly added to the molten salt until immobilization occurred (about 15 to 16% MgO). This material was cooled, ground, and sieved to make A #1130. Some of A #1130 was used to prepare CuCl_2 catholyte, C #1291. These powders were used to make cells which were tested on the single cell tester. (Table 10)

TABLE 9 SINGLE CELL TEST RESULTS FOR THE FREON BLENDED POWDERS.
THESE POWDERS WERE PREPARED TO TEST MgO AS A BINDER. ALL TESTING
WAS RUN AT 200°C

S/N	V _P	i _P	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT} PEAK	R _{INT} t ₉₀	R _{INT} t ₈₀	R _{INT} t ₇₀	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1863	1.22	22.3	0.07	0.12	0.20	X	X	25.5	31.1	Unfused MgO Anolyte
1864	1.65	186	5.20	14.5	26.7	1.64	1.96	1.22	1.54	Unfused Cab-O-Sil Anolyte Fresh Cells
1865	2.02	36.9	2.05	15.2	38.2	1.60	0.89	1.31	1.49	
1866	2.05	14.9	1.01	23.4	44.4	1.34	0.73	0.82	1.89	
1867	2.11	38.6	0.66	1.18	10.1	X	X	10.5	3.44	Unfused Cab-O-Sil 4 hours desiccation
1868	2.26	16.4	0.21	0.33	0.55	X	X	X	17.0	
1869	1.76	199	5.38	16.8	31.2	0.99	0.76	0.47	0.79	Fused Cab-O-Sil Anolyte Fresh Cells
1870	2.04	37.3	1.27	20.1	45.3	1.08	0.59	0.66	0.76	
1871	2.49	18.1	0.09	0.19	12.6	X	2.43	1.97	0.73	

TABLE 10 SINGLE CELL TEST RESULTS FOR CELLS MADE WITH
ELECTROLYTE POWDERS IMMOBILIZED WITH MgO

S/N	V _P	i _P	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Peak	t ₇₀		
					ohm·cm ²	ohm·cm ²	ohms	
2028	2.32	42.4	1.86	3.39	4.04	9.62	5	LiAlCl ₄ not desiccated
2029	1.40	158	3.11	4.05	4.37	10.0	.81	
2030	1.96	35.7	2.00	2.85	12.7	37.9	5	LiAlCl ₄ desiccated 3½ hours
2031	2.26	16.4	1.76	3.03	10.5	-	12.6	
2032	1.58	178	3.58	5.84	2.73	3.72	.81	NaAlCl ₄
2033	2.13	39.0	1.05	2.65	3.17	3.06	5	
2034	2.41	17.5	0.31	1.00	5.03	2.40	12.6	

All of the cell tests displayed large spikes, high internal resistance, short life times and poor energy density. The NaAlCl_4 cells showed evidence of flow and poor wetting of the MgO by the NaAlCl_4 .

CONCLUSION:

Cells which contained kaolin did not perform quite as well as cells that were made with Cab-O-Sil. The potential was slightly lower and the energy density was not as high. The main cause of the lower energy density was the significant increase in the internal cell resistance. The antiflow properties of the kaolin electrolytes appears to be at least as good as the Cab-O-Sil electrolytes. Kaolin is easier to handle and easier to incorporate into an anolyte. There is no apparent reason to pursue the substitution of kaolin for Cab-O-Sil.

Of the Illinois Mineral silicates tested Imsil-25 did make some very good cells. Imsil-25 prevents electrolyte flow. Approximately 4 times as much Imsil-25 as Cab-O-Sil is needed to prevent flow. There was no cold voltage observed with the cells made with either kaolin or Imsil-25. There was no increase in internal resistance with cells made with Imsil-25 as there was with cells made with kaolin. Imsil-25 is cheaper and easier to use than Cab-O-Sil but has a tendency to aggravate the spike phenomenon.

MgO is not a suitable antiflow agent for this thermal system. MgO does not wet NaAlCl_4 but does wet LiAlCl_4 .

SECTION VIII

ACID-BASE PROPERTIES OF THE ELECTROLYTE

The effects upon cell and battery performance due to changes in the acid-base properties² of the $\text{NaCl} \cdot \text{AlCl}_3$ mixtures which compose the electrolytes are not well known. It was anticipated that the cathode chloride would be much more soluble in an acidic catholyte than in a basic catholyte. The increased solubility should increase the cathode activity, which should increase the cell voltage. However, the mobility of the cathode active species would also be increased and it was anticipated that as the cathode active materials crossed the electrolyte an energy wasting corrosion reaction would take place at the anode as well as the energy producing cell reaction. It was believed that this energy wasting reaction could be retarded by using a suitable separator. If a basic anolyte was used with an acidic catholyte the reduced solubility of the cathode active species in the base would allow the anolyte/catholyte interface to act like a separator. The soluble cathode chloride would not cross the basic anolyte layer.

Another problem anticipated was the higher vapor pressure of acidic $\text{NaCl} \cdot \text{AlCl}_3$ mixtures. This could cause problems in safely preparing these electrolyte materials and could cause performance problems for both cells and batteries.

In addition to this it had already been observed that the conductivity of NaAlCl_4 cells decreased dramatically with an increase in acidity of the electrolyte.^{3,4} This is accounted for by an increase in the size of the Al (III) containing species in the acidic electrolytes, a decrease in the concentration

2. Reference. A.A. Fannin, Jr., L. A. King, and D. W. Seegmiller, "Chloroaluminate Equilibria in $\text{AlCl}_3 \cdot \text{NaCl}$ Melts," *Journal of the Electrochemical Society*, 119,801 (1972)
3. Reference. G. D. Brabson, J. K. Erbacher, L. A. King, and D. W. Seegmiller, "Exploratory Aluminum-Chlorine Thermally Activated Battery: Single Cell Experiments," FJSRL-TR-76-0002, January, 1976.
4. Reference. C. L. Hussey, J. K. Erbacher, L. A. King, "High Energy Density Pelletized Aluminum Chloride Thermal Batteries," FJSRL-TR-76-0003, January, 1976

of very mobil Na^+ ions, and the formation of a nonconducting Al_2Cl_5 layer at the anode/anolyte interface early in the cell discharge. Once again, some of these effects may be lessened by the use of an acidic catholyte and a basic anolyte.

The first single cell tests done for the acid-base experiments were with cells using CuCl_2 catholytes and 40 % LiAl anodes. There were four types of cells made:

- 1) basic anolyte and basic catholyte - these were control cells for the rest of the experiment
- 2) basic anolyte and acidic catholyte
- 3) acidic anolyte and acidic catholyte
- 4) acidic anolyte and basic catholyte

Representative tests of each type of cell was done with a 5 ohm load and at a temperature of 200°C . The following table represents these results.

TABLE 11 TYPICAL ACID-BASE SINGLE CELL TESTS
FOR CuCl_2 CELLS USING A 40 % LiAl ANODE

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	TEMP. & LOAD	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg		
1294	1.87	34.2	551	773	20.9	26.2	200°	Basic Anolyte Basic Catholyte
1295	1.87	34.2	593	824	22.3	28.4		Acidic Anolyte Basic Catholyte
1306	1.86	34.0	963	1536	35.0	50.1	5	Acidic Anolyte Acidic Catholyte
1310	1.90	34.8	781	1440	29.4	47.5	ohms	Basic Anolyte Acidic Catholyte

These cell test results are not individual cell tests but, rather, the average of the tests of three similar cells. Single Cell #1294 was just a normal test cell and was the control cell for this experiment. These results can be compared to cell tests which were reported two months previous to this experiment and which were constructed similarly to cell #1294. The results of the earlier cell tests can be summarized like this:

$$\begin{aligned}
 V_p &= 1.78V \\
 i_p &= 34.2 \text{ mA/cm}^2 \\
 t_{80} &= 600 \text{ seconds} \\
 t_{70} &= 1200 \text{ seconds} \\
 ED_{80} &= 24 \text{ Wh/kg} \\
 ED_{70} &= 40 \text{ Wh/kg}
 \end{aligned}$$

EARLIER CELLS

The later cell tests, which were done for this experiment, were made with different, but similar, batches of anolyte and catholyte and can be summarized like this:

$$\begin{aligned}
 V_p &= 1.78V \\
 i_p &= 34.2 \text{ mA/cm}^2 \\
 t_{80} &= 550 \text{ seconds} \\
 t_{70} &= 750 \text{ seconds} \\
 ED_{80} &= 21 \text{ Wh/kg} \\
 ED_{70} &= 26 \text{ Wh/kg}
 \end{aligned}$$

LATER CELLS

These two sets of single cell data provide some insight about the normal variation in cell performance. Considering this large variation there is little difference in the performance of the control cell and the cell with acidic anolyte and basic catholyte. As predicted the cell with the acidic catholyte and basic anolyte had the highest voltage but this could have been

due to statistical variance as well as to the effects of using an acidic catholyte. Single cell #1306, the cell made entirely from acidic electrolyte, had significantly longer life and a greater energy density than any of the other cells. Yet, this cell was made with both, an acidic anolyte and an acidic catholyte, and it was predicted that this combination would have the shortest life due to diffusion of the cathode active species and to increased internal resistance.

A similar series of cells was made with MoCl_5 catholytes (see Table 12).

TABLE 12 TYPICAL ACID-BASE SINGLE CELL TESTS
FOR MoCl_5 CELLS USING A 40 w/o LiAl ANODE

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	TEMP. & LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg		
1325	2.43	44.5	509	800	31.7	44.8	200°	Basic Anolyte Basic Catholyte
1339	2.46	45.0	488	776	31.1	44.4	&	Acidic Anolyte Basic Catholyte
1338	2.43	44.5	510	809	31.4	44.9	5	Acidic Anolyte Acidic Catholyte
1328	2.42	44.3	549	802	33.7	45.0	ohms	Basic Anolyte Acidic Catholyte

As was true for the CuCl_2 cells with 40 w/o LiAl in the anode, this type of cell (MoCl_5 catholyte with 40 w/o LiAl anode) had been made before this experiment. A summary of these data is:

$$V_p = 2.35V$$

$$i_p = 43.0 \text{ mA/cm}^2$$

$$t_{80} = 642 \text{ seconds}$$

EARLIER CELLS

$$t_{70} = 876 \text{ seconds}$$

$$ED_{80} = 37.7 \text{ Wh/kg}$$

$$ED_{70} = 47.5 \text{ Wh/kg}$$

Compare this summary to a similar summary about the later made cells.

$$V_p = 2.43V$$

$$i_p = 44.5 \text{ mA/cm}^2$$

$$t_{80} = 509 \text{ seconds}$$

LATER CELLS

$$t_{70} = 800 \text{ seconds}$$

$$ED_{80} = 31.7 \text{ Wh/kg}$$

$$ED_{70} = 44.8 \text{ Wh/kg}$$

These summaries provide a little more insight about the magnitude of the variance for single cell test results. This variance was apparently so high that it was necessary to make more cell tests on the four possible types of cells.

For the first series of tests the temperature was held constant at 200°C while the load resistance was varied (see Table 13).

Some of the data from Table 13, the peak voltage and current density, are illustrated with Figure 7. In each of the four sets of data it can be seen that as the current density of a cell is caused to increase the peak voltage is decreased. This is normal behaviour for any cell. It would appear from Figure 7 that at low current density the peak voltages of the four cell types were about the same. However, at the high current densities the cells with basic anolyte were superior to cells with acidic anolytes. This is reasonable. The acidic anolytes have higher internal resistances. Then it would be expected that this would have a greater effect on performance at higher current densities than at lower current densities.

TABLE 13 THE EFFECT OF VARIOUS TEST LOADS ON CuCl_2 CELLS
MADE WITH THE FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC
ANOLYTE, ACIDIC CATHOLYTE, BASIC ANOLYTE AND BASIC CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	LOAD	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	ohms	
(1279) (1272)	1.60	180	70	116	12.4	17.7	.81	<u>200°C</u> Basic Anolyte <u>Basic Catholyte</u>
1277	1.73	106	152	268	16.5	25.3	1.5	
1276	1.82	55.5	372	650	22.1	33.8	3	
(1271) (1270)	1.87	34.2	628	1263	23.2	40.1	5	
(1273) (1275)	1.92	13.9	2695	4150	41.2	57.4	12.6	
1278	2.05	7.5	5256	7816	43.8	60.2	25	
1321	1.60	181	82	138	14.5	21.3	.81	<u>200°C</u> Basic Anolyte <u>Acidic Catholyte</u>
1310	1.90	34.8	781	1440	29.4	47.5	5	
1311	1.96	14.2	2860	-	44.9	-	12.6	
1312	1.97	7.2	6760	8533	54.5	65.0	25	
1307	1.50	169	83	134	12.7	18.1	.81	<u>200°C</u> Acidic Anolyte Acidic Catholyte
1306	1.86	34	964	1534	35.0	50.1	5	
1309	1.93	14	3355	-	54.7	-	12.6	
1308	1.95	7	7150	9160	55.9	67.5	25	
1297	1.43	162	44	95	5.06	11.0	.81	Test Temperature <u>200°C</u> Acidic Anolyte <u>Basic Catholyte</u>
1301	1.84	56.1	302	407	18.7	23.2	3	
1295	1.87	34.2	593	824	22.2	28.4	5	
1296	1.93	14.0	2338	3023	36.1	43.8	12.6	
1300	1.90	7	6303	7835	48.9	57.3	25	

It was hoped that the decrease in performance caused by an increase in the internal resistance of the catholyte would be more than compensated for by an increase due to the increased activity of the cathode active species. From Table 13 it can be seen that, indeed, the cells with acidic catholytes did have superior lifetimes and energy densities. However, this was only readily apparent at the low current densities. Furthermore, the group of control cells, the basic anolyte/basic catholyte cells were also quite good at the low current densities. There was certainly no significant increase in the cell voltage due to use of an acidic catholyte. Perhaps the cathode active species was not significantly activated by the acidic nature of the catholyte or perhaps the catholyte was not as acidic as was believed.

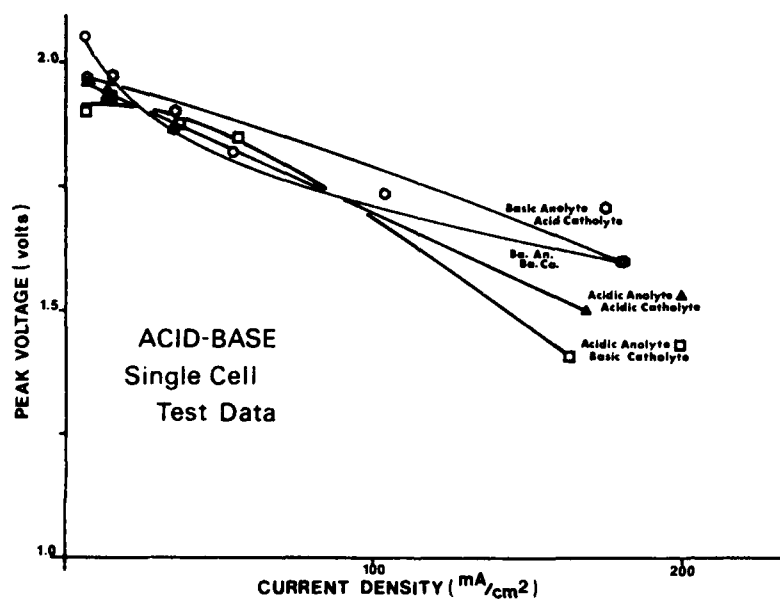


Figure 7. Single Cell Tests Results

The next experiment was to hold the load resistance at 5 ohms and vary the test temperature. These data are tabulated in Table 14.

TABLE 14 THE EFFECT OF VARIOUS TEST TEMPERATURES ON CuCl_2 CELLS MADE WITH FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC ANOLYTE, BASIC ANOLYTE, ACIDIC CATHOLYTE, BASIC CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	TEMP.	NOTES
	volts	mA/cm^2	seconds	seconds	mA/cm^2	mA/cm^2	$^{\circ}\text{C}$	
1280	1.89	34.8	763	1233	28.7	41.4	180	5 ohm Load ————— Basic Anolyte ————— Basic Catholyte —————
(1270)	1.87	34.2	628	1263	23.2	40.1	200	
(1271)	1.88	34.4	665	1100	25.6	37.3	240	
1282	1.89	34.6	595	835	23.4	29.9	280	
1283	1.88	34.4	245	1170	9.36	34.8	300	
1284	1.93	35.3	435	1295	17.2	41.5	320	
1285	1.95	36.7	346	982	14.0	32.5	340	
1319	1.87	34.2	633	1169	22.8	37.1	160	5 ohm Load ————— Basic Anolyte ————— Acidic Catholyte
1320	1.91	34.9	714	1357	26.7	44.6	180	
1310	1.90	34.8	781	1440	29.4	47.5	200	
1322	1.88	34.4	959	1383	35.8	47.3	240	
1324	1.91	34.9	427	1148	16.8	36.8	320	
1313	1.84	33.7	894	1415	31.2	44.6	160	5 ohm Load ————— Acidic Anolyte ————— Acidic Catholyte
1314	1.84	33.7	903	1568	31.7	48.9	180	
1306	1.86	34.0	964	1536	35.0	50.1	200	
1315	1.86	34.0	887	1362	33.0	45.5	240	
1316	1.88	34.4	339	534	13.9	19.2	280	
1317	1.89	34.6	432	1069	16.4	33.8	320	
1318	2.03	37.1	194	672	8.60	23.6	360	
1299	1.86	34.0	608	822	22.6	28.2	180	5 ohm Load ————— Acidic Anolyte ————— Basic Catholyte
1295	1.87	34.2	593	824	22.3	28.4	200	
1303	1.87	34.2	786	1062	30.1	37.5	240	
1304	1.88	34.4	698	972	27.4	34.8	280	
1305	1.94	35.5	613	1137	25.4	40.4	320	

In three out of four sets of data the peak voltage increased as the temperature increased. The exception was the set of cells made with a basic anolyte and an acidic catholyte.

The lowest voltage recorded was for the lowest temperatures and the cells made with both acidic anolyte and acidic catholyte. These same cells also produced the highest voltage but at the high temperatures. This is somewhat misleading because there was a tendency to form a "spike" in the activation curve when the test temperature was over 300°C. Actually there was very little difference in the peak voltages produced. Table 15 is a tabulation of average peak voltage and standard deviation for the data for each cell type in Table 6.

TABLE 15 AVERAGE VOLTAGE, STANDARD DEVIATION
AND 1 BANDS FOR THE FOUR DATA SETS IN TABLE 5

CELL TYPE	AVERAGE VOLTAGE	STANDARD DEVIATION	1 BAND
Basic Anolyte Basic Catholyte	1.8975	0.0276	1.925 1.870
Basic Anolyte Acidic Catholyte	1.8940	0.0182	1.912 1.876
Acidic Anolyte Acidic Catholyte	1.8857	0.0663	1.952 1.819
Acidic Anolyte Basic Catholyte	1.884	0.0321	1.916 1.852

It is reasonable to explain the low voltage for the acidic anolyte/acidic catholyte cells at low temperature due to increased melting point and decreased conductivity of the electrolyte. No explanation is offered for the tendency to form an activation spike at higher temperature or in an acidic catholyte.

The biggest difference expected in acidic and basic electrolytes was in internal resistance. Tables 16, 17, & 18 tabulate the internal resistance data that were accumulated during the tests described in Tables 12, 13, & 14. It was expected that the acidic electrolytes would cause their cells to have high internal resistances. However, this was not always the case. For example, in Table 17 the group of cells which displayed the least internal resistance was the group with the acidic anolyte and basic catholyte. There is no immediate explanation for why this group has a lower internal resistance. The control group, with a basic anolyte and a basic catholyte, was predicted to have the lowest internal resistance. Also, the internal resistance always increased as more current passed. The effect was about as great for low current density situations as for high current density cells. Finally, there is no apparent reason for why the internal resistance increased with temperature.

TABLE 16 INTERNAL RESISTANCE FOR TYPICAL CELLS OF EACH OF THE FOUR TYPES TESTED

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1294	1.87	551	5	200	.30	1.3	4.8	6.7	Basic Anolyte Basic Catholyte
1295	1.87	593	5	200	.90	1.6	3.0	7.6	Acidic Anolyte Basic Catholyte
1306	1.86	964	5	200	.98	1.1	4.5	10.6	Acidic Anolyte Acidic Catholyte
1310	1.90	781	5	200	1.2	4.8	10.1	X	Basic Anolyte Acidic Catholyte

TABLE 17 INTERNAL RESISTANCE FOR CuCl_2 CELLS OF EACH OF THE FOUR TYPES TESTED WITH CONSTANT TEMPERATURE AND A VARIABLE LOAD

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
(1272) (1279)	1.60	71	.81	200	1.5	2.9	3.1	X	Basic Anolyte
(1270) (1271)	1.87	628	5	200	.75	3.1	5.7	21.5	
(1273) (1275)	1.92	2695	12.6	200	.55	.80	8.1	14.4	Basic Catholyte
1278	2.05	5256	25	200	.35	X	X	X	Control Group
1321	1.60	82	.81	200	1.3	1.8	3.1	4.1	Basic Anolyte Acidic Catholyte
1310	1.90	781	5	200	1.2	4.8	10.1	X	
1311	1.96	2860	12.6	200	.73	X	9.0	X	
1312	1.97	6760	25	200	.36	X	X	X	
1307	1.50	83	.81	200	X	1.5	3.8	5.4	Acidic Anolyte
1306	1.86	964	5	200	.98	1.1	4.5	10.6	
1309	1.93	3355	12.6	200	3.7	4.9	10	16.7	Acidic Catholyte
1308	1.95	7150	25	200	1.4	1.6	17.7	41.9	
1297	1.43	44	.81	200	X	3.0	9.7	X	Acidic Anolyte
1295	1.87	593	5	200	.90	1.6	3.0	7.6	
1296	1.93	2338	12.6	200	.29	.31	2.8	4.0	Basic Catholyte
1300	1.90	6303	25	200	.29	.32	.70	6.6	

TABLE 18 INTERNAL RESISTANCE FOR CuCl_2 CELLS OF EACH OF THE FOUR TYPES TESTED WITH CONSTANT LOAD RESISTANCE AND A VARIABLE TEST TEMPERATURE

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1280	1.89	763	5	180	1.2	2.0	4.0	X	Basic Anolyte Basic Catholyte Control Group
1281	1.88	665	5	240	.30	2.0	5.5	X	
1283	1.88	245	5	300	.30	6.0	11.3	12.5	
1285	1.95	346	5	340	.14	3.8	9.9	X	
1320	1.91	714	5	180	1.2	3.5	5.0	10.7	Basic Anolyte Acidic Catholyte
1322	1.88	959	5	240	.29	2.0	5.5	12.9	
1324	1.91	427	5	320	.29	5.6	10.7	13.0	
1314	1.84	903	5	180	2.7	3.6	5.5	12.3	Acidic Anolyte Acidic Catholyte
1315	1.86	887	5	240	.29	2.6	6.7	13	
1317	1.89	432	5	320	.29	5.9	11.9	16.1	
1318	2.03	194	5	360	2.2	X	10.1	19.8	
1299	1.86	608	5	180	.29	2.3	3.3	5.5	Acidic Anolyte Basic Catholyte
1303	1.87	786	5	240	.29	1.3	3.3	7.8	
1304	1.88	698	5	280	.29	1.6	5.8	11.3	
1305	1.94	613	5	320	.57	4.1	10.2	12.8	

Similar sets of data were collected for MoCl_5 cells with 40 % LiAl anodes. These cells were very disappointing because there were very few noticeable differences in the acid-base electrolytes. Tables 19, 20, and 21 tabulate the internal resistance data for these cells. Once again there is no noticeable difference in the internal resistance of the four types of cells.

Looking at Tables 18, 19, and 20 it is interesting to notice the change in the internal resistance as the cell is discharged. For a CuCl_2 cell the internal resistance always started out low and gradually increased. The MoCl_5 cells start out with relatively high internal resistance which drops to a minimum value. Then, after hitting the minimum the internal resistance will start to gradually climb again. This pattern has been noted for the internal resistance of All LiAl/MoCl_5 cells made before. The only differences are the times when the minimum is reached. For example, the minimum occurred about t_{90} for cell #1325 but it occurred sometime after t_{70} for cell #1328 (Table 19). Once again, no real effect can be assigned to any particular combination of acidic or basic electrolyte.

TABLE 19 INTERNAL RESISTANCES OF MoCl_5 CELLS
OF EACH OF THE FOUR DIFFERENT TYPES

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1325	2.43	509	5	200	.70	.25	.28	.66	Basic Anolyte Basic Catholyte
1328	2.42	549	5	200	.93	.76	.56	.32	Basic Anolyte Acidic Catholyte
1338	2.43	510	5	200	.90	.25	.29	.33	Acidic Anolyte Acidic Catholyte
1339	2.46	488	5	200	2.1	.76	.28	.32	Acidic Anolyte Basic Catholyte

TABLE 20 THE EFFECT OF VARIOUS CURRENT DENSITIES ON
MoCl₅ CELLS AT CONSTANT TEMPERATURE AND WITH THE FOUR
POSSIBLE ACID-BASE TYPES

S/N	V _p	t ₈₀	load	Temp.	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	seconds	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1326	1.91	86	.81	200	1.1	1.5	.93	1.4	Basic Anolyte Basic Catholyte
1325	2.43	509	5	200	.70	.25	.28	.66	
1327	2.51	928	12.6	200	.55	1.2	.69	.79	
1329	1.96	91	.81	200	1.1	1.3	.96	1.3	Basic Anolyte Acidic Catholyte
1328	2.42	549	5	200	.93	.76	.56	.32	
1332	2.56	954	12.6	200	1.1	.60	.68	.77	
13X	2.43	510	.81	200	.90	.25	.29	.33	Acidic Anolyte Acidic Catholyte
1338			5						
X			12.6						
X	2.46	488	.81	200	2.1	.76	.28	.32	Acidic Anolyte Basic Catholyte
1339			5						
X			12.6						

TABLE 21 THE EFFECT OF VARIOUS TEST TEMPERATURES AT
CONSTANT LOAD FOR MoCl₅ CELL WITH A 40 w/o LiAl ANODE
AND A BASIC ANOLYTE AND ACIDIC CATHOLYTE

S/N	V _p	t ₈₀	load	Temp.	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	seconds	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1334	2.46	349	5	160	1.8	2.3	2.0	.96	Basic Anolyte
1335	2.51	387	5	180	1.3	.49	.82	.94	
1328	2.42	549	5	200	.93	.76	.56	.32	
1333	2.46	469	5	240	.23	.25	.56	1.3	Acidic Catholyte
1336	2.52	165	5	280	.23	.25	.55	.32	
1337	2.55	123	5	320	.23	.24	.27	.63	

It was felt that the lack of dramatic effects due to the use of acidic electrolyte may have been due to the fact that the electrolyte was not as acidic as was believed. The NaAlCl_4 purchased from Alcoa Aluminum contained 69 ^m/o AlCl_3 . This material was ground until it could pass through a #40 sieve and was mixed with 10 ^w/o Cab-O-Sil. The mixtures were then heated to 250°C in a covered vessel in the argon box. The fused mixes were then ground until they could all pass through a #40 sieve. It was felt that perhaps the excess AlCl_3 was all lost during the overnight heating at 250°C and that maybe the acid mixtures were no longer acidic.

For this reason it was decided to mix binder into the NaAlCl_4 mechanically instead of fusing it in. Since Cab-O-Sil does not mix well with salt mixtures at room temperature it was decided to use kaolin. So, a 40 ^w/o mixture of kaolin was mixed in ground NaAlCl_4 (69 ^w/o AlCl_3) by stirring and tumbling. The mixture was never heated and the mixing was done in the argon box so that none of the excess AlCl_3 could be lost. These electrolytes were surely acidic.

Some basic electrolyte (49.8 ^w/o AlCl_3) was made with kaolin so that all four types of cells could be made with kaolin containing electrolytes. Table 22 displays the results of representative cells at 200°C and 5 ohm loads.

TABLE 22 TYPICAL SINGLE CELL TEST RESULTS FOR CuCl_2
CELLS MADE WITH THE FOUR POSSIBLE COMBINATIONS OF
ACIDIC ELECTROLYTE MIXED WITH KAOLIN

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	
1355	2.03	37.1	603	1174	25.2	43.2	Basic Anolyte Basic Catholyte
1347	1.84	33.7	674	1294	23.2	39.2	Acidic Anolyte Basic Catholyte
1344	1.74	31.8	363	601	11.3	16.8	Acidic Anolyte Acidic Catholyte
1340	1.81	33.1	895	1379	30.9	43.0	Basic Anolyte Acidic Catholyte

Since the cells with the basic anolyte and the acidic catholyte were the best (as had been hoped) more cells were made like these and tested at constant temperature.

TABLE 23 TYPICAL SINGLE CELL TEST RESULTS FOR CELLS MADE WITH CuCl_2 , AN ACIDIC CATHOLYTE, A BASIC CATHOLYTE, AND USING KAOLIN FOR A BINDER. THE TEST TEMPERATURE WAS 200°C

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	load	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg		
1343	1.43	162	59	105	7.97	12.4	.81	Basic Anolyte Acidic Catholyte 200°C
1340	1.81	33.1	859	1379	30.9	43.0	5	
1342	1.91	13.9	2375	3250	35.8	45.5	12.6	
1341	1.94	7.1	6950	8460	52.3	60.9	25	

When the results in Table 11 are compared to the results in Table 22 it is actually a comparison of the suspect heated electrolytes with the nonsuspect electrolytes mechanically mixed with kaolin. The first impression formed while making this comparison is that the cells with Cab-O-Sil (Table 11) were, overall, better than the cells with kaolin. This was anticipated as a result of the kaolin containing cells reported prior to this experiment. Furthermore, it appears that many of the properties that were expected to be found in Table 11 did appear in Table 22. For example, the best cell was #1340 which had an acidic catholyte and a basic anolyte. The worst cell was #1344 which was made with both acidic anolyte and acidic catholyte.

Another good comparison of the heated electrolytes and the mechanically mixed electrolytes is Table 7 with Table 24. This comparison shows that the internal resistance of the kaolin cells is higher than the internal resistance of the Cab-O-Sil cells. This was also expected as a result of the work done prior to this experiment.

TABLE 24 INTERNAL RESISTANCE RESULTS FOR CELLS
MADE WITH CuCl_2 CATHODES, 40 w/o ANODES, AND ELECT-
ROLYTES WITH MECHANICALLY MIXED KAOLIN FOR A BINDER

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohm	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1355	2.03	603	5	200	.82	2.7	.68	4.3	Basic Anolyte Basic Catholyte
1347	1.84	674	5	200	1.8	3.0	4.1	8.1	Acidic Anolyte Basic Catholyte
1344	1.74	363	5	200	2.4	3.1	3.7	5.1	Acidic Anolyte Acidic Catholyte
1340	1.81	895	5	200	1.8	3.4	6.5	11.7	Basic Anolyte Acidic Catholyte
1343	1.43	59	.81	200	1.5	2.4	3.7	5.2	Basic Anolyte Acidic Catholyte 200 $^{\circ}\text{C}$
1340	1.81	895	5	200	1.8	3.4	6.5	11.7	
1342	1.91	2375	12.6	200	.73	4.8	9.9	24.9	
1341	1.94	6950	25	200	.36	X	14.1	46.2	

There was one other large difference in the heated and mechanically mixed electrolytes. When the tested cells were examined, post mortem, "air bubble" spaces were found in the mechanically mixed cells but not in the heated cells. This could be because most of the excess AlCl_3 had been lost in the heated electrolytes and very little was lost in the mechanically mixed electrolytes. Therefore, it is logical to believe that either the effect of the acidic electrolytes is not as great as was originally expected, or the full effect of the acidic electrolytes can be achieved with just a slight excess of AlCl_3 . That is, it appeared that an electrolyte with a composition of 50.2 m/o AlCl_3 could be just as effective as an electrolyte with 69 m/o AlCl_3 and the disadvantage of the volatile AlCl_3 would have been much less.

One further observation needs to be made about the acid-base experiments. At first glance it would appear that the acidic electrolytes have very little effect on cell performance. But, the use of acidic electrolytes has produced superior cells with about a 20% increase in energy density.

A large volume of single cell tests were used to demonstrate that acidic electrolytes could be expected to make superior cells. Batteries were made with those cells and the results will now be reported. Batteries #1019 & #1020 were made to test the acidic CuCl_2 electrolytes.

TABLE 25 TEST RESULTS FOR BATTERIES MADE WITH ACIDIC CuCl_2 ELECTROLYTES. THE TEST LOAD WAS 50 OHMS

S/N	V_p	i_p	Act.	t_{90}	t_{80}	t_{70}	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T_p	T_{Test}	Spec. r at 80%
	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm·cm ²
1019	25.8	48.5	0.55	.78	1.2	117	.117	.022	155	75	X
		+			+			+			
1020	20.9	38.2	0.84	.30	220	530	9.42	1.79	99	-55	19.6

These batteries displayed a very severe "spike". This was unexpected because the CuCl_2 system had not displayed a spike during single cell testing. Experience showed that one of the factors that effects the spike is high temperature. The battery performance was improved with judicious use of heat balancing and thermal buffers but this will be more fully reported upon later, under "Thermal Management".

A number of oxides were collected for possible use as cathode materials. A little preliminary testing was done to see how these materials would react with the electrolyte.

On a hot plate in the dry box two small crucibles were about 1/3 filled with electrolyte powder. One crucible contained acidic material (69 ^m/o AlCl₃) and one contained basic material (NaCl saturated). The heat was turned up until each sample melted. Then a small amount, 10 or 20 mg of oxide was sprinkled onto the surface of each melt and observed. A new melt was prepared for each oxide tested.

<u>MATERIAL TESTED</u>	<u>OBSERVATIONS: ACIDIC MELT</u>	<u>OBSERVATIONS: BASIC MELTS</u>
MoO ₃	powder turns light green-no evidence of solution-no evidence of gas formation	powder turns light green-much bubbling and gas formation-light colored smoke formed after the crucible was removed from the hot plate
CuO	no gassing or solution noticed	no gassing-the dark melt turned even darker
Fe ₂ O ₃	no gassing-solution turned light yellow-green-material at bottom of crucible was red	no gassing-solution turns dark green-powder at crucible bottom was red
TiO ₂	no gassing-no evidence of solution	moderate gassing-no color changes no other evidence of solution
V ₂ O ₅	light gassing-solution turns light yellow-green-orange powder turns red on crucible bottom	heavy gassing-solution turns light yellow green-orange powder turned blue grey on crucible bottom
WO ₃	no bubbling-powder turns lime green on crucible bottom	no bubbling-powder turns lime green on crucible bottom
NaVO ₃	solution turns light yellow green powder on crucible bottom turns light yellow orange	moderate gassing-solution dark green solution later turns to blue grey
Na ₃ VO ₄	slight gassing-solution turns light yellow green-powder turns yellow on crucible bottom	no gassing(!)-solution turns dark green-powder turns yellow orange on crucible bottom
Na ₆ V ₁₀ O ₂₈ · x H ₂ O	no gassing-solution turns dark green-powder at bottom of crucible turns blue grey	moderate gassing-solution turns dark green-some floating powder turns red

It appeared that a WO_3 catholyte should be quite stable. CuO would also be a good candidate for a storable catholyte. Fe_2O_3 was another likely catholyte material. It also appeared that a catholyte could be made a little more stable by making it a little more acidic. However, the excess $AlCl_3$ may have too great a vapor pressure to make the catholyte storable.

Because of the possible problem with $AlCl_3$ a new batch of acidic $NaAlCl_4$ was ordered and received which contains 52 m/o $AlCl_3$ instead of the former 69 m/o $AlCl_3$. This material is referred to as slightly acidic $NaAlCl_4$.

Some slightly acidic $NaAlCl_4$ (52 m/o $AlCl_3$) was made into an anolyte and catholyte. These two electrolytes were used to make cells. The results of the tests made on these cells are in Table 26.

TABLE 26 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH $NaAlCl_4$ WHICH CONTAINED 52 m/o $AlCl_3$

S/N	v_p	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} PEAK	R_{INT} t_{90}	R_{INT} t_{80}	R_{INT} t_{70}	TEMP. or LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	°C or ohms	
1853	1.90	34.8	3.36	35.3	42.0	3.00	1.54	1.38	0.80	160°	Fresh Cells 52 m/o $AlCl_3$ in both the anolyte and catholyte 5 ohms
1854	1.90	34.8	4.64	40.8	46.5	1.67	1.24	0.18	0.22	180°	
1855	1.92	35.1	5.23	49.0	57.3	1.10	0.62	0.35	0.40	200°	
1856	1.94	35.5	6.03	50.9	59.2	1.37	0.31	0.35	0.79	220°	
1857	1.94	35.5	7.13	52.0	58.7	1.37	0.61	0.69	0.39	240°	
1858	1.96	35.9	8.22	49.0	57.1	X	0.51	0.34	0.39	260°	
1859	1.97	36.0	8.31	27.4	33.6	1.39	0.92	3.58	7.81	280°	
1860	1.73	195	6.33	20.3	33.2	1.17	0.86	0.31	0.68	.81	Stored in dry box overnight 200°C
1861	1.97	36.0	3.80	40.7	44.5	X	0.61	0.34	0.78	5	
1862	1.99	14.4	4.67	55.2	62.4	0.34	0.38	0.43	0.49	12.6	

The energy densities measured at t_{80} and t_{70} were very good. The ED_{90} 's were not good. This is evidence of a very slight tendency to form a spike. Taken as a group these were among the test cells tested during this contract (Figure 8).

As a result of the work it was predicted that a superior cell could be made with the anolyte, $LiAlCl_4$, and with the catholyte, slightly acidic $NaAlCl_4$. The use of $LiAlCl_4$ as an electrolyte material will be further explained under "Alternate Electrolytes".

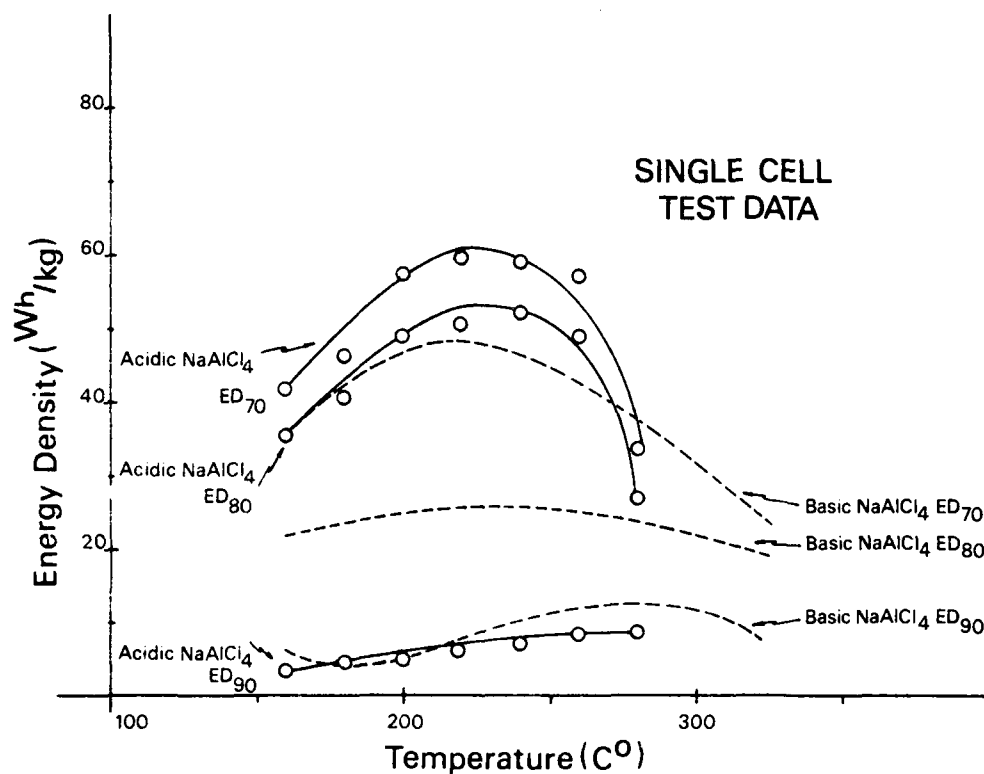


Figure 8. Single Cell Test Data. Basic $NaAlCl_4$ vs Acidic $NaAlCl_4$

SUMMARY & CONCLUSION

Some NaAlCl_4 containing 69 ^m/o AlCl_3 has been received from Alcoa Aluminum. This material was fused at 250°C and mixed with Cab-O-Sil to produce an acidic anolyte. A portion of this acidic anolyte was mixed with CuCl_2 (or MoCl_5) to produce an acidic catholyte. Using both acidic and basic anolytes and catholytes the four possible types of cells were constructed and tested. Later, it was suspected that the excess AlCl_3 was volatilized out of the NaAlCl_4 during the fusing process so new acidic electrolytes were prepared by mechanically mixing the NaAlCl_4 with 40 ^w/o kaolin powder. The four types of cells were duplicated and tested. Some of the specific properties of these cells were vague and confusing but the general conclusion that acidic electrolytes can make superior cells was demonstrated.

SECTION IX

ALTERNATE CATHODE CHLORIDES

In September of 1977, when this project began, it was believed that MoCl_5 was the optimum cathode material for the NaAlCl_4 thermal cell. During the last three years Seiler Research Laboratory at the Air Force Academy has published work which strongly suggested that some other heavy metal chlorides could produce even better cells than MoCl_5 ^{5,6,7}. A number of such cathode chlorides have been tested; iron (III) chloride, FeCl_3 , copper (II) chloride, CuCl_2 , tungsten (VI) chloride, WCl_6 , and chrome (III) chloride, CrCl_3 ,

Quite a large number of catholytes had to be prepared to test these materials. Most of these catholytes were regular test catholytes:

56 gms cathode chloride

26 gms anolyte

18 gms graphite

There were a few exceptions to this formula and these will be noted when necessary.

The first chloride tested was FeCl_3 . A test catholyte was made with FeCl_3 and a DSC spectrum was generated for this material. This DSC spectrum was interesting. The first feature was a large exotherm which started at about 147°C and peaked at 169°C . There were no "moisture" peaks at 100°C such as may be

5. Reference. J.C. Nardi, J. K. Erbacher, C. L. Hussey, "High Energy Density Pelletized Aluminum Chloride Thermal Batteries; Part II Cathode Screening", FJSRL-TR-77-0004, April, 1977.
6. Reference. J.K. Erbacher, C. L. Hussey, L. A. King, "The Discharge Behavior of a $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2$ Pelletized Thermal Cell", FJSRL-TR-77-0001, February, 1977.
7. Reference. R. L. Vaughn, L. A. King, "Discharge Characteristics of $\text{LiAl}/\text{NaAlCl}_4/\text{FeCl}_3$ Thermal Cells", FJSRL-79-0001, February, 1979.

expected in a MoCl_5 catholyte spectrum. The second feature was a broad endotherm which started to form at about 311°C . When the sample reached 327°C it was cooled back to 47°C and reheated. The only feature on the reheated spectrum was a small endotherm at about 149°C .

As the FeCl_3 testing progressed it was decided to make a catholyte which contained both FeCl_3 and MoCl_5 . For this purpose a test catholyte was made with MoCl_5 . This MoCl_5 catholyte was then mixed, 50:50, with the FeCl_3 catholyte to make a $\text{MoCl}_5/\text{FeCl}_3$ catholyte.

The DSC spectrum of the MoCl_5 catholyte was quite typical of a MoCl_5 catholyte with a large "moisture" peak of 107°C . This was followed by an exotherm which peaked at 145°C , and endotherm at 159°C and another endotherm at 181°C . The general shape of this spectrum was recognizable as a MoCl_5 catholyte except that it was generally more exothermic in the area between 107°C and 145°C . Upon cooling and reheating this sample, the baseline becomes flat with constant slope and with only three features - a large endotherm at 141°C , a small exotherm at 180°C , and a medium sized endotherm at 255°C .

When the above two catholytes were combined to make the $\text{MoCl}_5/\text{FeCl}_3$ catholyte a different DSC spectrum was generated. The two endotherms characteristic of a MoCl_5 catholyte were still present (103°C and 157°C). These were followed by an exotherm at 187°C and two other exotherms at 269°C and 275°C . These later two exotherms were too close to be completely resolved. Upon cooling and reheating this sample the only feature was an endotherm at 167°C .

It was noted that in each of the three spectra described above the combined area under the peaks in the reheated region of the spectra was much smaller than the combined area of the peaks in the spectra when the samples were heated the first time. This suggested that the catholytes might be more thermally

manageable if they were fused, ground, and sieved before making into cells. This practice is not uncommon in the thermal battery industry for anolytes but is usually not done for catholytes.

These two FeCl_3 catholytes have been tested in 22 single cell tests. These tests are organized into four groups:

- 1) FeCl_3 catholyte with 20 w/o LiAl alloy
- 2) $\text{FeCl}_3/\text{MoCl}_5$ catholyte with 20 w/o LiAl alloy
- 3) FeCl_3 catholyte with Anode #7*
- 4) $\text{FeCl}_3/\text{MoCl}_5$ catholyte with Anode #7*

Anode #7 contains only half as much LiAl as the 20 w/o LiAl alloy. This was used because this anode produces a smaller activation, high voltage peak than pure alloy.

The following is a tabulation of single cell results for a cell made from FeCl_3 catholyte with an anode of 20 w/o LiAl alloy.

TABLE 27 FeCl_3 & 20 w/o LiAl

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	LOAD
1162	1.50	169	89	107	14.5	16.4	.81
1161	1.75	107	151	185	17.8	20.4	1.5
1160	2.02	61.6	290	381	22.6	27.3	3
1159	2.18	39.9	322	424	16.8	20.5	5
1163	2.25	16.3	625	828	14.2	18.8	12.6
1164	2.24	8.2	736	1143	8.34	11.5	25

* Anode #7 is a mixture of 50% Al powder and 50% LiAl alloy (20 w/o). This will be discussed in more detail later in this report.

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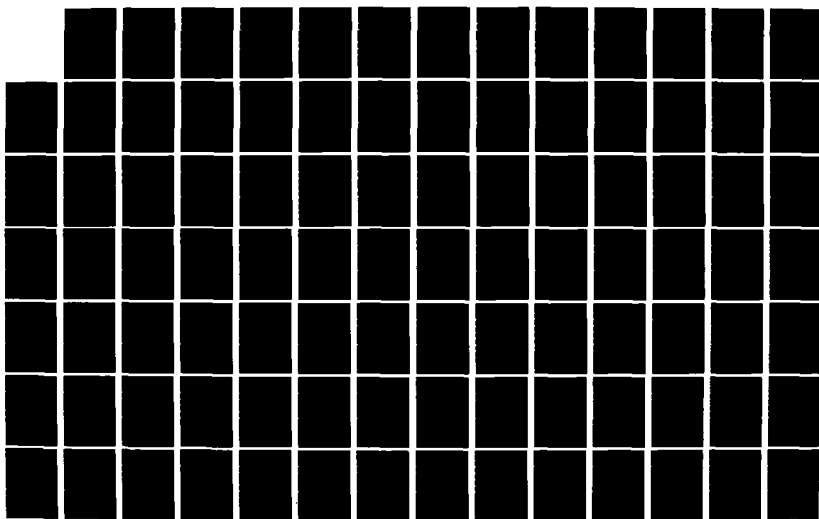
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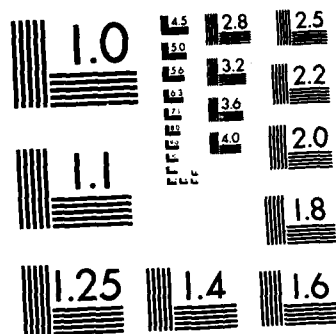
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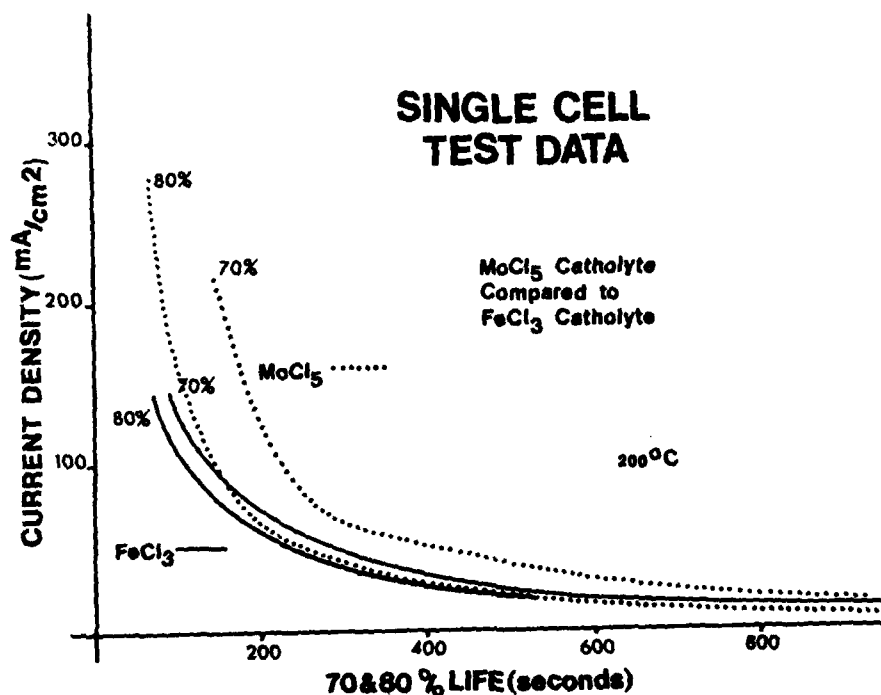


Figure 9. Single Cell Test Results Which Compare FeCl_3 With MoCl_5

Figure 9 charts current density vs. 80 & 70% lifetime. Examining these curves it can be seen that, for the 80% life, the FeCl_3 compares very closely to MoCl_5 at the lower current densities but at the higher current densities the FeCl_3 is inferior to the MoCl_5 . When the lifetime is measured to 70% of peak the FeCl_3 is entirely inferior to MoCl_5 . This is because the FeCl_3 loses potential very quickly in the 75% to 50% range. This is illustrated in Figure 10 which is a drawing of two typical discharge curves - one each for MoCl_5 and FeCl_3 .

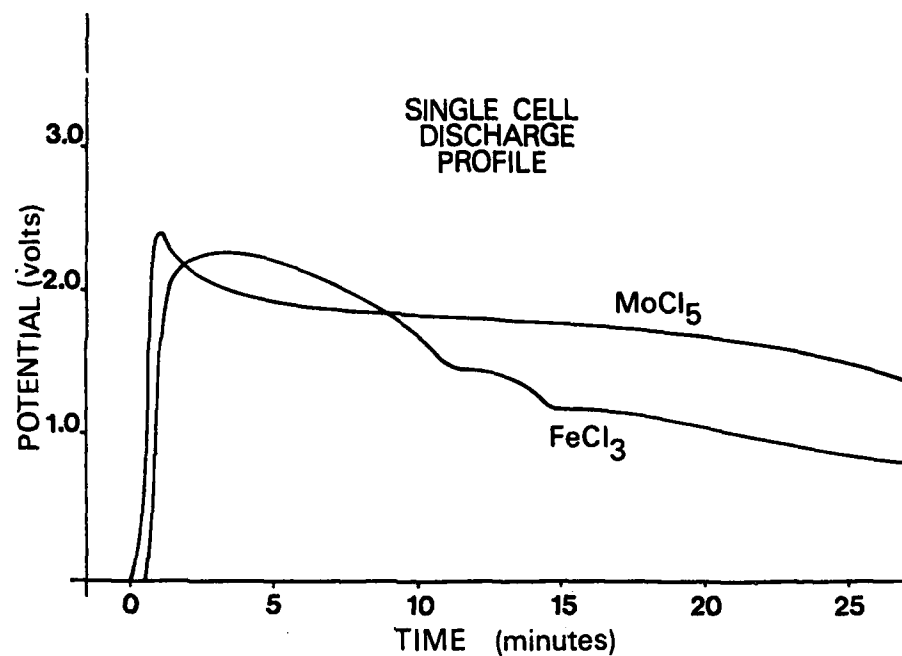


Figure 10. Typical Discharge Curves For FeCl₃ & MoCl₅

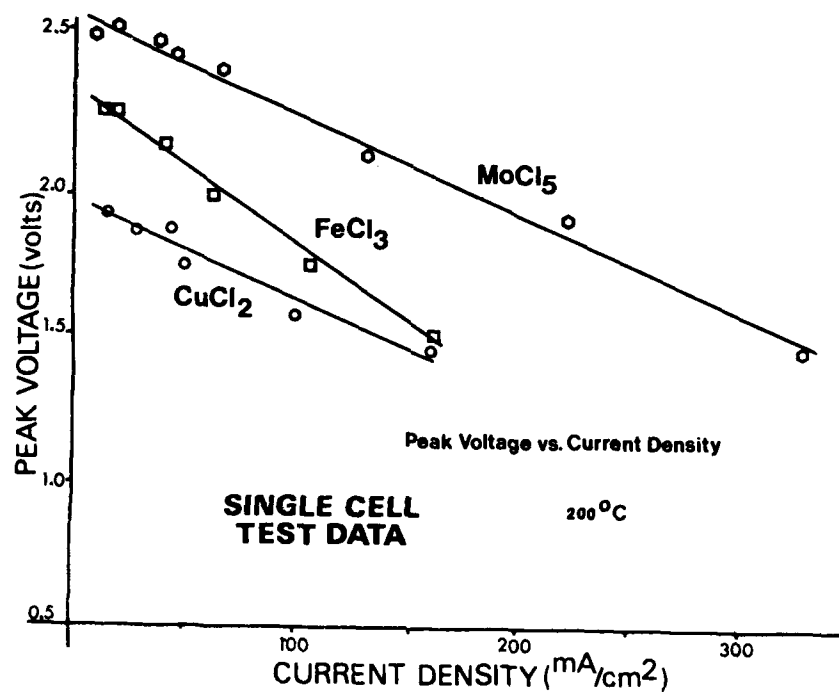


Figure 11. Peak Voltage vs. Current Density Comparisons For MoCl₅, CuCl₂, And FeCl₃

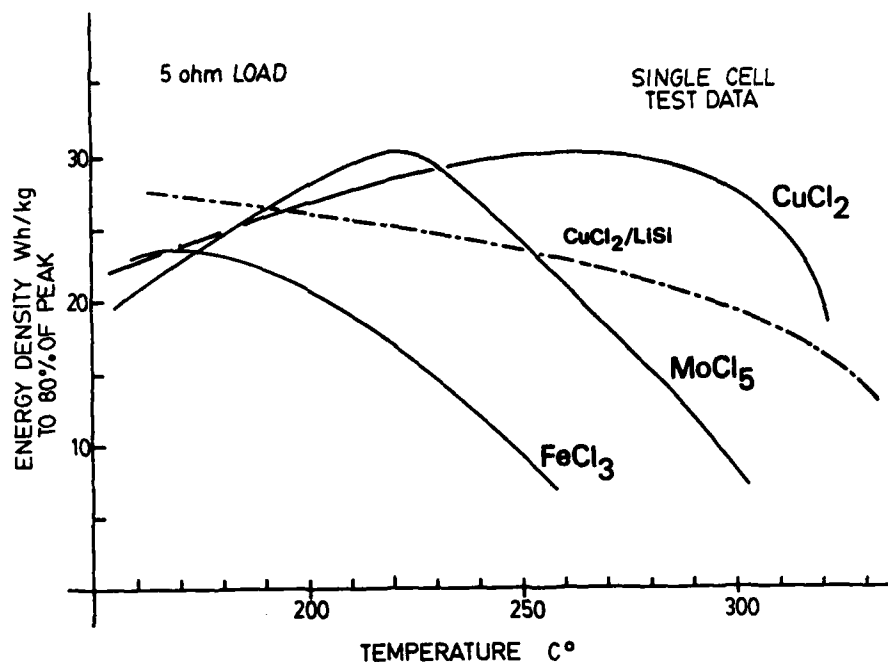


Figure 12. A Comparison Of Temperature Tolerance For FeCl_3 , CuCl_2 , And MoCl_5

Figure 11 is a peak voltage vs. current density chart which compares single cell results for MoCl_5 , FeCl_3 , and CuCl_2 . From this chart it can be seen that FeCl_3 tends to polarize much more severely than MoCl_5 .

Figure 12 is a chart of 80% life vs. temperature. It can be seen from this chart that FeCl_3 is quite subject to changes in temperature and has a much smaller useful range than does MoCl_5 . On the same chart it can be seen that CuCl_2 is a superior material.

In summary:

- a) FeCl_3 does not produce as high a voltage as MoCl_5 — about 5 to 10% less (Figures 10 and 11).

- b) FeCl_3 will not carry as much current as MoCl_5 catholyte (Figures 9 and 11).
- c) FeCl_3 is much more temperature sensitive than MoCl_5 (Figure 12).
- d) There is no "spike" or activation high voltage peak with FeCl_3 (Figure 10).
- e) Voltage regulation is difficult with FeCl_3 (Figure 10).
- f) FeCl_3 does not produce as great an energy density as MoCl_5 (Figure 12).
- g) The FeCl_3 catholyte appears to be even more sensitive to moisture than MoCl_5 catholyte. This material was difficult to rake while making cells on the hydraulic press.

FeCl_3 is not suited for either a long life battery or a high energy density battery. There was no activation high voltage spike with FeCl_3 . This was interesting because it had not been known whether the spike formed as a result of a reaction between the anode and anolyte or as a reaction at the cathode. The anode was not changed for these FeCl_3 cells but the spike disappeared. This certainly suggested that the spike was associated with the cathode and not the anode.

It was noticed that in the first few moments of life the FeCl_3 had a better discharge profile than MoCl_5 (Figure 10). This suggested that the MoCl_5 discharge curve could be straightened by mixing FeCl_3 into the catholyte. This was tried with catholyte C #1043.

Table 28 is a tabulation of all of the single cell results with this mixed $\text{MoCl}_5/\text{FeCl}_3$ catholyte.

TABLE 28 SINGLE CELL RESULTS WITH $\text{MoCl}_5/\text{FeCl}_3$
CATHOLYTE AND EITHER, 20 w/o OR ANODE #7

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	LOAD	NOTES
-	volts	mA	seconds	seconds	WH/kg	WH/kg	C°	ohms	
1177	1.82	206	120	176	27.6	35.7	200	.81	C #1043 & 20 w/o
1176	2.40	43.9	470	612	28.4	34.6	200	5	C #1043 & 20 w/o
1178	2.54	18.4	886	1236	23.3	30.1	200	12.6	C #1043 & 20 w/o
1179	2.79	49.4	19	69	5.26	12.3	160	5	C #1043 & 20 w/o
1180	2.36	43.1	495	715	28.2	37.5	180	5	C #1043 & 20 w/o
1174	1.79	202	109	146	25.0	28.7	200	.81	C #1043 & An #7
1173	2.31	42.3	436	565	24.5	27.7	200	5	C #1043 & An #7
1175	2.40	17.4	754	952	18.3	21.7	200	12.6	C #1043 & An #7

Catholyte #1043 did appear to help raise the discharge curve of the cell. Figure 13 is a sketch of a "typical $\text{MoCl}_5/\text{FeCl}_3$ cell discharge and a typical MoCl_5 cell discharge". The spike was not particularly affected as can be seen by the potential of 2.70 volts for cell #1179. The energy density for the higher current densities was not as good for $\text{MoCl}_5/\text{FeCl}_2$ as for MoCl_5 alone.

It is also noteworthy that for C #1037, the FeCl_3 catholyte, the cells all displayed an ohmic resistance (internal iR drop) which was an order of magnitude greater than for the MoCl_5 cells. When the FeCl_3 catholyte was mixed with the MoCl_5 catholyte to obtain C #1043 the cells displayed an iR drop more characteristic of a MoCl_5 cell than a FeCl_3 cell. Furthermore the iR drop in the FeCl_3 cells increased dramatically as the cell was discharge. Table 22 is a tabulation of some examples of the behaviour of the iR drop for FeCl_2 cells compared to $\text{MoCl}_5/\text{FeCl}_3$ cells.

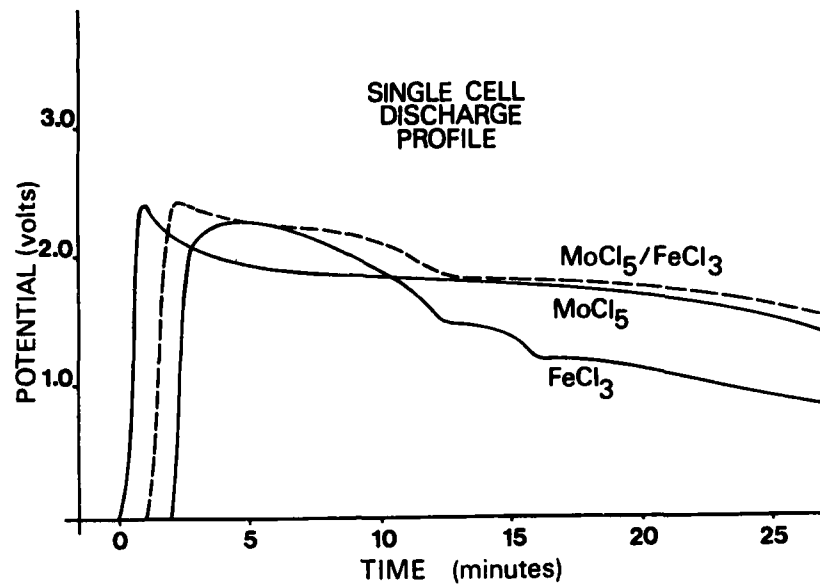


Figure 13. Single Cell Discharge Profiles
For a $\text{MoCl}_5/\text{FeCl}_3$ Type Cell

TABLE 29 SPECIFIC RESISTIVITIES
OF VARIOUS CELLS COMPARED

S/N	T	Load	SP. $R_{\text{INT}100}$	SP. $R_{\text{INT}90}$	SP. $R_{\text{INT}80}$	SP. $R_{\text{INT}70}$	NOTES
	$^{\circ}\text{C}$	ohms	$\text{ohm}\cdot\text{cm}^2$ at Peak	$\text{ohm}\cdot\text{cm}^2$ at 90%	$\text{ohm}\cdot\text{cm}^2$ at 80%	$\text{ohm}\cdot\text{cm}^2$ at 70%	
1028	200	5	2.33	1.26	0.85	0.64	MoCl_5 Cells 1001 - 1006
1029	200	1.5	2.39	1.26	1.24	1.51	
R_{INT} AT LOWEST MEASURABLE LIMIT WITH EXISTING EQUIPMENT - $R_{\text{INT}} = 1.5$							MoCl_5 Cells with LiCl 1056 - 1087 FeS_2 Cells 1008 - 1113
1160	200	3	4.42	3.68	3.81	5.26	FeCl_3 Cells 1159 - 1172
1165	160	5	8.17	5.93	6.83	-	
1166	180	5	9.15	5.62	5.64	-	
1170	200	5	2.55	2.52	6.39	3.62	
1173	200	5	.719	.264	.597	-	MoCl_3 FeCl_3 Cells 1173 - 1180
1175	200	12.6	.289	.324	.721	-	

In summary the FeCl_3 cells appeared to have a greater internal resistance than other cells tested so far. It should also be noted that this was only the first attempt to make cells with anything except MoCl_5 . These alternate cells were certainly not optimized. Some of the noted features of these systems could have changed dramatically with something as simple as a cell formula change. Only further experimentation could have revealed these features and therefore, any conclusions concerning the use of these materials must be considered preliminary.

Copper (II) chloride, CuCl_2 , was the second alternate cathode chloride considered. The initial test results were quite encouraging.

A number of test catholytes were prepared with CuCl_2 . A "fingerprint" DSC spectrum of these catholytes can be described. These samples were heated, cooled, and reheated. During the first heating, two endotherms were noted, a small one at 87°C and a larger one at 144°C . After cooling and reheating only one peak was noted, an endotherm at 159°C .

These materials were then used to make cells and the cells were tested with the single cell tester. Table 30 tabulates the single cell results made at constant test temperature. Table 31 is a tabulation of test results made with a constant 5 ohm load and varying test temperatures.

TABLE 30 TABULATION OF CuCl_2 SINGLE CELL RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	T	LOAD	NOTES
	volts	mA	seconds	seconds	WH/kg	WH/kg	$^\circ\text{C}$	ohms	
1182	1.45	164	97	153	14.0	20.0	200	.81	CuCl_2 Catholyte
1186	1.67	102	184	327	18.6	28.8	200	1.5	CuCl_2 Catholyte
1185	1.76	53.7	365	687	20.1	32.8	200	3	CuCl_2 Catholyte
1181	1.88	44.2	727	1469	26.3	46.3	200	5	CuCl_2 Catholyte
1184	1.85	28.2	1095	1805	32.1	63.0	200	6	CuCl_2 Catholyte
1183	1.93	14	379	2633	39.5	57.3	200	12.6	CuCl_2 Catholyte

From Table 30 it can be seen that the potentials for CuCl_2 cells are generally lower than for either MoCl_5 or FeCl_3 . Despite this handicap the energy density to 80 and 70% of peak is excellent. This is because the discharge curve is so straight (see Figure 14). The internal resistance of these cells was comparable to MoCl_5 cells.

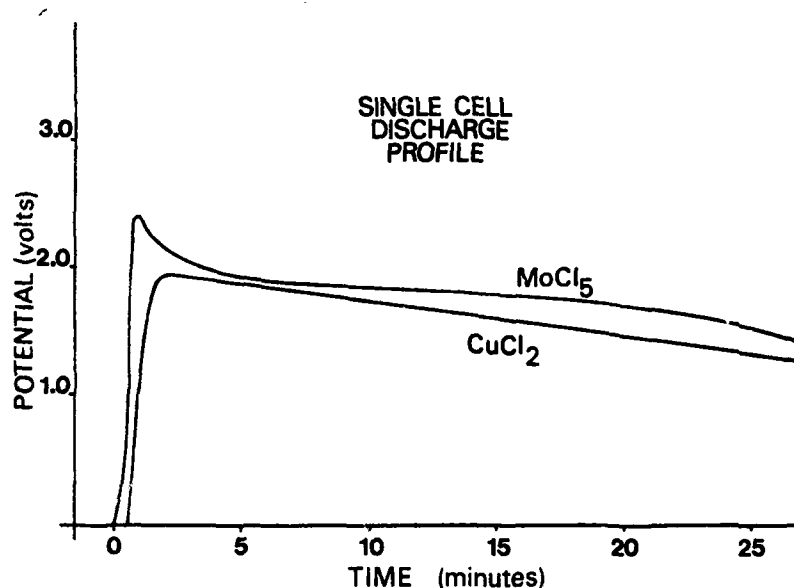


Figure 14. A Typical CuCl_2 Single Cell Discharge Curve Compared to a Typical MoCl_5 Discharge Curve

Figure 15 shows how the current density vs. lifetime curve compares with the MoCl_5 system. The conclusion is the CuCl_2 is at least equal to and is even superior to MoCl_5 at the lower current densities.

CuCl_2 cells were also tested at various temperatures. Figure 12 (see Table 31) is a graph of data points from single cell tests #1261 to #1269. The purpose of this figure is to show the superior temperature tolerance of the CuCl_2 catholyte. This is a large advantage for the CuCl_2 system.

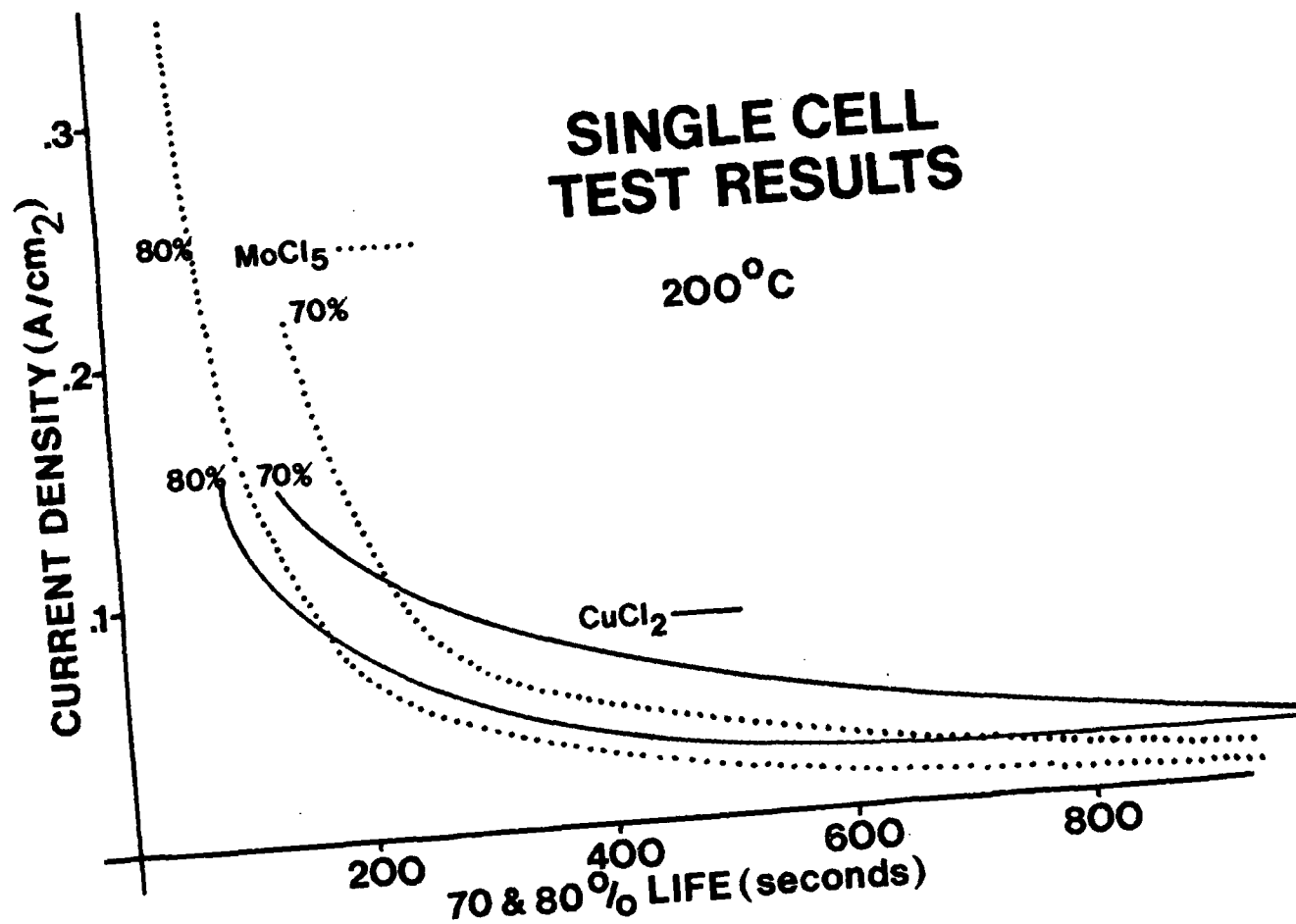


Figure 15. CuCl_2 Is Superior To MoCl_5 At The Low Current Densities

TABLE 31 CuCl_2 SINGLE CELL TEST RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	NOTES
-	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	$^{\circ}\text{C}$	-
1261	1.86	34	715	126	25.9	40.4	160	Test Load 5 ohms
1262	1.86	34	759	1180	27.5	38.6	180	
1263	1.83	33.5	635	940	22.5	30.3	200	
1264	1.85	33.9	694	1172	25.2	37.7	220	
1265	1.85	33.9	895	1203	32.9	40.9	240	
1266	1.87	34.2	619	896	23.5	30.9	260	
1267	1.87	34.2	771	1141	30.1	40.0	280	
1263	1.88	32.1	839	1286	32.2	44.2	300	
1269	1.91	34.9	538	1073	21.3	36.2	320	

CuCl_2 cells were also tested with a LiSi anode. These results will be discussed later in the "Alternate Anode" section of this report.

In conclusion, the CuCl_2 testing done so far demonstrates that the CuCl_2 is capable of producing energy at least as well as the MoCl_5 system with the additional advantages of greater temperature tolerance and greater moisture tolerance. There is the disadvantage of lower voltage with CuCl_2 cells.

It was concluded previously that FeCl_3 was not a desirable cathode material. However, FeCl_3 does have a higher peak voltage than CuCl_2 . Mostly for this reason FeCl_3 was mixed with CuCl_2 into one catholyte. This catholyte was tested in single cells #1196 thru #1225. These cells are divided in three groups by using three different anodes - 20 W/o LiAl, 28 W/o LiAl, and anode #7. Two catholytes were prepared. One catholyte contained 50 m/o FeCl_3 and 50 m/o CuCl_2 and one catholyte contained 50 W/o FeCl_3 and 50 W/o CuCl_2 . The results of these tests are presented in Table 32.

TABLE 32 $\text{FeCl}_3/\text{CuCl}_2$ SINGLE CELL TEST DATA

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{80}		NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg		Tests at 200°C
1197	1.64	328	55	92	10.2	13.7	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ 28 ^w /o LiAl
1196	2.31	42.3	118	195	11.7	17.6	5	
1198	2.34	17.0	485	970	11.6	19.6	12.6	
1200	1.55	175	100	155	16.3	22.5	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ 20 ^w /o LiAl
1199	2.19	40.1	230	450	12.3	20.3	5	
1201	2.34	17.0	504	1122	12.3	22.5	12.6	
1203	1.28	145	72	109	7.99	8.26	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ Anode #7
1202	2.18	39.9	234	544	12.6	23.8	5	
1204	2.24	16.3	557	947	12.3	18.2	12.6	
1206	1.56	176	75	105	12.9	16.3	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ 28 ^w /o LiAl
1205	2.20	40.3	240	490	13.1	22.3	5	
1207	2.38	17.3	527	1292	13.1	26.2	12.6	
1209	1.64	185	80	106	14.7	18.0	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ 20 ^w /o LiAl
1210	2.26	41.4	224	631	13.0	28.8	5	
1208	2.39	17.4	525	887	13.1	19.4	12.6	
1212	1.56	176	80	131	13.2	19.0	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ Anode #7
1211	2.19	40.1	242	547	13.1	24.2	5	
1213	2.24	16.3	586	911	12.3	17.2	12.6	

Figure 16 is a sketch of a typical FeCl_3 discharge curve, a typical CuCl_2 curve, and a typical $\text{FeCl}_3/\text{CuCl}_2$ curve. The effect of mixing the FeCl_3 was to increase the peak voltage but the lifetimes became shorter. Due to the relatively large increment between the peak voltages of CuCl_2 and FeCl_3 , the main effect of mixing the two in one catholyte was to create a high voltage plateau which lowered the energy density in a manner similar to the lowering

of the energy density due to the MoCl_5 spike. That is, mixing two cathode species does not appear to be feasible unless the peak voltages are close together. The cell did not appear to begin to utilize the CuCl_2 until the 80% of peak had already been reached.

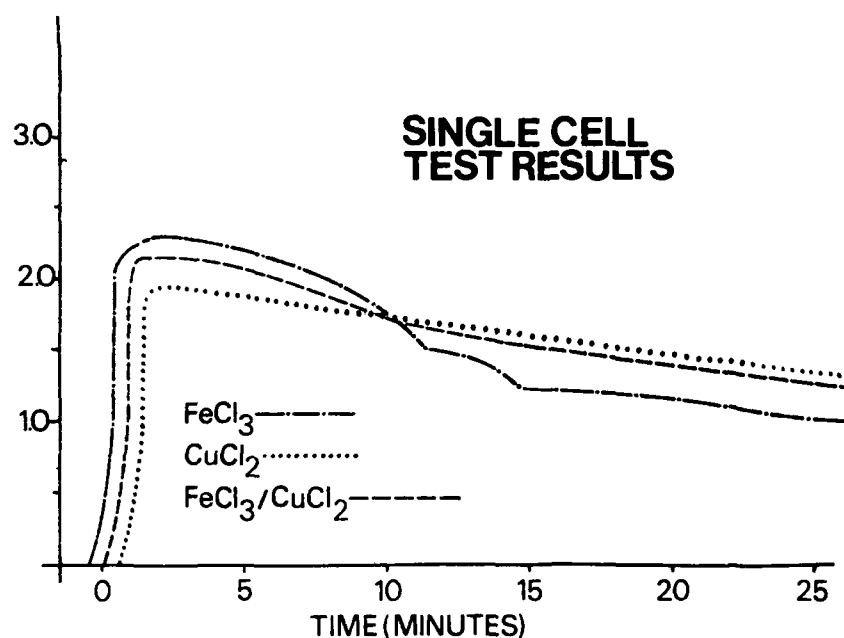


Figure 16. Typical Discharge Curves for FeCl_3 , CuCl_2 and $\text{FeCl}_3/\text{CuCl}_2$ Type Cells

Another cathode chloride was tungsten hexachloride, WCl_6 . WCl_6 catholyte was tested by single cell tests with both a 20 w/o LiAl anode and a 28 w/o LiAl anode. Once cell was tested with a catholyte which contained both CuCl_2 and WCl_6 . Table 33 is the single cell test data collected at 200°C with an anode of 28 w/o LiAl. Table 34 is the single cell test data for the cells at constant 5 ohm load and various temperatures.

TABLE 33 SINGLE CELL TEST DATA FOR
 WCl_6 CATHOLYTE AT 200°C

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}		NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	ohms	
1249	1.30	297	98	132	23.4	28.9	.4	WCl_6 Catholyte Anode - 28 W/o LiAl Test Temperature 200°C
1250	1.49	168	154	193	24.3	28.4	.81	
1251	1.76	107	229	291	26.6	31.5	1.5	
1252	1.90	57.9	342	562	23.2	33.3	3	
1255	1.98	36.2	495	632	21.5	31.6	5	
1253	2.03	31	562	934	20.9	30.6	6	
1254	2.11	15.3	1027	1485	19.5	25.6	12.6	

TABLE 34 SINGLE CELL TEST DATA FOR WCl_6
CATHOLYTE AT VARIOUS TEMPERATURES

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	°C	
1247	1.84	33.7	276	536	9.91	18.7	160	WCl_6 Catholyte Anode - 28 W/o LiAl Load Resistance 5 ohms
1248	1.95	35.7	500	878	21.2	32.2	180	
1255	1.98	36.2	495	832	21.5	31.6	200	
1256	2.03	37.1	424	776	19	30.1	220	
1257	2.04	37.3	288	362	13.5	15.8	240	
1258	2.04	37.3	226	285	10.7	12.6	260	
1259	2.12	38.8	130	169	6.74	8.07	280	

Figure 17 illustrates data from Table 33. The dotted curves represent MoCl_5 data generated previously. It can be seen that WCl_6 is at least as good as MoCl_5 at high current densities and is better than MoCl_5 at low current densities.

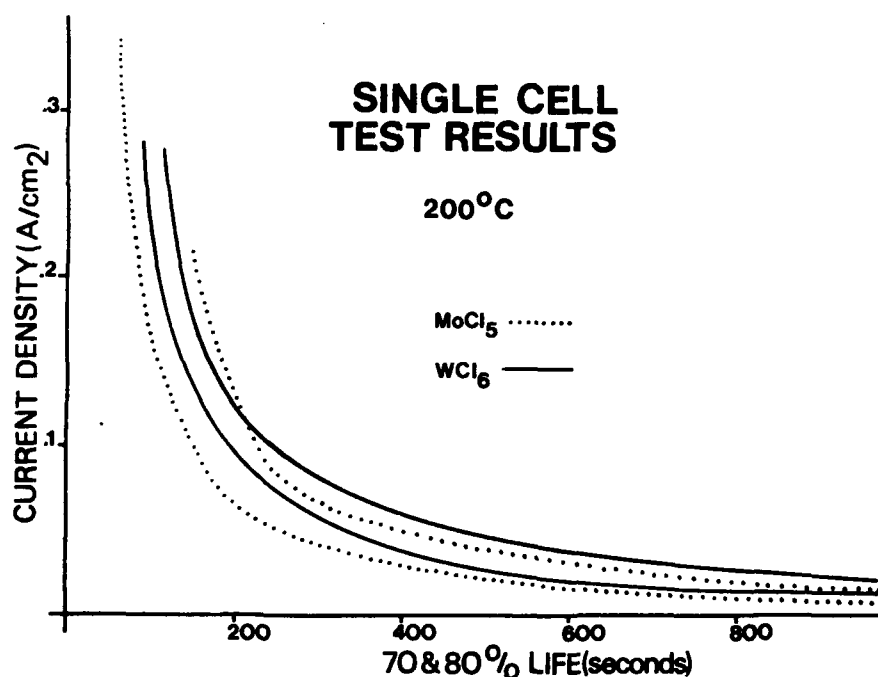


Figure 17. WCl_6 Single Cell Test Results compared to MoCl_5 Test Results

Figure 18 illustrates data from Table 34. It can be seen that WCl_6 does not have quite as wide a temperature tolerance range as MoCl_5 has.

Figure 19 shows a typical WCl_6 cell discharge curve relative to a typical MoCl_5 cell discharge curve. There is a tendency to produce a spike with WCl_6 but not as severely as with MoCl_5 . This reduced tendency for WCl_6 explains why WCl_6 performance looks so good compared to MoCl_5 .

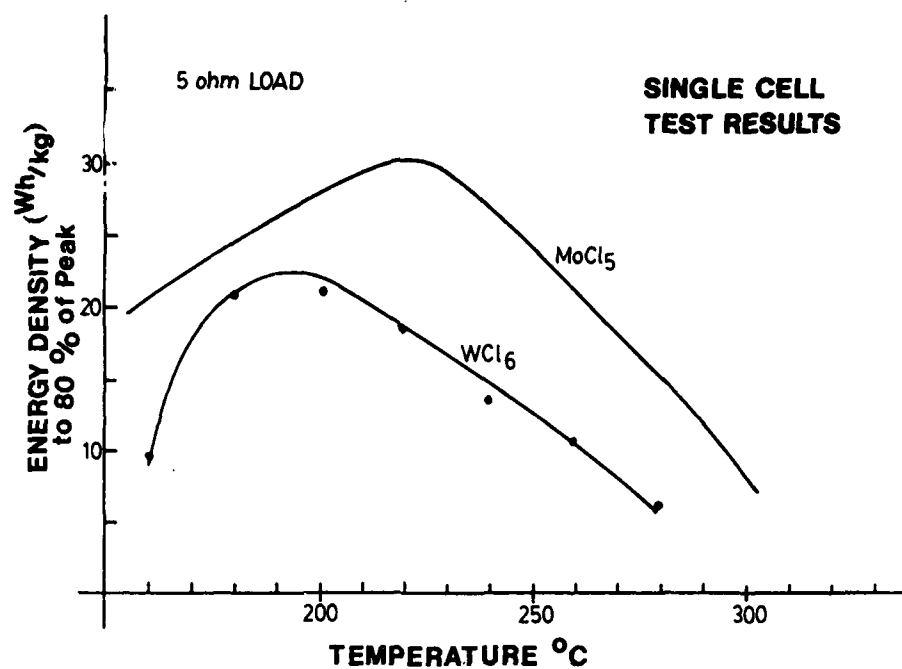


Figure 18. Temperature Tolerance of WCl₆ Compared to MoCl₅

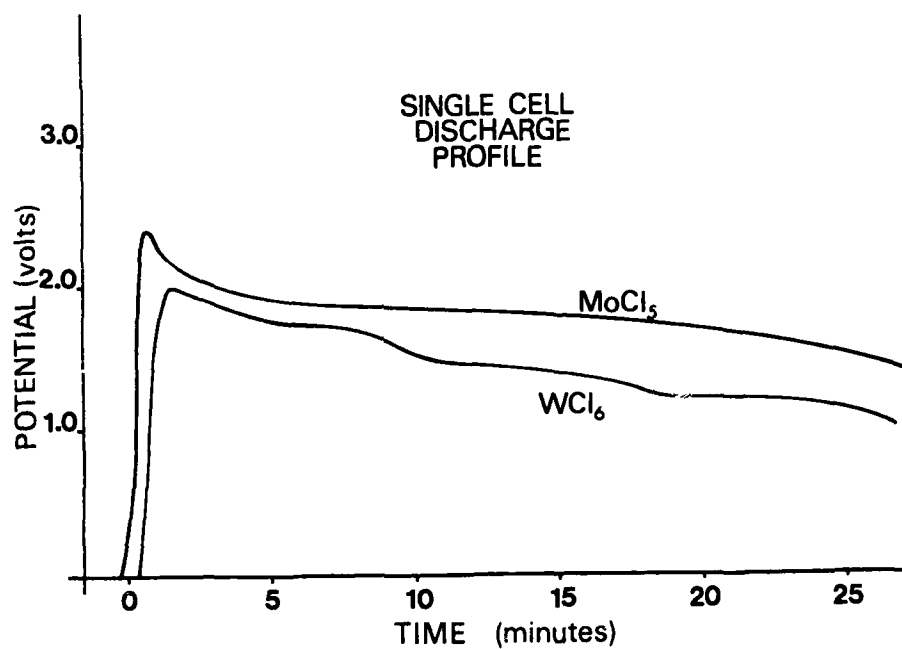


Figure 19. A Typical WCl₆ Discharge Curve

WCl_6 has a peak voltage even lower than FeCl_3 . It has been previously mentioned that FeCl_3 and CuCl_2 cannot be successfully mixed because their peak voltages are so relatively far apart. WCl_6 and CuCl_2 have peak voltages which are relatively much closer and so there could have been some benefit realized by mixing WCl_6 and CuCl_2 . This was done and one cell has been tested (Single Cell #1260). This cell was about as good as a WCl_6 cell. Figure 20 displays a typical $\text{WCl}_6/\text{CuCl}_2$ curve compared to a typical CuCl_2 discharge curve.

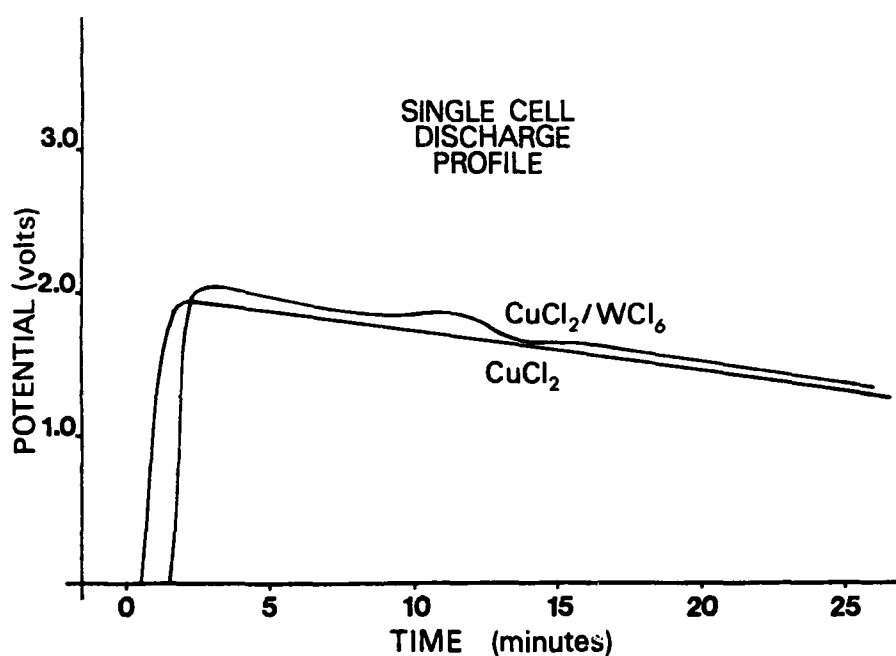


Figure 20. A Typical $\text{CuCl}_2/\text{WCl}_6$ Discharge Curve

To summarize, WCl_6 initially appeared to be a good cathode material with a relatively low peak voltage and a poor temperature tolerance. One possible use of WCl_6 is as an additive to increase the early voltage for the CuCl_2 catholytes. WCl_6 is presently an expensive material.

An interesting trend has been noted while testing these various cathode materials. It was first noted that cells made with MoCl_5 reached a maximum energy density as the current density increased. That is, the harder the cells worked the better they worked. Other cathode materials did not function this way. FeCl_3 cells displayed no correlation between energy density and current density. CuCl_2 cells behaved just opposite to MoCl_5 cells. That is, as the current density decreased the energy density increased, or, the easier the cells are allowed to work the better they work.

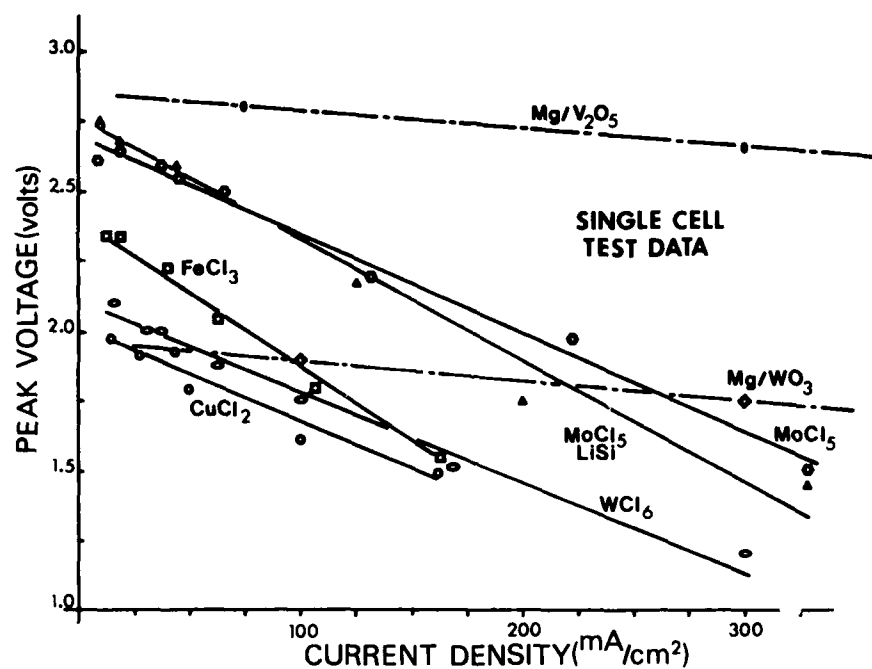


Figure 21. Polarization Curves for the NaAlCl_4 System Compared to the $\text{KCl} \cdot \text{LiCl}$ System

Figure 21 illustrates how the peak voltages vary with current density for a number of cathode and anode systems tested for this project. The behavior of MoCl_5 , CuCl_2 , FeCl_3 , and WCl_6 vs. a LiAl anode is plotted. In addition to this MoCl_5 is plotted vs. a LiSi anode. The dashed lines represent the behavior of the Eureka production systems $\text{Mg/V}_2\text{O}_5$ and MG/WO_3 . It appears that the slopes of all of the lines generated for NaAlCl_4 cells are similar and the slopes for all the $\text{KCl}\cdot\text{LiCl}$ lines are also similar. Furthermore, the slope of the $\text{KCl}\cdot\text{LiCl}$ lines is much closer to zero than the NaAlCl_4 lines. This indicates a severe polarization which may be a characteristic of the NaAlCl_4 system but which is not present in the $\text{KCl}\cdot\text{LiCl}$ system.

It is not known whether this polarization or any other polarizations which may be taking place in the cell are located at the anode or the cathode. It was proposed to study these polarizations with the use of a reference electrode inserted in the anolyte layer. This would indicate the relative sizes of the polarizations at both the anode and cathode. The reference electrode tests will be further explained later in this section of this report.

In summary, four cathode chlorides were used to make cells. MoCl_5 was considered the regular cathode material and FeCl_3 , CuCl_2 and WCl_6 were alternate cathode chlorides. Testing displayed unique discharge characteristics.

FeCl_3 was the first material tested. The peak voltage of FeCl_3 is almost as good as MoCl_5 with the advantage of no high voltage activation spike. FeCl_3 has the disadvantages of not being able to carry a high current, a shorter lifetime due to poor voltage regulation, a poor temperature range, and a moisture sensitivity at least as poor as MoCl_5 .

CuCl_2 has two large disadvantages: a relatively low peak voltage and relatively poor current carrying ability. However, CuCl_2 has some large advantages: a flat discharge curve for longer life, a wide range of temperature tolerance, much less sensitivity to moisture and long storage life.

WCl_6 is a good cathode chloride but it is expensive, has a tendency to form a spike, poor voltage regulation, and is somewhat volatile.

The best material for a high energy density battery is still MoCl_5 . However, for reliable, long life battery CuCl_2 is the best material because of the relative flatness of the discharge curve and the long storage life of CuCl_2 cells.

Cells made with this low temperature system have always displayed an unusual high voltage at initiation. This phenomenon has come to be called "the spike" phenomenon. In order to further examine the characteristics of the cell it was decided to put a reference electrode in the anolyte layer. Then the potential from the reference to the anode and from the reference to the cathode could be measured simultaneously with the anode to cathode potential.

The cells were special, two layer cells. The anode layer was composed of one stratum of 0.45 gm LiAl alloy and a second stratum of 1.75 gm anolyte. The cathode layer had one stratum of 1.75 gm anolyte and 1.90 gm catholyte. When stacked with the two anolyte layers together the resulting cell had a normal anode and cathode with double the normal amount of anolyte. The reference electrode was inserted about 1/16" into the gap between the two anolyte layers. The anode and cathode current collectors were the usual type nickel current collectors. High impedance recorders (10^7 ohms) were used to measure the reference voltages so that no current could flow through the reference. A special frame of 1/16" silicone glass material was used to hold the cell and reference electrodes in the single cell tester in such a way that the reference was not shorted to either other electrodes (see Figure 22).

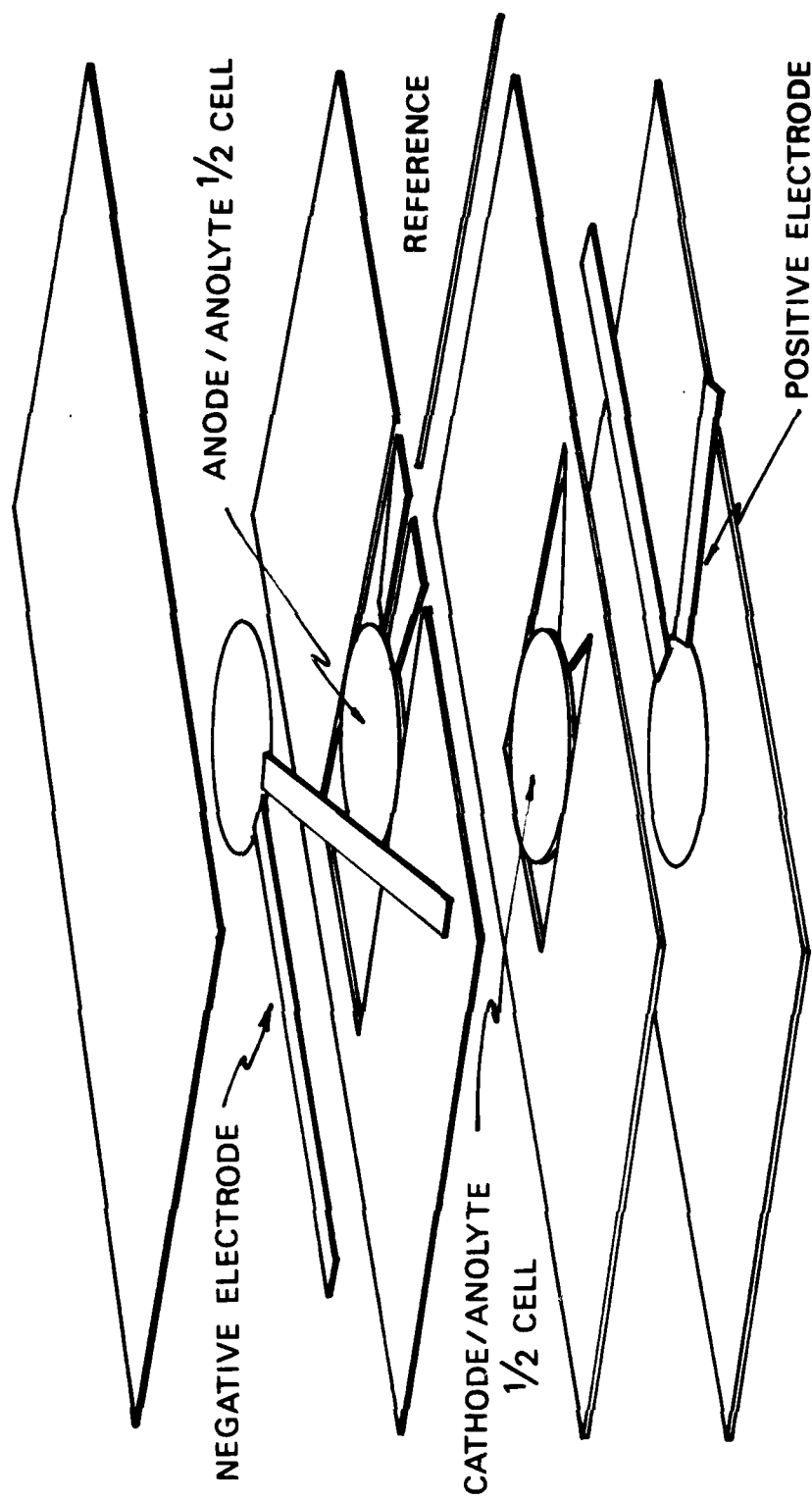


Figure 22. Reference Electrode Test Apparatus

The reference electrode was prepared by immersing the end of a glass micropipette into some molten NaAlCl_4 . The molten electrolyte wicked into the capillary forming a salt plug. The reference wire (Al, Alfa-Ventron, Wire, 0.127mm dia.) was then inserted into the open end of the capillary. The plugged end of the capillary was then reimmersed into the molten salt to melt the plug. The wire was then pushed a few tenths of a mm into the molten plug. The capillary was withdrawn from the molten electrolyte and allowed to cool. Some electrolyte adhered to the outside walls of the capillary but was easily chipped off with a knife.

The first R.E.T. (Reference Electrode Test) was done with an Al electrode a basic CuCl_2 catholyte, and a 28 % anode. There was no load on the cell.

The first twenty seconds of the test was complicated by electronic noise. When there was only a very small voltage on the recorder there was some unexpected oscillation on the three necessary recorder channels. In addition to this noise there was apparent shorting (or rapid changes of conductivity) at the surface of the reference electrode. Eventually the noise stopped and the three voltage traces were clean and easy to read. After about 80 seconds a 6 ohm load was put across the cell. At about 150 seconds a no load test was run (that is, the load was taken out of the circuit for about one second) to determine the internal resistance of the cell. Later the load was changed to 3 ohms, 1.5 ohm, and 0.81 ohms and the results observed. Table 35 is a tabulation of some selected voltage readings during the test.

The second R.E.T. was just a repeat of the first test to see how well they could be duplicated.

The first 60 seconds of the test were once again obscured by noise. There is no explanation for the significant differences in voltages for these

two tests. Note that for the internal resistance measurements the + to ref. component and the - to ref. components do not add up to the total resistance. This is due to the relatively crude, graphic measurements made from the recorder tapes.

The aluminum wire and glass capillary electrodes were rather large compared to the thickness of the various electrolyte layers. For this reason the reference electrode was changed to just a pure Al wire instead of the capillary. RET #3 was the first of these tests. The potentials measured in RET #3 are similar to RET #1. Once again the first part of the test was confused by noise.

TABLE 35 SELECTED DATA POINTS FROM R.E.T #1 ON A
BASIC CuCl_2 CATHOLYTE, 28 W/O LiAl , AND AN Al/NaAlCl_4
REFERENCE

time	$V_{+ \text{ to } -}$	R_{INT} + to -	$V_{+ \text{ to } R}$	R_{INT} + R	$V_{- \text{ to } R}$	R_{INT} - R	NOTES
seconds	volts	ohms	volts	ohms	volts	ohms	
0	Noise	-	Noise	-	Noise	-	No Load
20	1.97	-	1.35	-	0.63	-	
90	1.78	-	1.43	-	0.37	-	6 ohms
147	1.75	-	1.52	-	0.24	-	6 ohms
150	1.79	.137	1.54	0.07	0.26	0.07	No Load
390	1.54	-	1.43	-	0.12	-	6 ohms
392	1.62	0.31	1.45	0.08	0.16	0.15	No Load
478	1.50	-	1.39	-	0.13	-	3 ohms
479	1.59	0.18	1.44	0.10	0.17	0.18	No Load
534	1.33	-	1.31	-	0.02	-	1.5 ohms
536	1.55	0.25	1.41	0.11	0.13	0.13	No Load
659	1.00	-	1.13	-	-0.12	-	0.81 ohms
660	1.40	0.32	1.43	0.24	-0.02	0.08	No Load

A Silver wire (Alfa-Ventron, Stock No. 10303, 0.127 mm dia.) was the reference for R.E.T. #4. There was a change in reference potentials. The anode to reference changed from about 0.6 volts to about 1.8 volts and the cathode to reference changed from about 1.6 volts to about 0.7 volts.

This RET was not as noisy at the activation as the other tests have been. A spike was noted in the cell discharge. Notice (Figure 23) that the anode (V_- to R) also had a spike voltage but that the voltage at the cathode (V_+ to R) rose slowly and steadily for the first 67 seconds. This is the first evidence that the spike is caused an an anode reaction.

The 5th RET was with a tungsten wire reference. Again there were differences in the reference voltages. The anode to reference became about 2.0 volts and the cathode to reference potential was zero volts.

The first set of RET's was marred by the presence of excessive electrical noise at the cell activation. This noise hindered "spike" formation observation. It was felt that this condition would be corrected by increasing the surface area of reference wire inserted between the cell halves. Accordingly, 1 inch of wire was inserted in the cell instead of the usual 1/32 inch.

This procedure was a great improvement. Included in this report are several reproductions of activation portions of three of these new RET's (Figures 24, 25, and 26).

The spike can be well observed in all three figures. In all three figures there is a spike in the anode/reference trace at the same time there is a spike in the total cell trace. This is particularly interesting because a spike is normally not observed with the CuCl_2 system. Figures 27 and 28 are reproductions of the activation portions of two MoCl_5 RET's. The spike is well developed in Figure 27 but there is no spike in Figure 28. It can also be seen in Figure 28 that there is no spike in the anode contribution to the cell. This is further evidence that the anode is the source of the spike reaction.

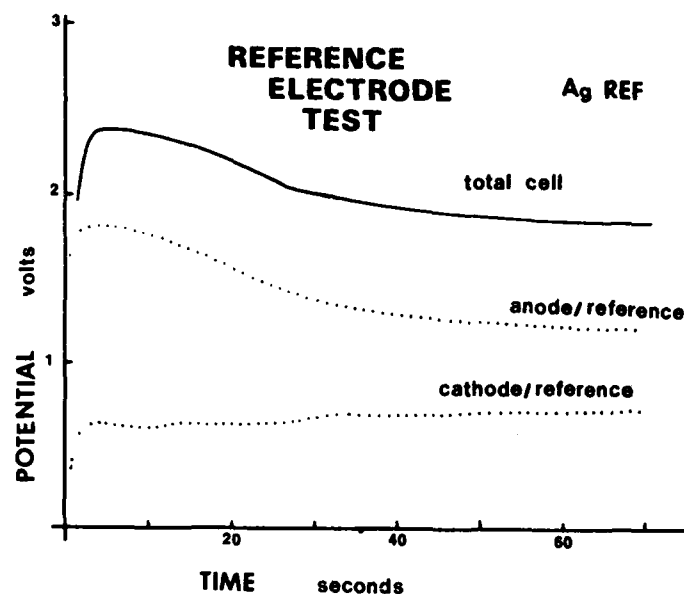


Figure 23. A Typical Reference Electrode Test

These RET's were activated under no load conditions. Various loads were then attached to the circuits, usually in this sequence, 5 ohm, 0.81 ohm, 12.6 ohm, 25 ohm and finally, 3 ohms. While the data for all the RET's will not be presented, the following table (Table 36) is a sample of the data taken for one CuCl_2 RET.

The internal resistance of a cell can be calculated by measuring a change in potential relative to a change in current;

$$R_{\text{INT}} = \frac{\Delta E}{\Delta I}$$

When the various loads were inserted (or removed) from the circuit there was a change in voltage and a change in current. Due to the fact that the load was

changed so often, little inference can be made about how internal resistance varies with time. However, it was noticed that for every test the internal resistance contributed by the anode/anolyte was larger than the internal resistance component contributed by the cathode/anolyte. This is, the current density of the cell appeared to be limited by the anode and not by the cathode.

It should be noted that the internal resistance of each component measured depends upon the position of the reference electrode relative to the position of the anode current collector and the cathode current collector. That is, for the measurements to be truly relative the reference wire must be exactly in the center of the anolyte layer. Since the present test setup does not insure that the reference wire will be exactly in the center of the anolyte the data generated, and any conclusions that result, will always contain a degree of uncertainty.

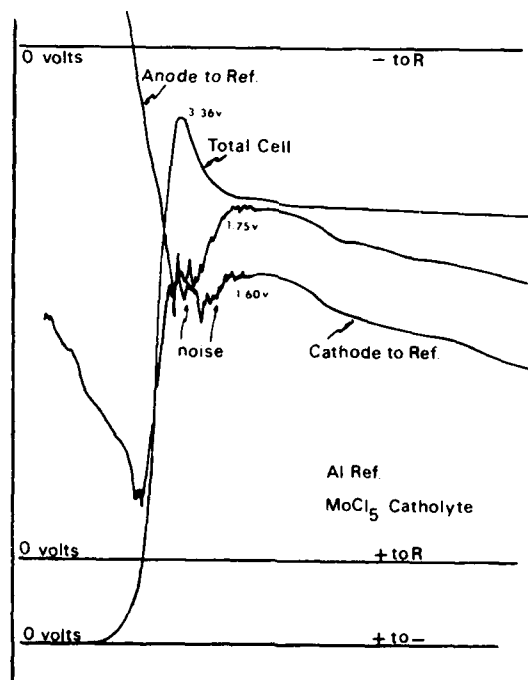


Figure 24. A Reference Electrode Test With An Aluminum Reference Wire

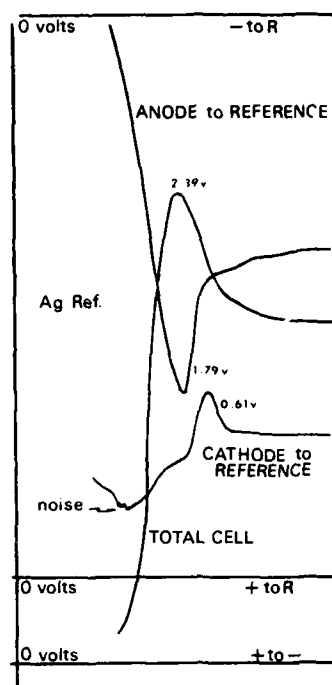


Figure 25. A Reference Electrode Test With A Silver Reference Wire

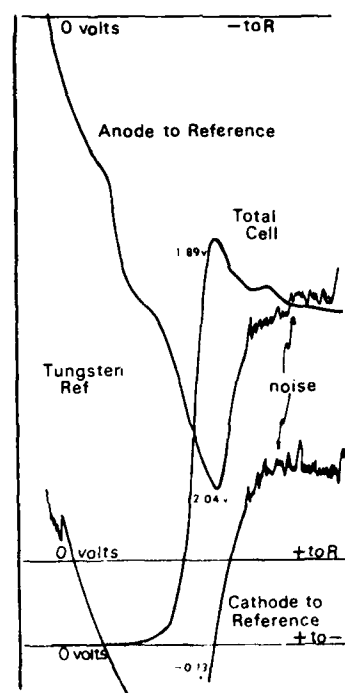


Figure 26. A Reference Electrode Test With A Tungsten Reference Wire

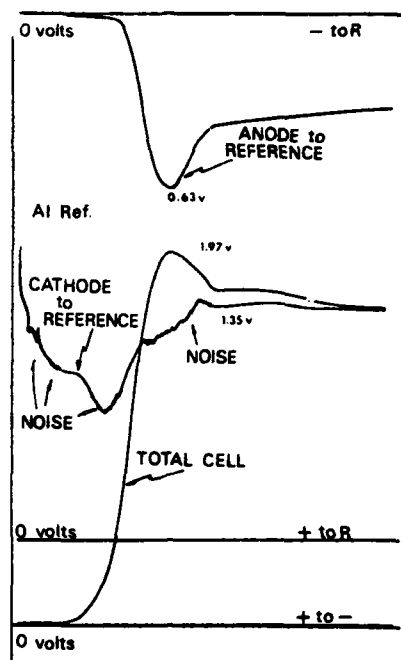


Figure 27. A MoCl_5 Cell Tested With An Aluminum Reference Wire Showing A Spike

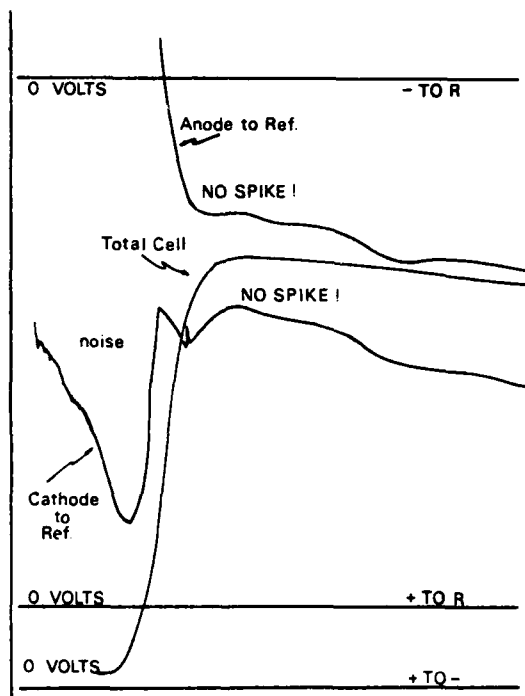


Figure 28. A Reference Electrode Test Showing No Spike

TABLE 36 VOLTAGE AND INTERNAL RESISTANCE DATA FOR RET 11.
THIS TEST WAS A CuCl_2 CELL WITH A Ag REFERENCE WIRE

Time	V_+ to -	R_+ to -	V_+ to Ref.	R_+ to Ref.	V_- to Ref.	R_- to Ref.	NOTES
seconds	Total Cell	ohms	Cathode	ohms	Anode	ohms	
10	1.90	X	0.55	X	1.35	X	No Load
13	2.65	X	0.63	X	2.02	X	V_p
17	2.12	X	0.82	X	1.29	X	No Load
30	1.90	X	0.73	X	1.17	X	No Load
110	1.85	X	0.73	X	1.12	X	No Load
112	1.73	.347	0.68	.145	1.04	.231	5 ohms
118	1.80	.202	0.71	.087	1.09	.145	No Load
124	1.83	X	0.71	X	1.11	X	No Load
125	1.37	.272	0.58	.077	0.77	.201	0.81 ohms
133	1.20	X	0.56	X	0.64	X	0.81 ohms
134	1.72	.351	0.68	.081	1.02	.324	No Load
139	1.81	X	0.70	X	1.06	X	No Load
140	1.76	.358	0.69	.072	1.01	.358	12.6 ohms
151	1.75	X	0.69	X	1.05	X	12.6 ohms
152	1.80	.360	0.71	.144	1.10	.360	No Load
157	1.81	X	0.71	X	1.10	X	No Load
158	1.79	.279	0.70	.139	1.09	.139	25 ohm
169	1.78	X	0.69	X	1.08	X	25 ohm
170	1.81	.421	0.70	.140	1.10	.281	No Load
174	1.81	X	0.70	X	1.10	X	No Load
175	1.62	.352	0.64	.111	0.98	.222	3 ohms
190	1.50	X	0.62	X	0.87	X	3 ohms

Another type of reference electrode test was done. The reference wire as Ag. The test temperature was 200°C . One cell each was tested across 0.4, 1.5, 5.0, and 12.0 ohm resistors. The current was interrupted every 10 seconds by disconnecting the load for 1 second. In this manner the internal resistance

of the cell is observed to change as a function of discharge time. Also, the cell internal resistance is divided into two sections; one section is associated with the anode and one section is associated with the cathode. Figure 9 is a reproduction of some typical results with a CuCl_2 cell and a Ag reference wire.

The upper portion of Figure 29 is a sketch of a typical discharge curve for a CuCl_2 RET type cell. On the same set of axes are displayed the potentials measured from the anode to the Ag reference and from the cathode to the Ag reference. It can immediately be seen that the shape of the activation portion of the curve is determined by the anode reaction. That is analogous to saying the "spike" is formed at the anode. It can also be seen that the cell voltage dropped off near the end of life as the cathode to reference voltage dropped off. It can be concluded that the cathode is being consumed before the anode.

The lower portion of the figure is a sketch of how the internal resistance varies with time. It can be seen that at initiation the anode resistance is higher than the cathode resistance. This could indicate a passivation coating on the LiAl alloy which burns off early in the life of the cell. However, once the cell has begun to discharge the anode resistance drops to a position well below the cathode and remains relatively constant during the remainder of the discharge. The cathode resistance does not remain constant but shows a significant maximum at about the time when the cell potential has reached 50% of peak. This maximum was observed at each discharge rate from 12 mA/cm^2 to 150 mA/cm^2 .

When this series of RET's was repeated for MoCl_5 cells it was again demonstrated that the spike originates in the anode reaction. However, there were two maxima in the cathode internal resistance curve: one at about 95% peak and another at about 85% peak.

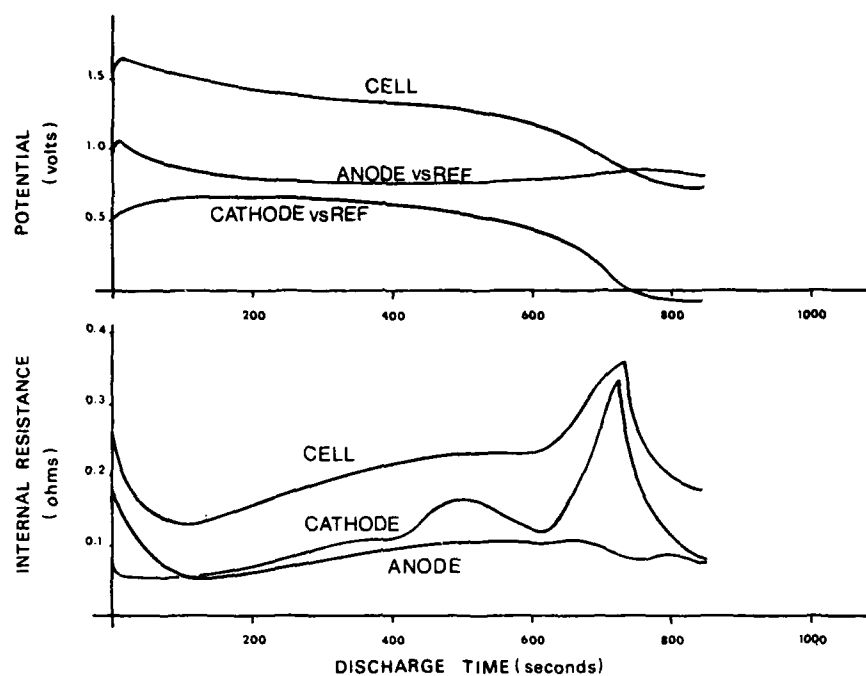


Figure 29. An R.E.T. With A CuCl_2 Cell Showing Potential And Internal Resistance Varying With Time

SUMMARY OF REFERENCE ELECTRODE TESTING:

The first reference electrodes were made by wicking molten NaAlCl_4 into a glass capillary into which was plunged a wire. This was too thick to be practical so just plain wire was used. Electrical noise usually prevented the initial part of the curve from being readable. Relative to an Al wire the anode voltage at initiation is about 0.6 volts and the cathode voltage is about 1.4 volts. Relative to a Ag wire the anode voltage is about 1.3 volts and the cathode voltage is about 0.7 volts. Relative to a W wire the anode voltage is about 2.0 volts and the cathode is about zero volts. In one test, evidence of spike formation was noticed and was assigned to the anode reaction site. In the

early part of the discharge curve the anode had an equal or larger impedance than the cathode but as time passed or when the cell had a relatively high current density the cathode impedance became greater than the anode impedance. This could explain why CuCl_2 cells do not work as well at high current densities as at lower current densities.

The electrical noise which has previously obscured the activation portion of the reference electrode tests has been mostly eliminated by increasing the surface area of the reference wire. It has been determined that the high voltage spike is caused by a high voltage anode reaction. Internal resistance measurements show that the current density of the cell is anode limited at the beginning of cell life and cathode limited as the cell polarizes near the end of life.

The cathode portion of the cell is consumed before the anode. The anode sometimes displays symptoms of a high resistance passivation layer. The cathode resistance reaches a sudden and very large maximum at various times during the discharge:

- a) at 50% peak of CuCl_2 cells;
- b) at 90% and 85% peak for MoCl_5 cells.

Overall, that is, except at certain specified times, the components of internal resistance of the cell due to each electrode is about the same.

CrCl_3 :

Another alternate cathode chloride was tested. The CrCl_3 used for this experiment was Alfa Ventron CrCl_3 , anhydrous, sublimed, 99%.

A fifty gram cathode was prepared by mixing 13 grams of anolyte with 9 grams of graphite and 28 grams of CrCl_3 with a mortar and pestle. It was difficult to sieve the mixture because the CrCl_3 tended to compact into small

hard flakes which could not be ground further. The catholyte was not as dense as the regular CuCl_2 catholyte. This material was used to prepare cells for testing. Table 37 contains the results of these tests.

TABLE 37 SINGLE CELL TEST DATA FROM
THE INITIAL SERIES OF CrCl_3 CELLS

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	LOAD	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	$^{\circ}\text{C}$	ohms	
1558	1.66	74.5	53	79	1.63	2.16	200	0.81	$\text{LiAl}/\text{NaAlCl}_4/\text{CrCl}_3, \text{C}$ Initial Tests
1559	1.23	22.5	442	990	7.09	13.4	200	5.0	
1560	1.50	10.9	97	1310	0.86	9.12	200	12.6	

These tests were immediately followed by a series of tests in which the test load was held constant at 5 ohms and the temperature of each cell test was varied. Table 38 is a tabulation of this test data.

Figure 30 illustrates the relationship between the energy density and the test temperature. The energy density reaches a maximum at about 300°C . For this reason another set of cells was tested as a constant test temperature of 300°C . These cells were all tested at various current densities. Table 39 is a tabulation of these cell results.

TABLE 38 SINGLE CELL TEST RESULTS FOR LiAl/
NaAlCl₄/CrCl₃,C CELLS AT CONSTANT LOAD AND
VARIABLE TEMPERATURE

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	NOTES
	volts	mA/cm ²	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	
1561	1.13	20.7	118	267	480	3.71	5.78	175	5 ohm Load LiAl/NaAlCl ₄ / CrCl ₃ ,C
1559	1.23	22.5	147	442	990	7.09	13.4	200	
1562	1.19	21.8	344	1031	1830	15.5	24.1	225	
1563	1.21	22.1	392	1150	1964	17.9	27.0	250	
1564	1.23	22.5	492	1350	2040	21.8	29.8	275	
1565	1.26	23.1	674	1174	2223	20.9	33.6	300	
1567	1.43	26.2	402	620	922	14.4	19.1	325	
1568	1.85	33.9	139	200	301	7.86	10.5	350	
1569	1.90	34.8	103	155	245	6.38	8.86	375	
1570	2.08	38.1	115	220	337	10.5	14.4	400	
1571	2.16	39.5	221	310	405	16.7	20.1	425	
1572	2.36	43.2	133	230	303	14.4	17.7	450	

TABLE 39 SINGLE CELL TEST RESULTS FOR LiAl/
NaAlCl₄/CrCl₃,C CELLS AT CONSTANT TEMPERATURE
AND VARIABLE CURRENT DENSITY

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	seconds	Wh/kg	Wh/kg	ohms	
1573	1.01	189	44	80	127	9.27	13.0	0.49	300°C LiAl/NaAlCl ₄ / CrCl ₃ ,C
1574	1.11	125	58	100	155	8.52	11.7	0.81	
1575	1.19	72.6	105	225	385	11.6	17.4	1.5	
1576	1.24	37.8	260	556	1091	15.6	26.0	3.0	
1565	1.26	23.1	674	1174	2223	20.9	33.6	5.0	
1577	1.51	11.0	7	1192	2951	10.6	22.7	12.6	
1578	1.70	6.2	7	21	2845	0.13	12.6	25	

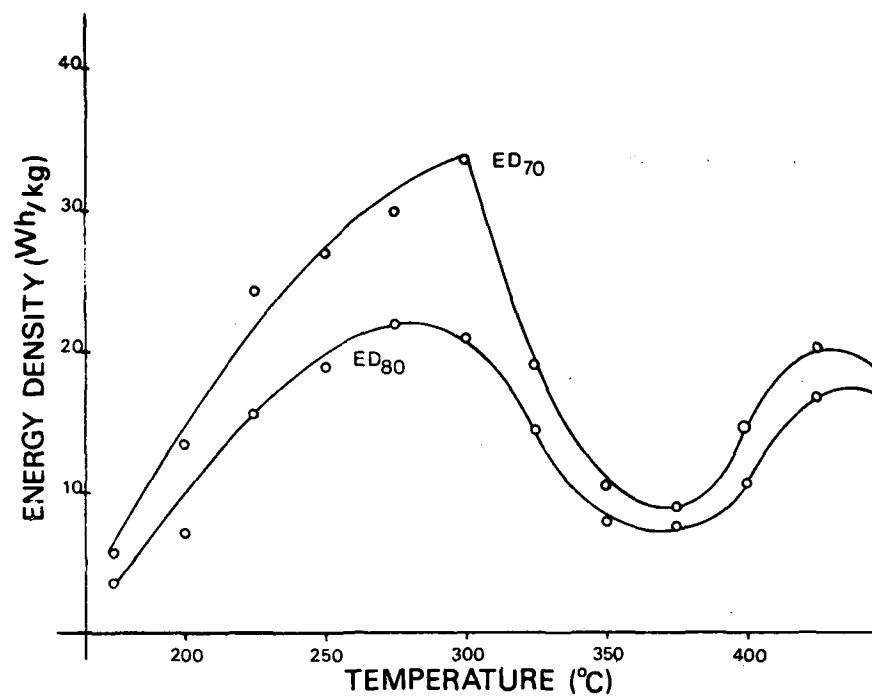


Figure 30. Energy Density vs. Test Temperature
For CrCl_3 Type Cells

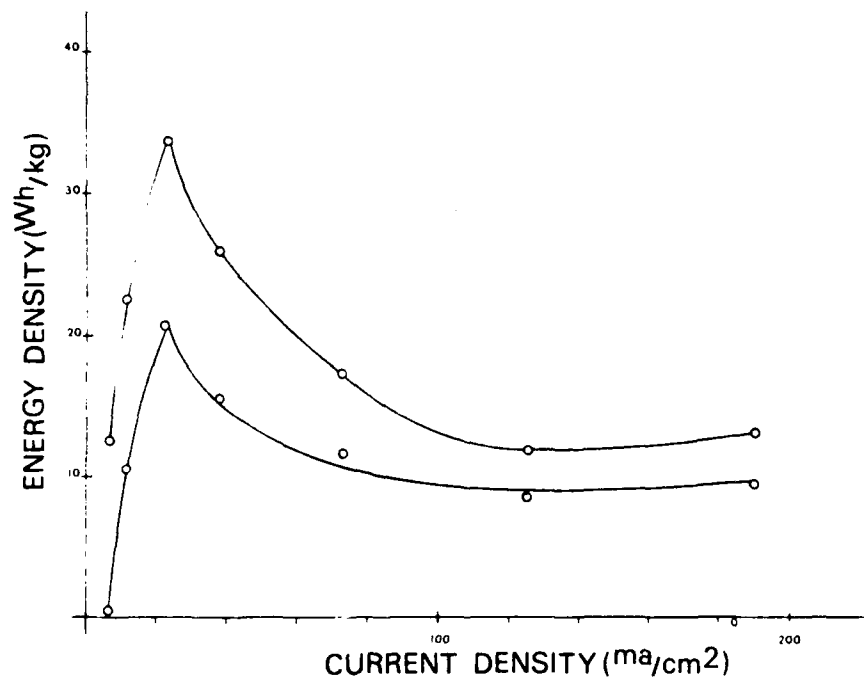


Figure 31. Energy Density vs. Current Density
For CrCl_3 Type Cells

Figure 31 shows the relationship between energy density and current density for these cells. There is a maximum at about 25 mA/cm^2 . This maximum is caused because the energy density falls off rapidly at current densities less than 25 mA/cm^2 . This is because at the low current densities the "spike" phenomenon becomes a greater factor. As the effect of the spike increased the lifetimes decrease and so does the energy density.

It was felt that perhaps CrCl_3 would be more active in an acidic catholyte. The material was prepared from the acidic NaAlCl_4 (69 m/o AlCl_3).

Cells were made from the 69 m/o AlCl_3 acidic catholyte and basic anolyte. The presence of the acidic catholyte had only a very minor effect in overall performance of the CrCl_3 cells.

The experiment seemed to indicate that CrCl_3 would be a relatively high temperature cathode material. Therefore, it was decided to try some cells with a higher temperature electrolyte – the $\text{LiCl}\cdot\text{KCl}$ eutectic. Table 40 shows the results of some cell tests with $\text{LiCl}\cdot\text{KCl}$ electrolyte and a catholyte of $2/3 \text{ CrCl}_3$ and $1/3 \text{ LiCl}\cdot\text{KCl}$. The anode was 20 w/o LiAl .

TABLE 40 SINGLE CELL TEST RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	LOAD	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	$^{\circ}\text{C}$	ohms	
1600	1.09	123	173	227	19.4	23.5	450	.81	LiAl/LiCl·KCl CrCl_3 Initial Test
1599	1.45	27	823	868	28.3	29.3	450	5	
1607	1.93	14	860	1060	17.3	20.4	450	12.6	
1603	1.22	223	1260	1470	29.0	32.4	400	5	LiAl/LiCl·KCl/ CrCl_3 Temperature Series
1604	1.33	24.3	1102	1231	31.4	33.8	425	5	
1599	1.45	26.5	823	868	28.3	29.3	450	5	
1605	2.12	38.8	170	185	9.24	9.76	475	5	

When Table 40 is compared to Tables 37 and 38 it can be seen that the LiCl·KCl was indeed a superior electrolyte for this application. The last four test results in Table 40 indicate a possible high temperature problem.

The next step was to try these powders with a magnesium anode. The results were interesting (Table 41).

TABLE 41 SINGLE CELL TEST RESULTS FOR Mg CELLS

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	seconds	Wh/kg	Wh/kg	Wh/kg	ohms	
1607	1.01	114	770	822	896	70.5	75.2	79.8	0.81	Mg/LiCl·KCl/CrCl ₃ 450°C
1608	0.99	112	730	790	845	64.6	69.1	72.3	0.81	
1606	1.34	24.5	34	236	>>1800	0.90	5.36	>>25.7	5	

Notice the relatively large lifetimes and energy densities (compare Table 41 with Tables 37, 38, and 40), especially at the high current densities. When the tapes were read activation was figured by taking 80% of peak. If 50% of peak had been used the energy density for these cells would have been about 100 Wh/kg. Figure 32 illustrates this unusual discharge curve.

SUMMARY OF CrCl₃ TESTS:

CrCl₃ is a high temperature cathode material unsuitable for use with this low temperature system. The peak voltage was low, the cathode reaction mechanism appears to be quite complex and the catholyte is not very temperature tolerant. CrCl₃ only worked well at high current density and will probably not store well.

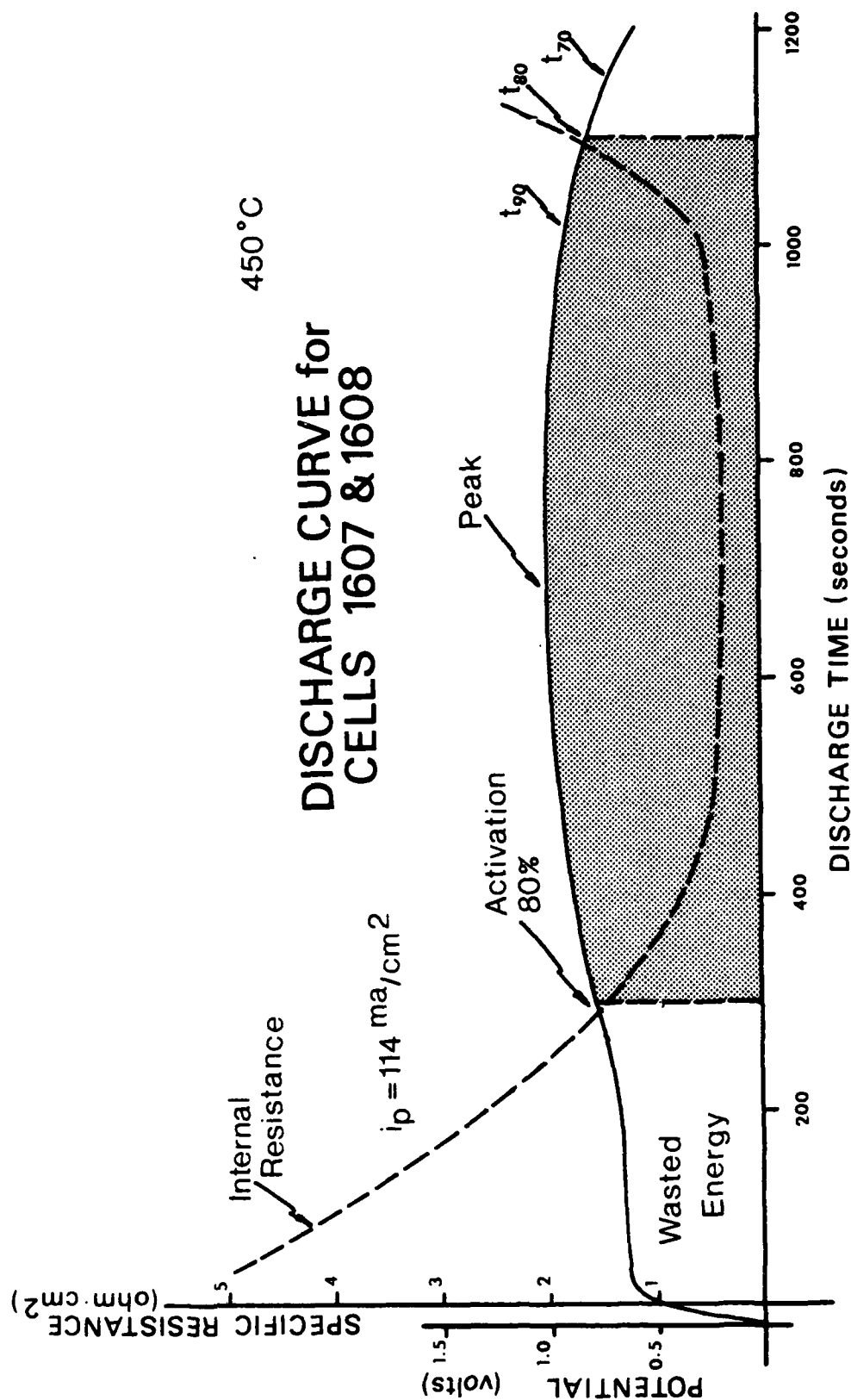


Figure 32. A Discharge Curve Of A CrCl₃ Type Cell Showing Internal Resistance

CuCl_2 FACTORIAL DESIGN STUDY:

The CuCl_2 system was optimized with a factorial design study. The factorial design method had been previously used to optimize the MoCl_5 system.

Four cell parameters were studied with respect to their effects upon nine cell variables. The four cell parameters chosen were:

$$x_1 = \frac{\text{anode weight}}{\text{anolyte weight}}$$

$$x_2 = \frac{\text{cathode weight}}{\text{anolyte weight}}$$

$$x_3 = \frac{\% \text{ CuCl}_2 \text{ in the catholyte}}{\% \text{ anolyte in the catholyte}}$$

$$x_4 = \frac{\% \text{ graphite in the catholyte}}{\% \text{ anolyte in the catholyte}}$$

The relative amounts of the three major catholyte components were varied between two extreme values. The relative amounts of the three major cell components were also varied between two arbitrarily chosen extreme values. The total cell weight was maintained constant at 4.10 ± 0.1 grams while the cell diameter was also maintained constant at 1.469". The cell thickness varied with each type of cell constructed.

The extreme values of x_1 were:

$$x_1 = \frac{\text{anode weight}}{\text{anolyte weight}} = 0.4 \text{ min. \& } 0.6 \text{ max.}$$

The extreme values for the other parameters were arbitrarily set at:

$$x_2 = \frac{\text{catholyte weight}}{\text{anolyte weight}} = 0.80 \text{ min. and } 2.70 \text{ max.}$$

$$x_3 = \frac{\text{CuCl}_2}{\text{NaAlCl}_4} = 1.3 \text{ min. and } 3.0 \text{ max.}$$

$$x_4 = \frac{\text{graphite}}{\text{NaAlCl}_4} = 0.3 \text{ min. and } 0.75 \text{ max.}$$

Using the above defined extremes there were four possible cell formulas:

Both parameters low

LL \equiv anode weight 0.74 grams
anolyte weight 1.86 grams
catholyte weight 1.49 grams

Anode minimum and cathode maximum

LH \equiv anode weight 0.40 grams
anolyte weight 1.00 grams
catholyte weight 2.70 grams

Cathode minimum and anode maximum

HL \equiv anode weight 1.03 grams
anolyte weight 1.71 grams
catholyte weight 1.37 grams

Both cathode and anode weights at maximum

HH \equiv anode weight 0.57 grams
anolyte weight 0.95 grams
catholyte weight 2.57 grams

There were also four possible catholyte formulations:

Both CuCl_2 and graphite at minimum

LL \equiv CuCl_2 50.00 %
graphite 11.54 %
anolyte 38.46 %

CuCl_2 at maximum and graphite at minimum

HL \equiv CuCl_2 69.77 %
graphite 6.98 %
anolyte 23.26 %

CuCl_2 at minimum with maximum graphite

LH \equiv CuCl_2 42.62 w/o
graphite 24.59 w/o
anolyte 32.79 w/o

Both CuCl_2 and graphite at maximum

HH \equiv CuCl_2 63.16 w/o
graphite 15.79 w/o
anolyte 21.05 w/o

Since there were four different cell formulations and each kind of cell could be made with any of the four different catholyte formulations there were a total of 16 different types of cells. These cells could be identified by the extreme of each of the four parameters. For example, the LHHL cell had x_1 and x_4 at minimum (low, L) and x_2 and x_3 at maximum (high, H). Then the LHHL cells had small anodes with large cathodes and their catholytes contained a relatively large amount of CuCl_2 and a relatively small amount of graphite.

At least three of each of the 16 cell types were tested. The three cell tests were averaged to provide one result. In some cases the spike phenomenon was so bad that one of the three results was vastly different from the others. In this case one or two more cells may have been prepared and the three results that were most alike were chosen and the others discarded. This may appear to be bias on the part of the experimenter but it is justified because it chooses cells with similar spikes. Since the spike is not one of the varied parameters or one of the measured variable results every effort should be made to hold it constant. An experiment of this nature must allow for the spike and since the spike phenomenon has not been quantized it can only be handled as a value judgement based upon the experience of the experimenter.

TABLE 42 SINGLE CELL TEST RESULTS FOR THE CELLS TESTED
FOR THE FACTORIAL DESIGN STUDY DONE TO OPTIMIZE THE
LiAl/NaAlCl₄/CuCl₂, C SYSTEM

S/N	V _p volts	t ₉₀ seconds	t ₈₀ seconds	t ₇₀ seconds	ED ₉₀ Wh/kg	ED ₈₀ Wh/kg	ED ₇₀ Wh/kg	PD ₈₀ Wh/dm ³	Spec r ohm·cm ²	Volume cm ³	Cold Voltage volts
H _H H _H	2.02	37	411	1479	1.54	14.0	41.7	26.2	2.73	2.193	0.57
	2.07	17	328	1256	0.74	11.6	36.9	21.7	1.93	2.193	0.74
	2.13	10	210	1110	0.45	7.57	32.5	14.2	1.53	2.193	2.97
H _H H _L	2.15	5.5	53	1001	0.26	2.05	29.9	4.09	2.24	2.054	2.77
	2.13	10	174	1030	0.46	6.53	31.2	13.0	2.24	2.054	2.94
	2.20	5	134	928	0.25	5.34	29.7	10.7	1.46	2.054	2.96
H _L H _L H	1.98	117	517	1377	4.67	17.5	38.9	31.5	1.62	2.277	2.31
	1.89	178	688	1412	6.48	21.3	37.8	38.4	2.12	2.332	0.01
	1.94	152	679	1561	5.83	22.0	43.1	38.7	1.25	2.332	1.05
H _L L _L L	2.02	38	471	1853	1.58	16.0	51.8	28.1	1.99	2.193	0.00
	2.00	74	662	1782	3.02	22.0	50.7	39.0	1.99	2.193	0.00
	2.00	92	785	2068	3.75	29.3	61.9	51.6	1.99	2.193	2.28
H _L L _L H	2.02	58	556	1564	2.41	19.0	45.1	31.5	1.19	2.499	2.93
	2.07	21	423	1525	0.92	15.0	45.0	24.8	1.16	2.499	2.92
	2.03	43	569	1492	1.81	19.5	43.6	32.3	1.57	2.499	2.96
H _L L _L L	2.00	81	707	1422	3.30	23.7	41.9	39.4	2.77	2.471	2.75
	1.86	229	845	1202	8.07	25.5	33.3	42.2	4.12	2.471	2.97
	2.00	54	612	1579	2.20	20.4	50.0	33.9	3.14	2.471	2.75
H _L L _L H	1.92	2.2	825	963	7.96	26.4	29.6	42.4	0.84	2.554	2.37
	1.98	137	704	909	5.47	23.6	28.7	37.9	1.22	2.554	2.53
	1.97	158	732	872	6.25	24.4	27.9	39.2	0.82	2.554	2.21
H _L L _L L	1.95	182	1112	1298	7.05	35.9	40.4	57.6	2.04	2.554	2.94
	1.96	173	1020	1310	6.77	33.3	40.4	53.6	1.23	2.554	2.91
	1.97	137	907	1216	5.42	29.8	37.4	47.8	1.62	2.554	2.88
L _H H _H H	2.03	12	268	1222	0.50	9.11	34.1	18.2	2.27	2.054	2.95
	1.98	58	445	1400	2.32	14.7	38.5	29.3	1.59	2.054	2.96
	1.98	14	318	1278	0.56	10.3	34.2	20.5	1.93	2.054	2.96
L _H H _L L	2.21	4.5	112	840	0.22	4.51	27.1	9.24	1.81	1.999	Noise
	2.18	7	122	726	0.34	4.80	23.0	9.84	2.19	1.999	0.04
	2.06	13	285	1173	0.56	9.98	33.9	20.5	1.93	1.999	2.78
L _H L _L H	1.98	123	590	1552	4.91	19.7	43.8	35.3	2.40	2.304	1.94
	1.93	168	707	1658	6.38	22.8	45.3	40.5	2.06	2.304	2.70
	1.90	192	743	1622	7.06	23.3	43.4	41.6	3.28	2.304	2.95
L _H L _L L	2.04	17	448	1760	0.72	15.3	50.0	31.5	1.18	2.193	2.90
	2.02	24	411	1438	1.00	13.9	40.5	28.6	2.34	2.193	2.98
	2.01	43	491	1780	1.77	16.5	49.6	33.9	2.34	2.193	0.06
L _L H _H H	1.86	237	1294	1759	8.36	38.2	48.4	68.0	1.26	2.304	2.75
	1.86	253	1432	1833	8.92	42.2	51.0	75.1	1.26	2.304	2.94
	1.87	212	1234	1689	7.55	36.7	46.4	65.3	2.51	2.304	2.22
L _L L _L L	1.84	236	1526	2131	8.14	43.8	56.8	77.0	3.71	2.249	2.62
	1.83	251	1058	1902	8.57	30.6	48.6	53.8	3.71	2.249	2.93
	1.82	273	1324	1773	9.22	37.6	47.1	66.1	X	2.249	2.94
L _L L _L H	1.89	201	661	758	7.32	20.7	22.9	36.9	1.26	2.332	2.24
	1.92	158	745	933	5.94	23.6	28.0	42.0	1.63	2.332	2.06
	1.84	266	878	970	9.18	26.1	28.1	45.9	0.86	2.332	2.84
L _L L _L L	1.85	278	1285	1444	9.70	37.8	41.3	64.9	1.70	2.338	2.82
	1.88	216	1328	1513	7.78	39.8	44.0	68.4	0.84	2.338	2.95
	1.85	271	1315	1500	9.45	38.6	42.6	66.3	2.10	2.338	2.94

Table 42 is a tabulation of the nine cell variables measured (or calculated) during this experiment. In addition to these, cell volume and cold voltage are included in Table 42.

Table 43 tabulates the relative position of each cell type with respect to the others. For example, notice that under the column marked V_p cell HHHH is listed as #1. This means that the HHHH cells had the highest voltage of all 16 cell types. Looking just one space to the right of the #1 a #16 can be seen. This means that the HHHH cells had the shortest lifetime at 90% of peak of all 16 types of cells tested. In every case the smaller the number in Table 43 the larger the actual value of the measured variable.

TABLE 43 THE RELATIVE STATUS OF EACH CELL TYPE

S/N	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	ED ₇₀	PD ₈₀	Spec R 80	Volume
HHHH	3	14	13	11	13	14	11	14	4	9
HHHL	1	16	16	13	16	16	13	16	4	10
HHLH	11	8	10	8	8	10	9	10	10	7
HHLL	6	10	9	2	10	8	1	7	5	9
HLHH	4	11	11	6	11	11	5	12	14	2
HLHL	10	9	7	9	9	7	8	9	2	3
HLLH	8	5	6	14	5	5	14	6	15	1
HLLL	9	6	4	12	6	4	10	4	11	1
LHHH	7	12	14	10	14	13	12	13	8	10
LHHL	2	15	15	15	15	15	15	15	6	11
LHLH	12	7	8	5	7	9	6	8	3	6
LHLL	5	13	12	4	12	12	4	11	7	9
LLHH	14	3	1	3	3	1	3	1	9	6
LLHL	16	2	3	1	2	3	2	3	1	8
LLLH	13	4	5	16	4	6	16	5	13	5
LLLL	15	1	2	7	1	2	7	2	12	4

Notice that, in Table 43, the cells identified as LLHL had the lowest peak but the highest t_{70} , the 2nd highest t_{90} , and the 3rd highest t_{80} . In contrast it has already been noted that the cell with the highest voltage had short lifetimes. Also notice that the relative ranks of the energy densities closely match the relative ranks of the lifetimes. This is logical because the energy density is directly proportional to the lifetime. However, the energy density is also directly proportional to the peak voltage but in Table 43 it can be seen that the V_p and ED were negatively correlated. This anomalous behavior is caused by the "spike" phenomena.

The spike was a real problem with this experiment. The peak voltages measured were not "true" peak voltage because the true peak voltages are biased by the addition of the spike. That is, the experiment would be better if the peak voltage could be separated in two portions - the true peak voltage and the spike voltage. It is believed that if the peak voltage could be corrected for the spike then the peak voltages would all be much more similar than they were observed in this experiment. This means that except for the spike the four parameters chosen have very little effect on the peak voltage.

Another good comparison is the energy density and the specific resistance. It is difficult to notice any correlation between energy density and resistance. While a strong correlation between resistance and energy density might be expected it did not occur. This is because the effect of the spike on overall cell performance was much greater than the effect of the internal resistance.

Notice also from Table 43 that the last four cell types had the best performances. An exception was the 80% lifetime of LLLH. This was probably due to the fact that this cell type had the 2nd smallest amount of CuCl_2 of all the cell types. Cell type HLLH had the smallest amount of CuCl_2 and it can be seen that it also had a relatively short 70% life. It is believed that these cells were running out of cathode material.

The data collected during this experiment can also be used to generate linear models of the nine variables of interest expressed in terms of the four parameters studied. Table 44 is a tabulation of all nine of the linear models generated from this data.

TABLE 44 THESE NINE LINEAR MODELS WERE GENERATED FROM THE DATA COLLECTED DURING THE FACTORIAL DESIGN STUDY

V_p	$= 1.997 - 0.034x_1 - 0.059x_2 - 0.031x_3 + 0.016x_4 - 0.026x_1x_2 + 0.013x_1x_3 + 0.007x_1x_4 + 0.028x_2x_3 - 0.033x_2x_4 + 0.001x_3x_4 + 0.002x_1x_2x_3 - 0.002x_1x_2x_4 - 0.008x_1x_3x_4 + 0.012x_2x_3x_4 - 0.002x_1x_2x_3x_4$
t_{90}	$= 119.75 + 27.23x_1 + 60.96x_2 + 30.54x_3 - 6.67x_4 + 29.73x_1x_2 - 14.44x_1x_3 - 4.19x_1x_4 - 12.17x_2x_3 + 24.38x_2x_4 - 14.88x_3x_4 - 9.94x_1x_2x_3 + 2.99x_1x_2x_4 + 4.15x_1x_3x_4 + 7.58x_2x_3x_4 + 9.98x_1x_2x_3x_4$
t_{80}	$= 690.5 + 102x_1 + 273.79x_2 + 88.83x_3 + 25.63x_4 + 109.17x_1x_2 - 81.17x_1x_3 - 9.38x_1x_4 - 91.67x_2x_3 + 98.79x_2x_4 + 47.96x_3x_4 - 54.0x_1x_2x_3 + 17.63x_1x_2x_4 + 15.29x_1x_3x_4 + 29.46x_2x_3x_4 + 48.63x_1x_2x_3x_4$
t_{70}	$= 1392.56 + 50.52x_1 + 4.81x_2 + 5.31x_3 + 51.98x_4 + 67.52x_1x_2 - 37.73x_1x_3 + 3.27x_1x_4 - 262.19x_2x_3 + 74.81x_2x_4 + 130.31x_3x_4 - 34.48x_1x_2x_3 + 65.02x_1x_2x_4 - 23.73x_1x_3x_4 + 3.40x_2x_3x_4 + 15.10x_1x_2x_3x_4$
ED_{90}	$= 4.44 + 0.83x_1 + 2.13x_2 + 1.20x_3 - 0.29x_4 + 0.94x_1x_2 - 0.54x_1x_3 - 0.19x_1x_4 + 0.42x_2x_3 + 0.86x_2x_4 - 0.52x_3x_4 - 0.36x_1x_2x_3 + 0.09x_1x_2x_4 + 0.14x_1x_3x_4 + 0.29x_2x_3x_4 + 0.37x_1x_2x_3x_4$
ED_{80}	$= 21.92 + 2.27x_1 + 7.75x_2 + 3.10x_3 + 0.70x_4 + 2.70x_1x_2 - 2.41x_1x_3 - 0.46x_1x_4 - 2.73x_2x_3 + 2.69x_2x_4 + 1.66x_3x_4 - 1.46x_1x_2x_3 + 0.46x_1x_2x_4 + 0.24x_1x_3x_4 + 0.811x_2x_3x_4 + 1.53x_1x_2x_3x_4$
ED_{70}	$= 39.93 + 0.40x_1 + 0.39x_2 + 0.38x_3 + 1.83x_4 + 1.35x_1x_2 - 0.79x_1x_3 - 0.15x_1x_4 - 6.45x_2x_3 + 1.45x_2x_4 + 3.72x_3x_4 - 0.77x_1x_2x_3 + 1.5x_1x_2x_4 - 0.69x_1x_3x_4 - 0.25x_2x_3x_4 + 0.75x_1x_2x_3x_4$
PD_{80}	$= 38.51 + 5.183x_1 + 12.00x_2 + 4.89x_3 + 1.12x_4 + 5.11x_1x_2 - 3.93x_1x_3 - 0.64x_1x_4 - 5.16x_2x_3 + 4.29x_2x_4 + 3.09x_3x_4 - 2.54x_1x_2x_3 + 0.52x_1x_2x_4 + 0.72x_1x_3x_4 + 1.03x_2x_3x_4 + 2.35x_1x_2x_3x_4$
$SPEC. R_{80}$	$= 1.9725 + 0.1054x_1 - 0.0446x_2 - 0.2758x_3 + 0.2933x_4 + 0.0125x_1x_2 + 0.0304x_1x_3 - 0.075x_1x_4 - 0.3054x_2x_3 + 0.3358x_2x_4 - 0.2104x_3x_4 - 0.0967x_1x_2x_3 + 0.0279x_1x_2x_4 - 0.0908x_1x_3x_4 - 0.1775x_2x_3x_4 + 0.0446x_1x_2x_3x_4$

These linear models can be used to determine the relative effects of each of the four studied parameters upon the nine variables of interest. They can also be used to examine the effects of the interactions of the four parameters upon the nine variables. For example, look at the linear model for t_{90} . Recall that this is an equation of the form:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_3 x_4 \\ + \beta_{10} x_3 x_4 + \beta_{11} x_1 x_2 x_3 + \beta_{12} x_1 x_3 x_4 + \beta_{13} x_1 x_3 x_4 + \beta_{14} x_2 x_3 x_4 + \beta_{15} x_1 x_2 x_3 x_4$$

Notice that, for t_{90} , β_2 (the coefficient of x_2) is almost 50% of β_0 . Furthermore, is the largest of all 15 coefficients in this equation. Therefore, it can be said that the 90% life is greatly influenced by x_2 (the relative size of the cathode). The eight most significant coefficients listed in order are:

$$\begin{aligned} &x_2 \\ &x_3 \\ &x_1 x_2 \\ &x_1 \\ &x_2 x_4 \\ &-x_3 x_4 \\ &-x_1 x_3 \\ &-x_2 x_3 \end{aligned}$$

Notice that the next four coefficients are about the same size -- about 25% of β_0 . Then, not only is the cathode size important but so is the anode size, the amount of CuCl_2 in the cathode and the interaction of x_1 and x_2 . What this may really be telling us is that the amount of anolyte is an important factor for t_{90} . Now, refer back to Table 42 and notice that the cells with the longest 90% lifetimes were the last four cells. These cells all had minimum values of x_1 and x_2 , or, in other words they all had large anolytes. Therefore, we are

led to the conclusion that for a long 90% lifetime the cell should have a relatively large anolyte layer. It could be that a large anolyte layer is needed as a sink to collect the reaction products from the electrodes and delay the inevitable polarization which brings the cell voltage below the 90% of peak.

Similar observations can be made for the 80% lifetimes. The analysis changes with the 70% life. Recall that the most significant factor in the linear model for t_{90} (β_2) was almost 50% of the constant β_0 . However, for t_{70} the most significant factor (β_8) is only about 20% of β_0 and, actually, none of the coefficients have much of an effect on the 70% life. The single most significant influence upon t_{70} was β_8 , the coefficient of the $x_2 x_3$ term and this coefficient is negative. This tells us that x_2 (the relative size of the cathode) and x_3 (the relative amount of CuCl_2 in the cathode) can interact to seriously lower the 90% life. This has already been observed for cells HLLH and LLLH.

These same observations can be made from the linear models generated for the energy densities. It has already been observed that a large energy density is correlated to a long lifetime. The linear models reinforce this though by showing that the factors that are responsible for a long life are also responsible for a high energy density. The same observations apply to the packing density except for minor changes due to differences in cell thickness.

Now observe the most significant factors for the peak voltage:

$$\begin{aligned} & -x_2 \\ & -x_1 \\ & -x_2 x_4 \\ & -x_3 \\ & -x_2 x_3 \\ & x_1 x_2 \end{aligned}$$

These are very similar to the most significant factors for t_{90} , t_{80} , ED_{80} , and PD_{80} except that they are all, anomalously, negative. The anomaly has already been blamed on the spike. Notice also the relatively small magnitude of these coefficients. Even the most significant coefficient is only about 2 or 3% of β_0 . This can be interpreted such that none of the four studied parameters have much effect upon the peak voltage. However, there was a large range of peak voltages (1.82v to 2.21v). Then it follows that some factor other than the four studied does indeed have a profound effect upon the peak voltage. This has already been identified as the spike phenomenon.

Finally, observe the linear model for the specific resistance measured at the 80% lifetime. The five most important factors are (these five are greater than 10% of β_0):

$$x_2 x_4$$

$$-x_2 x_3$$

$$x_4$$

$$-x_3$$

$$x_3 x_4$$

Notice that all five of these involve x_3 or x_4 in some way. The x_4 terms are positive (the relative amount of graphite in the catholyte) and two of the three x_3 terms are negative (the relative amount of $CuCl_2$ in the catholyte). As a result of the reference electrode tests explained earlier in this section it was observed that the internal resistance of a cell changed during discharge. It was further noted that these changes appeared to be dependent upon the cathode species. Now, again note that the most significant factors for the internal resistance involved the nature of the cathode. The negative value on the x_3 terms could be interpreted

as a lack of graphite (rather than a negative influence of an abundance of CuCl_2). It should be noted that positive terms in this model tend to increase the specific resistance and not decrease it.

SUMMARY:

The optimum cell formula was:

anode weight $0.75 \pm .1$ grams
anolyte weight $1.85 \pm .1$ grams
catholyte weight $1.50 \pm .1$ grams
Total Weight $4.10 \pm .1$ grams

The optimum catholyte formula was:

anolyte weight 21.05 grams
 CuCl_2 weight 63.16 grams
graphite weight 15.79 grams
Total Weight 100.00 grams

These optimum designs utilize a large anolyte layer with a relatively large amount of CuCl_2 in the catholyte. Because of a spike the cells with the highest potentials had the shortest lives. Also the optimum cells were cells that showed no tendency to form a spike. The cells designated LLLH and HLLH had short 70% lifetimes because they contained an inadequate amount of CuCl_2 . These cells can be used to define the lower limit of CuCl_2 tolerable in a cell. There was no evidence of any cell life being anode limited and the lower limit of anode mass was not determined. Because both electrodes were known to contain adequate reaction mass and since there was no correlation between internal resistance and useful lifetime the cell life-time must depend upon polarization of one or both electrodes. None of the four parameters studied had much effect on voltage within the range of study. The same was true of internal resistance. Before a truly optimum cell could be developed the spike had to be controlled.

CONCLUSION:

As this program was started the cathode active material was MoCl_5 . CuCl_2 , FeCl_3 , WCl_6 , and CrCl_3 were considered viable alternates. When the program was about at midpoint a serious storage problem developed with MoCl_5 and the "alternate", CuCl_2 , became the regular cathode material. For this reason CuCl_2 was optimized with a factorial design study.

FeCl_3 showed the advantages of high peak voltage, good energy density and little apparent tendency to form a spike. However, FeCl_3 also had the disadvantages of not being able to carry current, shorter lifetime due to poor voltage regulation and an undesirable discharge curve profile, a relatively small temperature range, a moisture sensitivity problem and a possible storage problem.

WCl_6 was a good performer but it is relatively expensive. Has a tendency to form a spike, has poor regulation and is volatile.

CrCl_3 turned out to be useful only at high temperatures.

CuCl_2 had the disadvantages of low peak voltage and relatively poor current carrying ability. However, these were compensated for by some large advantages: a flat discharge curve profile, a wide temperature range, a much less sensitivity to moisture, and a long storage life.

One of the techniques used to study the alternate cathode chlorides was the use of single cell testing with reference electrodes inserted into the anolyte layer. As a result of these tests it was demonstrated that the anode was the reaction site for the spike phenomenon. It was also learned that the internal resistance of a LiAl/CuCl_2 cell was highest in the anode at activation but as the cell discharges the cathode area resistance slowly but linearly increases until useful cell life has passed. This cathode polarization is aggravated by operating at high current density and the CuCl_2 must necessarily be a low current density system if it is to be a long life system.

SECTION X

ALTERNATE CATHODE MATERIALS (NOT CHLORIDES)

FeS_2 was one of the first alternate cathode materials tested.

A test catholyte was prepared using FeS_2 instead of MoCl_5 . The DSC spectrum of this material was generated and displayed a large exotherm at 167°C . One would normally expect to find a large endotherm at that temperature which would be interpreted as the heat of fusion. It appeared that the FeS_2 was reacting with the electrolyte. Because of this the first catholyte was diluted with 50 % additional anolyte. When the diluted catholyte was tested an exotherm did not appear but there was a small endotherm at 143°C and a large endotherm at 167°C . This is actually very similar to the DSC Spectrum usually obtained for a somewhat moist anolyte.

A third catholyte was prepared by mixing 66 % FeS_2 with 34 % anolyte. This material produced a DSC spectrum similar to a moist anolyte with no evidence of an exotherm.

A second sample of the first catholyte was tested and again the large exotherm was noted. This sample was cooled and tested again. On the second heating the only thermal feature noted was an endotherm at 170°C . The exotherm had not appeared upon reheating the sample.

There was no explanation for the inconsistent appearance of an exotherm near the melting points of these materials. Perhaps the heat of reaction for FeS_2 and the anolyte is very close to the heat of melting and the exotherm (or endotherm) can be lost in samples of different relative FeS_2 concentrations. To test this a series of Anolyte/ FeS_2 mixtures was prepared and DSC spectra for these generated.

A series of mixtures of anolyte and FeS_2 were made and DSC spectra were generated for each. The sample program was:

- | | |
|-----------------------|------------------------|
| 1) pure anolyte | 5) 66% FeS_2 |
| 2) 15% FeS_2 | 6) 90% FeS_2 |
| 3) 30% FeS_2 | 7) 100% FeS_2 |
| 4) 50% FeS_2 | |

Each sample was heated, cooled, and reheated.

As the sample became more concentrated with FeS_2 the DSC spectra became more exothermic. The spectra did not consist of a number of well defined features which changed progressively as the percentage of FeS_2 increased.

A catholyte was made of 45 ^{w/o} A #1030 with 45 ^{w/o} FeS_2 and 10 ^{w/o} graphite. This material was made into cells with Anolyte #1030 and 20 ^{w/o} LiAl anode. These were used for single cell test #1152 to #1158. Table 45 is a tabulation of the test results.

TABLE 45 TABULATION OF FeS_2 SINGLE CELL TEST RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	T	LOAD	NOTES
	volts	mA	seconds	seconds	wh/kg	wh/kg	°C	ohms	
1152	1.34	24.9	35	46	.719	-	200	5	C #1039, A #1030, 20 ^{w/o} LiAl
1153	1.59	11.5	77	137	.857	-	200	12.6	
1154	1.21	22.1	91	291	1.38	3.61	250	5	
1155	1.55	28.3	26	177	0.68	-	300	5	
1156	1.49	27.3	160	175	3.56	-	340	5	
1157	1.46	26.7	74	134	1.92	2.89	380	5	
1158	1.43	26.2	99	207	2.41	4.09	420	5	

The conclusions of all the cell testing were:

- a) The FeS_2 cathode is far inferior to any cathode chloride tested so far,
- b) The FeS_2 performs better at higher temperature.

In conclusion it can be stated that FeS_2 does not appear to be a good cathode material and further use of this material is not anticipated with this electrolyte.

It was mentioned earlier in this report that MoO_3 was also tried as an alternate cathode material. The preparation of the catholyte was described under " MoCl_5 Catholyte Particle Size Growth". Cells were made with these materials and they were tested.

The catholyte was used with 28 % LiAl and a basic NaAlCl_4 anolyte with the usual weight setting of 0.45 gm anode, 1.75 gm anolyte, and 1.9 grams catholyte to prepare the first MoO_3 cells. The cells averaged 0.081 inches thick. These cells were tested on a single cell tester. These were cells #1374 through #1378.

TABLE 46 TABULATION OF MoO_3 SINGLE CELL TEST RESULTS

S/N	V_p	t_{90}	t_{80}	t_{70}	ED_{90}	ED_{80}	ED_{70}	LOAD	NOTES
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	Wh/kg	ohms	
1377	0.94	36	47	66	2.25	2.84	3.63	0.81	Basic Anolyte
1375	2.11	84	107	139	4.27	5.22	6.33	5	
1376	3.37	X	X	X	X	X	X	No Load	
1379	2.07	109	122	169	5.65	6.19	7.72	5	Acidic Anolyte
1380	0.99	36	47	61	2.51	3.16	3.81	.81	
1381	2.40	270	305	444	7.29	8.08	10.5	12.6	
1382	3.12	X	X	X	X	X	X	No Load	

Single cells 1374 and 1375 initiated in a manner similar to MoCl_5 cells. The activation was noticeably slower. The peak voltages were only about 2.11 volts and a peak of about 2.45 volts could be expected with MoCl_5 cells. The lifetimes were very short. The energy densities for the MoO_3 cells were an order of magnitude greater than for FeS_2 cells but were an order of magnitude lower than for MoCl_5 cells. Both cells displayed over 2.1 volts of cold voltage.

The next cell was a no load test. The cell formed a peak to 3.37 volts which quickly dropped off to about 2.28 volts. The cell held this voltage for about 40 seconds and then climbed to 2.88 volts in the next 220 seconds. At 320 seconds a 5 ohm load was attached and the voltage fell off very quickly.

Cell #1377 was tested across an 0.81 ohm resistor. The voltage was extremely low ($V_p = 0.94\text{v}$). The activation was also quite low. These cells had a relatively good energy density. The biggest problem noticed with these cells is a severe polarization. Cell #1378 was tested at 260°C with no improvement in performance.

A second set of cells were made with this same catholyte. These cells were made with an acidic anolyte. These were cells #1379 thru 1382. There was a noticeable improvement with these cells but they still displayed severe polarization. When these cells were tested they emitted a white or yellowish "smoke". This "smoke" was not noticed with the previous set of cells made with basic anolyte.

The cells were allowed to cool in the dry box and were then removed and examined post-mortem.

SUMMARY OF MoO_3 CATHOLYTE CELL TESTING:

- 1) MoO_3 catholytes produce at least as great as voltage as MoCl_5 catholytes;
- 2) MoO_3 cells have much greater internal resistance and tend to polarize more than MoCl_5 cells;
- 3) MoO_3 cells produce yellow smoke in the presence of an acidic NaAlCl_4 anolyte but to a much less degree in the presence of a basic anolyte;
- 4) MoO_3 requires the addition of graphite in the catholyte;
- 5) the double peaks of the no load tests may be indicative that the MoO_3 reacts with the NaAlCl_4 anolyte to form a new catholyte. That is, it appears that fusing the catholyte mix causes the MoO_3 to react with the NaAlCl_4 to form a more active cathode species;
- 6) the presence of the yellow crystals, which are so similar to the white yellow crystals reported during the examination of the catholyte particle growth phenomenon, indicate that the MoO_3 catholyte would not be any more stable than the MoCl_5 catholyte;
- 7) the Mo species in a MoO_3 catholyte apparently diffuse through the cell even faster than the species in the normal basic MoCl_5 catholyte;
- 8) the basic MoO_3 catholyte appears to be quite stable.

WO_3 , Fe_2O_3 , CuO

Some more cathodic oxides were tested. The first was WO_3 . The results were not very dramatic. Also tested was CuO and Fe_2O_3 . MoO_3 has been tested before but not with a basic catholyte. Table 46 shows how each type of cell performed over a similar density range at 200°C .

TABLE 47 SINGLE CELL TEST RESULTS FOR FOUR ALTERNATE CATHODE OXIDES AT 200°C AND VARIOUS RESISTIVE LOADS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	Spec. R Peak	Spec. R 80	Load	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm	
1463	0.80	98.8	39	58	1.75	2.32	1.21	2.32	.81	W ₂ O ₃
1461	1.36	24.9	133	257	2.58	4.32	4.48	2.08	5	
1465	1.82	13.2	40	150	0.54	1.64	47.2	1.86	12.6	
1474	1.28	145	28	35	3.27	3.80	1.30	1.87	.81	CuO
1473	1.85	33.9	255	306	9.46	10.8	3.35	2.80	5	
1475	1.90	13.8	622	793	9.59	11.5	8.18	5.23	12.6	
1483	0.77	87	20	34	0.80	1.19	X	2.50	.81	Fe ₂ O ₃
1482	1.87	34.2	71	86	2.73	3.13	1.98	2.26	5	
1484	2.20	16.0	44	309	0.93	4.81	5.05	2.28	12.6	
1491	1.33	156	48	59	6.12	7.03	X	1.88	.81	MoO ₃
1490	2.22	40.6	113	150	6.62	8.01	3.47	4.01	5	
1492	2.46	17.8	244	389	6.90	9.54	2.75	4.80	12.6	

It can be seen from Table 46 that the best material was either CuO or MoO₃. As is true with the analog chlorides the Mo cathode could carry more current than the Cu cathode but a low current density the Cu cathode showed superior lifetimes and greater energy density. The chloride cathodes produced about 5 times as much energy as their oxide analogs. W₂O₃ produced less energy than could have been expected from the Mo and Cu performance.

Some more tests were run at constant load (5 ohms) and various temperatures. Only the results for the W, Cu and Mo systems will be shown here (Table 47). The Fe results were no better than those reported in Table 48.

TABLE 48 SINGLE CELL TEST RESULTS FOR THREE ALTERNATE CATHODE OXIDES AT 5 OHMS AND VARIOUS TEMPERATURES

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	Spec. R Peak	Spec. R 80	Temp.	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1467	1.41	25.8	115	171	2.43	3.28	2.91	0.48	175	W ₂ O ₃
1461	1.36	24.9	133	257	2.58	4.32	4.48	2.08	200	
1468	1.43	26.2	191	445	3.98	7.94	3.53	1.82	225	
1469	1.42	26.0	251	611	5.14	10.7	4.23	1.82	250	
1470	1.53	28.0	105	461	2.52	8.87	2.38	0.87	275	
1472	1.55	28.4	130	397	3.13	8.07	2.67	1.27	300	
1476	1.76	32.2	186	238	6.59	7.82	4.60	3.26	175	CuO
1473	1.85	33.9	255	306	9.46	10.8	3.35	2.80	200	
1477	1.85	33.9	208	266	7.68	9.19	3.08	2.80	225	
1478	1.84	33.7	240	333	9.12	11.5	2.23	1.41	250	
1479	1.83	33.5	265	339	9.79	11.7	3.88	2.47	275	
1480	1.87	34.4	294	361	11.6	13.4	2.51	4.33	300	
1446	2.09	38.2	133	167	6.83	7.97	42.4	X	175	MoO ₃
1490	2.22	40.6	113	150	6.62	8.01	3.47	4.01	200	
1497	2.08	38.1	90	130	4.53	5.85	1.77	2.20	225	
1498	2.12	38.8	64	85	3.13	3.85	2.47	1.55	250	

Notice from Table 48 that CuO performed relatively well across the entire temperature range but did best at the high extreme. W₂O₃ and MoO₃ reached their peak output at more moderate temperatures. Once again this behavior is similar to the chloride analogs. Notice that the energy density at 70% increased dramatically for W₂O₃ at higher temperatures but the 80% energy density did not. This is because of a bad "spike" with the W₂O₃ system which was not as much in evidence with the CuO and MoO₃ cathodes. The Cu cathode was clearly superior in these tests even though the voltage was less.

SUMMARY OF OXIDE CATHOLYTE TESTING:

- 1) transition metal oxide analogs of the transition metal chlorides which have been used for cathodes have been tested;
- 2) the oxides produce about 5 times less energy than the corresponding chlorides;
- 3) the relative behavior of the oxides is similar to the behavior of the chlorides;
- 4) while none of the oxides perform as well as the chlorides the CuO system is the best of the oxides;
- 5) based on these results the oxides appear to require a higher temperature than their chlorides analogs;
- 6) MoO_3 is not an exact analog of MoCl_5 ;
- 7) MoO_3 makes a superior current producing cathode but CuO makes a superior long life, low energy density cathode.

CARBON MONOFLUORIDE:

Another new cathode material, carbon monofluoride, CF, has been tested. This material was delivered by Mr. Dick Marsh during the occasion of a program status review at the Eureka plant.

A catholyte was prepared by mechanically mixing 18.6 gm CF (labeled AP) with 8.4 gm of A #1084 and 3 gm of graphite. This material was labeled C #1201. This formula contains more cathode material (62% vs 56%) than a regular catholyte mix and less graphite (10% vs 18%).

An attempt was made to make regular test cells with this catholyte, A #1084, and 28 ^w/o LiAl. However, the catholyte layer always delaminated and crumbled away from the rest of the cell.

In order to test the catholyte two layer pellets of 28 % LiAl and A #1084 were made. Then single layer pellets of the catholyte were prepared. The reason for the delamination of the three layer cells became evident when the single layer catholyte pellets were compacted. The finished pellets expanded in diameter by from 1/8" to 1/4" as soon as they were ejected from the die cavity. These pellets were compacted at about 28,000 PSI. The average thickness of one catholyte pellet was 0.039" which the thickness of the anode/anolyte pellet was 0.042". These pellets were used to make cells for testing by stacking the smaller anode/anolyte pellets on top of the catholyte pellet.

The first cell was tested at 150°C. The beginning of the test was all open circuit. There was a high spike of 2.9V which dropped in 15 seconds to 1.5V. Then the voltage slowly increased to 1.9V in about 300 seconds. At this point a 75Ω resistor was switched into the circuit to test the current carrying ability of the cell. The voltage dropped immediately to 0.04 volts. This was not surprising because the melting point of the electrolyte is greater than 150°C. Therefore, the temperature was slowly increased.

All the while the temperature was increasing the cell was being watched for visible signs of deterioration (gas, smoke, bubbling, etc.). At 200°C the O.C. V was 2.04 volts. The test was then discontinued. The next cell was tested at 200°C and open circuit. The test displayed a 2.46 volt spike. The potential after the spike was about 2.04 volts. When a 12.6Ω load was switched into the circuit the voltage dropped to 0.28V. As in the previous test the temperature was slowly increased. At 230°C the load was switched in and the voltage read 0.47v. The temperature was allowed to continue to increase and the current carrying ability of the cell also kept increasing -- at 260°C the voltage went from 2.14 to 0.77v; at 280°C the voltage dropped from 2.14 to 1.02v; at 290°C the voltage dropped from 2.12v to 1.0v. The temperature was raised to 305°C and the test was discontinued. There was no visible deterioration of the cell.

In an attempt to improve the conductivity of the catholyte another formula was mixed. This catholyte, C #1203, contained 9 gm CF, 19 gm A #1084, and 3 gm graphite. Once again it was necessary to make two pellet cells. It was difficult making catholyte pellets because of "blow-by".

The first cell was tested at 175°C initially. The cell reached 2.80v spike and dropped off to 1.91v. Then the voltage slowly rose to 2.04v. Where a 12.6Ω resistor was switched into the circuit the voltage dropped from 2.01v to 1.10v. It is interesting to note that for the cells made with the first catholyte, C #1201, the internal resistance was 90% iR drop and 10% polarization. For cells made with the second catholyte, C #1203, just the opposite was true — the internal resistance was 10% iR drop and 90% polarization.

CONCLUSION:

The CF material is still a good catholyte candidate but some method must be found to put it into some usable form.

TiS₂ & TiS₃:

Approximately 10 gms TiS₂ was received from Wright-Patterson. This material was mixed with LiAlCl₄ anolyte and graphite to make up a catholyte (C #1231):

10 gms TiS₂

4.6 gms A #1096 (LiAlCl₄ with 12 % Cab-O-Sil)

3.2 gms graphite

The mixture was ground and passed through a #40 sieve.

Due to the exceptionally small amount of catholyte the press could not be set in properly. Each cell was unique. The cell anodes were 35% Mg and 54% LiAl (28 ^W/o Li) that weighed 0.45 grams. The anolyte was a LiAlCl₄ electrolyte that weighed 1.75 ± .1 gm. The catholyte varied but was usually about 1.10 gms. The cells were about 0.065" thick. Table 49 shows the results of the tests.

It can be seen from Table 49 that the peak voltage was very low. The low peak voltage coupled with the short life caused very low energy densities. The internal resistances were good. It appears that TiS₂ is not a very good low temperature thermal battery cathode material. An attempt was made to charge these cells but did not work well. TiS₂ will be abandoned.

TiS₃:

A 4.4 gram sample of TiS₃ was also received from Wright-Patterson. This material was used to prepare a NaAlCl₄ catholyte (C #1237).

4.4 gm TiS₃

2.1 gm A #1094

1.4 gm graphite

Once again the cells had light catholytes (about 1.4 grams). The cells were about 0.068" thick.

Apparently TiS₃ is not a good cathode material for this application.

TABLE 49 SINGLE CELL TEST RESULTS
FOR CELLS MADE WITH TiS_2 CATHOLYTES

S/N	V_p	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} PEAK	R_{INT} t_{90}	R_{INT} t_{80}	TEMP.	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	C°	ohms	
1872	1.28	23.4	0.76	1.00	2.29	1.23	0.94	1.05	150	5	TiS_2
1873	1.35	24.7	0.78	1.09	1.47	1.17	1.32	0.92	180	5	
1874	0.91	103	1.08	1.83	3.91	0.37	0.22	0.23	180	.81	TiS_2
1873	1.35	24.7	0.78	1.09	1.47	1.17	1.32	0.92	180	5	
1875	1.44	10.5	0.68	0.99	1.29	0.94	1.06	0.59	180	12.6	
1876	1.59	29.1	3.06	5.56	7.11	1.03	1.63	1.30	180	5	Charged
1877	0.76	13.9	1.18	2.25	3.60	0.68	0.77	0.85	180	5	Charged & Cooled
1878	1.66	27.6	0.93	1.65	2.45	2.82	0.80	0.45	200	5	TiS_2 at 5 ohms
1879	1.56	28.5	0.50	1.13	2.74	1.04	0.78	0.43	260	5	
1880	1.58	28.9	0.32	1.76	2.68	0.71	0.28	0.43	320	5	

CONCLUSION:

FeS_2 , TiS_2 , TiS_3 , CF, and a number of heavy metal oxides were tested.
No cathode material was found to be equal to or superior to the heavy metal chlorides.

SECTION XI
ALTERNATE GRAPHITES

One pint samples of eight different graphites were received from Asbury Graphite Mills, Inc., in Asbury, New Jersey. Asbury sent samples of the five major types of graphites: amorphous, crystalline, flake, synthetic, and primary. These materials were all supposed to be submicron particle size and were supposed to come from different source. Asbury Mills sent data sheets with each sample. The following table (Table 50) is a condensed tabulation of the sample characteristics.

TABLE 50 GRAPHITE PROPERTIES

NO.	TYPE	ORIGIN	%C	% SiO ₂	% Al ₂ O ₃	% Fe _x O _y	A.P.D. μ
5530	Natural Amorphous Graphite	Mexico	82.9	8.9	6.1	1.7	.62
M785	Natural Sirlanke Graphite	Sirlanke	96.0	1.8	.58	.35	.85
S-5131	Flake	Sirlanke	96.2	1.85	.95	.30	.75
M470	Artificial	Japan American German	98.8	.068	.05	.21	.70
M980	Flake	Malagasy	99.1	.11	.063	.25	.82
7105	Artificial	American	99.8	.094	.004	.035	.45
7101	Artificial	American	99.8	.050	.006	.056	-#100*
M870	Natural Flake	Malagasy	99.9	.013	.005	.009	0.72
Fisher #64	Grade #38	-	99.5	-	-	-	-#325**

These graphites were used to prepare regular test CuCl₂ catholytes. These catholytes were used to make regular test cells with 28 % LiAl anodes. At least five cells were tested with each type of graphite (about 60 cells total).

* Most (99%) of this material will pass through a #100 sieve.

** 96.79% of this material will pass through a #325 sieve.

The test results were exceptional in the fact that nothing dramatic happened. Almost all of the eight graphites performed in identical behavior. There was one notable exception. The crude Mexican graphite did not work very well. Figures 33 and 34 illustrate this point well.

Figure 34 shows energy density vs. current density for 10 types of cells. Eight types of cells are represented by the eight different graphite samples and two additional cell types which used mixtures of graphites. The first thing noticeable about the data in Figure 34 is how it falls into groups. This says that the different graphites performed almost identically at the high current density range. One notable exception is represented by the black dots on Figure 34 – the Mexican amorphous graphite. This catholyte would not carry current. Also, it can be noticed that the other seven graphites made their individuality better known at the lower current density ranges. At low current density graphites #7101 and S-5131 were somewhat superior to the others. At the lower current densities a spike began to effect the discharge curve of some of the samples and this explains the increased spread in the data points.

Figure 33 compared peak voltages with current density. This chart was drawn to illustrate how little difference there was due to the presence of the different graphites.

An interesting observation was made while examining the DSC spectra of the catholytes made with the eight different samples of graphite. For six of the catholyte spectra the traces were featureless until the endotherm was reached that probably represents the heat of fusion of the NaAlCl_4 in the catholyte. However, for two samples, this endotherm was difficult to resolve from a large exotherm that occurred at about the same temperature. These two

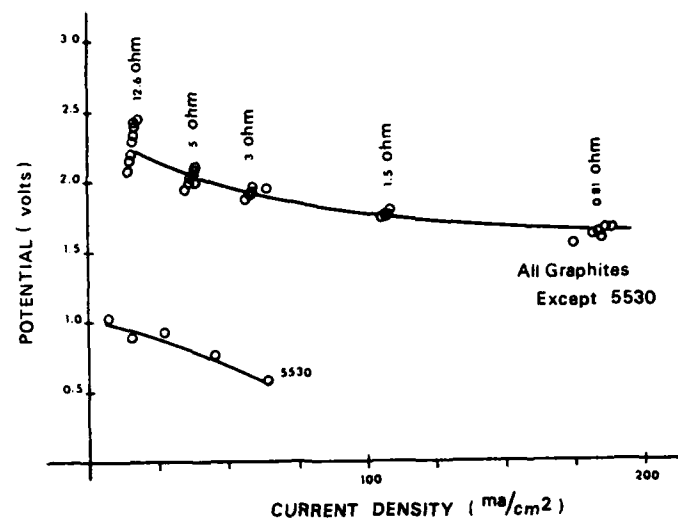


Figure 33. Potential vs. Current Density Comparing Different Graphites

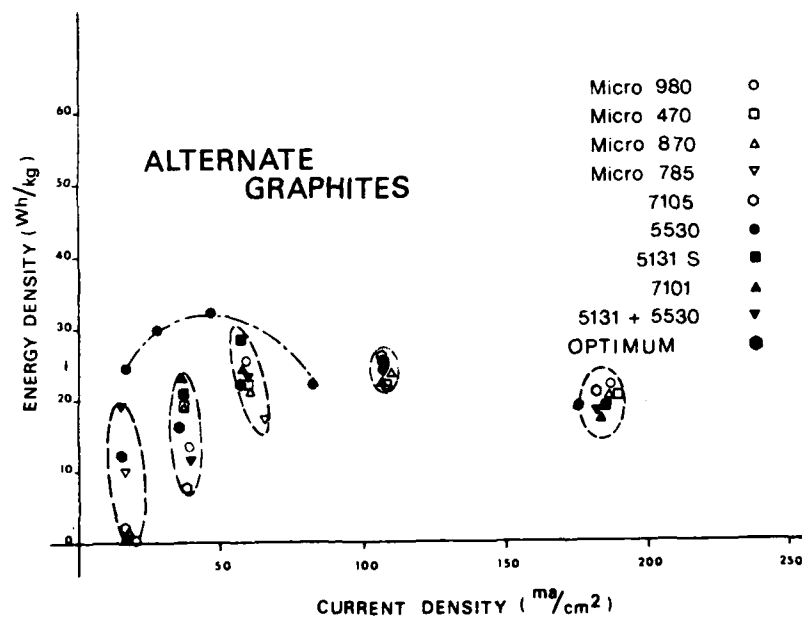


Figure 34. Energy Density vs. Current Density Curves Comparing Different Graphites

samples were of catholytes prepared with graphites designated MICRO 980 and MICRO 470. A second sample of MICRO 470 was tested to see if these results would repeat. The large exotherm was once again present.

For most of the DSC samples tested the sample is heated, allowed to cool, and then reheated. It should be noted that with the sample that contained the MICRO 470 the exotherm was observed during both heatings.

About a week later a second catholyte was prepared with MICRO 470 and was tested. Once again the large exotherm, coincident with the endotherm which generally accompanies melting, was observed.

A sample of the pure graphite was tested for 47°C up to 327°C and no features were observed in the spectrum at all. That is, the trace was a straight line and there was no hint of a feature at the 145°C to 165°C region.

At the present time there is no explanation for this exotherm.

After the first series of cell tests it was determined that two of the alternate graphite samples tested made cells that performed better than the others. However, at that time it was not determined whether either of these (#7101 or #S-5131) was superior to the Fisher #64 which had been used for all of the previous work done for this contract. To determine the superior graphite, three catholytes were prepared.

Upon examining the test results it was noticed that at similar discharge rates, i.e., 204 mA/cm², the energy densities measured were all practically the same. The Fisher #64 cells were slightly better. At the 37 mA/cm² rate the data were again similar with the Fisher #64, usually somewhat better. Graphite #S-5131 displayed an anomalous superior ED₇₀. One of each type of cell was vacuum desiccated for an additional two hours. Once again the three types of cells performed similarly with the Fisher #64 cell slight superior.

CONCLUSIONS:

- 1) of the nine different graphites tested and compared most seemed to make materials that performed about equally well;
- 2) three samples, #7101, #S-5131, and Fisher #64 performed better than the others; of these three, Fisher #64 was slightly superior;
- 3) one sample, #5530, was completely unsuitable for cell use;
- 4) the superior materials were more pure and of smaller particle size than most of the others; among the poorer performing samples were the least pure and coarsest samples;
- 5) the difference in the worst performance and the average performance is large while the difference in the best performance and the average is small; that is, many of the new materials were found to be inferior to the Fisher #64 but none were found to be superior;
- 6) there is still no clear indication of which impurity is most damaging to cell performance and there still is no clear indication of which particle size is optimum;
- 7) it has been found that the graphite makes a significant contribution to optimum cell performance. Evidence of this is the large difference in the best and the worst tests.

SECTION XII

A SULFUR CATHODE

Cells with sulfur catholytes have been tested. A regular test catholyte was prepared 56 % sulfur with 26 % NaAlCl_4 anolyte and 18 % graphite. Regular test cells were prepared with 28 % LiAl . Table 51 shows typical test results.

TABLE 51 SINGLE CELL TEST RESULTS FOR CELLS MADE WITH SULFUR CATHOLYTE

S/N	V_P	i_P	ED_{90}	ED_{80}	ED_{70}	R_{INT} PEAK	R_{INT} t_{90}	R_{INT} t_{80}	R_{INT} t_{70}	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm	
1768	0.76	86	1.3	2.7	3.8	3.7	3.7	4.8	3.3	0.81	Sulfur Catholyte
1769	1.33	24	0.6	2.2	5.8	3.4	3.4	2.9	4.2	5	
1770	1.20	9	0.4	1.2	3.0	7.8	3.7	8.0	6.1	12.6	
1771	0.79	15	0.9	2.6	3.7	6.1	7.2	10.4	6.7	5	160°C
1772	0.71	13	0.4	1.1	1.6	6.1	5.9	6.5	7.3	5	180°C
1769	1.33	24	0.6	2.2	5.8	3.4	3.4	2.9	4.2	5	200°C
1773	2.11	39	11.0	13.7	16.1	2.9	3.9	4.4	5.6	5	Charged
1774	2.02	37	5.9	8.3	10.2	2.1	2.9	3.2	4.0	5	Charged

As can be seen From Table 51 the cells did not perform well. The voltages were low and the internal resistances were high. The lifetimes were very short so the energy densities were very small. One of the reasons for this poor performance was the mobile catholyte.

An attempt was made to charge a couple of cells. One cell was placed in the single cell tester at 180°C. A 25 ohm resistor was put across the anode and cathode. Finally a 3.5 volt D.C. signal was passed through the resistor for 105 minutes. This was cell #1773. Cell #1774 was "charged" across a 50 ohm resistor for 5 hours at a rate of 1.0 to 1.2 amps. The power supply was turned off and the cell was allowed to cool. The cooled cells were then tested in the usual manner. The result was an order of magnitude increase in performance.

A new $\text{LiAlCl}_4/\text{S}_8$ catholyte was prepared and, with a LiAlCl_4 anolyte and 35% Mg anode, cells were prepared. These cells had two large differences from the previous S_8 cells:

- a) the LiAlCl_4 electrolyte, and;
- b) the anode containing 35% Mg.

The first three cells were tested just as they were made (see Table 52). No attempt was made to charge them. These cells were not much better than the ones tested before. There was an improvement in the internal resistance.

It was believed that these cells could be charged but there was no set pattern or procedure for charging. The next cell (S/N 1884) was charged, in the single cell tester at 160°C, at a rate of 2.0 amps until the voltage across the cell was 4.20v. The power supply was removed and the still hot cell was discharged across a 5 ohm resistor. When the cell had discharged to about t_{60} the load was removed and the cell was again charged up to 4.20v at a rate of 2.0 amps. Again the hot cell was discharged across a 5 ohm load.

The single cell tester was set twenty degrees cooler (to 140°C) and cell 1885 was then charged to 4.5v at a rate of 2.0 amps. The cell was disconnected from the power supply and removed from the single cell tester until

it reached room temperature. The cell tester was turned up to 150°C and the cell was discharged across a 5 ohm resistor.

Cell 1886 was charged at a slower rate, 1.5 amps up to 4.5v. The power supply was disconnected and the still hot cell was discharged across a 5 ohm resistor.

Cell 1887 was charged at the higher rate, 2.0 amps but only up to 4.1v. It was discharged hot. For the remainder of this report when a cell is discharged by attaching a load immediately after it has been charged and is still hot and activated, it will be described as "discharged hot". If a cell is removed from the hot tester platens and allowed to cool to room temperature before it is again inserted between the platens and tested it will be described as "discharged cool".

The next two cells, 1888 and 1889, were charged at a rate of 1.5 amps to 4.6v. They were then kept between the hot platens and the voltage was held constant at 4.6 volts for one hour. During this hour the current dropped to about 0.25 amps. Cell 1888 was discharged hot and cell 1889 was discharged cool.

Cell 1890 was only charged up to 3.25v before being discharged hot. Cell 1891 was only charged at a rate of 1.0 amps up to 4.6v. This cell was discharged hot.

Cells 1892 and 1893 were both charged at a rate of 1.5 amps up to 4.5v and both cells were discharged cool but the cooling procedure was a little different for each cell. After charging cell 1892, the power supply was not taken out of the circuit. That is the cell was allowed to cool with a constant 4.5v across the cell. Then the power supply was taken out of the circuit, the load applied, the cell activated and discharged. Cell 1893 was cooled with 4.1 volts across it.

TABLE 52 SINGLE CELL TESTS FOR CELLS MADE OF LiAlCl_4/S AND ANODES OF 35% Mg. THE CHARGING SEQUENCE WAS USUALLY DIFFERENT FOR EACH KIND OF CELL. THESE CELLS WERE DONE MOSTLY TO DEVELOP THE CHARGING METHOD.

S/N	V_p	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} PEAK	R_{INT} t_{70}	TEMP & LOAD	NOTES
	volts	mA/cm^2	Wh/kg	Wh/kg	Wh/kg	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$^{\circ}\text{C}$ and ohms	
1881	0.40	45.2	X	X	0.61	2.04	1.86	160 $^{\circ}$ 0.81 Ω	Cells not Charged
1882	1.09	19.9	0.66	2.13	4.09	2.26	0.35	160 $^{\circ}$ 5 Ω	
1883	1.16	8.4	X	2.92	4.80	X	X	160 $^{\circ}$ 12.6 Ω	
1884	1.88	34.4	25.5	29.9	32.7	X	6.71	160 $^{\circ}$ 5 Ω	This cell was charged, tested, and recharged and tested
	1.94	35.5	10.5	14.1	19.5	7.3	8.66	160 $^{\circ}$ 5 Ω	
1885	1.83	33.5	23.5	26.6	29.0	7.92	15.5	150 $^{\circ}$ 5 Ω	Discharged Cool
1886	1.78	32.6	26.0	28.0	30.8	8.81	8.74	150 $^{\circ}$ 5 Ω	Discharged Hot
1887	2.05	14.9	22.9	27.6	29.1	9.97	7.20	160 $^{\circ}$ 12.5 Ω	Discharged Hot
1888	1.63	29.8	21.8	26.3	28.3	10.9	14.1	150 $^{\circ}$ 5 Ω	These cells charged for 1 hr. at 4.6v
1889	1.76	32.2	15.2	19.5	24.1	X	9.47	150 $^{\circ}$ 5 Ω	
1890	1.73	31.7	17.9	22.7	26.4	10.9	9.47	150 $^{\circ}$ 5 Ω	Charged to 3.25v
1891	1.61	29.5	17.4	19.5	21.4	20.2	13.1	140 $^{\circ}$ 5 Ω	Charged to 4.60v
1892	1.94	35.5	26.8	30.7	32.2	5.77	5.47	150 $^{\circ}$ 5 Ω	Cooled at 4.5v
1893	2.01	36.8	25.1	30.7	32.5	4.05	5.92	150 $^{\circ}$ 5 Ω	Cooled at 4.2v
1894	1.84	33.7	21.0	23.7	25.3	6.25	11.9	160 $^{\circ}$ 5 Ω	Stored 1 Day
1895	1.82	33.3	16.8	18.8	20.4	5.86	17.1	160 $^{\circ}$ 5 Ω	Stored 3 Days

Cells 1894 and 1895 were charged and cooled and then stored in the dry box before testing. Cell 1894 was stored for 1 day and cell 1895 was stored for 3 days.

These tests showed that there was a least an order of magnitude difference in the uncharged and charged cells. The charged cells had consistently good 90% energy densities. All of these sulfur cells have had high internal resistances.

The best charging procedure found was;

- 1) activate the cell, no load;
- 2) charge the cell at a constant rate of 1.5 amps until the voltage climbs to 4.2v;
- 3) hold the voltage constant at 4.2v until the diminishing current reaches a minimum;
- 4) remove the cell from the hot platens;
- 5) when the cell reaches room temperature remove the constant 4.2v.

There was evidence of catholyte flow for each cell tested. The sulfur was obviously flowing. To remedy this it was decided to mix the sulfur with kaolin.

A Petri dish half filled with sulfur was placed on a hot plate in the fume hood. The temperature was allowed to increase slowly until the sulfur melted to a clear yellow melt (about 1 hour). Then a volume of calcined kaolin (about 1/4 the original volume of S_8) was slowly stirred into the molten sulfur. The kaolin wetted immediately. The Petri dish was removed from the hot plate and allowed to cool. The cooled melt came out of the Petri dish easily and was easily ground and sieved. This material was used with A #1096 to make a catholyte (C #1241).

Another mixture of sulfur and kaolin was prepared like this. One volume of kaolin was mixed with 2 volumes of sulfur. The two powders were mechanically mixed and poured level into a Petri dish. The mixture was slowly heated on a hot plate until the S_8 melted and wetted the kaolin. The mixture was cooled, ground, and sieved before being used to prepare a catholyte (C #1243). These powders were used to make cells with the 35% Mg anodes and the $LiAlCl_4$ electrolytes. Table 53 contains the results of these cells.

TABLE 53 SINGLE CELL TEST RESULTS OF CELLS PREPARED WITH SULFUR FUSED WITH KAOLIN. THE TOP CELL HAS NOT BEEN CHARGED, THE MIDDLE CELL WAS DISCHARGED COOL, AND THE BOTTOM CELL WAS DISCHARGED HOT. ALL TESTS WERE AT 160°C ACROSS A 5 OHM LOAD.

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{90}	R_{INT} t_{80}	R_{INT} t_{70}	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1899	0.82	15.0	1.01	1.78	2.54	11.0	9.00	8.20	10.5	1/3 Kaolin
1900	1.98	36.2	33.0	38.2	40.1	4.97	2.88	4.11	4.61	Fused With
1901	1.92	35.1	23.7	29.9	32.3	8.82	5.18	8.80	7.81	The Sulfur

These cells were much better than the cells not mixed with kaolin. For a cell not mixed with kaolin the ED₉₀ might be expected to be from 20 to 25 Wh/kg. However, after adding the kaolin the expected value of the ED₉₀ went to 30 to 35 Wh/kg and ED₈₀ went to 35 to 40 Wh/kg. It was also noticed that the cells discharged cool always did better than the cells discharged hot.

These cells appeared to have more than enough sulfur so three tests were made with cells larger than normal anodes. It had always previously been believed that the cell lives were cathode limited. However, it was possible

that the 35% Mg anodes had caused the cells to be anode limited. However, the heavy anode cells did not perform as expected.

Whenever any of these sulfur cells were tested some yellow condensation formed on the cooler mica insulators. It was believed that this was sulfur. In an attempt to operate the cells a little cooler a catholyte was prepared from A #1106, the mixed LiAlCl_4 and NaAlCl_4 anolyte. This was C #1245.

TABLE 54 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH MIXED, LiAlCl_4 ELECTROLYTE. ALL
TESTS ARE AT 160°C AND 5 OHMS. THE LAST THREE
CELLS WERE MADE FROM PARTIALLY FUSED CATHOLYTE

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{90}	R_{INT} t_{80}	R_{INT} t_{70}	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1910	1.11	20.3	1.02	1.89	3.87	7.37	4.55	3.45	5.79	Not Charged
1911	1.90	34.8	28.7	32.7	35.4	7.01	3.32	5.50	6.47	Discharged Cool
1912	1.93	35.3	29.8	34.8	38.1	8.35	3.23	3.31	3.39	Discharged Hot

These cells were not particularly good. However, a second set of cells (S/N 1910, 1911, 1912) were a little different. Some catholyte, C #1245, was heated in a Petri dish on a hot plate in the dry box. As the temperature slowly increased from room temperature some white-yellow, very fine droplets condensed on the lid of the Petri dish. Cells made with these materials were superior to cells with unfused catholyte. It is also interesting to note that when these cells were tested the white-yellow droplets that usually form on the cooler mica of the cell tests did not form.

It was believed that LiAlCl_4 made superior electrolyte for sulfur cells. However, it was also felt that an acid electrolyte would be superior to an alkali saturated electrolyte. Some more sulfur cells were tested with a LiAlCl_4 electrolyte made acidic by mixing with acidic NaAlCl_4 (69 m/o AlCl_3).

TABLE 55 SINGLE CELL TEST RESULTS FOR
CELLS PREPARED WITH SULFUR CATHOLYTES

S/N	V_P	i_P	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{90}	R_{INT} t_{80}	R_{INT} t_{70}	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1913	1.06	19.4	1.31	1.89	2.86	5.18	5.20	6.83	5.93	Not Charged
1914	1.92	35.1	24.6	27.1	29.1	6.74	2.97	3.93	4.12	Discharged Hot
1915	1.90	34.8	22.5	24.6	26.3	8.30	3.56	4.61	5.17	Discharged Cold
1916	1.86	34.0	8.88	12.1	15.9	2.75	2.47	2.44	2.01	Charged 3½ Hrs.
1917	0.96	17.6	0.95	1.54	2.50	8.78	8.20	2.70	7.19	Not Charged
1918	1.96	35.9	25.9	30.1	32.5	5.04	2.08	3.86	4.37	Discharged Hot
1919	1.99	36.4	25.9	30.9	33.5	5.83	2.60	3.21	2.95	Discharged Cold
1920	0.89	16.3	1.16	1.77	2.28	10.8	10.7	13.8	5.62	Not Charged
1921	1.93	35.3	18.0	21.5	22.9	4.16	2.40	2.36	4.43	Discharged Hot
1922	2.01	36.8	13.1	21.2	22.9	7.71	3.92	4.37	3.95	Discharged Cold
1923	1.11	20.3	1.72	2.55	3.64	2.38	5.47	2.35	4.55	Not Charged
1924	1.91	34.9	29.5	34.8	37.2	7.98	5.41	4.85	4.80	Discharged Hot
1925	1.73	31.7	10.2	18.9	22.4	23.2	10.6	13.9	15.6	Discharged Cold
1926	1.99	36.4	29.0	32.9	34.7	5.64	2.62	4.13	3.98	160°C
1927	2.05	37.5	27.9	33.1	35.1	4.39	2.80	3.14	2.86	180°C
1928	2.03	37.1	25.4	29.0	30.4	3.71	2.27	3.73	3.21	200°C
1929	2.10	38.4	19.5	27.6	29.8	3.63	2.47	4.43	3.46	220°C

Cells #1913 - 1915 (see Table 55) were the first of these cells to be tested. The results were not particularly good. Cell #1916 was charged for $3\frac{1}{2}$ hours. It was worse than the others. None of these cells were as good as the best cells tested previously.

Previous experience showed that fusing the catholyte could be beneficial, so, the catholyte was fused, reground, and sieved. It seemed to work. There was a small increase in capacity and voltage. However, these cells still were not particularly good.

Another set of cells were made with a large anolyte layer and a small catholyte layer. The anode was unchanged. These cells (#1920 - 1922) were only about $\frac{2}{3}$ as good as the other cells so this approach was abandoned.

The next set of cells were made with large anodes. These did show significant improvement (#1923 - #1925). Cell #1924 was the best cell tested during this series of tests.

None of the above mentioned cells were better than the cells made earlier. It was believed that these cells would be better. One possible explanation for this is the use of a mixture of NaAlCl_4 and LiAlCl_4 . The mixture sounds good but practical experience at this facility has demonstrated that this particular combination has always been disappointing. The reason it was used was because an acidic catholyte matrix was desired. Ideally an acidic LiAlCl_4 should have been used. The mixture of NaAlCl_4 (69 m/o AlCl_3) with LiAlCl_4 (LiCl saturated) was just a substitute. It was felt that perhaps an acidic NaAlCl_4 catholyte would be better than the mixed catholyte even if it wasn't as good as an acidic LiAlCl_4 catholyte.

So, a new catholyte, C 1249, was prepared from the slightly acidic NaAlCl_4 (52 m/o AlCl_3). The tests of cells made with this catholyte were #1926 -

#1929. These cells were all tested across a 5Ω resistor; all were tested at different temperatures; and these cells were tested after cooling from the charging temperature to room temperature. These cells, taken as a group were not much better than any other group of cells tested. They still were not superior to the cells tested previously and they were certainly not superior to cells made with CuCl_2 .

CONCLUSION:

Thermal battery cells can be made from elemental sulfur. These cells have no capacity unless charged. The best way to charge the activated cells is at a rate of 1.5 amps up to a voltage of 4.2 volts. The voltage should be held constant at 4.2v until the current drops to a minimum. The voltage should be maintained while the cell is allowed to cool to room temperature. The capacity of the charged sulfur cells is significant but not necessarily superior to CuCl_2 cells. The capacity to t_{90} for charged sulfur cells is superior to CuCl_2 cells.

Sulfur was the best cathode material, except for metal chlorides, tested during this program. It had the advantages of being cheap, in good supply, of being easy to work with, of being a moderate energy producer, of not being volatile and, therefore, quite storable. However, it was not an extraordinary energy producer, its storage life is still quite doubtful, and the cells have to be charged before they are useful.

SECTION XIII

CATHOLYTES IMMOBILIZED WITH BINDERS

Post mortem examinations of many of the first MoCl_5 batteries showed symptoms of possible electrolyte flow. To correct this possible problem a catholyte was prepared which contained 10 ^{w/o} Cab-O-Sil.

An anolyte was prepared by mixing and fusing 40 ^{w/o} Cab-O-Sil into NaAlCl_4 . This anolyte was then mixed into a test catholyte.

26 mg 40 ^{w/o} Anolyte

56 mg MoCl_5

18 gm Graphite

The test catholyte then contained 10 ^{w/o} Cab-O-Sil.

The DSC spectrum of the catholyte displayed very small peaks. The tests were repeated with a larger sample but once again only very small peaks were observed.

It was difficult to make cells with this material because the bulk density of the catholyte was so low. One cell was finally constructed and it had a total weight of only 2.8 grams instead of 4.1 grams. The lifetime of this cell was very poor.

In some more recent work it became advantageous to make some anolytes by mechanically mixing kaolin with NaAlCl_4 instead of the usual fusion of Cab-O-Sil into NaAlCl_4 . In order to prevent flow of the molten salts it was necessary to use 40 ^{w/o} kaolin. Catholytes made with this anolyte contained 10 ^{w/o} kaolin. These cells were just as dense as regular test catholyte and there was no difficulty making cells.

The cells tests were rather unexciting. The peak voltages and energy densities were slightly lower than for cells made with regular test catholyte. This was because of a significant increase of resistance in the cells. There was no evidence of flow in any of these cells. Kaolin can be used as a binder in situations where fusing the electrolyte is not desirable.

CONCLUSION:

Due to the early MoCl_5 work it was believed that catholyte flow was a problem. It was thought that the problem could be solved by adding binder to the catholyte. Cab-O-Sil was not effective because it must be fused into the mix. Kaolin was effective because it was only necessary to mechanically mix in the kaolin. However, when MoCl_5 was abandoned and CuCl_2 was substituted the problem of catholyte flow became irrelevant.

SECTION XIV

ALTERNATE ELECTROLYTES

Three alternate electrolyte materials have been tested:

- 1) LiCl:KCl eutectic
- 2) LiAlCl₄
- 3) acidic NaAlCl₄ & acidic LiAlCl₄

LiCl:KCl

In view of some of the storage problems which occurred during storage testing some new cell material combinations were tried. FeS₂ is a very stable material but it has previously been determined that it only functions well at temperatures too high for NaAlCl₄. For these reasons cells were made with LiCl·KCl eutectic anolyte.

Two catholytes were used with these cells - FeS₂ and a mixture of FeS₂ and graphite. Two anodes were used - LiAl and Mg. Some cells were also made with V₂O₅ catholytes as control cells.

An FeS₂ catholyte was prepared by mixing 66 ^{w/o} FeS₂ with 33 ^{w/o} LiCl·KCl eutectic anolyte. This same anolyte was used to make the cells. The anode was LiAl, 20 ^{w/o}. The cell formula was:

Anode	0.50 gm <u>±</u> .1
Anolyte	1.20 gm <u>±</u> .1
Catholyte	<u>1.30 gm <u>±</u> .1</u>
Total Wt.	3.00 gm <u>±</u> .1

A similar catholyte was made with graphite with this formula:

3 parts LiCl-KCl eutectic anolyte

6 parts FeS₂

1 part graphite

While the cell without graphite produced an energy density greater than any NaAlCl₄ cell yet tested the cells with carbon in the catholyte produced even more (Table 56).

Another set of cells was made with Mg anodes (Table 56). Once again the cells with FeS₂/carbon mixture were superior.

TABLE 56 SINGLE CELL TEST RESULTS FOR CELLS USING LiCl-KCl ELECTROLYTES, AND FeS₂ CATHODES. THE CATHODES WHICH CONTAINED GRAPHITE WERE SUPERIOR

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	Spec. R Peak	Spec. R 80	Load	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohms	
1505	1.13	128	270	300	28.8	38.3	2.41	2.64	.81	LiAl FeS ₂
1504	1.70	31.1	1173	X	54.3	X	.964	4.49	5	
1506	2.02	14.7	1770	1892	38.6	40.6	X	X	12.6	
1513	1.61	182	244	276	61.7	67.0	.367	.690	.81	LiAl FeS ₂ , C
1515	1.82	33.3	1140	1177	60.1	61.4	.970	3.42	4	
1514	2.09	15.2	950	1522	22.3	32.6	.656	2.42	12.6	
1517	1.06	120	443	732	39.2	58.5	.825	.746	.81	Mg FeS ₂
1516	1.25	22.9	2160	3042	47.2	60.4	.434	1.04	5	
1518	1.47	10.7	6066	X	64.5	X	3.60	1.14	12.6	
1521	1.19	134	633	903	76.4	99.1	.145	.156	.81	Mg FeS ₂ , C
1520	1.48	27.1	1795	4465	48.8	105	1.79	.452	5	
1524	1.63	11.8	380	9819	5.12	101	.835	.524	12.6	

Note in Table 56 that the Mg cells were superior to the LiAl cells even though they had a lower voltage. So far in this program the cell with the highest energy density measured to 80% of peak has been cell #1521, a LiAl/KCl·LiCl/LiCl·KC, FeS₂, C type cell. This cell was producing current at a rate of 134 mA/cm² (max.) and energy at a rate of 76 Wh/kg to 80% and 99 Wh/kg to 70%. The best cell to 70% was #1520 which produced 105 Wh/kg.

It has been observed that NaAlCl₄ electrolytes do not function well with oxide cathodes. However, for this series of cells the electrolyte was LiCl·KCl. This electrolyte works well with oxides. Therefore, V₂O₅ catholyte was tried with both LiAl and Mg anodes. These cells were also tested at 350°C, 400°C, 450°C and 470°C. The low extreme of 350°C is too low for this electrolyte. The cells at 400°C were usually the best tests.

TABLE 57 SINGLE CELL TEST RESULTS FOR
CELLS OF THE M/LiCl·KCl/V₂O₅ TYPE

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	Spec. R Peak	Spec. R t ₈₀	Load	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohms	
1527	2.76	311	60	75	44.3	51.7	.74	1.64	.81	LiAl/LiCl· KCl/V ₂ O ₅
1526	3.05	55.8	212	265	30.4	35.6	X	3.81	5	
1529	2.32	262	76	126	38.9	56.2	.78	1.22	.81	Mg/LiCl· KCl/V ₂ O ₅
1528	2.60	47.6	242	376	21.7	31.1	1.23	3.24	5	

TABLE 58 THE 400°C CELL TESTS
WERE USUALLY BETTER

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	Spec. R Peak	Spec. R t ₈₀	Temp	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1508	0.88	16.1	133	197	1.61	2.12	21.5	26.9	350	LiAl/LiCl· KCl/FeS ₂
1500	1.66	30.4	1450	1683	62.7	69.4	2.79	X	400	
1504	1.70	31.1	1173	X	54.3	X	0.94	4.49	450	
1511	1.77	32.4	728	X	37.1	X	0.91	X	470	
1515	1.66	30.4	1862	2038	78.9	84.0	0.97	3.1	400	LiAl/KCl· LiCl/FeS ₂ ,C
1512	1.82	33.3	1140	1177	60.1	61.4	0.30	2.1	450	
1519	1.29	23.6	2456	3145	55.4	66.5	0.84	1.02	400	Mg/LiCl· KCl/FeS ₂
1516	1.25	22.9	2160	3042	47.2	60.4	0.43	1.04	450	
1522	1.27	23.2	1553	1963	33.7	40.0	0.42	2.04	400	Mg/LiCl/ KCl/FeS ₂ ,C
1520	1.48	27.1	1795	4465	48.8	105.1	1.79	0.45	450	

CONCLUSION:

From these tests it was concluded that FeS₂ is a good cathode material but only at the relatively high temperature of 400° to 450° and then with the LiCl·KCl electrolyte. As good as they were, none of these cells were of an optimum configuration.

LiAlCl₄:

Some LiCl saturated LiAlCl₄ was received from Alcoa. To test this material the LiAlCl₄ was mixed with 10 % Cab-O-Sil, fused, ground, and sieved like a regular NaAlCl₄ anolyte. This anolyte was mixed with CuCl₂ and graphite to make a LiAlCl₄ catholyte. Some cells were made with both LiAlCl₄ electrolytes, some with LiAlCl₄ anolyte and NaAlCl₄ catholyte and vise versa. Table 59 shows some single cell test results

TABLE 59 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH LiAlCl₄ ELECTROLYTE POWDERS

S/N	V _p	i _p	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT} Peak	R _{INT} t ₇₀	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm-cm ²	ohm-cm ²	ohm	
1756	1.61	182	11.5	19.8	22.5	X	1.2	0.8	Li ⁺ anolyte and Li ⁺ catholyte
1750	1.89	35	37.7	53.3	54.3	0.3	X	5	
1758	1.93	14	27.3	42.7	43.4	0.7	0.3	12.6	
1759	1.60	181	4.4	16.2	22.1	2.1	X	0.8	Na ⁺ anolyte and Li ⁺ catholyte
1760	2.22	41	2.4	9.5	34.2	1.7	3.0	5	
1761	2.27	17	1.4	8.8	43.2	2.4	4.2	12.6	
1762	1.42	160	6.9	13.7	20.7	2.3	3.1	0.8	Li ⁺ anolyte and Na ⁺ catholyte
1763	1.90	35	4.8	14.4	22.1	3.2	2.7	5	
1764	1.94	14	3.1	4.0	22.5	2.8	0.9	12.6	

It can be seen that the data in Table 59 are divided into three horizontal ranks. The three cells represented in the top rank were made with both electrolytes, anolyte and catholyte, made with LiAlCl₄. With the middle rank, only the catholyte contained LiAlCl₄ and for the bottom rank, only the anolyte contains lithium.

For many of these cells the t_{90} 's and t_{80} 's were quite long but the t_{70} 's were only a little longer than the t_{80} 's. This is why the ED_{80} 's and ED_{70} 's are so similar for some of the tests. That is because the voltage suddenly started to drop just after t_{80} . This is particularly evident with the cells made with both $LiAlCl_4$ electrolytes, S/N 1750 & 1758. Also evident in this set of data was the exceptionally large ED_{90} (37.7 Wh/kg) for cell 1750.

The cells made with the lithium electrolyte were very good cells and they performed as well as, or even better than, analogous $NaAlCl_4$ cells. To understand this, the data for cells 1756, 1750, and 1758 should be compared to analogous $NaAlCl_4$ test data.

The cells made with both $LiAlCl_4$ in the catholyte and anolyte were tested for temperature dependence. A series of cells was tested from 100°C to 300°C , to 20°C intervals, across a 5 ohm resistor. Table 60 is a tabulation of these test results.

TABLE 60 SINGLE CELL TEST RESULTS OF CELLS MADE FROM ELECTROLYTES PREPARED WITH $LiAlCl_4$ AND TESTED ACROSS A 5 OHM RESISTOR AT VARIOUS TEMPERATURES

S/N	V_F	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} Peak	R_{INT} t_{70}	TEMP	NOTES
	volts	mA/cm^2	Wh/kg	Wh/kg	Wh/kg	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$^\circ\text{C}$	
1745	0.31	6	0.14	0.20	X	437	X	100	$LiAlCl_4$ anolyte & $LiAlCl_4$ catholyte & $CuCl_2$ & 28 W/o $LiAl$
1746	1.00	18	0.88	1.2	2.1	33	38	120	
1747	1.81	33	7.6	25.1	32.5	3.7	4.1	140	
1748	1.86	34	27.8	42.8	45.2	1.7	0.4	160	
1749	1.91	35	17.5	51.1	53.3	0.6	0.4	180	
1750	1.89	35	37.7	53.3	54.3	0.3	X	200	
1751	1.88	34	33.8	43.2	44.2	0.6	0.4	220	
1752	1.88	34	32.7	X	X	0.3	X	240	
1753	1.88	34	27.0	32.8	34.8	0.3	X	260	
1754	1.88	34	13.2	18.0	19.1	0.3	X	280	
1755	1.89	35	14.1	17.3	18.2	0.3	1.6	300	

These data are further illustrated by Figure 35. Figure 35 shows how energy density varies with the test temperature. There are two groups of curves. The solid lines represent the energy densities measured to t_{90} , t_{80} , and t_{70} for cells prepared with LiAlCl_4 electrolytes. The dotted lines represent analogous data for cells prepared with NaAlCl_4 . The NaAlCl_4 data was taken from single cell tests #1180 thru #1192.

A number of observations can be made from Figure 35. First, the three energy density curves for the NaAlCl_4 cell are relatively even spaced but the LiAlCl_4 , ED_{80} and ED_{70} curves are quite close together. This is because $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2$ cells have very flat discharge curves and the $\text{LiAl}/\text{LiAlCl}_4/\text{CuCl}_2$ cells tend to drop off very quickly after t_{80} .

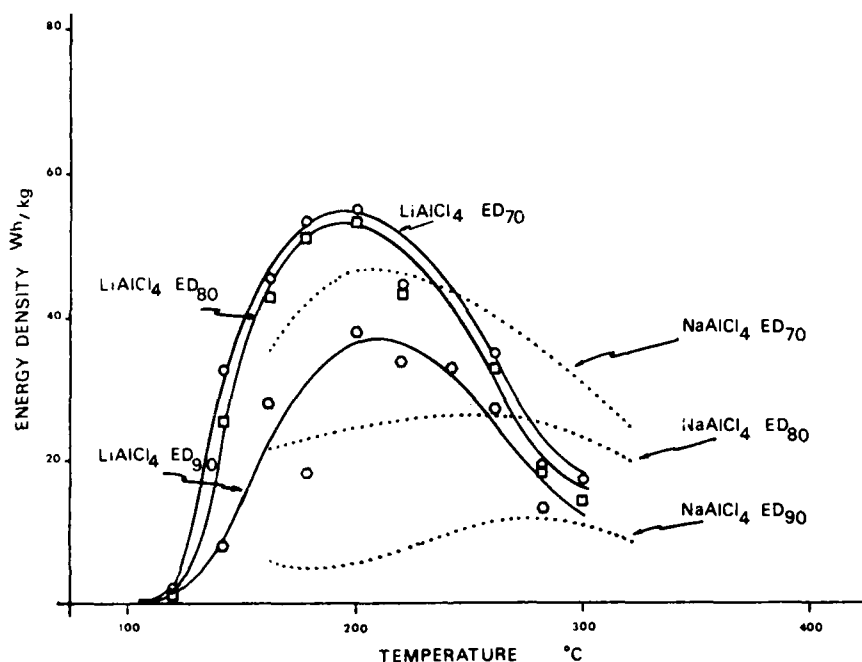


Figure 35. Energy Density vs. Temperature Curves Comparing LiAlCl_4 And NaAlCl_4 Type Cells

Second it could be observed that the energy densities of the LiAlCl_4 cells were generally much greater than the NaAlCl_4 cells. This is not completely true because the NaAlCl_4 data points are "old". That is, more recent $\text{NaAlCl}_4/\text{CuCl}_2$ cell tests would cause one to expect a better ED_{80} and ED_{70} than is shown from these data (because of vacuum desiccation, new press procedures, superior graphites, etc., which were unknown when the "old" data were collected). However most of the advances in the NaAlCl_4 cell technology have had little effect upon t_{90} or ED_{90} . Most of their impact has been upon t_{80} and t_{70} . Therefore, the observation that there is a large, significant increase in ED_{90} is valid.

Third, it has been noticed that the NaAlCl_4 cells appear to be less affected by temperature change than LiAlCl_4 cells. However, it was noticed that, by mixing LiAlCl_4 and NaAlCl_4 it could be possible to prepare cells with a very large temperature independence.

An electrolyte was prepared by mixing equal weights of NaAlCl_4 and LiAlCl_4 . To this mixture 10 % Cab-O-Sil was blended in to prepare an anolyte. The mixture was fused and sieved. This anolyte was blended with CuCl_2 and graphite to make a catholyte.

The results of these tests were not very good (Table 61). There was a noticeable "spike" above 180°C . This caused all of the t_{90} 's to be short and all of the ED_{90} 's were small. The ED_{80} 's gradually increased to a maximum of 19.4 Wh/kg at 240°C . The ED_{70} 's did not reach a maximum even at 300°C . The ED_{70} 's from 240°C or hotter were respectable but still not exceptional.

The last two cells were an attempt to lessen the spike by vacuum desiccating the cells, in a vacuum oven at 165°C , for three hours, just prior to testing. While the spike was lessened somewhat the lifetimes were also considerably shortened. A post mortem examination showed a grey darkening at

the anode/anolyte interface such as has been previously reported for cells stored in hot storage battery units. For this reason it was felt that the anodes may have been affected by the overnight storage in a vacuum oven held at 165°C.

Post mortem examination of all of the cells made with LiAlCl_4 have displayed symptoms of minor electrolyte flow. For this reason a new anolyte, A #1096, has been prepared with 12 % Cab-O-Sil and tested.

TABLE 61 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH ELECTROLYTES OF BOTH NaAlCl_4 AND LiAlCl_4
BLENDED TOGETHER

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{70}	TEMP	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1776	0.70	12.8	0.56	0.90	1.12	38.3	41.1	100	5 ohm Load
1777	1.30	23.8	1.45	2.97	5.02	20.0	12.7	120	
1778	1.53	28.0	4.41	8.67	15.1	12.9	6.6	140	
1779	1.83	33.5	2.91	5.86	25.2	9.0	2.5	160	
1780	1.95	36.7	3.02	7.71	27.7	4.64	2.31	180	
1781	2.03	37.1	2.22	10.0	31.5	3.08	1.51	200	
1782	2.04	37.3	2.09	13.1	34.8	2.08	0.75	220	
1783	2.05	37.5	2.00	19.4	41.1	1.56	0.19	240	
1784	2.08	38.1	2.12	19.2	36.6	1.56	0.19	260	
1785	2.15	39.3	2.35	15.4	44.0	1.01	1.76	280	
1786	2.22	40.6	2.11	12.4	52.4	1.71	0.14	300	
1787	1.61	182	3.91	13.9	22.4	2.95	1.23	240	0.81 ohm
1783	2.05	37.5	2.00	19.4	41.1	1.56	0.19	240	5 ohm
1788	2.24	16.3	1.02	6.38	49.3	1.22	0.44	240	12.6 ohm
1789	2.06	37.7	2.33	5.45	20.8	3.56	1.12	240	5 ohm
1790	2.11	15.3	1.08	7.29	27.7	3.86	0.47	240	

These cells made with this material were not particularly good. They were similar in performance to the previous set of cells made with the mixture of NaAlCl_4 and LiAlCl_4 . The post mortem of those cells also showed a darkened anode. These cells were also stored overnight in a vacuum oven at 165°F . It is therefore suspected that the poor performance was caused by the overnight storage in the vacuum oven.

Earlier some cell tests were reported with cells made from anolyte prepared with LiAlCl_4 and catholyte prepared with NaAlCl_4 . At that time it was noted that, while the difference between t_{90} and t_{80} was large, the cell died very quickly after t_{80} . It was thought that one possible cause for this behavior was that the anode, which contained 35 % Mg, was being consumed too quickly. For this reason a set of cells was made with cells that had large anodes.

The test results show that the use of a large anode (made larger at the expense of the anolyte) did not cause an improvement. The cells tested earlier were, overall, better. It is interesting that, once again, the best operating temperature was 240°C . For this reason, two more cells were made and tested at 240°C and different resistive loads (0.81Ω and 12.6Ω).

It was suspected that the above cells would have done even better if fresh LiAl was used so a new batch was opened. There was an apparent small improvement made. Because of this improvement the series of cells run earlier was repeated with noticeable improvement. One of these cells was tested at 260°C and had superior results.

Finally, it was recalled that all cells were being routinely desiccated overnight before testing. It was thought that perhaps this practice had an unknown negative effect on cell performance.

When it became evident that routine cell desiccation had a degrading effect upon the cells more of the earlier LiAlCl_4 cell tests were repeated.

Table 62 contains many of these cell tests.

TABLE 62 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH BOTH ELECTROLYTES, NaAlCl_4 AND LiAlCl_4

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{70}	LOAD or TEMP.	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm-cm ²	ohm-cm ²	ohms or °C	
1829	1.77	32.4	22.1	46.7	50.9	0.62	1.56	160°	LiAlCl ₄ anolyte NaAlCl ₄ catholyte 5n Fresh Cells
1830	1.78	32.6	31.8	48.8	51.7	1.20	0.22	180°	
1831	1.79	32.8	35.5	48.5	51.3	0.60	0.43	200°	
1832	1.83	33.5	34.5	51.8	55.0	0.90	1.08	220°	
1833	1.81	33.1	38.9	48.0	50.4	0.89	0.21	240°	
1834	1.78	32.6	38.9	45.4	47.3	0.31	0.22	260°	
1835	1.79	32.8	35.9	41.2	43.0	0.60	0.85	280°	
1836	1.68	190	15.8	33.0	44.1	0.54	1.15	.81n	240°C
1833	1.81	33.1	38.9	48.0	50.4	0.89	0.21	5n	
1837	1.86	13.5	30.9	35.6	36.8	0.38	1.05	12.6n	
1838	1.93	14.0	22.9	39.2	41.3	2.13	0.50	12.6n	Stored 48 hours
1839	1.99	36.4	5.33	29.5	47.3	2.61	1.53	160°	NaAlCl ₄ anolyte LiAlCl ₄ catholyte 5n
1840	2.04	37.3	4.99	27.2	51.9	1.56	0.19	180°	
1841	2.09	38.2	6.03	30.2	57.0	2.54	1.90	200°	
1842	2.20	40.3	3.08	5.87	20.3	2.42	x	200°	3 hours Dess.
1843	1.61	182	10.2	22.7	38.1	0.57	0.97	.81n	Light anolyte Heavy catholyte 200°C
1844	1.80	32.9	21.7	37.9	49.3	1.20	0.43	5n	
1845	1.85	13.4	26.5	36.1	41.7	0.74	0.53	12.6n	
1846	1.81	33.1	26.1	42.7	49.7	0.43	0.60	5n 240°C	Light An. Heavy Cath.

The first eleven tests in Table 62 were made with cells which had LiAlCl_4 anolytes and NaAlCl_4 catholytes. These eleven tests are divided into three groups. The first group of seven cells were all tested across a 5 ohm resistor but the test temperature was different for each test. The next group of three cells were all tested at 240°C but each was tested across a different resistor. The last cell S/N 1838 was tested at 240°C across a 12.6 ohm resistor (as was S/N 1837) but it had been stored for 48 hours in the dry box prior to testing. This was not a "fresh cell" but it was not a desiccated cell either.

The first thing to be noticed about these data is how similar they all are. The energy densities are consistently good across the entire temperature range. There is a difference across the current density range but they are still all good. This is somewhat illustrated in Figure 36. For further information compare Figure 36 with Figure 35.

Cell S/N 1838 was stored for 48 hours in the dry box just to test the effect of storing cells in the dry box. This test shows that this cell was as good or better than the other cells and was apparently not affected by the storage. This shows that it was the desiccation responsible for the earlier poor cell performance and not just the storage alone.

The remaining eight cells in Table 62 are made with NaAlCl_4 anolytes and LiAlCl_4 catholytes, just opposite of the previous eleven cells. These tests are divided into four groups. The first group of three tests (cells S/N 1839, 1840, 1841) were tested across a 5 ohm load but at varying temperatures. This series was much shorter than the previous series. Notice the significant drop in the energy densities at t_{80} . The energy densities at t_{70} were as good as for the earlier series of cells. This is because of these cells had a slight

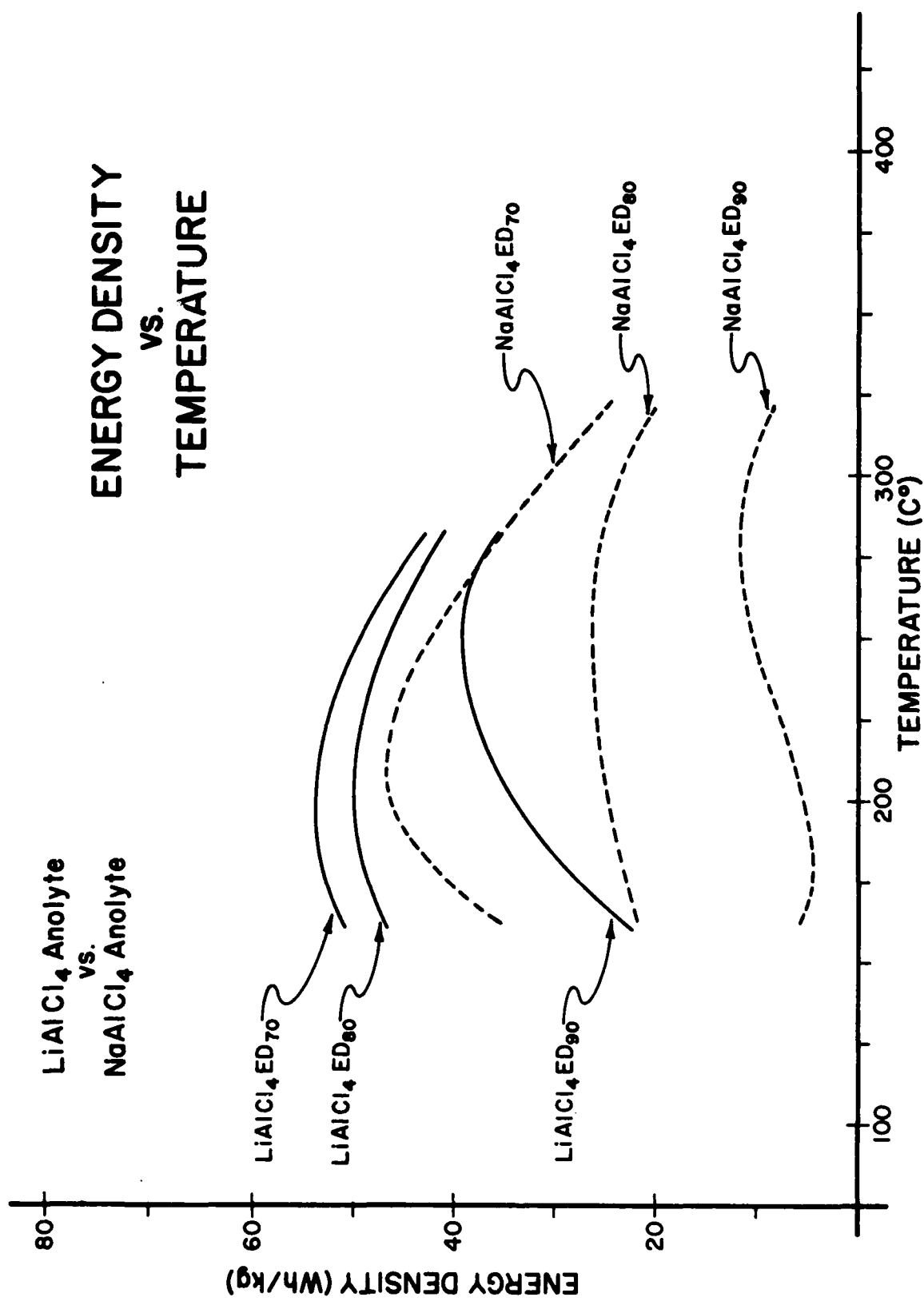


Figure 36. Energy vs. Temperature

tendency toward spike formation. This tendency was not very strong but not much is needed to seriously impair performance. Because of this tendency one cell was vacuum desiccated. This was cell S/N 1842. The cell performance was very poor with a large reduction in energy density and a large increase in internal resistance.

The next four cells were made with a slightly different cell formula:

anode = 0.45 gm \pm .1 gm (normal weight)

anolyte = 1.60 gm \pm .1 gm (lighter than normal)

catholyte = 2.05 gm \pm .1 gm (heavier than normal)

Total Weight = 4.10 gm \pm .1 (normal weight)

The regular cell formula was chosen after a factorial design study was done on cells similar to these. However, these tests were influenced by a significant spike tendency. These recent cell tests did not have a great tendency to form a spike. Therefore, it was possible that the regular cell formula was not the optimum. Since previous experience has demonstrated that the cell life is cathode limited it was decided to make cells with a larger catholyte, holding the anode the same. The idea did not work. These cells (S/N 1843, 1844, 1845, and 1846) had lower energy densities than the other cells.

Another previously reported experiment was the mixing of LiAlCl_4 and NaAlCl_4 to make up one anolyte. The cell tests were not particularly good. Since there was a possibility the poor performance was caused by the routine cell desiccation these tests were repeated with fresh cells. Table 63 contains the results of these newer tests.

TABLE 63 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH ELECTROLYTE POWDERS OF LiAlCl_4 AND
 NaAlCl_4 MIXED TOGETHER

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{70}	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohms	
1847	1.72	194	10.9	23.4	33.8	0.97	0.35	.81	Mixed elect- rolyte in anolyte & catholyte 200°C
1848	2.05	37.3	0.81	29.9	48.3	1.08	0.74	5	
1849	2.18	15.8	0.21	13.4	47.4	1.28	0.88	12.6	
1850	1.50	169	10.0	17.4	24.6	1.59	1.63	.81	Mixed Anolyte NaAlCl_4 Catholyte 200°C
1851	1.81	33.1	8.33	33.6	50.6	0.60	2.47	5	
1852	1.95	14.2	2.16	29.8	54.5	3.46	2.93	12.6	

The first three cells in Table 63 are exactly analogous to cells reported in Table 61. Both, the catholyte and anolyte, were made from a 50:50 mixture of NaAlCl_4 and LiAlCl_4 . These fresh cells were much superior to the desiccated cells. The internal resistances were much smaller.

Another set of cells were made with a mixed anolyte and a regular NaAlCl_4 catholyte. Since thermal shock is known to be a spike producer, and because the mixture is believed to require less heat to become active than the unmixed salts, it was expected that the spike tendency would be reduced with this particular combination. The tests of the cells (S/N 1850, 1851, and 1852) showed this to indeed be the case with a significant increase in the 90% energy density and modest increases in the 80% and 70% energy densities.

At that time it was noted that, while the difference between t_{90} and t_{80} was large, the cell died very quickly after t_{80} . It was thought that one possible cause for this behavior was that the anode, which contained 35 % Mg, was being consumed too quickly. For these reason a set of cells was made with cells that had large anodes. The data from these cell tests are reported in Table 64.

TABLE 64 SINGLE CELL TEST RESULTS FOR CELLS PREPARED WITH LiAlCl_4 ANOLYTES, NaAlCl_4 CATHOLYTES, AND LARGE ANODES

S/N	V_p	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} Peak	R_{INT} t_{70}	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	
1930	1.73	31.7	18.9	39.9	50.5	0.94	2.99	180°C 5Ω
1931	1.74	31.8	21.8	41.1	50.0	0.92	2.52	200°C 5Ω
1932	1.73	31.7	20.3	37.4	48.7	1.53	4.93	220°C 5Ω
1933	1.76	32.2	29.5	45.9	55.4	1.21	0.87	240°C 5Ω
1934	1.76	32.2	27.4	43.1	52.8	0.91	2.10	260°C 5Ω
1935	1.77	32.4	31.6	45.2	50.8	0.91	2.52	280°C 5Ω
1936	1.77	32.4	28.0	X	43.8	0.61	7.86	300°C 5Ω
1937	1.46	165	10.9	17 5	25.0	1.52	2.53	240°C .81Ω
1938	1.80	13.1	31.5	47.3	54.8	1.53	4.17	240°C 12.6Ω
1940	1.75	32.0	27.4	42.3	51.5	1.21	2.94	Fresh
1941	1.84	13.4	33.6	51.7	57.0	1.52	2.09	LiAl Alloy

The results in Table 64 show that the use of a large anode (made larger at the expense of the anolyte) did not cause an improvement. The cells tested earlier were, overall, better. It is interesting that, once again, the best operating temperature was 240°C. For this reason, two more cells, #1937 and #1938, were made and tested at 240°C and different resistive loads (0.81Ω and 12.6Ω).

It was suspected that the above cells would have done even better if fresh LiAl was used so a new batch was opened. Cells made with this material were #1940 and #1941. There was an apparent small improvement made. Because of this improvement the series of cells run in August was repeated with noticable improvement (cells #1941 - #1952).

CONCLUSION:

A significant quantity of high quality LiAlCl_4 was prepared for this program by Alcoa Aluminum. This material was successfully fabricated into anolytes and catholytes. These electrolyte powders were used to prepare cells and, ultimately, batteries which eventually performed better than any other materials tested for this program.

ACIDIC ELECTROLYTES:

Some slightly acidic NaAlCl_4 (52 m/o AlCl_3) was received and made into an anolyte and catholyte. These two electrolytes were used to make cells. The results of the tests made on those cells are in Table 65.

Because these tests were so good cells were made with a catholyte prepared with this slightly acidic NaAlCl_4 and an anolyte was prepared from the LiAlCl_4 . These cell tests are shown in Table 66. These cells were made with a larger than normal anode.

TABLE 65 SINGLE CELL TEST RESULTS FOR CELLS MADE WITH NaAlCl_4 WHICH CONTAINED 52 m/o AlCl_3

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{70}	TEMP. or LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C or ohms	
1853	1.90	34.8	3.36	35.3	42.0	3.00	0.80	160°	Fresh Cells 52 m/o AlCl_3 in both the anolyte & catholyte 5 ohms
1854	1.90	34.8	4.64	40.8	46.5	1.67	0.22	180°	
1855	1.92	35.1	5.23	49.0	57.3	1.10	0.40	200°	
1856	1.94	35.5	6.03	50.9	59.2	1.37	0.79	220°	
1857	1.94	35.5	7.13	52.0	58.7	1.37	0.39	240°	
1858	1.96	35.9	8.22	49.0	57.1	X	0.39	260°	
1859	1.97	36.0	8.31	27.4	33.6	1.39	7.81	280°	
1860	1.73	195	6.33	20.3	33.2	1.17	0.68	.81	Stored in dry box overnight 200°C
1861	1.97	36.0	3.80	40.7	44.5	X	0.78	5	
1862	1.99	14.4	4.67	55.2	62.4	0.34	0.49	12.6	

TABLE 66 SINGLE CELL TEST RESULTS MADE FOR CELLS MADE WITH LiAlCl_4 ANOLYTE AND SLIGHTLY ACIDIC NaAlCl_4 CATHOLYTE. THESE CELLS HAD ANODES MADE HEAVY AT THE EXPENSE OF THE ANOLYTE

S/N	V_p	i_p	ED ₉₀	ED ₈₀	ED ₇₀	R_{INT} Peak	R_{INT} t_{70}	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	
1953	1.75	32.0	15.7	34.0	46.2	1.53	1.30	180°C 5Ω
1954	1.77	32.4	18.6	37.0	53.0	1.80	2.09	200°C 5Ω
1955	1.77	32.4	17.2	34.4	43.8	1.51	2.10	220°C 5Ω
1956	1.77	32.4	22.2	37.9	47.4	0.91	1.69	240°C 5Ω
1957	1.77	32.4	22.0	37.7	48.9	1.51	2.48	260°C 5Ω
1958	1.78	32.6	27.3	41.4	46.4	0.91	5.86	280°C 5Ω
1959	1.78	32.6	26.0	35.6	37.7	0.60	12.5	300°C 5Ω
1960	1.78	32.6	26.2	43.1	52.6	0.91	2.09	240°C 5Ω
1961	1.36	153	8.23	12.7	17.4	1.80	2.32	240°C .81Ω
1962	1.84	13.4	21.2	41.1	52.4	1.52	1.05	240°C 12.6Ω
1963	1.77	32.4	21.1	38.1	51.6	2.66	2.10	260°C 5Ω

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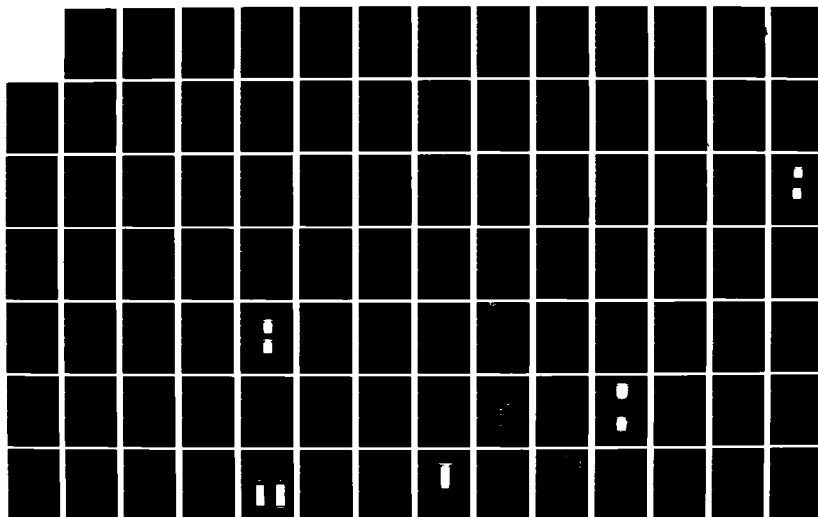
ADVANCED THERMAL BATTERIES(U) NATIONAL UNION ELECTRIC
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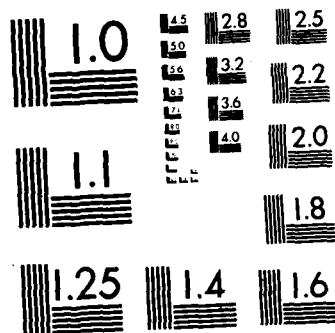
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MICROCOPY RESOLUTION TEST CHART
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Once again, the best cells were at somewhat higher than normal test temperatures. The overall performance of these cells was not as good as the cells tested previously.

Any attempt to make anolyte from the slightly acidic LiAlCl_4 was unsuccessful. A yellow-green liquid condensed upon the inside of the lid of the large reaction vessel inside the dry box. The material in the bottom of the reaction vessel was composed of "wetted" Cab-O-Sil, grey colored particles which were probably LiAlCl_4 which was not mixed with Cab-O-Sil, hard white particles, and much "unwetted" Cab-O-Sil. All of the hard particles were ground to a powder and returned to the reaction vessel for a second heating at 180°C for $\frac{1}{2}$ hour. There was no apparent change and the mixture was abandoned.

Other attempts to make anolyte from the acidic LiAlCl_4 at lesser temperatures also failed. The acidic LiAlCl_4 has been abandoned for this system.

A second batch of LiAlCl_4 was received from Alcoa. Some of this material was unfiltered and unpurified. Some of this material was purified but unfiltered. These materials were used to prepare cells and the cells were tested on the single cell tester.

The cell test results for the purified and unpurified LiAlCl_4 electrolytes were almost identical. This would indicate that the purification step is unnecessary. However, it should also be noted that the exact nature of the purification step, as well as the exact quality of the unpurified material, has not been specified by Alcoa. It may be that the purification step is not needed because the unpurified material is in reality, quite pure. It may also be that the purification is unnecessary because it is not effective.

During the testing of the many different LiAlCl_4 and NaAlCl_4 , both basic and acidic, electrolytes it was believed that the optimum cell formula developed as a result of the Factorial Design Study could be improved upon.

For this reason a number of cells were prepared and tested. These cells were made with LiAlCl_4 anolytes, have anodes of 35% Mg and 65% LiAl, and had CuCl_2 catholytes made from slightly acidic NaAlCl_4 .

TABLE 67 SINGLE CELL TEST RESULTS FOR CELLS WITH LiAlCl_4 ANOLYTES AND $\text{NaAlCl}_4/\text{CuCl}_2$ CATHOLYTES

S/N	V_p	i_p	ED_{90}	ED_{80}	ED_{70}	R_{INT} Peak	R_{INT} t_{70}	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohms	
1964	1.39	157	16.3	26.3	36.7	0.59	2.66	.81	70 w/o CuCl_2
1965-1967	1.69	33.8	19.1	34.1	42.9	2.60	6.29	5	10 w/o C
1968	1.76	12.3	55.4	66.7	70.9	0.73	1.09	12.6	Regular Cell
1969-1971	1.52	169	10.5	23.3	35.0	1.93	3.60	.81	70 w/o CuCl_2
1972-1974	1.73	31.7	26.6	48.7	57.2	1.99	5.98	5	10 w/o C
1975-1977	1.87	13.3	39.1	53.9	59.3	1.88	1.59	12.6	Heavy Anode
1978-1980	1.60	181	12.4	22.0	32.7	1.02	2.80	.81	70 w/o CuCl_2
1981-1983	1.77	32.4	41.0	52.9	60.5	0.87	4.26	5	15 w/o C
1984-1986	1.81	13.1	37.5	47.9	52.6	3.68	5.99	12.6	Regular Cell
1987-1989	1.23	139	8.17	13.7	18.6	2.88	6.08	.81	70 w/o CuCl_2
1990-1992	1.60	29.4	27.3	46.7	49.8	2.52	9.67	5	5 w/o C
-	-	-	-	-	-	-	-	-	Regular Cell
1993-1995	1.65	182	10.6	17.3	25.4	0.91	2.85	.81	70 w/o CuCl_2
1996-1998	1.77	32.5	23.3	37.0	45.6	0.87	6.30	5	15 w/o C
1999-2001	1.82	13.2	26.6	38.9	47.4	1.38	4.26	12.6	Heavy Cathode

Some of these cells were among the best cells tested during this program. Cell #1968 was the best cell tested during this program. However, the best cell was not considered the optimum cell because of the relatively low energy density at a discharge rate of 33.8 ma/cm^2 .

CONCLUSION:

The best cells tested during this program were the following types;

anode: 35 %w/o Mg & 65 %w/o LiAl (28 %w/o Li);
0.45 gm

anolyte: basic LiAlCl_4 with 12 %w/o Cab-O-Sil;
1.75 gm

catholyte: 70 %w/o CuCl_2 ; 10 %w/o graphite; 20 %w/o
 NaAlCl_4 (52 %m/o AlCl_3 ; NaAlCl_4 immobilized
with 10 %w/o Cab-O-Sil); 1.90 gm

Total Cell Weight: 4.10 gm

The new optimum cell formula is:

anode: 35 %w/o Mg & 65 %w/o LiAl (28 %w/o Li);
0.75 gm

anolyte: basic LiAlCl_4 with 12 %w/o Cab-O-Sil;
1.25 gm

catholyte: 70 %w/o CuCl_2 ; 15 %w/o graphite; 15 %w/o
 NaAlCl_4 (52 %m/o AlCl_3 ; NaAlCl_4 immobilized
with 10 %w/o Cab-O-Sil); 2.50 gm

Total Cell Weight: 4.10 gm

SUMMARY & CONCLUSION OF ALTERNATE ELECTROLYTE STUDY:

The regular electrolyte for this program was alkaline NaAlCl_4 . These alternate materials have been considered:

- a) LiAlCl_4
- b) acidic NaAlCl_4 & LiAlCl_4
- c) $\text{LiCl} \cdot \text{KCl}$

$\text{LiCl} \cdot \text{KCl}$ was used principally as a material to make control units for all tests. It was also used for high temperature experiments.

LiAlCl_4 proved to be a superior anolyte material. Acidic LiAlCl_4 could not be successfully immobilized and has been abandoned.

Acidic NaAlCl_4 also proved to be a superior electrolyte material. Catholytes prepared with NaAlCl_4 (52 ^m/o AlCl_3) have performed better than any other catholyte material. The practice of mixing NaAlCl_4 with LiAlCl_4 was not particularly beneficial.

During the testing of these various materials it was discovered that the practice of routinely desiccating cells in a vacuum oven seriously retarded their performance.

Also as a result of these experiments a new optimum cell was developed. The new optimum cell formula is:

anode: 35 ^w/o Mg 65 ^w/o LiAl (28 ^w/o Li);

0.75 gram

anolyte: basic LiAlCl_4 with 12 ^w/o Cab-O-Sil;

1.25 grams

catholyte: 70 ^w/o CuCl_2 ; 15 ^w/o graphite; 15 ^w/o

NaAlCl_4 (52 ^m/o AlCl_3 ; NaAlCl_4 immobilized
with 10 ^w/o Cab-O-Sil); 2.50 grams

Total Cell Weight: 4.10 grams

SECTION XV

PREFUSED CATHOLYTE

Early in the program it was speculated that prefusing the catholyte prior to cell fabrication would be beneficial to performance. However, when the first MoCl_5 cell was heated the volatile MoCl_5 was lost. When MoO_3 was used as a catholyte material it was also fused into the catholyte (see this report, Section IV). However, the MoO_3 reacted with the electrolyte to form the same product as the MoCl_5 catholyte.

Catholyte prefusion was abandoned until sulfur was used as a catholyte (see this report, Section XII). With CuCl_2 the cathode active material collects in zones or grains and leaves a relatively inhomogeneous catholyte.

CONCLUSION:

The practice of prefusing the catholyte was found to be beneficial only with the sulfur catholyte. Prefusing heavy metal catholytes has been abandoned.

SECTION XVI

FREON BLENDING

Freon blended anolyte has been prepared. Freon, 40 ml., and 10 grams of calcined Cab-O-Sil were placed in the blender in the hood in dry room #3 and blended for 2 minutes. NaAlCl_4 , 90 grams, was added and blended for 2 more minutes. An additional 300 ml. of freon was added to compensate for evaporation. This mixture was poured into an aluminum pan. The mixture was so thick that about 25% was left behind in the blender. The mixture was allowed to dry by placing it in front of the slightly open fume hood door and allowing the dry room air to pass over it. The dry material was then fused for 2 1/2 hours at 160°C to 170°C . When cool the fused powder contained both grey and white lumps which easily passed through a #40 sieve without grinding. This freon blended anolyte was labeled A #1080.

A catholyte was prepared by mechanically mixing and grinding 28 gm CuCl_2 with 13 gm A #1080 and 9 gm graphite. This catholyte was labeled C #1197.

These powders were used to make cells. It should be noted that the cells were relatively thin (0.07" compared to 0.084" usually observed). In addition to being thinner it was possible to use more pressure to make the cells than with conventional powders (30 TONS FORCE compared to 12 TONS for conventional cells).

The cells displayed a large spike when tested but this was corrected by vacuum desiccation.

A second anolyte was prepared. This time cells were made with the anolyte before it was fused. These cells were only 3.5 grams because the anolyte was so light and fluffly. The energy densities of these cells were relatively high. This experiment was repeated to see if there was any real

merit to non-fused electrolytes. The good results did not reproduce the second time.

The next experiment was to freon blend a CuCl_2 catholyte. Graphite, 9 grams, was mixed with 300 ml. of freon in a blender for 2 minutes. Then 13 grams of freon blended A #1082 and 28 grams of CuCl_2 were blended for 2 minutes. An additional 100 ml. of freon was added to compensate for evaporation. This blend was poured into a small ceramic dish in the fume hood in dry room #3 until it dried. The dry powder was further desiccated in a vacuum oven for 3 additional hours at 165°F . This material, when cool, was easily passed through a #40 sieve. This catholyte was labeled C #1199. Cells were made and tested with these materials.

The next experiment was to prefuse the freon blended catholyte. The catholyte was heated in a dry box in a 1000 ml. beaker on a hot plate. A thermometer just touching the powder read 190°C to 200°C for 45 minutes. This material was allowed to cool and passed through a #40 sieve. Cells were made and tested. Once again the spike was removed by vacuum desiccation.

In addition to the NaAlCl_4 electrolytes, some freon blending was done on $\text{LiCl}\cdot\text{KCl}$ electrolytes. The procedure was the same. That is, the freon and Cab-O-Sil was mixed and then the $\text{LiCl}\cdot\text{KCl}$ was added. Cells were made with normal production catholyte and magnesium with half the cells made with freon blended anolyte and half made with production anolyte. From the test data it appears that at the highest current density the cell made with freon blended anolyte was a 25% better energy producer than the cell made with regular anolyte.

The next experiment was to make a freon blended V_2O_5 catholyte. V_2O_5 , 75 grams, was blended with 300 ml. freon for 2 minutes. Next 18.5 grams KCl and 20.5 grams LiCl was added and blended for an additional 2 minutes. An additional

200 ml. of freon was used to wash the mixture out of the blender into a ceramic pan. After the freon had evaporated away in the fume hood in dry room #3 the powder was put in a vacuum oven at 250°C for 2 hours. Cells were made with this catholyte and tested.

Freon blending was used during the testing of MgO as an alternate binder. This preparation was described under Section VIII, Alternate Binders.

SUMMARY AND CONCLUSION:

The freon blended powders were made. These included freon blended anolytes and catholytes with both electrolyte systems, NaAlCl_4 and $\text{LiCl}\cdot\text{KCl}$. The freon blended powders compact better. It would be easier to control the particle size distribution of the final product of freon blended powders.

With the NaAlCl_4 system freon blended powders form a very severe spike. This can be removed by vacuum desiccation. The bad spike is probably caused by the additional handling necessary because of the need to evaporate away the freon. Other than better handling capabilities there is no apparent reason to apply the freon blending to the NaAlCl_4 system. There is no apparent improvement in performance.

One group of cells was made with a freon blended NaAlCl_4 anolyte which was not fused. These cells showed significant performance increases. This performance was not reproducible.

For $\text{LiCl}\cdot\text{KCl}$ electrolytes there were all of the advantages of better handling (better flow and compactability) without the disadvantages of spike formation. There did appear to be about a 25% increase in performance with the freon blended electrolytes. However, not enough cells have been tested to make an accurate judgement.

SECTION XVII
ALTERNATE ANODES

Early work with this battery system demonstrated the presence of a high voltage activation spike. It was felt that the size and shape of this spike was in some way dependent upon the activity of the lithium in the lithium anode. Mostly in an effort to test this theory and lessen the spike a number of alternate anodes were made and tested.

The several anodes which were tested shall now be listed.

- Anode #1 - 28 ^{w/o} LiAl alloy
- Anode #2 = 20 ^{w/o} LiAl alloy
- Anode #3 = 1/3 Al with 2/3 LiAl alloy (20 ^{w/o})
- Anode #4 = 2/3 Al with 1/2 LiAl alloy (20 ^{w/o})
- Anode #5 = 1/2 Al with 1/2 LiAl alloy (28 ^{w/o})
- Anode #6 = 26.6% Al
53.4% LiAl (20 ^{w/o})
20.0% A #1030
- Anode #7 = 2/5 Al & 2/5 LiAl (20 ^{w/o}) & 1/5 A #1030
- Anode #8 = LiSi alloy which contains 58 ^{w/o} Lithium
- Anode #9 = 50 ^{w/o} Al and 50 ^{w/o} LiSi alloy
- Anode #10 = 25 ^{w/o} Al and 75 ^{w/o} LiSi alloy
- Anode #11 = 40 ^{w/o} LiAl alloy
- Anode #12 = 40 ^{w/o} LiAl (-#80 + #270)
- Anode #13 = LiSi (-#80 + #270)
- Anode #14 = 3 parts LiAl (20 ^{w/o})
1 part Mg
1 part KCl·LiCl (50:50)

Anode #15 = 10 w/o Mg & 90 w/o LiAl (28 w/o Li)
Anode #16 = 20 w/o Mg & 80 w/o LiAl (28 w/o Li)
Anode #17 = 30 w/o Mg & 70 w/o LiAl (28 w/o Li)
Anode #18 = 40 w/o Mg & 60 w/o LiAl (28 w/o Li)
Anode #19 = 50 w/o Mg & 50 w/o LiAl (28 w/o Li)

Single cell results with Anode #1 & #2 have been previously described. There is very little difference between 28 w/o and 20 w/o LiAl except for a slight reduction in the height of the high voltage activation spike. This reduction is too small to be a "cure" for the spike problem and is usually perceived as a lower peak voltage. Therefore, it was concluded in previous work that 28 w/o LiAl was a superior anode material. However, recognition of the activation spike makes this not necessarily true.

It was felt that the small change in the size and shape of the spike was caused by a reduction in Li in the anode so an anode was prepared by mixing 1 part of Al granules with 2 parts 20 w/o LiAl. The Al was sieved and only the material which passed through a #40 sieve was used. This was done because of the difficulty in obtaining LiAl alloys which contain less than 20 w/o Li, in a useful form. This was named Anode #3.

Anode #3 was used with a regular anolyte and test catholyte RC-13 to make tests cells. These cells were tested and numbered 1114 thru 1119. These data are tabulated in Table 68.

It can be seen from these data that the peak voltage is still quite good. Observing the discharge curves shows that the spike is almost entirely gone. However, the curve dropped off too quickly, resembling the shape of a negative exponential curve.

TABLE 68 SINGLE CELL TEST RESULTS
FOR CELLS USING ANODE #3

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	LOAD	NOTES
	volts	mA	seconds	seconds	Wh/kg	Wh/kg	°C	ohms	
1114	2.49	45.6	400	604	25.6	40.0	200	5	1/3 Al & 2/3 LiAl (20 ^{w/o})
1115	2.58	18.7	792	1232	21.7	30.6	200	12.6	
1116	2.02	228	130	163	28.1	-	200	.81	
1117	2.43	44.5	486	691	30.0	-	180	5	
1118	2.41	44.1	488	716	29.5	-	160	5	
1119	2.45	44.8	91	239	6.28	-	300	5	

In a further attempt to smooth out the discharge curve another anode was mixed with 2/3 Al & 1/3 LiAl (20^{w/o}). This anode was tested in cells #1120 through 1135. There was no significant change except that the 70% life became shorter. It appeared that the anode was running out of lithium too quickly. Therefore another anode was made of 1/2 Al & 1/2 LiAl (28^{w/o}). This anode produced a little smaller energy density with no significant change in the shape of the discharge curve.

Two more anodes were made which contained anolyte. That is, 20^{w/o} anolyte was mixed into the anode material. This was done to, both, increase the conductivity of the anode and to act as a thermal buffer for the anode. This was done to Anode #3 (the mixture was renamed Anode #6) and to a mixture of 1/2 Al & 1/2 LiAl (20^{w/o}) (named Anode #7). The materials were tested in cells #1136 through #1151. There was no significant improvement with these salt containing anodes except than the activation time was shorter.

To summarize, adding Al powder to the LiAl alloys had the effect of minimizing the spike and flattening the discharge curve. The discharge curve was in general shaped like a negative exponential curve with the 80% life about 2.5 times larger than the 90% life and the 70% life about 7 times longer than the 90% life. As the concentration of lithium in the anode became less so did the 70% life although the 90% and 80% lives were not particularly affected. Adding 20 % anolyte to the anode increased the energy density about 5%. Adding Al to the anode tended to slow activation but adding anolyte restored the activation. The 90% life was improved most with less significant improvements in the 80 and 70% lifetimes.

The LiSi alloy was first tested in single cell tests #1226 to #1244. These included some cells with MoCl_5 catholyte and CuCl_2 catholyte. This also includes one anode mixed with 50 % Al powder.

Table 69 is a tabulation of all the single cells made with MoCl_5 catholyte and tested at 200°C with varying loads.

TABLE 69 SINGLE CELL TEST RESULTS, 200°C

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm	
1229	1.40	334	129	160	39.8	46.1	.4	$\text{MoCl}_5/\text{LiSi}$ 200°C
1227	1.76	199	180	226	39.9	46.6	.81	
1232	2.21	135	171	233	31.3	39.0	1.5	
1233	2.30	70.1	370	-	35.5	-	3	
1226	2.48	45.4	474	694	31.3	41.6	5	
1228	2.64	19.2	810	1240	23.6	32.7	12.6	
1234	2.75	10.1	960	1810	11.3	21.6	25	

These data are illustrated with Figure 37. It can be seen from Figure 37 that the LiSi appears to make a significant improvement in the life-time at high current densities. There was little improvement at low current densities. This has exaggerated the "the harder you work it the better it works" trend for MoCl_5 catholytes. Just the opposite is true for CuCl_2 . This has been previously noted for CuCl_2 with an LiAl anode. WCl_6 seems to behave similarly to MoCl_5 in the presence of LiSi.

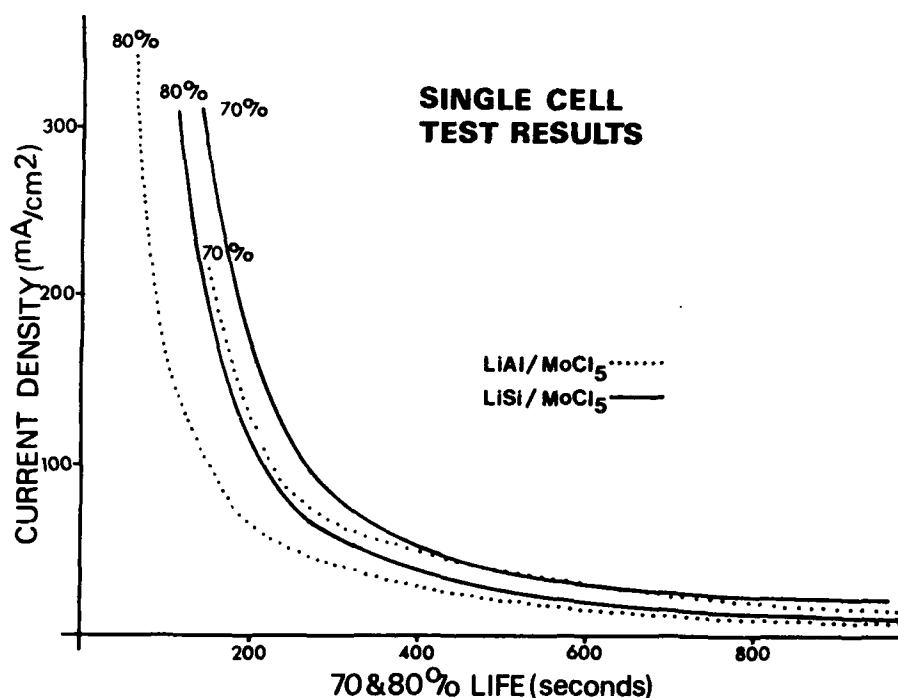


Figure 37. A comparison Of LiAl And LiSi Single Cell Test Results

Table 70 is a tabulation of the single cell test data for $\text{MoCl}_5/\text{LiSi}$ cells made at constant 5 ohm load and various temperatures.

The data in Table 70 are illustrated in Figure 38. The use of LiSi did not affect the temperature tolerance range of MoCl_5 catholytes much at all.

TABLE 70 SINGLE CELL TEST RESULTS, AT VARIOUS TEMPERATURES

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	NOTES
	volts	mA/cm^2	seconds	seconds	Wh/kg	Wh/kg	$^{\circ}\text{C}$	
1230	2.20	40.3	166	336	8.54	14.8	160	$\text{MoCl}_5/\text{LiSi}$ 5 ohm Load
1231	2.33	42.6	402	671	22.8	33.9	180	
1226	2.48	45.4	474	694	31.3	41.6	200	
1236	2.46	45.0	389	556	27.8	35.3	220	
1237	2.52	46.1	290	441	21.3	28.6	240	
1238	1.83	33.5	550	1050	18.7	31.5	260	

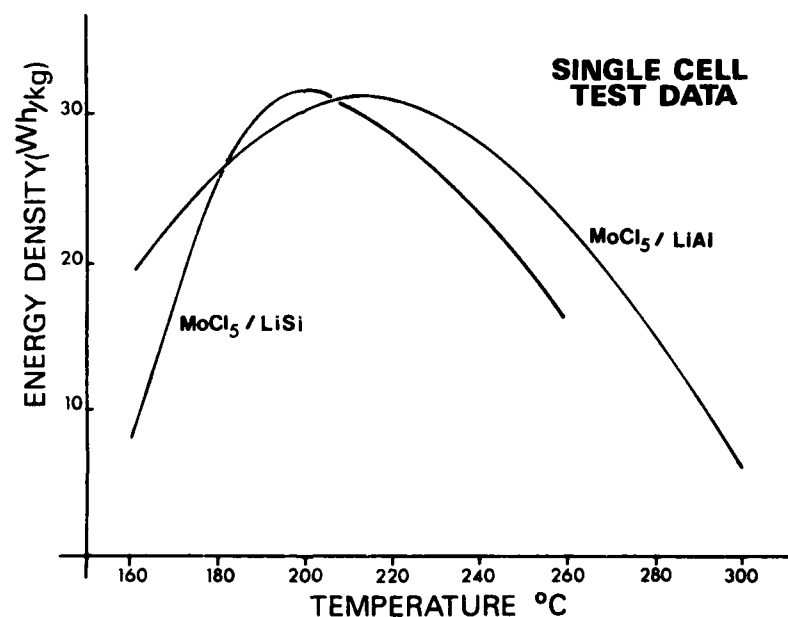


Figure 38. The Temperature Tolerance Of LiSi Cells

Using LiSi with MoCl_5 catholyte did greatly lessen the effect of the activation spike. This significantly changes the shape of a typical discharge curve for a MoCl_5 catholyte as can be seen in Figure 39. This is interesting because using LiSi alloy with CuCl_2 caused a spike to form. Because of this, granular aluminum was mixed with the LiSi to make Anode #9. Mixing Al with LiAl alloy reduced the spike with MoCl_5 catholyte and adding Al to the LiSi reduced the spike with the CuCl_2 catholytes.

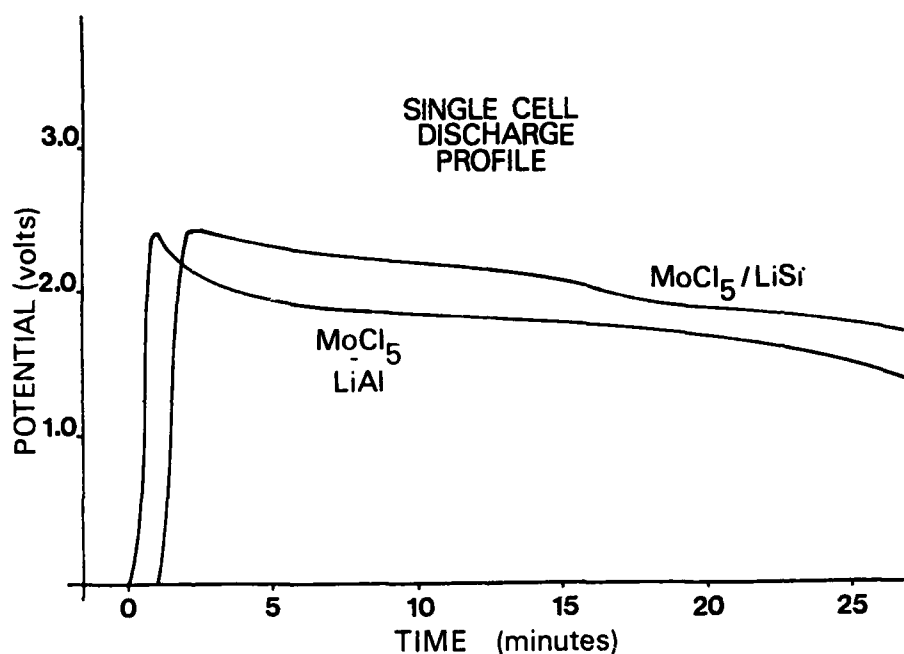


Figure 39. The Effect Of LiSi Upon A Typical MoCl_5 Discharge Curve

Some 40 ^{w/o} lithium LiAl alloy was tested. The first tests were run with single cells made with a catholyte that had been stored about two months in a screw cap jar in a dry room. These cells displayed a severe spike. The spike was so bad that the cells were not treated quantitatively.

It was noticed while preparing these bad cells that the edges appeared to smear more than usual. For this reason some cells had their edges abraded with emery paper. However, this treatment made no noticeable effect on the cell performance. This has also been the case for other cells filed earlier in this project. That is, smeared edges do not appear to be an immediate problem with this system.

It was speculated that the bad spike was caused either by use of the 40 ^W/o LiAl or by use of an aged (and deteriorated) catholyte. A new test catholyte was prepared. There was no appreciable spike in the single cell tests for cells made from this new catholyte so it can be concluded that the deteriorated catholyte caused the spike and not the 40 ^W/o LiAl alloy.

Two other catholytes were prepared from CuCl_2 and these were used to make cells to test the 40 ^W/o LiAl. Table 71 presents data collected for CuCl_2 cells made with 40 ^W/o LiAl and at various current densities.

The energy density was not as high as would be expected for a MoCl_5 cell in the moderate to high current density regions. The energy density was quite good for the low current density discharges. This has been noted before in previous progress reports. Cells #1275 & #1278 had "record" high energy densities. Once again the CuCl_2 appears to be best for a long life low current density battery.

Table 72 and Figure 12 illustrate the superior temperature tolerance of CuCl_2 .

TABLE 71 40 ^w/o LiAl SINGLE CELL TEST RESULTS, 200°C

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm	
(1272) (1279)	1.60	180	71	116	12.4	17.7	.81	CuCl ₂ Catholyte 40 ^w /o LiAl Anode 200°C
1277	1.73	106	152	268	16.5	25.3	1.5	
1276	1.82	55.5	372	650	22.1	33.8	3	
(1270) (1271)	1.87	34.2	628	1263	23.2	40.1	5	
(1273) (1275)	1.92	13.9	2695	4150	41.2	57.4	12.6	
1278	2.05	7.5	5256	7816	43.8	60.2	25	

TABLE 72 40 ^w/o LiAl SINGLE CELL TEST RESULTS, AT VARIOUS TEMPERATURES

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	°C	
1280	1.89	34.8	763	1233	28.7	41.4	180	5 ohm Load CuCl ₂ Catholyte 40 ^w /o LiAl Anode
1281	1.88	34.4	665	1100	25.6	37.3	240	
1282	1.89	34.6	595	835	23.4	29.9	280	
1283	1.88	34.4	245	1170	9.36	34.8	300	
1284	1.93	35.3	435	1295	17.2	41.5	320	
1285	1.95	36.7	346	982	14.0	32.5	340	

To summarize, the 40 ^w/o LiAl makes an excellent anode material. With the MoCl₅ catholyte the tendency to form a spike is enhanced. The voltage and energy density are enlarged for both the CuCl₂ and the MoCl₅ system. The combination of 40 ^w/o LiAl anode, CuCl₂ catholyte and low current density produced excellent cell performance.

Two other samples of 40 ^W/o LiAl and LiSi were received for testing. In each case these materials were specified to pass through a #80 sieve and be retained on a #270 sieve. Both of these materials reacted violently to the atmosphere at the hand press in the dry room. These materials were finer than the previous lot. When a small sample of the fine LiAl was initially open on the cell press the sample jar became quite hot, the alloy darkened considerably and the particle size of the darkened alloy pieces increased. Cells were made with the material (S/N 1538 - S/N 1547) but they were not extraordinary. There was a rather severe spike with the low current density cells.

The moisture level of the dry room was immediately measured at 2.0% R.H. Apparently this moisture level is high enough to cause a visible reaction with the high lithium alloy.

The LiSi sample was also opened in a dry box. This material became quite warm in the press room. After just a few minutes the powder started to glow dark red. At this point the lid was screwed on the sample jar. The material continued to heat until it became bright red. The experiment was ended and the material was allowed to burn up on a large volume of water outside the building.

A more practical anode (Anodes #14 - #19) was made after a visit to Sandia Laboratory. There an improved LiAl anode was made by adding 10% Mg to the anode mix to give it better mechanical strength. Since it is believed at Eureka that the smallest powdered LiAl anode that is possible to make on existing equipment still contains an abundance of Li, it was decided to try this approach.

The first experiment was with 3 parts LiAl (20 ^W/o), 1 part Mg, and 1 part KCl·LiCl (50:50). Three regular CuCl₂ type cells were made with this anode and three cells were made with the plain 20 ^W/o LiAl anode (as control units). Table 73 contains the results of these cell tests.

TABLE 73 SINGLE CELL TESTS FOR CELLS MADE
WITH Mg IN THE ANODE. ALL TESTS AT 200°C

S/N	V _p	i _p	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT} Peak	R _{INT} t ₉₀	R _{INT} t ₈₀	R _{INT} t ₇₀	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohms	
1799	1.66	188	7.28	18.1	29.9	1.54	0.74	1.03	0.25	0.81	NaAlCl ₄
1800	2.12	38.8	0.77	7.59	45.6	0.79	2.21	1.24	0.71	5	Control
1801	2.69	19.5	0.18	0.20	0.51	3.06	X	X	0.67	12.6	Units
1802	1.56	176	10.1	19.5	28.3	0.57	0.47	0.33	0.91	0.81	LiAl, Mg
1803	1.95	35.7	2.93	34.1	49.1	2.15	0.90	0.67	1.15	5	LiCl·KCl
1804	1.99	14.4	2.94	53.3	59.6	0.68	0.52	0.84	2.87	12.6	200°C

A quick glance at the energy densities in Table 73 show that the cells that contained Mg were significantly superior to the control cells. The least improvement was with the cells tested across the 0.81 ohm resistor. The greatest improvement was across the 12.6 ohm resistor. This was because of a bad spike which was present in the control cells but not in the Mg cells.

Because of this success another series of cells were prepared. These cells were made with anodes that contained varied (but controlled) amounts of Mg. They ranged from 0% to 50% Mg. Table 74 contains the results of the cell tests made with these cells. These anodes were made from 28^{w/o} LiAl and contained no KCl·LiCl (50:50).

TABLE 74 SINGLE CELL TEST RESULTS FOR CELLS MADE
WITH ANODES THAT CONTAINED VARIOUS AMOUNTS OF Mg

S/N	V _p	i _p	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT} Peak	R _{INT} t ₉₀	R _{INT} t ₈₀	R _{INT} t ₇₀	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohms	
1805	1.85	209	4.39	8.94	19.2	1.13	1.39	0.91	1.28	.81	0% Mg
1806	2.25	41	0.74	3.96	32.6	1.24	1.33	1.19	1.02	5	
1807	2.52	18	0.18	0.46	10.6	X	1.85	2.03	1.53	12.6	
1808	1.80	209	4.89	10.8	22.8	1.26	1.53	0.98	1.10	0.81	10% Mg
1809	2.21	40	0.84	6.53	43.8	1.78	1.33	0.68	1.37	5	
1810	2.70	20	0.11	0.16	0.80	3.14	X	0.67	0.35	12.6	
1811	1.76	199	5.61	12.0	26.6	1.36	1.71	1.09	1.18	0.18	20% Mg
1812	2.18	40	1.05	7.93	45.0	1.49	0.55	1.21	1.04	5	
1813	2.33	17	0.26	1.19	45.7	4.68	0.66	0.72	2.46	12.6	
1814	1.74	1.97	4.80	11.9	25.6	1.48	1.86	0.75	1.18	0.81	30% Mg
1815	2.04	37	2.34	16.2	52.0	1.56	1.16	0.65	0.74	5	
1816	2.18	16	0.74	10.5	62.6	3.13	2.07	0.39	0.94	12.6	
1817	1.64	186	4.87	15.9	26.8	1.84	1.26	1.06	0.70	0.81	40% Mg
1818	2.03	37	1.97	10.6	50.4	1.55	1.16	1.62	0.75	5	
1819	2.06	15	1.07	19.0	59.8	0.66	0.73	0.81	0.47	12.6	
1820	1.54	174	8.06	20.2	27.5	2.15	1.11	1.18	1.43	0.81	50% Mg
1821	2.04	37	2.09	8.69	45.5	2.55	2.27	0.98	0.74	5	
1822	2.06	15	1.38	18.4	56.8	2.62	0.73	0.41	0.47	12.6	
1823	2.01	37	0.35	0.86	X	X	9.72	X	X	5	3 hours additional vac. dess
1824	2.13	16	0.79	3.86	30.9	7.55	16.0	14.5	4.44	12.6	

The effect of the gradual increase in the Mg in the anode can better
be seen in Table 75.

TABLE 75 SINGLE CELL TEST RESULTS FOR CELLS MADE
WITH VARYING AMOUNTS OF Mg ARRANGED IN ORDER OF
INCREASING MAGNESIUM

S/N	V _p	i _p	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT} Peak	R _{INT} t ₉₀	R _{INT} t ₈₀	R _{INT} t ₇₀	LOAD	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohms	
1805	1.85	209	4.39	8.94	19.3	1.13	1.39	0.91	1.28	.81	0% Mg
1808	1.80	209	4.89	10.8	22.8	1.26	1.53	0.98	1.10	.81	10% Mg
1811	1.76	199	5.61	12.0	26.6	1.36	1.71	1.09	1.18	.81	20% Mg
1814	1.74	197	4.80	11.9	25.6	1.48	1.86	0.75	1.18	.81	30% Mg
1817	1.64	186	4.87	15.9	26.8	1.84	1.26	1.06	0.70	.81	40% Mg
1820	1.54	174	8.06	20.2	27.5	2.15	1.11	1.13	1.43	.81	50% Mg
1806	2.25	41	0.74	3.96	32.6	1.24	1.33	1.19	1.02	5	0% Mg
1809	2.21	40	0.84	6.53	43.8	1.78	1.33	0.68	1.37	5	10% Mg
1812	2.18	40	1.05	7.93	45.0	1.49	0.55	1.21	1.04	5	20% Mg
1815	2.04	37	2.34	16.2	52.0	1.56	1.16	0.65	0.71	5	30% Mg
1818	2.03	37	1.97	10.6	50.4	1.55	1.16	1.62	0.75	5	40% Mg
1821	2.04	37	2.09	8.69	45.5	2.55	2.27	0.98	0.74	5	50% Mg
1807	2.52	18	0.18	0.46	10.6	X	1.85	2.03	1.53	12.6	0% Mg
1810	2.70	20	0.11	0.16	0.80	3.14	X	0.67	0.35	12.6	10% Mg
1813	2.33	17	0.26	1.19	45.7	4.68	0.66	0.72	2.46	12.6	20% Mg
1816	2.18	16	0.74	10.5	62.6	3.13	2.07	0.39	0.94	12.6	30% Mg
1819	2.06	15	1.07	19.0	59.8	0.66	0.73	0.81	0.47	12.6	40% Mg
1822	2.06	15	1.38	18.4	56.8	2.62	0.73	0.41	0.47	12.6	50% Mg

By examining Table 75 it can be seen that none of the ED₉₀'s were very good but the best ones were measured across the 0.81 ohm resistor. They appear to be relatively independent of the amount of Mg in the anode. For the cells tested across the 5 and 12.6 ohm resistors there does appear to be an increase in ED₉₀ with an increase in Mg in the anode.

The ED_{80} 's appear to increase as the % Mg is increased and this was the same for all three discharge rates. This was also true for the ED_{70} 's.

It is interesting to note that the largest ED_{80} was for the cell that was tested across the 0.81 ohm resistor and which had an anode of 50% Mg and 50% alloy. This can be explained with the "spike". These cells displayed a "spike" in the discharge curve. The spike is always most severe for cells discharged at the low rate (17 mA/cm^2 or across the 12.0 ohm resistor) and least severe for the high discharge rate (200 mA/cm^2 or across the 0.81 ohm resistor). Furthermore, the presence of a greater amount of Mg in the anode also tended to suppress the "spike". This is particularly evident in the ED_{90} 's of the 5 and 12.6 ohm tests.

It can be noticed that the best cells were at about 30% or 40% Mg and the cells that contained 50% Mg were also very good.

It is not understood how there could have been a "spike" at all. These cells were desiccated in a vacuum oven for at least 8 hours prior to testing. In an attempt to remove the spike two cells were vacuum desiccated for an additional 3 hours. These were cells #1823 and #1824 at the bottom of Table 74. The experiment did not work. The cells were worse instead of better.

In summary, it has been found that Mg granules can be mixed with LiAl alloy granules to fabricate a superior cell. Cells made with Mg in the anode have superior mechanical strength and shearability. Furthermore, cells which contain Mg in the anode have displayed superior electrochemical performance. The LiAl alloy is the most expensive material in the cell and it has been demonstrated that the anode need contain only half as much LiAl as previously believed. Anodes containing up to 50% Mg have been tested successfully.

CONCLUSION:

It has been assumed that lithium is the active anode material. An attempt was made to maximize the amount of lithium in the anode by using alloys with high lithium concentrations such as LiAl (40 ^m/o Li) and LiSi (56 ^m/o Li). However, as the amount of Li was increased in the anode the tendency to form a high voltage activation spike also increased. Through another course of experimentation it was discovered that the cell was cathode limited and high lithium concentrations were not needed anyway. It was also discovered that the spike could be partially controlled by protecting the lithium from sudden thermal shock. For this reason anodes were made with the granular LiAl alloy diluted with granular Al or Mg. The dilution experiments were successful producing a Mg, LiAl anode that was mechanically and electrochemically superior with improved performance and that was less expensive to fabricate. An optimum anode was formulated with 35 ^w/o Mg and 65 ^w/o LiAl alloy (28 ^m/o Li).

SECTION XVIII

CELL REPRODUCIBILITY

A cell which has good reproducibility can be fabricated repeatedly over a relatively long period of time, maintaining consistent physical properties (weight, thickness, shape, etc.), and resulting in a finished cell which functions in a repeatable and predictable manner.

In the early days of this program reproducibility was very poor due to the presence of the activation spike and due to the poor cell fabrication methods. However, fabrication methods have been improved and the spike is better understood and more controllable than before.

The test cells are now made on a manually operated hydraulic press fitted with a 1.469" diameter circular die. It has proven very easy to make three layer thermal cells on this press. The total cell weight can be easily maintained at 4.10 grams \pm 0.1 gram. The cells produced are rigid, firm with only very slight bowing, and with only a slight tendency to crack or delaminate. The cell edges do not appear to smear appreciably.

By controlling the spike the cell performance can be quite reproducible. For example, examine once again the data of pages 47 & 49 . These cells were made at different times, months apart, from different materials, for different purposes and still performed quite similarly. This was not the case with all of the cells produced. The cell made with FeS_2 on the catholyte bowed, cracked, and started to crumble within minutes after fabrication.

CONCLUSION:

It can be stated that the cells for this program are quite reproducible and are at least as good as existing thermal cell systems.

SECTION XIX

ELECTROLYTE MIXED WITH ANODE ALLOY

The reference electrode tests indicated a relatively high impedance at the anode. In an attempt to improve this condition a series of cells were made and tested with various amounts of anolyte mixed into the anode. Cells were made with 10 %^{w/o}, 20 %^{w/o}, 30 %^{w/o}, and 40 %^{w/o} anolyte in the anode. A group of control cells without anolyte in the anode were also made. These cells were tested across 0.81, 5.0, and 12.0 ohm loads. One set of cells was made with MoCl_5 and one set was made with CuCl_2 .

It was noticed that the cells that contained from about 10 %^{w/o} to 30 %^{w/o} were easier to fabricate. That is, the anode layer compacted better. The effect of adding anolyte to the anode upon the noise in the cell could not be determined because there was no noise in any of the cells.

These conclusions can be made from this experiment:

- 1) Adding anolyte to the anode does not have much effect on internal resistance of the cell.
- 2) Adding anolyte to the anode does not have much effect on the energy density of the cell.
- 3) Adding 40 %^{w/o} anolyte to the cell may tend to reduce the concentration polarization which occurs in the cell under high current conditions.
- 4) Adding anolyte to the anode aids anode compacting and improves the mechanical properties of the cell.
- 5) Cell resistance usually starts out high — it then reaches a minimum and again starts to increase. This applied to both MoCl_5 and CuCl_2 cells.

A mixture of 30 gm NaAlCl_4 and 30 gm of LiAl (28 %w/o) were mechanically mixed in the dry box and heated in a porcelain evaporating dish on a hot plate. The temperature of the hot plate was turned up slowly. The mixture seemed to fuse all at once. That is, one second it was a free flowing powder and then it suddenly fused. Five seconds later the entire contents of the dish were fused into a solid mass. This mass was removed from the dish, reground, and made to pass (100%) through a #40 sieve. The reground material was used to make CuCl_2 cells and was tested to see what effect the fusion could have on the observed cold voltage or spike. The results of the tests were not much different from results of the tests on the control cells.

The actual fusion is difficult to describe. One would expect the salts to melt and, because of the unfused solid metal, form a metallic paste. However, some of the larger crystals of salt could be seen to melt and about one second later the metal started to darken and the darkened areas radiated away from the sites of the melted crystals. Just two or three seconds after the first salt crystal was observed to melt the mixture had become a solid grey mass. That is, it appeared that the LiAl had reacted with the molten salt. Note that there was no Cab-O-Sil in the mixture.

In order to more closely examine the possibility of a reaction between the alloy and the salt a new mixture was prepared and tested with a DSC. The DSC spectrum showed a large exotherm just after fusion of the salt. The test was repeated with a mixture of regular test anolyte and LiAl alloy with similar results. That is, it appears that the reaction between the molten salt and alloy was exothermic. No evidence of this has been observed at this facility before.

It was already observed that the anode/anolyte interface is relatively polarized at initiation. This polarization seems to diminish as current passes through the cell. As even more current passes through the cell the cathode/anolyte interface seems to polarize. So, as current passes through the cell, the anode seems to "unpolarize" while the cathode polarizes. It could be that the above describes fusion reaction of alloy and anolyte is responsible for this initial anode polarization.

Another alloy/salt mixture containing 25 ^{w/o} NaAlCl₄ was fused and re-ground. Cells were made with this material and tested. The cell tests were not significantly better or worse than regular test cells. There is no apparent advantage of using NaAlCl₄ with the alloy and so this procedure was not pursued further. There is some interest in the nature of the fusion reaction and the meaning of the large exotherm in the DSC spectrum of the alloy/salt mixture.

A series of batteries (battery construction will be discussed later in this report) was prepared which had anodes made with $\frac{1}{2}$ anolyte and $\frac{1}{2}$ LiAl alloy (28 ^{w/o}). The purpose was to make an anode easy to compact which would store well and help to eliminate noise in the discharge. Two of these batteries have been tested (Table 76). The noise was not eliminated.

TABLE 76 BATTERY TEST DATA FOR BATTERIES MADE WITH ANODES THAT CONTAINED $\frac{1}{2}$ ANOLYTE AND $\frac{1}{2}$ LiAl ALLOY AND WHICH HAD BEEN STORED AT 165°F

S/N	Storage Time	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _{Peak}	Spec. R t ₈₀	NOTES
		volts	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	ohm-cm ²	
1067	1 Day	24.1	74	129	163	11.9	2.17	88	62.2	Anodes: $\frac{1}{2}$ A #1066 & $\frac{1}{2}$ LiAl (28 ^{w/o})
1066	1 Week	24.0	69	109	Noise	10.3	1.87	86	48.9	

CONCLUSION:

There appears to be a tendency for the anode to polarize a little slower when electrolyte is mixed into the anode. However, the effects observed when electrolyte is added to the anode are minimal and so, the procedure will not be further pursued.

SECTION XX
CELL FABRICATION AND PROCESSING

Two main problems have occurred while making cells:

- 1) the cells tend to crumble, delaminate, and break before they can be used, and
- 2) it is difficult to shear the cells.

The breakage problem has already been mentioned as a storage problem.

Of more immediate interest are cells that break as they come out of the cell die. This problem can be cured by changing the ram pressure on the press. This pressure needs to be adjusted for almost every combination of anode, anolyte, and catholyte and can be easily determined by trial and error.

Sometimes the edges of a cell tend to smear and cause local shorting. This can usually be cured by making the cells oversize and punching out a smaller cell. However, cells made with this system did not punch well. The LiAl was very brittle. It was found that those cells could be punched after Mg was mixed with LiAl alloy. The center hole had never been successfully punched in those cells until Mg was added to the anode. Center holes can also be drilled with common twist drills.

It was believed that perhaps the moisture content of raw Cab-O-Sil was causing storage problems. A quantity of Cab-O-Sil was baked in a vacuum oven at 160°F for eight days before it was fused with NaAlCl_4 . This was anolyte #1060.

Cells were made from 28 ^{w/o} LiAl, anolyte A #1060, and a MoCl_5 catholyte. As a result of these cell tests it was concluded that there was no significant change in cell performance resulting from the 8 day vacuum desiccation received by the Cab-O-Sil.

The second experiment was to proceed to calcine the Cab-O-Sil. That is, the Cab-O-Sil was heated to 500°C for 16 hours. The hot Cab-O-Sil was allowed to cool in the dry box interchange and when cool was taken on into the dry box.

The calcined Cab-O-Sil was tested with a DSC and the spectrum was identical to the DSC spectrum of "as received" Cab-O-Sil. The DSC was taken up to 650°K. The spectrum was featureless for the total range.

Some graphite was desiccated in a vacuum oven at 165° and 2 mm Hg for 16 hours. This graphite was used with the anolyte made with the calcined Cab-O-Sil to prepare a catholyte. These materials were used to make cells and the cells were tested.

From the cell test data one could conclude that the cells made with desiccated inerts were superior overall. However, at the low current density the "spike" was exaggerated. This is probably due to the decreased internal resistance. In some instances the "as received" cells were superior. This is once again caused by a suppressed "spike" probably caused by higher internal resistance. It does appear that the internal resistance of the cell is lowered by using desiccated materials.

As a result of these tests it has been concluded that there is merit in desiccating graphite and calcining Cab-O-Sil and from that time on all regular test anolytes and catholytes contained desiccated inerts.

A series of batteries was made from the specially prepared electrolytes. The Cab-O-Sil was calcined at 500°C and the graphite was desiccated at 165°F in vacuum oven overnight. These batteries were stored at room temperature. Table 77 contains the battery test results.

TABLE 77 TEST DATA FOR STORAGE BATTERIES MADE TO TEST THE EFFECTS OF DESICCATION OF THE CAB-O-SIL AND GRAPHITE IN THE ELECTROLYTES. THE ENERGY DENSITY IS EXPRESSED IN TERMS OF Wh/kg. THE TEST LOAD WAS 25 OHMS.

S/N	STORAGE TIME	V_p	t_{90}	t_{80}	t_{70}	ED_{80}	ED_{80}	T_{Peak}	R_{INT} t_{80}	NOTES
		volts	seconds	seconds	seconds	IDEAL	ACTUAL	°C	ohm·cm ²	
1068	Control	25.2	40	145	330	13.8	2.51	99	29	Calcined Cab-O-Sil & Desiccated Graphite
1069	1 week	25.3	37	152	350	14.5	2.63	97	31	
1073	2 wks	22.6	45	140	282	10.8	1.95	96	45	
1074	1 mth	22.5	18	55	134	4.2	0.77	72	80	
1076	3 mths	15.8	3	21	38	0.8	0.14	88	224	CuCl ₂

Serious deterioration can be seen as a large decrease in peak voltage and a large increase in internal resistance.

Battery #1076 was examined post mortem. Three prominent features were noted. First, it was noted that the battery did not appear to be as hot as the others. That is, the heat paper was light green and the heat paper and quinargo were not fused together. This was previously noted and reported for battery #1074.

The second feature was a dark grey layer noted at the anode/anolyte interface. The grey material appears to start at the anode/anolyte interface and continue upward into the anode eventually thinning out into nothing. None of the grey material appears to be in the anolyte — it all appears to be in the anode. This grey layer has been noted before in post mortem battery examinations but not in single cell examinations. However, a black layer often is apparent in single cell post mortems. Then it could be theorized that the grey layer is characteristic of cells stored in batteries in an oven at 165°F. While the nature

of the grey material is unknown it is quite reminiscent of the reaction product observed when an attempt was made to fuse NaAlCl_4 into the LiAl anode (see Section XIX, "Electrolyte Mixed With Anode Alloy", this report).

To gain more information about the grey material, the next battery in the series, which was originally planned to be tested at 6 months, was removed from the oven and opened. A few cells were broken open and examined under a microscope at 10X, 20X, and 40X. The LiAl layer was badly darkened and "blued". There was no hint of a "grey layer". Another cell was chosen and tested at 200°C across a 5 ohm resistor. The test data showed that the cell had an unusually short t_{90} and t_{80} which correspondence with the low ED_{90} and ED_{80} . The internal resistances were usually high.

Post mortem examination of the cell showed the "grey layer" in the anode. Also present at the anode/anolyte layer was some reddish material characteristic of Cu metal or Cu_2O . This is the first time a grey layer has been noticed in a single cell post mortem. It should also be noted that the cell was discharged to past t_{60} and single cell tests are usually stopped at about t_{70} .

The third feature noticed in the post mortem examination of battery #1076 was a considerable number of broken cells and, particularly, the anode edges had crumbled. These crumbled edges explain the noise in the discharge. This was probably caused by poor mechanical preparation of the cells and has probably already been cured by sharpening the press dies.

The conclusion of this is that there appears to be a change in the anode, particularly at the anode/anolyte interface, characterized by a darkening and bluing of the LiAl before the cell is discharged and the formation of a dull grey material after discharge, aggravated by hot storage inside a battery.

VACUUM DESICCATION OF CELLS:

One time it was noticed that the "spike" appeared to be removed after some cells were vacuum desiccated. The spike had been a nuisance and it would have been real progress if the process of vacuum desiccation would have removed it. This process was tried a couple years ago with the MoCl_5 cells and was abandoned because the cells were so badly degraded by the treatment. Now it is known that the MoCl_5 catholytes are not stable in a vacuum oven. The process that wouldn't work for the MoCl_5 cells might have worked quite well for the CuCl_2 cells.

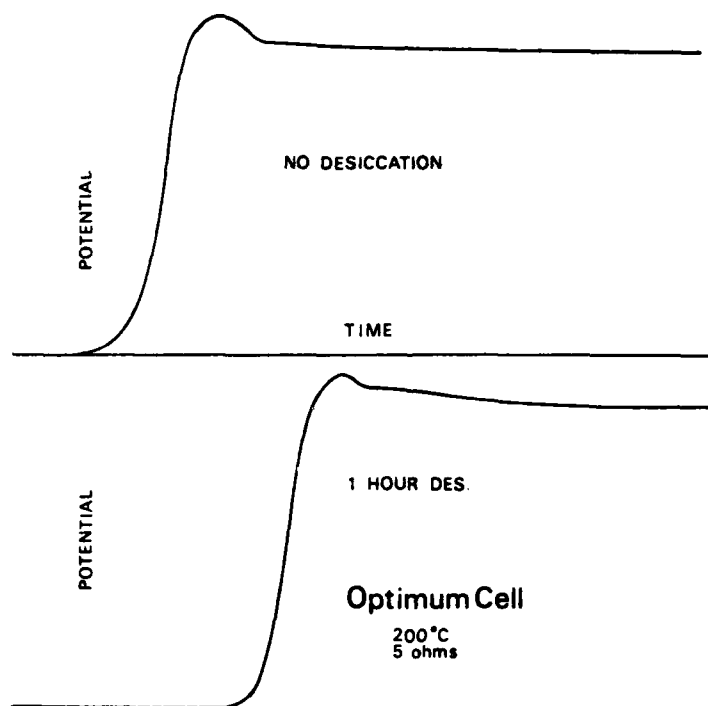


Figure 40. Discharge Curves Comparing "Wet" And Dry Cells

This process was first noted when some of the factorial design cells were tested and displayed large spikes. These were vacuum desiccated for one hour at 165°C (single cell #1557 for example) and when they were retested there was a reduced spike (Figure 40).

Next, some of the cells tested during the alternate graphite study were vacuum desiccated at 165°F for 3 hours and the spike was entirely removed (Figure 41).

When freon blending began many of these cells displayed bad spikes and, once again, these were removed by vacuum desiccation (Figure 42).

Finally, a set of cells was made and tested specifically to observe this process (Figure 43).

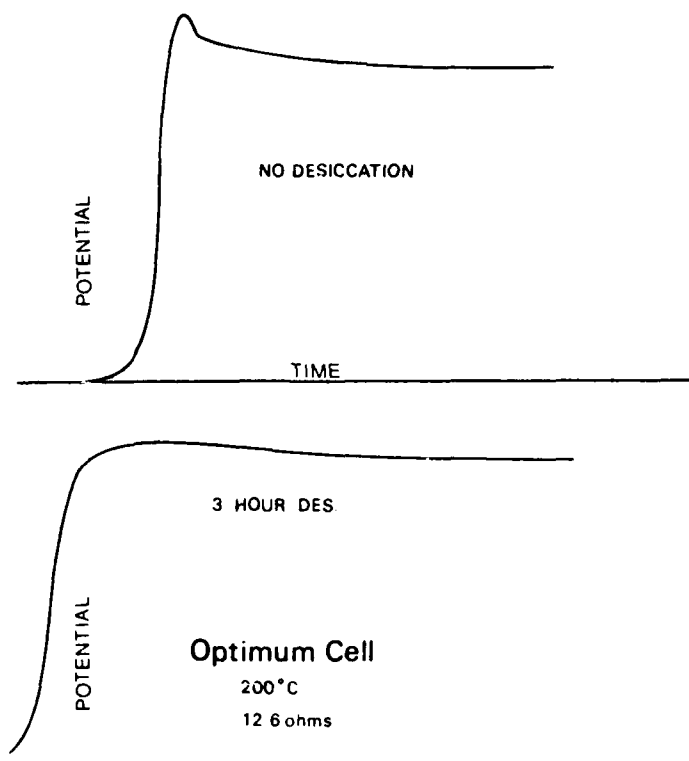


Figure 41. Discharge Curves

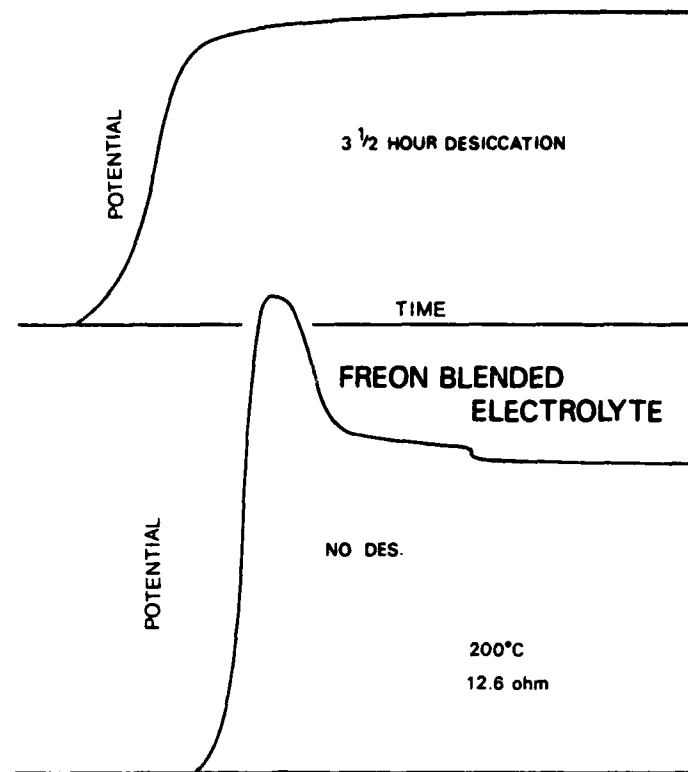


Figure 42. Discharge Curves For Freon Blended Cells Showing The Effect Of Desiccation On Spike Formation

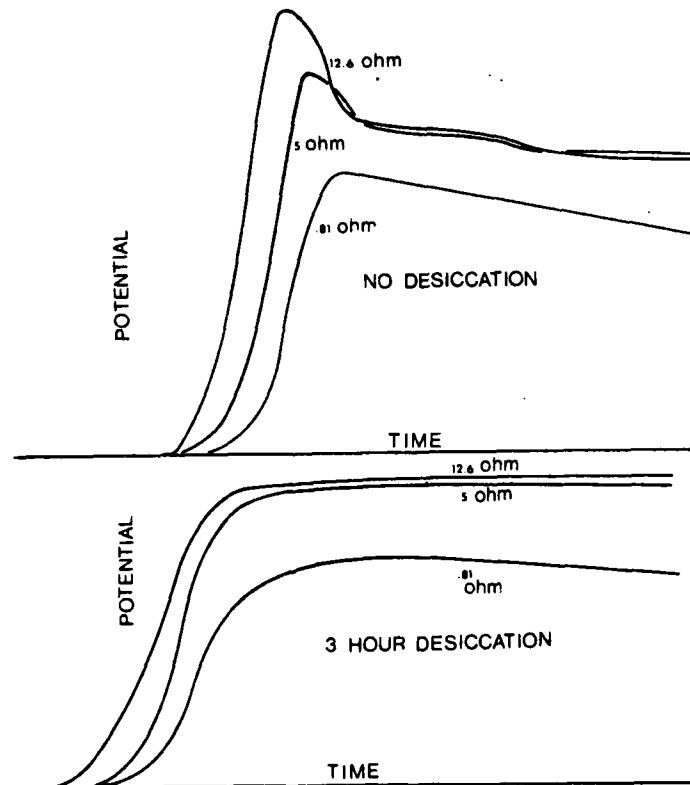


Figure 43. Discharge Curves Demonstrating The Effect Of Desiccation Upon Spike Formation

It was the conclusion of this work that the spike could be removed from the CuCl_2 cell by the vacuum desiccation. The mechanism of the "fix" involved an increase of internal resistance.

At a later instance, when some $\text{LiAlCl}_4/\text{NaAlCl}_4$ type cells were being tested, a spike was noticed. This was just a small spike. An attempt was made to lessen the spike by cell desiccation. While the spike was lessened somewhat the lifetimes were also considerably shortened. A post mortem examination showed a grey darkening at the anode/anolyte interface such as has been previously reported for cells stored in hot storage battery units. For this reason it was felt that the anodes may have been affected by the overnight storage in a vacuum oven held at 165°C . The tests were repeated at a later date with fresh cells.

During another instance some cells were made to test the amount of Cab-O-Sil in a LiAlCl_4 anolyte. These cells were not particularly good. They were similar in performance to the previous set of cells made with the mixture of NaAlCl_4 and LiAlCl_4 . The post mortem of those cells also showed a darkened anode. These cells were also stored overnight in a vacuum oven at 165°F . It is therefore suspected that the poor performance was caused by the overnight storage in the vacuum oven. These tests were also repeated with fresh cells.

As a result of these and similar tests it was decided that the process of vacuum desiccation of cells should only be used to try to "fix" cells which have displayed a large spike. It would have to be concluded that indiscriminate use of cell desiccation is to be avoided. Apparently the cell desiccation suppresses the spike by causing a reaction in the cell, which can be detected by an increase in internal resistance. If there is no spike to suppress then the increased internal resistance is entirely negative to cell performance and the cell should not be desiccated.

CONCLUSION:

The two largest fabrication problems which have occurred are cells that are easily broken and cells that are difficult to shear or punch. Both problems are correctable by maintaining well machined press dies, maintaining the proper press pressure, and by adding a ductile material such as Mg to the brittle LiAl alloy anode.

It was developed that the cells are very sensitive to moisture. The cells are four orders of magnitude more conductive while in the uninitiated state than are LiCl-KCl type cells under similar circumstances. It has been found that the anode/anolyte interface is particularly sensitive to moisture and degradation on storage. For this reason the practice of vacuum desiccation of all cells prior to testing was initiated. However, this practice was discontinued when it was discovered that the vacuum desiccation caused a serious retardation of cell performance. It is believed to be better practice to protect a cell from moisture than to try to dry out a moist cell.

SECTION XXI
BATTERY BUILDING

The first battery design was a 10 cell series stack in a 2 inch tall by 2 inch diameter steel can. The design was the same as for batteries made for the feasibility study of this system except that the can was a different size and therefore there were some differences in insulation and in the header and match assembly. This design was extremely simple to reproduce and was considered a "test battery" until some major design change was made. Figure 44 is a diagram which represents the test battery design. Figure 45 is an x-ray photograph of battery S/N 1001.

The cells were a disk, 1.469" diameter, with no center hole. The anode was $0.5 \pm .1$ gm 28 ^W/o LiAl alloy.

The anolyte was $1.3 \pm .1$ gm Anolyte #1004 and the catholyte was $2.3 \pm .1$ gm Catholyte #1015. The press compacting pressure was about 110,000 PSI. The total cell weight was 4.1 gm and the cell thickness was 0.070 inches.

The heat paper was LSS 15%, 430 cal/gm, 115 cal/in², solid disk, 1.469" diameter. The cell connectors were 0.004" nickel. The fuze strips were LSS 8%, 430 cal/gm, 130 cal/in², 5/16" wide.

The stack was pressed at 5,000 lbs. force and again pressed at 5,000 lbs. while in the case. The closing pressure was 300 lbs. of force on the header. The finished battery, S/N 1001, weighed 220 gms with a volume of 6.28 in³ or 103 cm³.

The test was conducted at room temperature and the battery was discharged across a 35 ohm resistor. The activation was .81 seconds. The peak voltage was 22.3 volts (2.23 volts/cell), with a peak current of 637 mA and a peak current density of 58.3 mA/cm². The energy density generated at 90% of peak

WRIGHT-PATTERSON TEST BATTERY

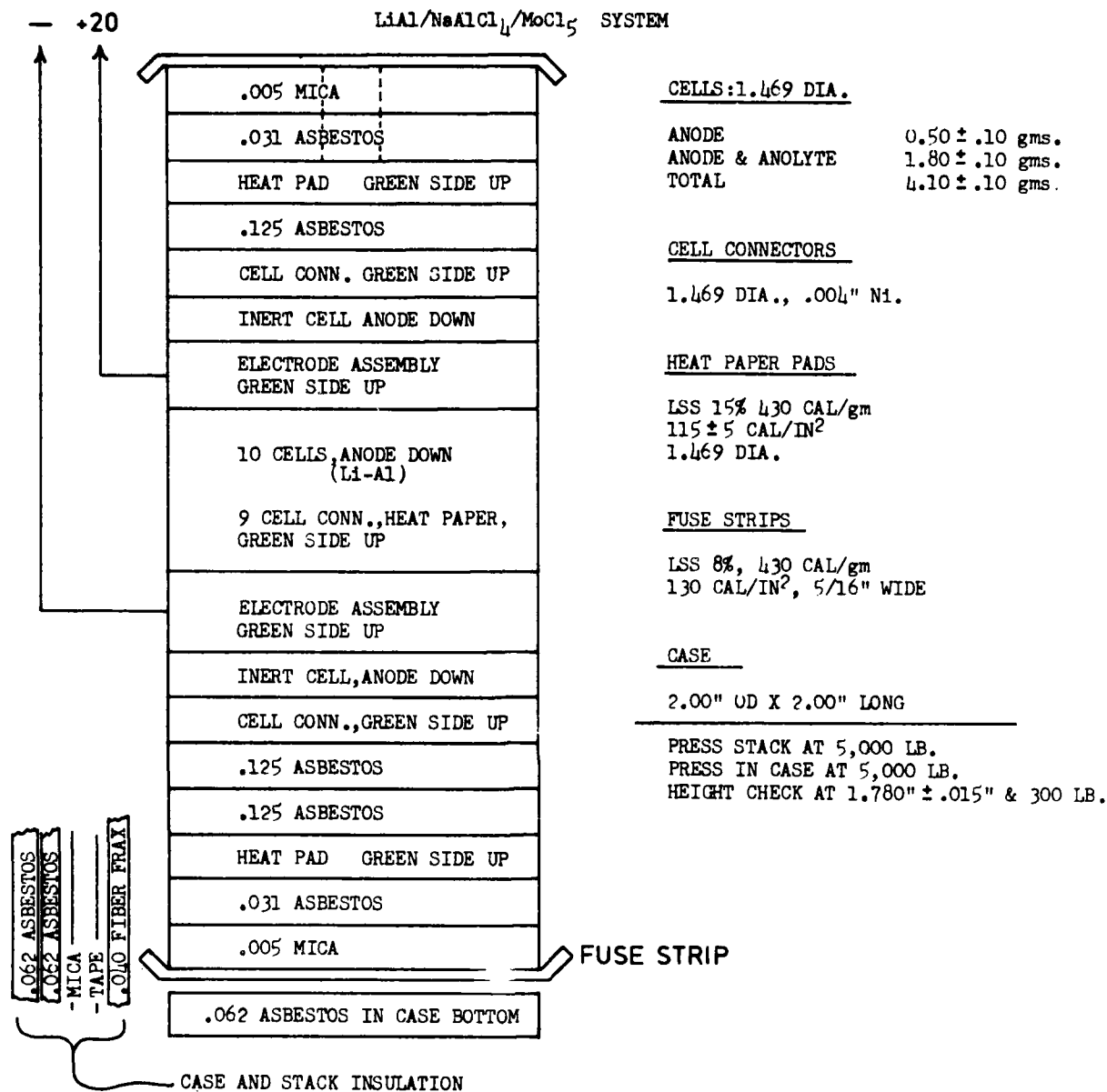


Figure 44. A Schematic Diagram Of A Wright-Patterson Test Battery



Figure 45. X-Ray Photograph Of Battery S/N 1001

was approximately 6.60 Wh/cm^3 . The internal resistance was measured once (at about 90% peak) and was 0.35 ohm (at about 90 seconds into life). The 90% life was 76 seconds, the 80% life was 150 seconds, the 70% life was 217 seconds, the 60% life was 403 seconds. The skin temperature was monitored with a thermocouple. The skin temperature was initially 27°C ; 137°C after 242 seconds; 148°C after 400 seconds; 149°C after 455 seconds, and 150°C after 570 seconds. The peak temperature was 150°C . During this discharge there was no easily measurable electrical noise. The battery did not vent or deform.

Battery #1002 was similar to #1001. This battery was fabricated with MoCl_5 cells, 115 cal/in^2 heat paper, 28 w/o LiAl anodes. This battery was the control unit for a series of batteries made for storage testing. Batteries #1002 to #1006 were all tested at room ambient temperature

TABLE 78 STORAGE BATTERY TEST RESULTS

S/N	V_p	i_p	t_{90}	t_{80}	t_{70}	ED 80 IDEAL	ED 80 ACTUAL	LOAD	NOTES
	volts	mA/cm^2	seconds	seconds	seconds	Wh/kg	Wh/kg	ohms	
1002	24.4	53.8	110	240	330	22.4	3.58	35	Control Unit
1003	22.8	59.6	30	134	326	10.3	1.96	35	Stored 28 days at 70°C before testing
1004	8.9	23	103	149	203	1.94	0.37	35	Stored 28 days at 70°C with + and - terminals shorted
1005	20.9	239	18	85	122	25.5	4.84	8	Stored 5 months at room ambient temperatures
1006	15.8	181	47	95	145	16.3	3.09	8	Stored 28 days at R.A. with + and - terminals shorted & 4 months at R.A. unshorted

Battery #1003 was similar to #1002 except that it was stored for 28 days in an oven maintained at 71°C. The battery was allowed to reach room temperature prior to testing. The battery produced a peak voltage and current of 22.4 volts and 651 mA with a current density of 59.6 mA/cm². The battery activated in 1.22 seconds. The lifetime to 90% of peak was 30 seconds; to 80% of peak was 134 seconds. The battery produced 10.2 Wh/kg based on 41 grams of cell weight and 1.96 Wh/kg based on 216 grams of total battery weight.

Comparing the results from Batteries #1002 and #1003 show that the hot storage definitely appeared to hurt the battery performance. The peak voltage was 6.5% lower, all of the early lifetimes were shorter and the energy density was 45% lower.

It was observed during single cell testing that short 90% and 80% lifetimes were indicative of a high voltage activation spike. Therefore, the relative failure of Battery #1003 could be caused by spike formation. However, the peak voltage was lower than before storage, not higher. While the hot storage may have caused a spike formation there is obviously material deterioration or the peak voltage would not have dropped off.

Battery #1004 was exactly like #1003 except it was stored with the plus and minus terminals shorted together. This battery had only about 1/3 as high a voltage ($V_p = 8.19v$) as the control battery. This battery only produced about 1/10 the energy density of the control unit. Obviously, the storage left the battery seriously depleted and deteriorated.

Battery #1005 was stored for about 5 months at 25°C before testing. The terminals were not shorted together. The peak voltage was smaller and the lifetimes shorter but the energy density to 80% was longer. This was because the test was 8 ohms instead of the usual 35 ohms. This allowed the maximum current density to

be up around 239 mA/cm^2 instead of 63 mA/cm^2 . The single cell studies indicate that the LiAl/MoCl_5 system produces a higher energy density at higher current densities. The lower voltage is also explainable by the heavier load. Therefore, the conclusion of this test seems to be that the battery was not seriously deteriorated by room temperature storage for 5 months.

Battery #1006 was the last battery of this series. It was stored at room temperature for the first month with the plus and minus terminals shorted together and with the short removed for the balance of the storage time. Battery #1006 performed significantly worse than #1002, the control unit.

Batteries #1013 & #1014 were two more storage batteries. These batteries were constructed similar to #1002 except that the heat paper was 120 cal/in^2 . These batteries were constructed 5 June 1978 and were tested 29 August 1978. They were stored at room temperature. These two batteries were made just to get an indication of repeatability.

There was an indication of spike formation ($t_{90} = 14$ seconds and t_{80} at about 74 seconds) but the repeatability was quite good (see Table 79).

TABLE 79 STORAGE AND REPEATABILITY BATTERY TEST RESULTS.
THESE BATTERIES WERE TESTED AT ROOM TEMPERATURE ACROSS AN
8 OHM LOAD

S/N	V_p	i_p	Act.	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	Spec. r at 90%
	volts	mA/cm^2	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	$\text{ohm}\cdot\text{cm}^2$
1013	21.8	249	1.80	14	74	108	0.97	4.5 ^a	11.2
		+			+	+		+	
1014	21.8	249	1.72	15	75	107	1.04	4.63	13.4

Early cell studies indicated that MoCl_5 catholytes might not have an acceptable shelf life. For this reason some CuCl_2 batteries were made for storage testing. The first set of batteries were stored at room temperature and were tested after being stored for various intervals of time.

TABLE 80 BATTERY TEST RESULTS FOR CuCl_2 BATTERIES STORED AT ROOM AMBIENT TEMPERATURE. ALL BATTERIES TESTED AT ROOM TEMPERATURE AND ACROSS A 25 OHM LOAD

S/N	STORAGE TIME	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}
						ACTUAL		at Peak	at t_{70}
		volts	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm.cm ²	ohm.cm ²
1027	Control	19.3	62	183	333	1.07	2.75	17.4	36.4
1028	1 week	20.3	15	108	282	0.28	1.71	16.2	32.9
1029	1 mth	19.7	45	111	215	0.83	1.80	15.8	13.1
1050	3 mths	19.7	38	115	311	0.71	1.81	26.0	44.2
1070	6 mths	19.1	34	110	287	0.59	1.61	31.9	55.9
1077	1 year	19.2	20	82	217	0.34	1.19	29.2	57.5

Figure 46 illustrates the data in Table 80. The upper curve is a plot of the peak voltage. It can be seen that the peak voltage did not change across the entire year of storage. The middle curve is a plot of how the internal resistance changed as the year progressed. This internal resistance measurement was measured at t_{70} . The R_{INT} at one month was unusually low. Except for this point the internal resistance showed a gradual increase across the one year interval. The bottom curve is a plot of the actual battery energy density measured at t_{80} . This showed a severe drop after the first week of storage followed by a much less, gradual drop to the end of the year. The significant point is the severe drop at the beginning of the storage period.

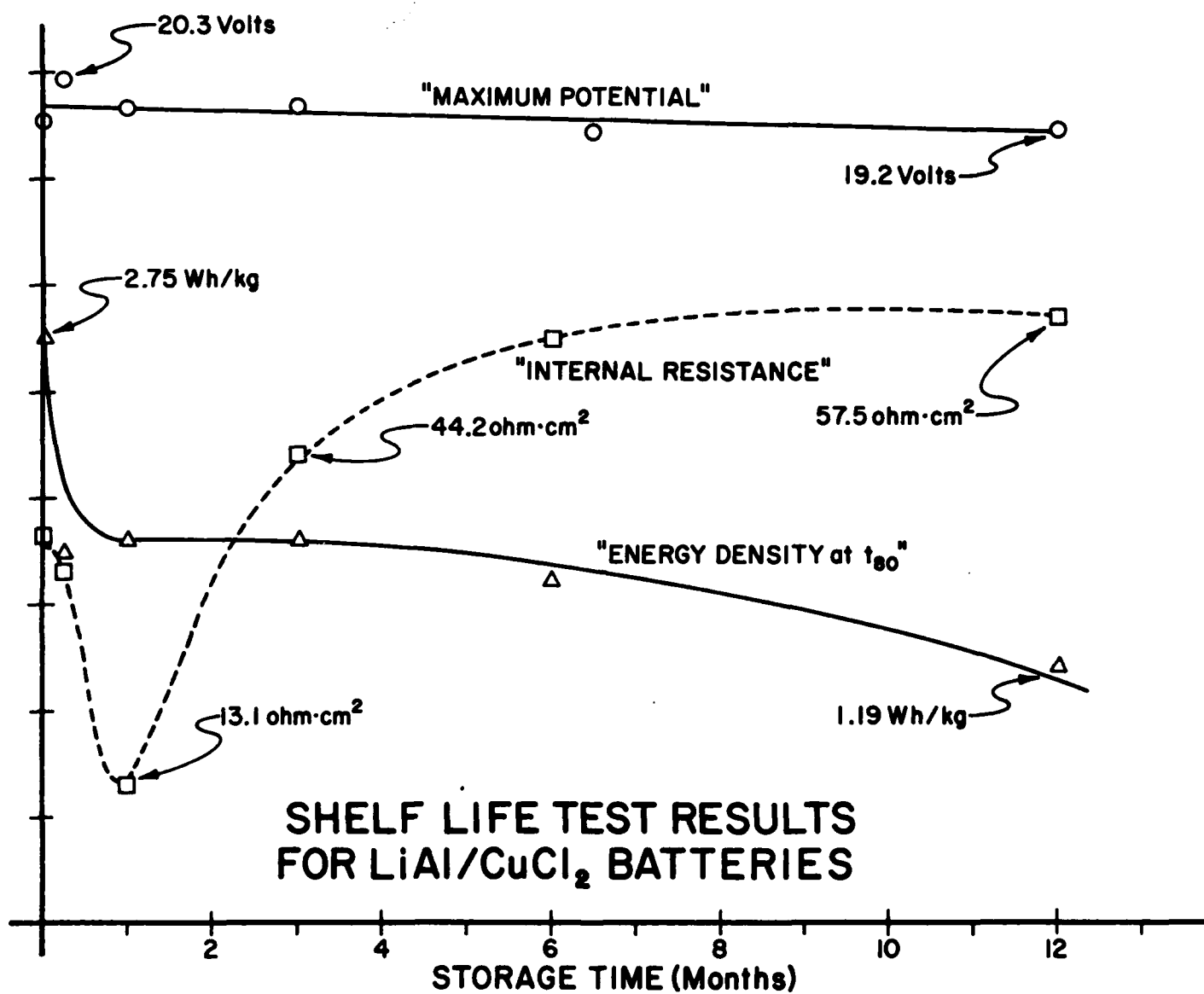


Figure 46. Battery Test Results For CuCl₂ Batteries Stored At Room Temperature

One year is a long time to store a set of batteries and to wait for test results. It was decided to store the batteries at 165°F as an accelerated storage test.

TABLE 81 BATTERY TEST RESULTS FOR CuCl_2 BATTERIES STORED AT 165°F. ALL BATTERIES TESTED AT ROOM TEMPERATURE ACROSS A 25 OHM LOAD

S/N	STORAGE TIME	V_p volts	t_{90} seconds	t_{80} seconds	t_{70} seconds	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}
						ACTUAL		at Peak	at t_{70}
						Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²
1027	Control	19.3	62	183	333	1.03	2.75	17.4	36.4
1038	1 day	20.1	66	153	308	1.20	2.51	X	61.4
1037	1 week	19.6	64	150	281	1.11	2.35	14.1	49.8
1036	2 weeks	19.5	62	138	247	1.08	2.16	16.9	44.2
1035	3 mths	13.8	25	52	86	0.22	0.60	120	225
1034	3 mths	9.5	SECOND TEST			X	X	X	X

It can be seen from the data in Table 81 that there was not the severe performance drop at the beginning of the storage period as there was with the previous set of batteries. However, at three months the performance was extremely poor. The discharge curve was very noisy. A post mortem examination of these batteries showed cells with crumbled edges and the LiAl/anolyte interface was very dark. It appeared that the cells did not survive physically and that the anode was degraded at the anode/anolyte interface. Specifically, the individual cell layers were delaminating; the individual particles of metal or salt were becoming uncompact from the whole.

At about this time in the program it was discovered that MoCl_5 was not storable and so these tests were not done with MoCl_5 batteries.

While it was known that the MoCl_5 was not storable it was not known to what extent the LiAl anode was going to be storable. In all of the above mentioned series there was visible evidence of anode degradation. It was felt that this degradation was aggravated by the "moist" air inside the sealed battery. For this reason some batteries were filled with dry argon. This was done by drilling a small hole in the header and placing the battery in a vacuum chamber. After the vacuum was held on the battery for one hour it was relieved by filling the chamber with dry argon. The hole in the header was then sealed. The first batteries to be backfilled were sealed by soldering the hole shut. However, this procedure overheated the batteries and destroyed the electric matches. So, the soldering procedure was replaced by filling the holes with an epoxy. The epoxy procedure was quite successful. Table 82 contains the battery test results for these backfilled batteries. These batteries were all stored at 165°F .

Figures 47, 48, and 49 illustrate some of the data from Table 82. The scales on the axes of these figures are the same as the scales on Figure 45 so that direct comparisons can be made.

Figure 47 illustrates how the peak voltage varied as the batteries were stored longer and longer. Notice that testing was after only three months of storage of the MoCl_5 batteries. However, the CuCl_2 batteries were not being degraded nearly as fast.

In order to add some perspective to these results it would be interesting to compare them with a better understood system such as $\text{Mg/LiCl}\cdot\text{KCl/V}_2\text{O}_5$. The $\text{Mg/V}_2\text{O}_5$ system has been a thermal battery standard for 25 years and is well characterized. It is believed that if a series of $\text{Mg/V}_2\text{O}_5$ batteries had been made and tested under exactly analogous conditions there would have been no

TABLE 82 BATTERY TEST RESULTS FOR BOTH CuCl_2 AND MoCl_5 BATTERIES BACKFILLED WITH ARGON. ALL TESTS WERE CONDUCTED AT ROOM AMBIENT TEMPERATURE AND ACROSS A 25 OHM LOAD

S/N	STORAGE TIME	V_p volts	t_{90} seconds	t_{80} seconds	t_{70} seconds	ED		R_{INT}	
						ED ₉₀	ED ₈₀	R_{INT}	R_{INT}
						ACTUAL		at Peak	at t_{70}
						Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²
MoCl ₅ BATTERIES									
1056	Control	28.3	56	190	275	1.49	4.28	4.93	9.71
1057	1 week	25.9	20	158	272	0.46	2.88	16.6	13.6
1058	2 weeks	25.3	26	144	256	0.56	2.52	19.2	12.4
1059	1 mth	23.9	35	121	194	0.67	1.95	18.8	18.0
1071	3 mths	6.8	25	37	55	0.05	0.06	20.4	17.4
CuCl ₂ BATTERIES									
1060	Control	24.7	73	203	380	1.44	3.46	12.4	34.9
1061	1 day	25.2	61	252	574	1.24	4.32	7.7	45.5
1062	1 week	23.2	41	127	454	0.72	1.90	29.2	80.5
1063	2 weeks	23.7	32	130	390	0.58	1.97	31.2	76.2
1072	3 mths	21.9	22	112	276	0.34	1.45	52.5	120
1075	6 mths	20.3	20	110	348	0.26	3.13	79	110

measurable difference in performance after 1 year storage at 165°F. The peak voltage would not have dropped, the energy density would not drop and the internal resistance would not change. If these hypothetical $\text{Mg/V}_2\text{O}_5$ batteries were included in Figures 47, 48, and 49 they would appear as straight lines with almost zero slopes.

Figure 48 illustrates how the energy densities changed. There is a well formed curve with a large negative slope for the MoCl_5 data points. The battery capacity was completely degraded after the first three months of storage

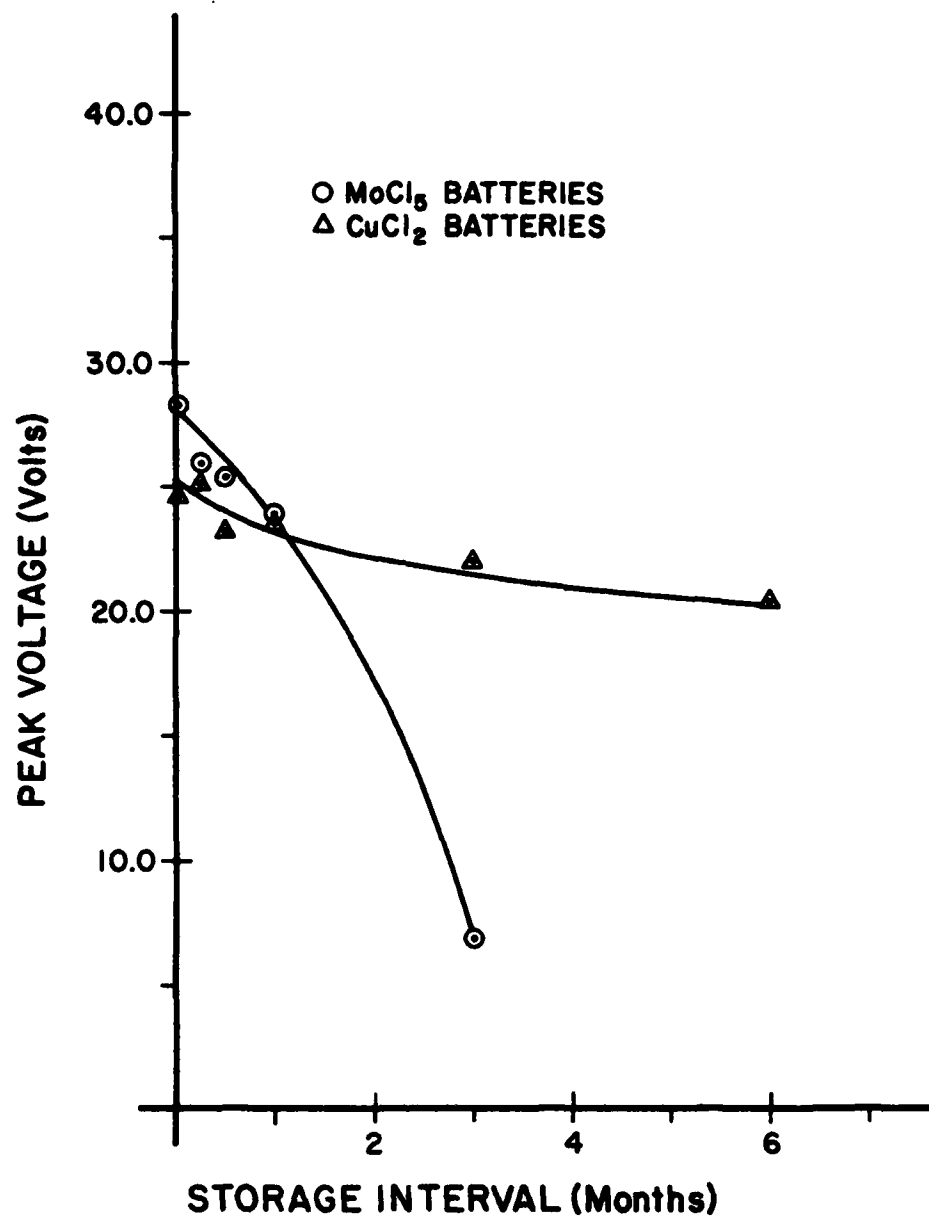


Figure 47. Peak Voltage vs. Storage Time

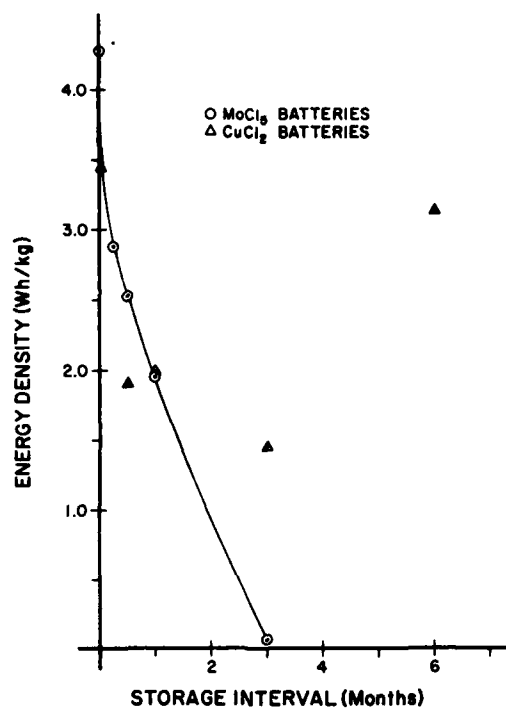


Figure 48. Energy Density vs. Storage Time

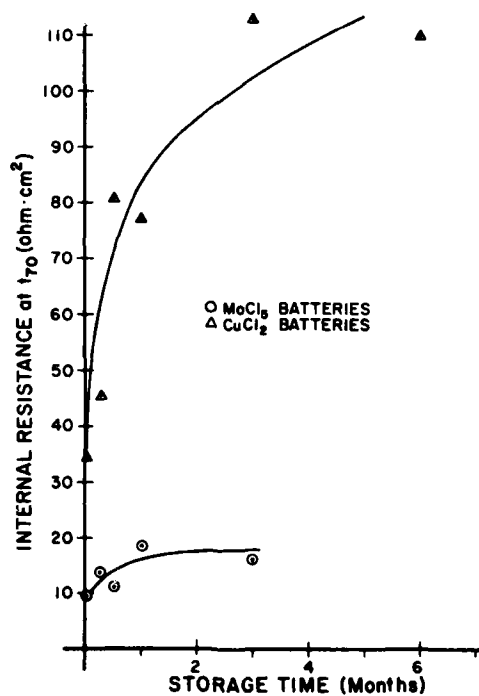


Figure 49. Internal Resistance vs. Storage Time

at 165°F. But the data for the CuCl_2 batteries is so scattered that no attempt has been made to fit a curve to the data points. It certainly cannot be concluded that the energy density of the CuCl_2 batteries was degraded upon storage at 165°F.

However, looking at Figure 49 one can see evidence that the internal resistance of the batteries were indeed increasing with storage time and the increase was even greater with the CuCl_2 batteries than with the MoCl_5 batteries.

These results can be interpreted to mean that the batteries made with tetrachloroaluminate electrolytes and LiAl anodes were being seriously degraded by storage at 165°F. While the CuCl_2 batteries were better than the MoCl_5 batteries they were still much worse than a conventional battery such as the $\text{Mg/V}_2\text{O}_5$ batteries previously described. Furthermore, the differences in degradation indicated that the two batteries (MoCl_5 and CuCl_2) were being degraded by different mechanisms.

By the time these tests were completed the volatile nature of the MoCl_5 catholytes was well known. What was needed was a mechanism for the degradation of the CuCl_2 batteries. It was known that the CuCl_2 catholyte was not volatile and was quite stable. It was believed that degradation of the LiAl anode was the cause of the degradation in performance. There was also evidence that cells with anodes of compacted LiAl powders were becoming uncompact upon long storage.

When the batteries were backfilled with dry argon it was insured that any moisture had to come from internal battery components. It was believed that perhaps the asbestos insulators in the can needed more desiccation so the open battery was stored for eight days in a vacuum oven held at 160°F and was not

removed from the oven until just prior to welding the header into place. The batteries were then backfilled with dry argon and epoxied shut. One battery was tested immediately and one battery was tested one month later. Table 83 contains the test results.

TABLE 83 BATTERY TEST RESULTS FOR BATTERIES THAT HAD BEEN VACUUM DESICCATED FOR EIGHT DAYS PRIOR TO CLOSING. THESE WERE CuCl_2 BATTERIES THAT WERE BACKFILLED WITH DRY ARGON. THESE BATTERIES WERE TESTED AT ROOM AMBIENT TEMPERATURE ACROSS A 25 OHM RESISTOR

S/N *	STORAGE TIME	V_p volts	t_{90} seconds	t_{80} seconds	t_{70} seconds	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	NOTES
						ACTUAL		at Peak	at t_{70}	
						Wh/kg	Wh/kg	ohm.cm ²	ohm.cm ²	
1060	Control	24.7	73	203	380	1.44	3.46	12.4	34.9	Not Desiccated
1064	None	24.4	51	205	442	0.98	3.31	19.4	61.4	Desiccated
1065	1 mth	22.6	27	121	380	0.45	1.67	39.0	71.4	Desiccated

* Batteries S/N 1051, 1052, and 1053 were made similar to the other batteries in this series except that they were stored in an oven at a temperature in excess of 200°F and the electric match assemblies were desensitized by the temperature. The batteries were consequently destroyed while trying to put them in new cases with new matches.

It can be seen from the data in Table 83 that the vacuum desiccation was not effective in extending storage life.

Some other batteries were constructed with cells that contained electrolyte in the anode. Mixing electrolyte with the LiAl alloy was an attempt to protect the anode. The discharge curves for these batteries were very noisy and only two batteries were tested. After only a week the rest of the test was abandoned (Table 84).

TABLE 84 BATTERY TEST RESULTS FOR BATTERIES MADE WITH ANODES THAT CONTAINED ELECTROLYTE. THESE BATTERIES WERE VACUUM DESICCATED PRIOR TO CLOSING AND WERE THEN BACKFILLED WITH DRY ARGON. THESE ARE CuCl_2 BATTERIES TESTED AT ROOM TEMPERATURE ACROSS A 25 OHM LOAD.

S/N	STORAGE TIME	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	NOTES
		volts	seconds	seconds	seconds	ACTUAL		at Peak	at t_{70}	
						Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	
1064	None	24.4	51	205	442	0.98	3.31	19.4	61.4	No Salt In Anode
1067	1 day	24.1	74	129	163	1.35	2.17	14.7	85.5	Electrolyte
1066	1 week	24.0	69	109	Noise	1.28	1.87	19.3	88.8	In Anode

The final attempt to improve the storage life of the CuCl_2 battery was to include all of the above mentioned techniques (except electrolyte in the anode) and to make cells out of electrolytes that were prepared with calcined Cab-O-Sil and vacuum desiccated graphite. The battery test results are in Table 85.

TABLE 85 BATTERY TEST RESULTS FOR BATTERIES MADE WITH ELECTROLYTES WHICH CONTAINED CALCINED CAB-O-SIL AND VACUUM DESICCATED GRAPHITE. THESE WERE CuCl_2 BATTERIES TESTED AT ROOM AMBIENT TEMPERATURE AND ACROSS A 25 OHM LOAD.

S/N	STORAGE TIME	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}
		volts	seconds	seconds	seconds	ACTUAL		at Peak	at t_{70}
						Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²
1068	Control	25.2	40	145	330	0.82	2.51	14.6	49.0
1069	1 week	25.3	37	152	350	0.76	2.63	12.2	43.7
1073	2 weeks	22.6	45	140	282	0.73	1.95	34.9	42.7
1074	1 mth	22.5	18	55	134	0.29	0.77	52.8	115
1076	3 mths	15.8	32	21	38	0.03	0.14	X	260

It can be seen from the data in Table 85 that there was no improvement. It would have to be concluded that either the "cures" did not work or else the theory about the mechanism is wrong. If the theory about the mechanism is wrong then the "cures" are for the wrong phenomena and will not be effective. Post mortem and pre-mortem examination of many storage battery cells have shown that the anode/anolyte interface does change with storage time. Furthermore, the LiAl anode has a tendency to crumble. At the elevated storage temperature of 165°F the change was somewhat faster. However, it may be that this change, while it might be easily observable, is not responsible for the degraded battery performance.

CONCLUSION TO SHELF LIFE TESTING:

Batteries constructed with cells made with MoCl_5 catholyte have no shelf life at all. The MoCl_5 catholyte is volatile and the cells are subject to self discharge. Batteries constructed with CuCl_2 type cells have much longer shelf lives. A CuCl_2 battery can be stored for about one year with about a 10% capacity loss. The CuCl_2 batteries have about a 66% capacity loss after only about six months storage at 165°F. Much of this capacity loss in the CuCl_2 system occurs in the first couple weeks of storage. Simultaneous with the CuCl_2 performance degradation there is a reaction at the anode/anolyte interface. It is believed, but has not been proven, that this reaction is brought about by moisture contamination inside the cell components. The attempts to improve shelf life by protecting the system from moisture were not successful.

HEAT BALANCE AND THERMAL MANAGEMENT:

When a battery is constructed the amount of heat the stack needs to produce must be balanced with the thermal requirements of the electrolyte salts. Enough heat is needed to fuse the electrolyte. If too little heat is available the salts will freeze too quickly and shorten the useful life. If too much heat is present unproductive and parasitic reactions can be accelerated. The cells will polarize too quickly and again shorten the useful life.

To balance a battery the heat requirements are estimated and batteries are made and tested. An ideal, perfectly balanced system could be tested both hot and cold and the useful lifetimes would be at optimum and the same for each test. From the Nernst equation it would be expected that the voltage of the cold test would be lower than for the hot test.

Battery #1007 was made similar to Battery #1001 except that 96 cal/in² heat paper was used instead of 130 cal/in². The activation was longer and the energy density was less so 115 cal/in² was decided upon as ideal.

Battery #1008 was made similar to #1002. Actually Battery #1008 was made prior to fabrication of #1002 and #1008 was used to prove in a new cell formula:

Anode 0.45 ± .1 gm

Anode & Anolyte 2.20 ± .1 gm

Cell 4.1 ± .1 gm

The heat paper was 115 cal/in². Since this battery performed well the storage batteries (later numbered #1002 through #1006) were made similar to this.

Batteries #1009 & #1010 were made similar to #1002, the new cell design. These batteries were the first batteries tested after being conditioned for hot and cold testing. That is, each battery was placed in a chamber at either 60°C (#1009) or -55°C (#1010) for at least 4 hours prior to testing. The batteries were removed from the chamber and fired within 5 minutes to insure that the inside of the battery was truly at the test temperature during initiation.

It can be seen from the data sheets that the batteries are quite well thermally balanced (Table 86). The hot and cold batteries have almost the same output. The voltage is slightly lower for the cold battery and the internal resistance is higher. The activation is longer for the cold battery. These performance characteristics are normal for thermal battery operation. The energy densities were quite similar.

TABLE 86 HOT AND COLD BATTERY TEST RESULTS

S/N	Temp.	P _v	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	Spec. r at 90%	Spec. r at 80%
	°C	volts	mA/cm ²	seconds	seconds	seconds	seconds	ohm·cm ²	ohm·cm ²
1009	60	23.1	264	1.13	22	72	103	2.36	3.21
1010	-55	21.4	245	1.70	22	75	119	528	6.41

Whenever some new material is included into a battery design the battery may need to be thermally balanced again. Some good examples of batteries made for this reason are S/N 1011 & 1012 made to test 20^{w/o} LiAl alloy; S/N 1015 & 1016 made to test 40^{w/o} LiAl alloy; and S/N 1017 & 1018 made to test 58^{w/o} LiSi alloy.

TABLE 87 BATTERY TEST RESULTS FOR BATTERIES
MADE TO TEST DIFFERENT MATERIALS

S/N	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	Test Temp	Test Load	NOTES
	volts	seconds	seconds	seconds	ACTUAL		°C	ohms	
					Wh/kg	Wh/kg			
1011	20.2	52	95	118	3.08	4.08	-45	8	To Test: 20 ^{w/o} LiAl/MoCl ₅
1012	21.8	26	78	96	1.79	4.64	85	8	
1015	23.2	16	61	97	1.29	3.63	85	8	To Test: 40 ^{w/o} LiAl/MoCl ₅
1016	20.9	28	78	169	1.80	3.78	-45	8	
1017	24.0	21	61	86	1.80	3.90	85	8	To Test: 58 ^{w/o} LiSi/MoCl ₅
1018	19.7	64	108	145	3.64	5.43	-45	8	
1019	25.8	0.78	1.20	117	0.02	0.02	73	50	To Test: Acidic NaAlCl ₄ Electro- lytes with 28 ^{w/o} LiAl/CuCl ₂
1020	20.9	0.30	220	530	0.01	1.79	-51	50	
1090	28.9	1.5	465	800	0.01	2.60	75	95	To Test: 28 ^{w/o} LiAl/LiAlCl ₄ /CuCl ₂
1091	25.3	235	360	450	1.23	1.76	-55	95	

It can be seen from the data in the above Table 87 that the batteries in the first three sets of test were relatively well balanced. Apparently changing the alloy material has a relatively small effect on the heat balance. The last two sets of batteries were quite unbalanced. The evidence of this is the great difference in the lifetimes. For example, t₈₀ for S/N 1019 was 1.20 seconds but t₈₀ for S/N 1020 (the cold test) was 220 seconds. Apparently changing the electrolyte has a much greater effect on heat balance than changing the anode alloy.

In the cases where the original heat estimate proves to be incorrect adjustments are made in the calorie value of the heat paper until the balance is made. For example consider battery series S/N 1090, 1091, 1092, 1093, 1094, and 1095.

TABLE 88 BATTERY TEST RESULTS THAT DEMONSTRATE THERMAL BALANCING

S/N	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	ED ₇₀	R _{INT}	R _{INT}	TEST	NOTES
					ACTUAL			t _{Peak}	t ₇₀	TEMP	
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1090	28.9	1.5	465	800	0.01	2.60	4.05	X	62.3	+75	150 cal/in ²
1091	25.3	235	360	450	1.23	1.76	2.05	12.5	189	-55	
1092	33.5	X	X	X	X	X	X	X	X	+75	180 cal/in ²
1093	26.6	185	425	575	1.06	2.16	2.17	8.11	55.2	-55	
1094	26.2	430	745	935	2.41	3.82	4.49	3.98	79.9	+75	130 cal/in ²
1095	25.8	120	180	237	0.65	0.91	1.10	16.5	158	-55	

Notice in battery set S/N 1090/1091 the cold life was much shorter than the hot life. Therefore the calorie value of the heat paper was increased from 150 cal/in² to 180 cal/in². The results of this increase can be seen in S/N 1092/1093. The hot test was a catastrophic failure. The readout was too noisy to provide any useful information. The cold test was good. Note that the lifetimes and energy densities did increase but the shortened t₉₀ showed that a spike was creeping into the cold discharge. The next tests, with heat paper of 130 cal/in² were an attempt to remove the spike. Tests S/N 1094/1095 showed no spike for either the hot or cold tests but the cold test had short life again. The heat had to be kept low to prevent a spike but had to be kept high to prevent premature freezing.

Another example of heat balancing was when a new battery case was received and "proved in". See Figure 50 for an x-ray of the new battery design. These were batteries S/N 1039, 1040, 1041.

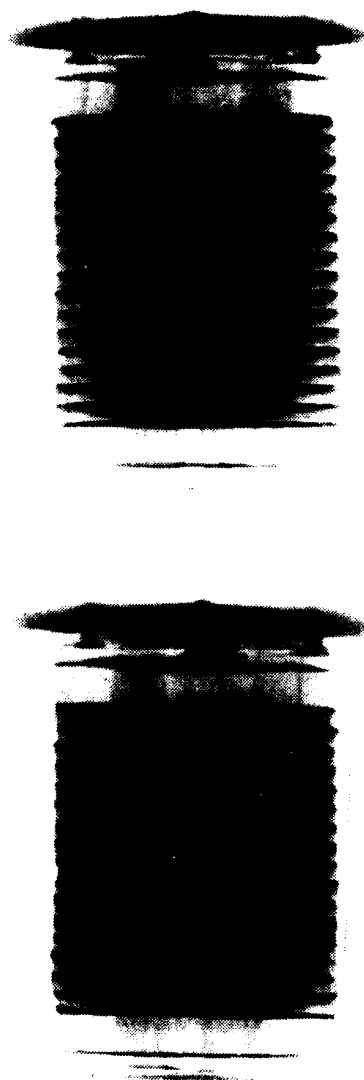


Figure 50. X-Ray Photograph Of New Battery Design

TABLE 89 BATTERY TEST RESULTS ILLUSTRATING
A ROUTINE HEAT BALANCE TRIAL

S/N	V_P	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	TEST TEMP	NOTES
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	at t_{90}	at t_{70}		
1030	7.5	HEAT PAPER DID NOT IGNITE: FUZE STRIPS IGNITED			X	X	X	X	Cold	85 cal/in ²
1031	6.7				X	X	X	X	R.A.	
1032	0.0				X	X	X	X	Hot	
1039	27.4	41	165	405	0.94	3.38	8.9	30.0	Hot	New case design 25 ohm load; CuCl ₂ ; 100 cal/ in ² heat paper
1040	27.1	55	147	426	1.24	2.95	24.9	45.3	R.A.	
1041	18.3	7	9	13	0.07	0.09	X	X	Cold	
1042	29.4	4	82	276	0.10	1.93	8.4	21.1	Hot	120. cal/in ²
1043	26.4	69	139	220	1.47	2.66	36.9	65.3	Cold	

The batteries were first made with 100 cal/in² heat paper. The room ambient and hot tests looked good but the cold test was too short so hotter heat paper was used (120 cal/in²). In this case the cold tests were good but the hot tests began to degrade. It was finally decided 115 cal/in² would be ideal for this design

Notice also in Table 89 tests S/N 1030, 1031, and 1032. These batteries were made with 85 cal/in² heat paper. The heat paper did not ignite. Only the fuze strips ignited. Heat paper at calorie values of less than 100 cal/in² is not very dependable.

The single cell tester was originally constructed with independent temperature controls on each platen. Taking advantage of this capability a series of cells was tested with anode and cathode platens at different temperatures. In every case the upper platen was the hotter of the two. The experiment was done to investigate the effects of heat upon spike formation and is directly related to the use of quinargo thermal buffers in the heat assemblies of the batteries.

The upper platen was always the hotter so the cells were always tested in pairs - one cell was tested with the anode up (anode hot) and the second cell was tested anode down (cathode hot). Some of the cells were tested under load and some were tested no load. Some cells were constructed with anolytes which contained IMSIL-25 and some of the cells used Cab-O-Sil as a binder. Table 90 is a tabulation of the 22 cells tested during this experiment.

The first cells were tested with the upper platen at 200°C and the lower platen at 40°C. It can be seen from Table 90 that the cells with hot anode produced a greater peak voltage than the cells with hot catholytes (A, B, C, and D). The rise times were slow and there was no hint of a spike for either loaded or unloaded cells. It was concluded that the 40°C lower platen was too cold for any meaningful data.

Accordingly the lower platen temperature was raised to 150°C. The upper platen temperature was maintained at 200°C. From Table 90 (E, F, G, and H) it can be seen that the peak voltage increased and the rise time was reduced to about normal. However, there was a severe spike associated with the no load tests but only a minor spike with the 5 ohm tests. The cells with the hot anodes once again had the highest peak voltage except for cells E and F. These were confused due to the presence of a spike.

TABLE 90 TEST RESULTS FOR SINGLE CELLS TESTED WITH
THE UPPER PLATEN HOTTER THAN THE LOWER PLATEN

S/N	Cathode Temp.	Anode Temp.	V _p	Rise Time	Spike	NOTES
	C ^o	C ^o	volts			
A	40	200	1.42	Slow	None	No Load
B	200	40	1.14	Slow	None	No Load
C	40	200	0.41	Slow	None	5 ohms
D	200	40	0.12	Slow	None	5 ohms
E	150	200	2.42	Normal	20%	No Load
F	200	150	2.69	Normal	30%	No Load
G	150	200	1.78	Normal	2%	5 ohms
H	200	150	1.64	Normal	5%	5 ohms
I	200	350	1.78	Fast	None	5 ohm load, ED ₉₀ = 11.3 Wh/k
J	350	200	2.12	Fast	20%	Cab-O-Sil 5 ohm load, ED ₉₀ = 0.33 Wh/k
K	150	400	1.80	Fast	4%	No Load
L	400	150	1.93	Fast	20%	No Load
M	150	400	1.43	Slow	(bad)	5 ohm
N	400	150	0.56	Fast	(double) (peak)	5 ohm
O	150	400	1.87	Fast	None	No Load
P	400	150	2.89	Fast	50%	No Load
Q	150	400	1.80	Fast	None	5 ohm
R	400	150	2.18	Fast	25%	5 ohm
S	150	400	1.59	Fast	None	0.81 ohm
T	400	150	1.65	Fast	6%	0.81 ohm
U	150	400	1.83	Fast	None	12.6 ohm
V	400	150	2.45	Fast	33%	12.6 ohm

Cells A through H were made with the IMSIL-25 anolyte and catholyte. The next two cells were made with regular Cab-O-Sil materials. Also, for the next two tests the upper platen was turned up to 350°C with the lower platen only turned up to 200°C. The results of these cell tests were very dramatic because a large spike was observed for the hot cathode test but no spike was noticed during the hot anode test. As a result of this spike the energy density to 90% for the hot anode test was 11.3 Wh/kg compared to 0.38 Wh/kg for the hot cathode test.

The next set of cells (K, L, M, and N) were tested with the upper platen at 400°C and the lower platen at 150°C. After cells I and J it was expected that the cells with the cooler cathodes would perform well but they did not. So this set of cell tests was repeated with cells made from Cab-O-Sil electrolytes (cells O, P, Q, and R). These cells performed as expected - similar to I and J with no spike observed for the cells with cold cathodes. These cells were so dramatic that four more were tested with a 12.6 ohm load and an 0.81 ohm load. In each case the cells with the hot cathode displayed prominent spikes while the cells with relatively cool cathodes did not.

An attempt was made to repeat on of these differential platen temperature tests with a reference electrode. However, the RTE cells have double thick anolytes and so did not react to the various temperatures the way the regular cells did. The cold cathode test formed a relatively narrow peak in the anode. The hot cathode produced a broad peak during the activation. There was a corresponding broad peak in the anode and a small peak, later, in the cathode trace. Could this second peak explain the multiple peaks sometimes observed during activation? About the only conclusion that can be made from this test is that the shape of the discharge curve during activation is similar to the shape of the anode to

reference discharge curve. As the cell reaches the end of its life and shape of the discharge curve is similar to the cathode to reference discharge curve.

CONCLUSION TO THE PLATEN TEMPERATURE DIFFENTIAL TESTS:

As a result of this work it was learned that even CuCl_2 batteries could form a pike if the cathode was not protected from overheating. To do this some batteries were made with asbestos thermal "buffers" inserted into the cell connector/heat source assembly on the cathode side. It is believed that the CuCl_2 cathode should be protected from the heat paper flash.

Batteries S/N 1021, 1022 and 1023 were the first of these batteries to be constructed with a thermal buffer inside the case. For battery S/N 1021 a disk of 0.003" asbestos paper was placed between the inert side of the heat pad and the nickel cell connector. This was done to protect the cathode from the flash of the heat paper. S/N 1022 was made with 0.003" disks of asbestos paper tucked into the heat assemblies between the nickel cell connector and the active side of the heat pad. This was done to protect the anode from the flash. A third battery, S/N 1023 was made with asbestos disks on both sides of the heat paper disk. This was done to protect both the anode and cathode equally. Table 91 contains the results of the tests of these batteries. These batteries were all tested at room ambient temperature across a 25 ohm load.

These batteries were CuCl_2 batteries made with cells that were prepared with acidic NaAlCl_4 . The anodes were LiAl (40 % Lithium). These anodes were particularly liable to form a spike. When the discharge curves turned out to be very straight it appeared that the buffers were going to work as intended.

TABLE 91 TEST RESULTS FOR BATTERIES CONSTRUCTED WITH QUINARGO HEAT BUFFERS IN THE CELL CONNECTORS

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _p	T _{Test}	Spec. r at 80%
	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm·cm ²
1021	20.2	73.9	1.11	99	169	284	15.5	2.93	219	25	18.0
	+			+	+		+		+		
1022	19.8	72.5	0.83	99	165	245	14.6	2.73	201	25	58.7
	+			+	+		+		+		
1023	20.7	75.9	1.0	77	129	207	12.4	2.33	240	25	30.0

Three more batteries were made and tested. These batteries did not contain asbestos buffers but they were made from cooler heat paper, 100 cal/in².

TABLE 92 BATTERY TEST RESULTS WITH A 25 OHM LOAD

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _p	T _{Test}	Spec. r at 80%
	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm·cm ²
1024	21.7	79.4	0.54	1.06	113	325	10.4	1.98	141	75	4.71
	+			+	+		+		+		
1026	19.0	70.6	1.00	72	252	7350	19.7	3.74	117	25	15.1
	+			+	+		+		+		
1025	18.0	65.7	2.34	104	206	355	14.7	2.79	89	-55	19.0

Notice that the short 90% life and longer 80% life indicate a bad spike for the hot test. The cold test was quite linear and the room temperature test was somewhere between these. This is another indication that a thermal buffer may be necessary to prevent thermal shock from causing a spike at activation.

Three other batteries were made and tested. These batteries were similar to previously made CuCl_2 batteries except for the heat paper. This heat paper had an inert layer on both sides of the paper. There were no asbestos buffers in the cell connectors.

TABLE 93 BATTERY TEST RESULTS FOR BATTERIES PREPARED WITH HEAT PAPER THAT HAD TWO INERT LAYERS

S/N	V_p	i_p	Act.	t_{90}	t_{80}	t_{70}	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T_{Test}	Spec. r at 80%
	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°F	ohm·cm ²
1049	26.3	96.2	1.08	60	176	386	19.2	3.42	165	18.2
1047	26.3	96.2	1.02	40	134	331	14.6	2.60	R.A.	22.1
1048	23.4	85.6	2.76	49	82	107	7.09	1.27	-65	77.9

These test were successful in removing the spike from the activation. This paper was too cold and 120 cal/in² would have been better.

Some batteries were made with cells of the optimum cell design. These cells had LiAlCl_4 anolytes and slightly acidic NaAlCl_4 catholytes. The first trial was with 150 cal/in² heat paper (Table 94).

TABLE 94 BATTERY TEST RESULTS FOR BATTERIES MADE WITH THE OPTIMUM CELL DESIGN AND 150 CAL/IN² HEAT PAPER. THE BATTERIES WERE TESTED ACROSS A 95 OHM LOAD

S/N	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	ED ₇₀	TEMP.	R_{INT}	R_{INT}
	volt	sec.	sec.	sec.	Actual				Peak	t_{70}
					Wh/kg	Wh/kg	Wh/kg	°C	ohm.cm ²	ohm.cm ²
1078	28.7	15	360	680	1.01	1.96	3.30	75	8.02	62.6
1079	25.2	260	410	513	1.37	2.00	2.34	-55	12.5	23.6

Notice that the hot test displayed a bad spike. This was not the case with the cold test. Notice that the ED_{70} was smaller for the cold test even though it did not display a spike. This was probably caused by the premature freezing of the electrolyte in the cold test. The next batteries were made with 105 cal/in^2 heat paper but there were asbestos thermal buffers in the heat paper subassemblies.

TABLE 95 TEST RESULTS FOR BATTERIES CONSTRUCTED WITH 150 CAL/IN^2 HEAT PAPER AND ASBESTOS THERMAL BUFFERS. THESE BATTERIES WERE TESTED ACROSS A 95 OHM LOAD.

S/N	V_p	i_p	t_{90}	t_{80}	t_{70}	ED_{90}	ED_{80}	ED_{70}	TEMP	R_{INT}	R_{INT}
						Actual				Peak	t_{70}
	volts	mA/cm ²	sec.	sec.	sec.	Wh/kg	Wh/kg	Wh/kg	°C	ohm·cm ²	ohm·cm ²
1080	30.9	29.8	1.85	145	505	.01	0.92	2.68	75	10.0	41.1
1081	25.2	24.3	245	381	474	1.33	1.86	2.17	-55	11.7	22.4

Notice from Table 95 and Figures 51 and 52 that adding the asbestos thermal buffers appeared to have no effect on battery performance. Also Figure 52 indicates that the electrolytes are fusing very quickly. The next batteries were built with 180 cal/in^2 heat paper, Table 96.

TABLE 96 BATTERY TEST RESULTS FOR BATTERIES MADE WITH 180 CAL/IN^2 HEAT PAPER AND WITH A THERMOCOUPLE AT THE SIDE OF THE STACK

S/N	V_p	i_p	t_{90}	t_{80}	t_{70}	ED_{90}	ED_{80}	ED_{70}	TEMP	R_{INT}	R_{INT}
						Actual				Peak	t_{70}
	volts	mA/cm ²	sec.	sec.	sec.	Wh/kg	Wh/kg	Wh/kg	°C	ohm·cm ²	ohm·cm ²
1082	24.7	23.8	265	420	525	1.33	1.95	2.28	-55	12.7	192
1084	29.9	28.8	2.0	310	720	0.02	1.83	3.71	+75	5.9	58.8

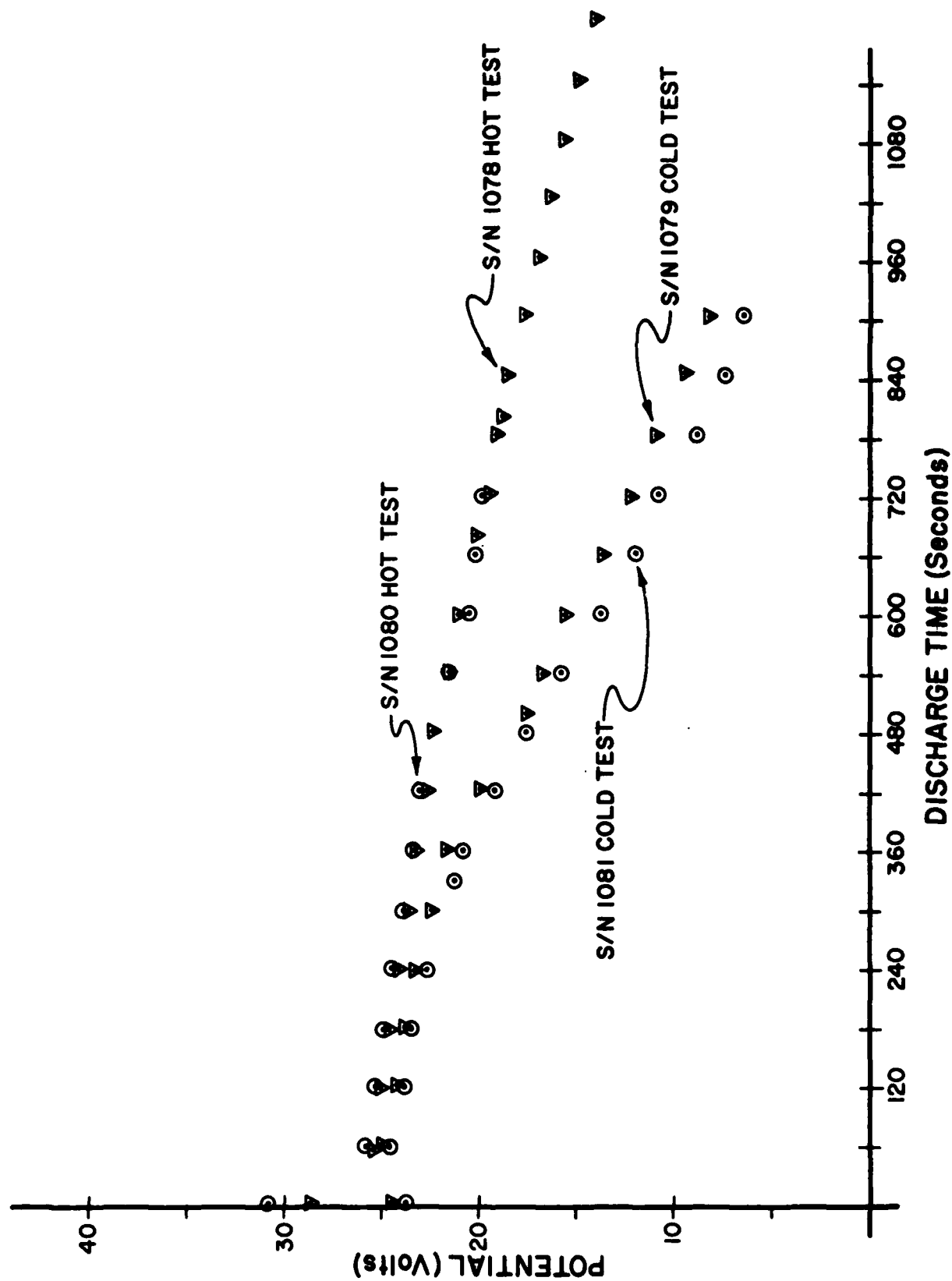


Figure 51. Discharge Curves Illustrating The Effect Of Asbestos Thermal Buffers

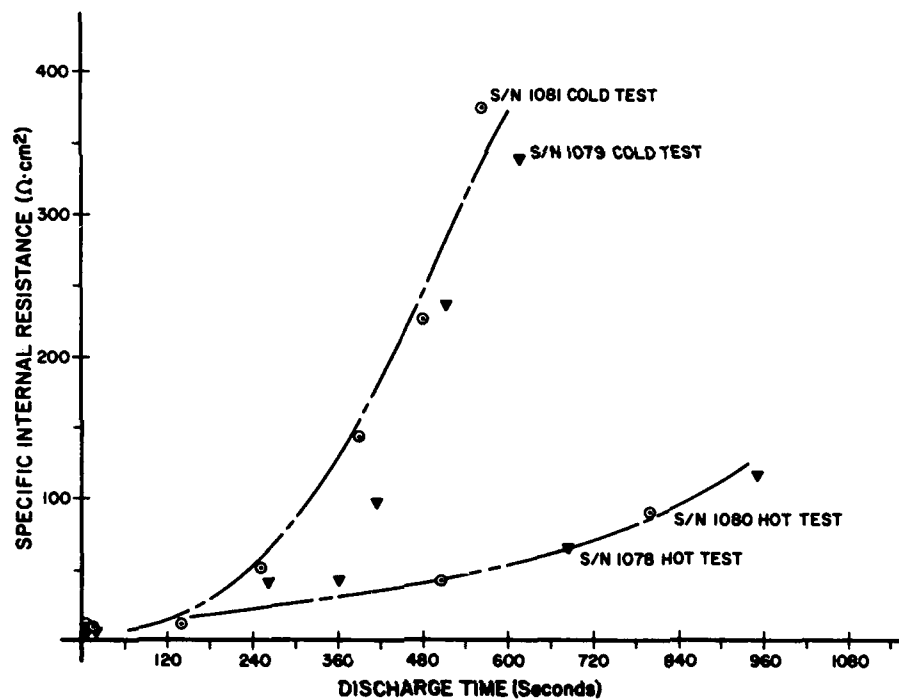


Figure 52. Curves Illustrating The Effect Of Asbestos Thermal Buffers Upon Internal Resistance

These batteries were not particularly good. They still displayed a spike during the hot test.

For these tests a thermocouple was taped to the cell stack inside the battery can. Figure 53 shows how the temperature at the side of the stack varied with time as the two batteries discharged. Notice that for battery S/N 1082, the cold test, this thermocouple never read above 120°C.

The next two batteries also had thermocouples taped to the side of the stack and a second thermocouple was taped to the case so the change in internal stack side temperature could be monitored simultaneously with the skin temperature (Table 97, Figure 54).

TABLE 97 BATTERY TEST RESULTS ACROSS A 95 OHM RESISTOR WITH THE INTERNAL STACK SIDE TEMPERATURE MEASURED SIMULTANEOUSLY WITH SKIN TEMPERATURE

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	ED ₇₀	TEMP	R _{INT}	R _{INT}
	Actual						Peak	t ₇₀			
	volts	mA/cm ²	sec.	sec.	sec.	Wh/kg	Wh/kg	Wh/kg	°C	ohm.cm ²	ohm.cm ²
1086	31.0	29.8	2.00	130	555	0.02	0.82	2.90	75	7.73	23.9
1088	25.7	24.8	280	565	785	1.52	2.75	3.49	-55	6.14	93.0

The battery performance was quite similar to the previous tests. Notice from Figure 55 that the voltage of the cold test (S/N 1085) began to fall off rapidly as the stack temperature approached 140°C.

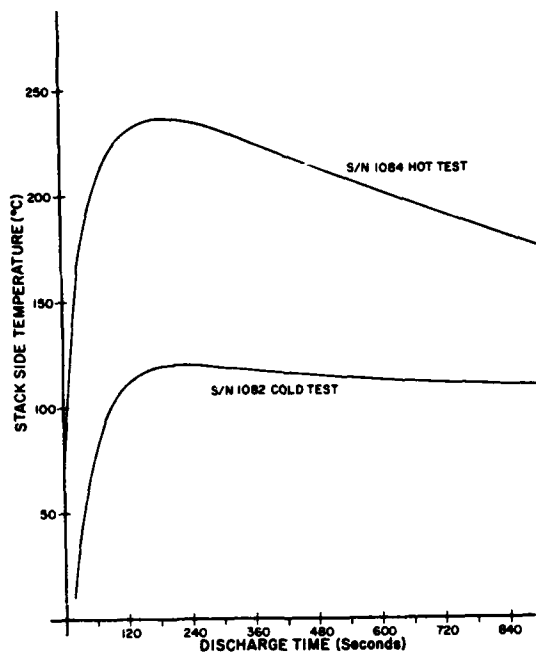


Figure 53. Stack Temperature vs. Time

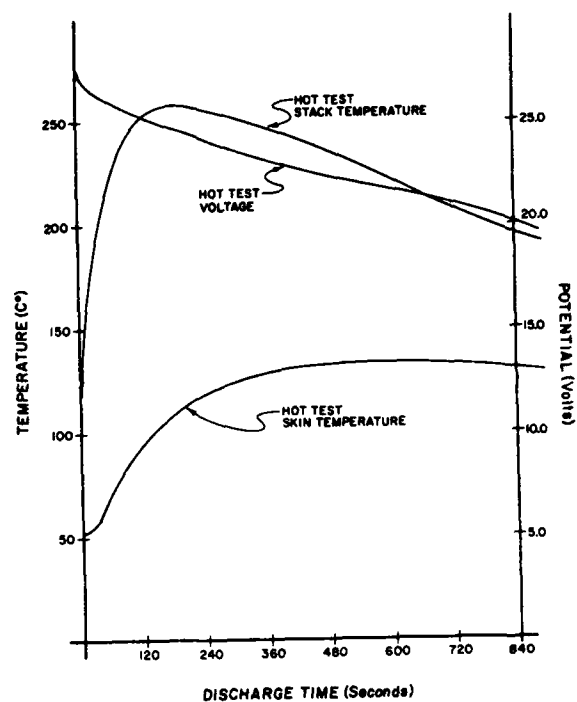


Figure 54. Stack And Skin Temperature Compared To A Discharge Curve For A Hot Test

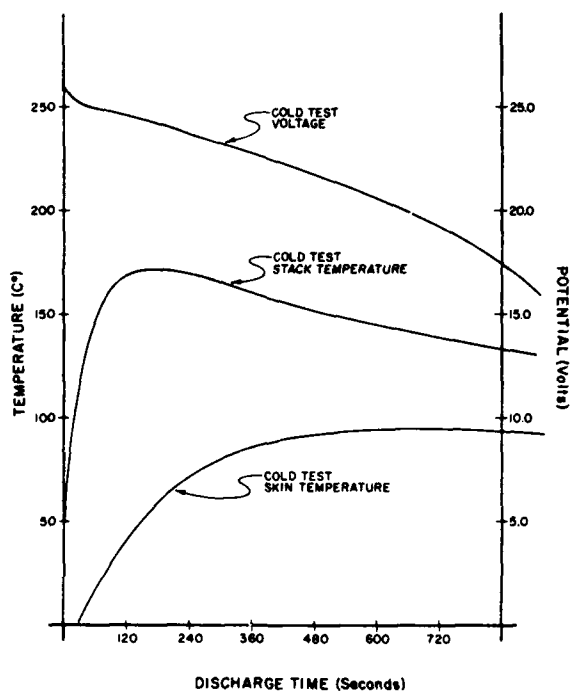


Figure 55. Stack And Skin Temperature Compared To A Discharge Curve For A Cold Test

The next two batteries also contained two thermocouples but in different positions. The 7th and 8th cells were separated and an additional heat paper/cell connector assembly was installed in the space. This caused two heat assemblies to be adjacent to each other. These were spread apart and a thermocouple inserted between two asbestos disks, which, in turn, were inserted into a cell connector and installed between the two heat assemblies. Figure 56 illustrates the various positions of the different thermocouple measurements. There was a second thermocouple at the side of the stack. Table 98 contains the battery test data.

TALBE 98 BATTERY TEST RESULTS FOR BATTERIES PREPARED WITH ONE THERMOCOUPLE AT THE STACK SIDE AND ONE AT THE STACK CENTER

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	ED ₇₀	TEMP.	R _{INT}	R _{INT}
	Actual									Peak	t ₇₀
	volts	mA/cm ²	sec.	sec.	sec.	Wh/kg	Wh/kg	Wh/kg	°C	ohm·cm ²	ohm·cm ²
1089	26.9	25.9	275	625	940	1.58	3.19	4.32	75	3.96	33.0
1088	25.8	24.8	240	550	830	1.27	2.59	3.51	-55	4.10	87.0

Figure 57 shows how the center stack temperature varied with time.

Notice from Figure 57 that the center of the stack realizes the flash of the heat paper but the side of the stack does not. Notice also that the center temperatures were always higher than the side heats. Also notice that the temperature of the center of the stack was never below the melting point of the electrolyte salts. Also notice from Table 97 that there was no spike on either the hot or cold test.

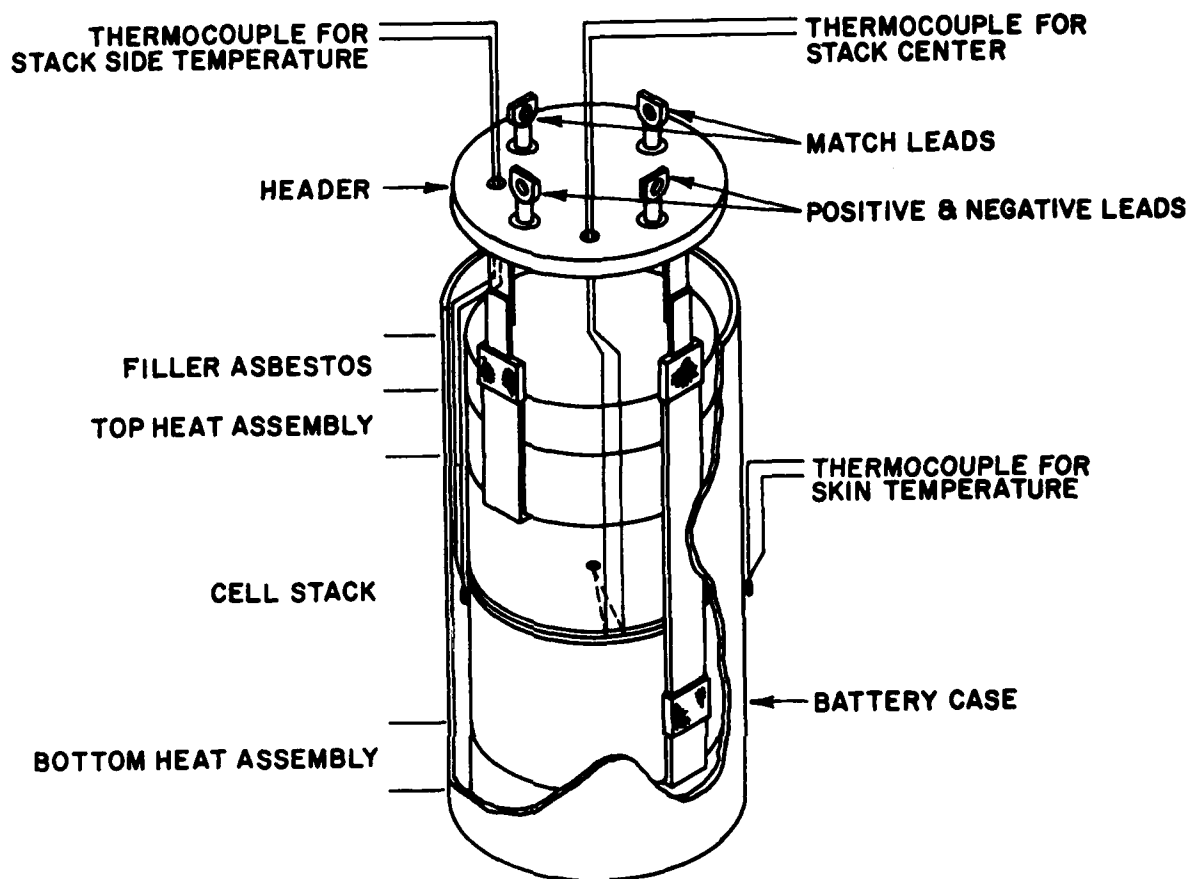


Figure 56. A Diagram Of The Test Battery And Various Positions For Thermocouple Placement

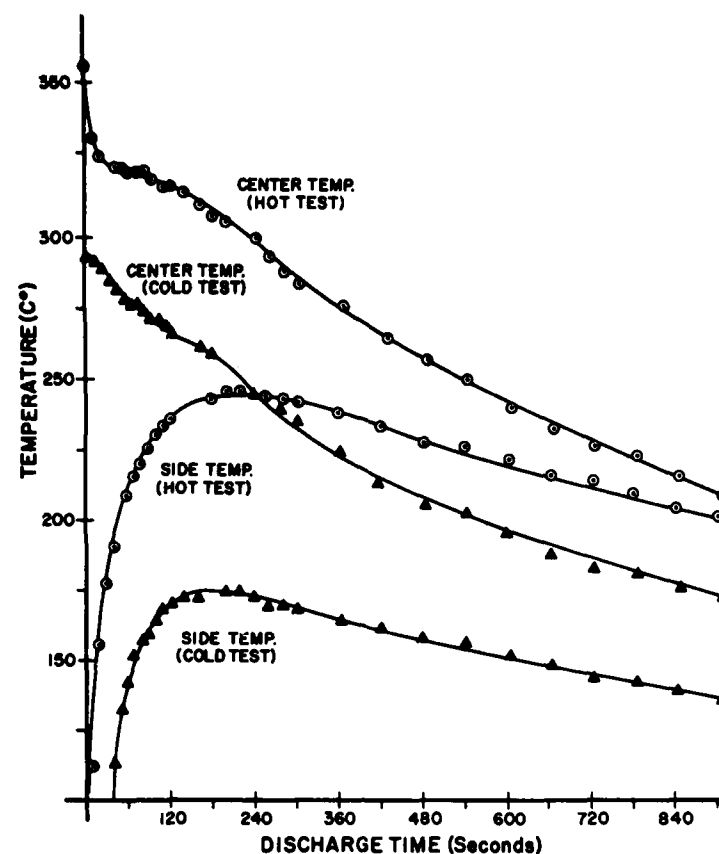


Figure 57. Temperature For Stack Center and For Stack Side vs Time

From these thermocouple data it can be seen that the life of the battery is not limited by the internal temperature. The stack is not freezing until well after t_{80} . The problem was not to keep the cells hotter for a longer period of time but to heat the cells more consistantly for a longer period of time. That is, the problem was to try, as near as possible, to approach the conditions of a single cell test with two constantly heated platens. In order to heat the cells in the stack more evenly a number of schemes were tried.

One scheme was to wrap the stack with heat paper. This was done because the thermocouple tests clearly showed that the edges of the cells were always about 50 C° cooler than the centers of the cells.

Batteries S/N 1090/1091 were made with 150 cal/in² heat paper and appeared too hot. Batteries S/N 1094/1095 were made with 130 cal/in² heat paper and were too cold. So, batteries S/N 1096/1097 were made with 130 cal/in² heat paper with 130 cal/in² heat paper wrap. Table 98 contains these test results.

TABLE 99 BATTERY TEST RESULTS ILLUSTRATING THE USE OF HEAT WRAP. ALL BATTERIES WERE TESTED ACROSS A 95 OHM RESISTOR

S/N	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	Test Temp °C	NOTES
	volts	seconds	seconds	seconds	Actual		t _{Peak}	t ₇₀		
					Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²		
1090	28.9	1.53	465	800	0.01	2.60	X	62.3	75	150 cal/in ² heat pads, no wrap
1091	25.3	234	360	450	1.23	1.76	12.5	189	-55	
1092	33.5	-	-	-	-	-	-	-	75	180 cal/in ² heat pads, no wrap
1093	26.6	185	425	575	1.06	2.16	8.11	55.2	-55	
1094	26.2	430	745	935	2.41	3.82	3.98	79.9	75	130 cal/in ² heat pads, no wrap
1095	25.8	120	180	237	0.65	0.91	16.5	158	-55	
1096	28.7	15	600	930	0.10	3.23	X	29.9	75	130 cal/in ² heat pads, 130 cal/in ² wrap
1097	25.3	205	325	410	1.06	1.56	12.4	106	-55	
1098	29.0	5.25	590	940	0.04	3.23	X	39.7	75	Same as 1096/1097 except wrap is nearer to case then to cell stack
1099	25.3	260	475	625	1.34	2.24	8.24	111	-55	
1100	28.0	190	710	1010	1.20	3.84	7.96	45.4	75	130 cal/in ² heat pads 175 cal/in ² wrap
1101	25.5	330	590	740	1.73	2.83	16.4	64.2	-55	
1102	27.2	280	530	725	1.68	2.88	8.02	82.4	75	Same as 1100/1101 except the stacks were vacuum desiccated overnight
1103	25.8	220	425	570	1.19	2.07	36.4	186	-55	

From the earlier experiments it was suspected this was too low but the 130 cal/in^2 heat wrap was supposed to make up the difference. This appeared to be the case for the cold test (which was similar to S/N 1091) but there was a spike for the hot test.

In order to suppress the spike the next two batteries were made similar to S/N 1096 & 1097 except that 0.155" of asbestos wrap was placed between the stack and the heat wrap. This was to lessen the thermal shock of the heat wrap flash. However, Table 99 shows that 1097/1098 were almost identical in performance to 1096/1097.

The next two batteries were made with 130 cal/in^2 stack heat but with 175 cal/in^2 heat wrap. A spike was expected with the hot test but the test was done to observe the change in the cold test. The cold test was improved considerably but the hot test did not display as bad a spike as was expected. Because of this another set of batteries was prepared similar to S/N 1100 & S/N 1101 but this time the stack was vacuum desiccated overnight before the battery was canned and closed. The results were difficult to appraise. The spike was gone from the hot test but the lifetimes were shorter. This is similar to results noticed when single cells were vacuum desiccated and, in fact, was the reason vacuum desiccation of cells was discontinued.

At this point it appeared that the cells were probably good and that the spike was caused by the thermal shock of the heat source ignition flash. This line of thought was responsible for the spiral heat wrap experiments. When the heat wrap burns it probably applies quite a thermal shock to the edge of the cells. In order to lessen this shock the wrap was cut into strips $5/32$ " wide and the strips were taped end to end to get one long strip (about 75" long). The idea was to wrap this long strip around the stack so that it would burn slowly and the calories would be delivered slowly.

To test this, the 5/32" strips were stuck to a long piece of 1/4" glass wrap tape. Then a second piece of 1/2" glass wrap tape was applied to the top so the long strip was completely covered with tape (Figure 58). This taped wrap assembly was wrapped around the outside of one empty battery can. It made two complete layers. One end of the strip was then ignited. It took 18 seconds for the strip to burn. It would have taken longer but during the test some of the tape on the inside layer burned through and ignited the outer layer too early.

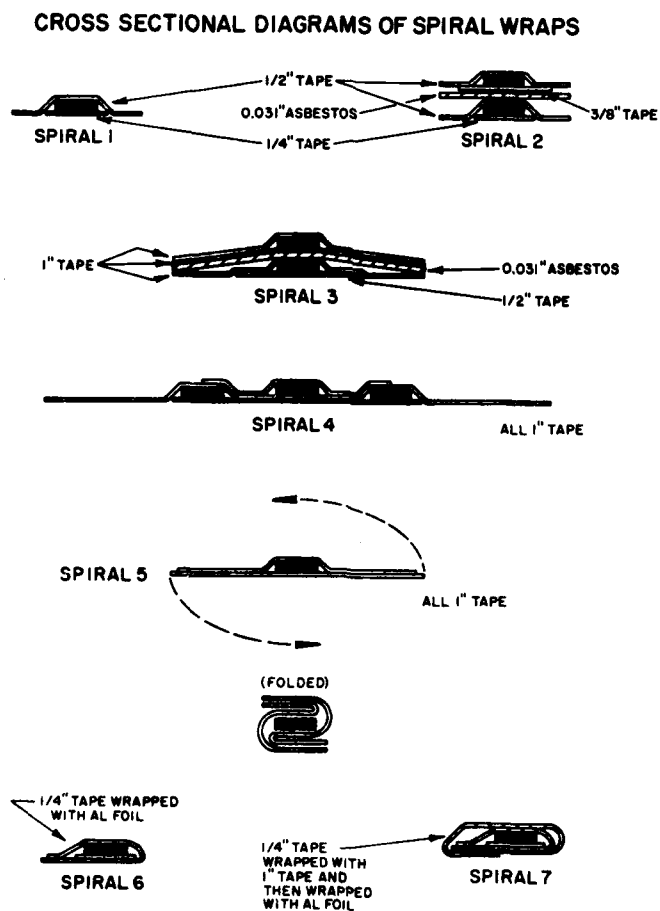


Figure 58. Various Spiral Wrap Designs

Because of the preignition of the outer spiral layer the two layers were separated by a layer of asbestos (0.031" thick). This was generally successful except that the flame shot out from under the asbestos and in a closed environment could have preignited the outside layer. That is, it only worked because it wasn't inside a battery.

Spiral 3 was made with 1/2" tape on the bottom and 1" tape on the top in an effort to contain the flame front. Flames once again shot out from under the asbestos wrap.

Spiral 4 was another method of wrapping with only tape but the tape burned through in a few places and again preignited the more outward layer.

With Spiral 5 the heat paper was completely wrapped with at least two layers of tape. This wrap burned for 15 seconds. It was very thick and would have consumed considerable volume inside a battery. Also, in spite of the double layer the tape still burned through in one piece.

Spiral 6 was prepared by placing the wrap on a 1/4" wide strip of tape and then wrapping the strip with a 3/4" wide strip of Al foil. However, the tape burned through and melted the foil.

Spiral 7 was wrapped completely with tape and then rewrapped with foil. This scheme worked.

Two 80" long spirals were made and wrapped around battery stacks. The batteries were closed and tested (S/N 1104 & 1105) (see Figure 59 for an x-ray photograph of S/N 1103). The test results (Table 100) will be further detailed later in this report. The batteries worked but there was still a bad spike. This indicates that the source of the thermal shock was probably the stack heat and not the heat wrap. The heat wrap could aggravate the situation but was not the primary cause.

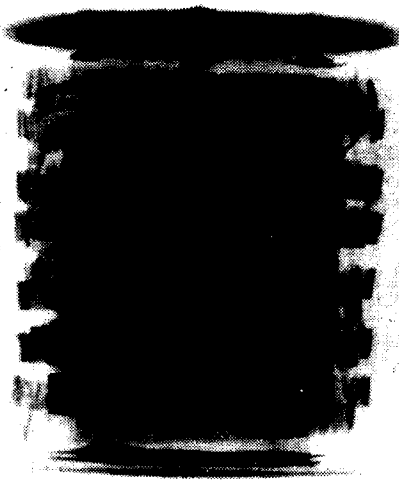


Figure 59a. An X-ray Photograph of S/N 1104
Showing The Spiral Wrap

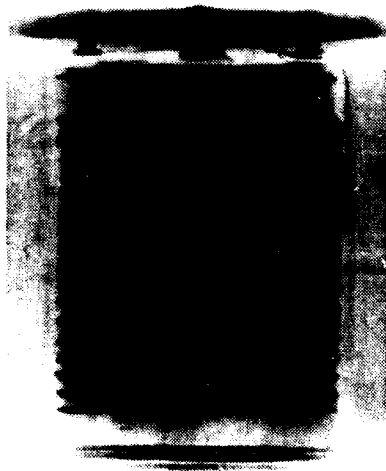


Figure 59b. An X-ray Photograph of S/N 1102
Showing Normal Heat Wrap

TABLE 100 BATTERY TEST RESULTS FOR BATTERIES MADE WITH SPIRAL HEAT WRAP. THESE BATTERIES WERE TESTED ACROSS A 95 OHM LOAD

S/N	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	Test	NOTES
	volts	second	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1104	30.1	0.32	330	620	.003	1.92	X	57.2	75	130 cal/in ² stuck with 170 cal/in ² spiral heat wrap
1105	24.8	190	305	400	1.00	1.49	24.5	81.7	-55	

These batteries were both successful and unsuccessful. That is, they activated and functioned normally without venting or electrical noise but the hot test still displayed a bad spike. Furthermore, the cold test had a short life. There was nothing unusual in the post mortem examination of these batteries.

It has long been known that thicker cell connectors can slow activation. It was hoped that thicker cell connectors would buffer the thermal shock of the heat source ignition flash.

For this reason the next two batteries were prepared with 0.015" thick cell connectors instead of 0.004" thick cell connectors as usual. The stack heat was 180 cal/in². There was no wrap heat.

Batteries S/N 1106 & 1107 were made with the thick cell connectors (0.015" thick). The results of the tests were a good hot test but a very short cold test. The next two batteries, S/N 1108 & 1109 were made with the 0.015" thick cell connectors with 180 cal/in² heat paper and 175 cal/in² heat wrap. These test results are in Table 101. The hot test was almost identical to S/N 1106 but the cold test was much better. Therefore, adding the 175 cal/in² wrap did help the cold test without hurting the hot test. However, the cold test was still not very good. The cold test indicated that more heat was needed.

TABLE 101 TEST RESULTS FOR BATTERIES MADE WITH THICK
(0.015" NICKEL) CELL CONNECTORS. ALL BATTERIES TESTED
ACROSS A 95 OHM RESISTOR

S/N	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	Test	NOTES
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm-cm ²	ohm-cm ²	Temp °C	
1106	26.1	430	780	1010	1.81	2.98	4.01	97.5	75	180 cal/in ² stack, no wrap, thick cell connectors
1107	25.4	105	170	230	0.42	0.63	29.1	111	-55	
1108	26.3	420	745	995	1.75	2.83	12.0	131	75	180 cal/in ² stack, 175 cal/ in wrap, thick cell connector
1109	27.0	165	340	530	0.72	1.33	42.3	66.6	-55	
1110	26.2	360	685	900	1.50	2.58	8.02	91.3	27	230 cal/in ² stack, no wrap, thick cell connectors
1111		PREMATURELY IGNITED								
1112	26.3	350	630	780	1.43	2.42	4.01	90.3	75	230 cal/in ² stack, no wrap, thick cell connectors
1113	25.4	240	375	480	0.95	1.37	8.24	134	-55	
1114	29.3	10.4	370	660	0.05	1.56	-	76.7	75	254 cal/in ² stack, no wrap, thick cell connectors
1115	25.8	285	480	605	1.15	1.78	8.11	110	-55	

The next two batteries, S/N 1110 & 1111 were made with the thick cell connectors and 230 cal/in² heat paper in the stack. Due to the increase in stack heat from 180 to 230 cal/in² no wrap was used.

Unfortunately, battery S/N 1111 was prematurely ignited while the leads were being spot welded to the header. The remaining battery S/N 1110 was fired at room temperature. The results of the test, as seen in Table 101 were not

particularly good except that there was no spike. Because there was no spike another set of batteries, S/N 1112 & 1113, were made to repeat these tests at the normal hot and cold test temperatures. The results of the 230 cal/in² stack heat was to shorten the hot life and to lengthen the cold life. The discharge curves were quite linear for both tests.

The next set of batteries were made with 254 cal/in² heat paper. These were batteries S/N 1114 & 1115. There was a significant increase in life times for the cold test but there was a bad spike for the hot tests.

Enough batteries were made and tested to make some conclusions about the heat balance of the batteries. Consider a thin cell connector of 0.004" Ni which has a volume of 0.2221 cm³. If the density of Ni is taken to be 8.9 gm/cm³ and the heat capacity is taken to be 0.13 cal/cm·C^o, then the amount of heat needed to increase the temperature of a cell connector by 225 C^o is:

$$0.221 \text{ cm}^3/\text{cell conn.} \times 8.9 \text{ gm/cm}^3 \times 0.13 \text{ cal/cm} \cdot \text{C}^{\circ} \times 225 \text{ C}^{\circ} = \underline{\underline{57.82 \text{ cal.}}}$$

Similar calculations for a 0.015" thick Ni cell connector yields 216.8 cal. It was earlier observed that for the thin cell connectors the 130 cal/in² heat paper was too cold and 150 cal/in² heat paper was just a little too hot. Assuming that 145 cal/in² is optimum, one heat pad generates 245.7 calories. It was shown above that 57.8 calories were used to heat the cell connector so that there is available 187.9 calories to heat the cell.

$$145 \text{ cal/in}^2 \times 10.93 \text{ cm}^2 \times \left(\frac{1''}{2.54 \text{ cm}}\right) = 245.7 \text{ calories}$$

$$245.7 \text{ calories} - 57.8 \text{ calories} = \underline{\underline{187.9 \text{ calories}}}$$

The data from batteries S/N 1106 to S/N 1115 indicates that with the thick cell connectors 230 cal/in² is good but 254 cal/in² is much too hot. If 230 cal/in² is assumed optimum for the thick cell connectors then calculations similar to those above indicate that 216.8 calories are used to heat the thick cell connectors 225°C and 172.9 calories are available to heat the cell.

Consider that at room temperature a battery stack is at about 25°C. If the heat paper raises this 225°C then the stack temperature will be about 250°C. The stack temperature for a cold test (-55°C) will be about 170°C and a hot test will be about 300°C. It has previously been reported in this report that the CuCl₂ catholyte performs well within this temperature range but drops off quickly above 300°C. These data seems to fit well with the above thermal speculation.

Therefore, it is believed that the cells should optimally receive about 180 calories/cell at initiation.

Now consider that the calories do not remain the battery but slowly leak out of the battery case walls. The activation times of the batteries have not previously changed significantly with a 85 cal/in² change in heat paper. This is because there was an accompanying change in cell connector thickness. The additional calories are absorbed by the thicker cell connectors and are later released into the stack and out of the battery. The effect is not to raise the battery temperature but to keep the battery hot for a longer time. More physical evidence of this observed phenomenon is a longer life time without an increase in battery skin temperature.

CONCLUSION:

It has been demonstrated that it is necessary to deliver at least 180 calories to these cells for optimum performance. The use of heat sinks can greatly reduce the spike and increase the life of the batteries.

Fe/KClO₄:

The Fe/KClO₄ heat source has good heat sink properties. Therefore, some batteries were made with the Fe/KClO₄ disks. The stack heat was 254 cal/in² heat pellets. The pellets were used with 0.015" thick cell connectors.

The experiment was a failure. The heat pellets failed to ignite for either the hot test or the cold test. The Fe/KClO₄ powder had been stored in the dry room for a very long time (about 4 years) so a new batch was unsealed and opened. The new material was tested by igniting heat pellets while between heat sinks.

TABLE 102 TEST RESULTS FOR BATTERIES MADE WITH Fe/KClO₄ HEAT PELLETS. ALL BATTERIES TESTED ACROSS A 95 OHM RESISTOR

S/N	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	TEST TEMP °C	NOTES
					Actual		t _{Peak}	t ₇₀		
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²		
1116	*	*	*	*	*	*	*	*	75	Old Heat Powder
1117	*	*	*	*	*	*	*	*	-55	Failed To Ignite
1120	23.1	160	245	320	0.54	0.72	X	136	-55	Fresh Heat Powder
1121	27.8	85	660	1020	0.39	2.51	X	31.9	+75	Ignited

More batteries were made similar to S/N 1116/1117 except that a thin piece of asbestos was placed between the heat disk and the cell connector. The results were not surprising. There was a spike for the hot test but the cold test was quite good. This experiment was done before the conclusions were drawn about the thermal properties of the battery. If this experiment were to be repeated today 230 cal/in² heat pellets would be used instead of the 254 cal/in² that were used.

OPTIMUM CELLS:

The optimum cell formula has previously been described in this report. In review, these cells were made with LiAlCl_4 anolytes and slightly acidic NaAlCl_4 catholytes. A number of batteries were made to test these optimum cells.

TABLE 103 BATTERY TEST RESULTS FOR BATTERIES
MADE WITH THE OPTIMUM CELL FORMULA

S/N	V_p	t_{90}	t_{80}	t_{70}	ED ₉₀	ED ₈₀	R_{INT}	R_{INT}	TEST	NOTES
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	TEMP	
1118	28.8	15	550	970	0.08	2.03	X	47.0	+75	250 cal/in ² heat paper - sodium based catholyte
1119	25.4	330	630	830	1.29	2.22	8.3	135	-55	
1120	27.3	85	660	1020	0.39	2.51	X	31.9	+75	230 cal/in ² Fe/KClO ₄ heat pellets
1121	23.1	160	245	320	0.50	0.72	X	136	-55	
1122	33.6	0.7	30	215	0.005	0.17	X	101	+75	250 cal/in ² heat paper; Na based electrolytes
1123	27.2	175	490	700	0.79	1.92	7.96	65.6	-55	
1125	20.6	410	730	950	1.11	1.80	5.22	72.6	+75	only 11 cells in S/N 1124 - 230 cal/in ² heat paper in both batteries; 175 cal/in ² wrap
1124	25.3	440	730	960	1.67	2.56	12.4	70.0	-55	
1126	-	-	-	-	-	-	-	-	-	S/N 1125 ignited during welding; 230 cal/in ² Fe/KClO ₄ heat pellets with quinargo
1127	25.5	165	305	420	0.64	1.07	-	70.4	-55	
1129	25.5	490	840	1100	1.21	1.90	4.10	64.5	+75	280 cal/in ² heat pellets with quinargo; 0.030" steel heat sinks
1128	25.8	135	310	390	0.33	0.68	16.4	110	-55	
1130	25.4	500	910	1210	1.21	2.00	4.10	52.8	+75	400 cal/in ² heat pellets with quinargo; 0.030" steel heat sinks
1131	25.7	130	305	400	0.32	0.67	16.7	75.8	-55	

The first two batteries (1118 & 1119) were made with 250 cal/in² heat paper. The next two batteries were made with 230 cal/in² heat pellets.

Batteries S/N 1122 & S/N 1123 were made with cells that were prepared entirely from slightly acidic NaAlCl₄. The heat source was 250 cal/in² heat paper. The data from S/N 1122 & S/N 1123 can be compared to the data from S/N 1118 & S/N 1119. There was a greater "spike" with the NaAlCl₄ batteries. This could have been caused by the nature of the electrolyte. It may also have been caused by the thermal imbalance caused by using the heat paper proper for a LiAlCl₄ anolyte/NaAlCl₄ catholyte battery in a NaAlCl₄/NaAlCl₄ type battery. This design will not be further pursued.

The next two batteries were again of the optimum cell design. These batteries contained 230 cal/in² heat paper with 175 cal/in² wrap. There is a discontinuity in these battery tests. The hydraulic press broke down while the cells were being prepared. Battery S/N 1124 was stacked and assembled. Only 11 cells remained for battery S/N 1125. Battery S/N 1124 was conditioned at -55°C and tested. When it became clear that the press would not be fixed for quite some time battery S/N 1125 was assembled 3 cells light and tested hot (at 75°C). These tests were actually quite good.

During earlier tests batteries made with the Fe/KClO₄ heat source were undependable because the heat source would not always burn. It was felt that the heat source lost too much heat to the cell connectors and failed to continue to burn. To prevent this heat sinking problem disks of 0.005" asbestos were placed between the faces of the heat disks and cell connectors. These batteries were to test this system. However, battery S/N 1126 was ignited during welding. It is interesting to note that the worker who ignited the battery during welding reported an absence of the usual flaming and gassing expected when a battery made

with the conventional Zr/BaCrO_4 heat source is prematurely ignited. The remaining battery was tested cold and the results of the test were very similar to batteries S/N 1120 & S/N 1121.

The next four batteries were rather different. The heat sources were separated from the cells with 0.030" thick, mild steel heat sinks. Figure 60 is an x-ray photograph of one of these batteries. The hot test was good but the results of the cold test indicated more heat was needed. The next set of batteries contained hotter heat pellets (400 cal/in^2). There was very little change in performance.

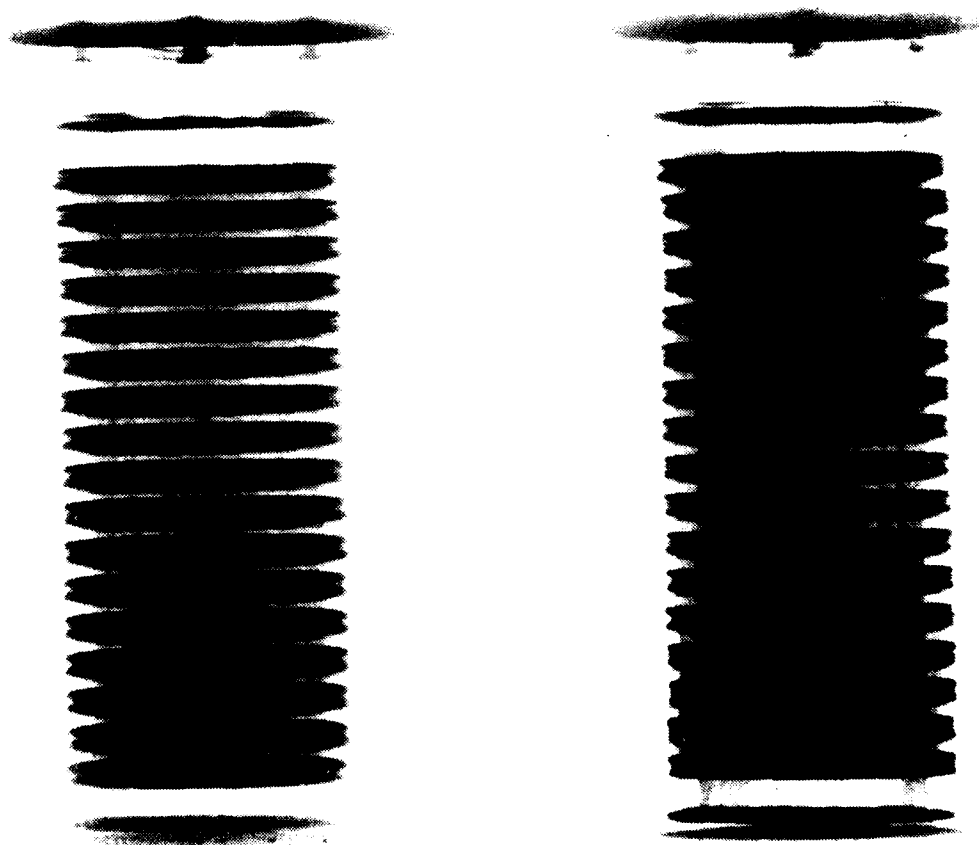


Figure 60. X-ray Photographs Of Batteries Constructed With 0.030" Steel Heat Sink/Buffers

FINAL DESIGN:

Among the batteries in the last series of tests (S/N 1117 to S/N 1131) were the batteries with the longest lifetimes. These batteries performed well because of one test parameter and three design changes. The test parameter was the discharge rate of about 25 mA/cm^2 which was quite favorable for long life testing. The three significant design characteristics were:

- 1) cells made with anolytes composed of LiAlCl_4
and catholyte composed of slightly acidic NaAlCl_4 ;
- 2) the Fe/KClO_4 heat source;
- 3) and, finally the use of heat sink/thermal buffers
to protect the cells from thermal shock upon
initiation.

The next series of batteries were made and tested to improve upon a battery constructed around the above mentioned points. See Table 104 for the test results of these batteries.

The first four batteries contained heat sink/thermal buffers made of disks compacted from basic NaAlCl_4 anolyte. These disks were about 0.030" thick and weighed 1.50 gm. These disks were inserted into 0.004" nickel cell connectors. The Fe/KClO_4 heat disks were also inserted into 0.004" nickel cell connectors. The reason for using salt type heat sinks was to cut down on the weight of the battery. Figure 61 is an x-ray photograph of S/N 1134. The lifetimes of the first two batteries were relatively short so the heat was increased from 339 cal/in^2 to 407 cal/in^2 . This caused a significant improvement in both the hot and cold tests.

TABLE 104 BATTERY TEST RESULTS FOR BATTERIES MADE
TO IMPROVE ON THE FINAL DESIGN. ALL BATTERIES TESTED
ACROSS A 95 OHM LOAD

S/N	V _P	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	R _{INT}	R _{INT}	TEST	NOTES
					Actual		t _{Peak}	t ₇₀	TEMP	
	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	°C	
1132	27.4	109	386	607	0.38	1.14	8.08	165	75	NaAlCl ₄ heat sink /thermal buffers; 339 cal/in ² heat disks
1133	26.7	56	233	373	0.18	0.64	X	144	-55	
1134	26.4	195	466	687	0.63	1.33	8.14	106	75	salt heat sinks & 407 cal/in ² heat disks
1135	24.6	225	359	466	0.62	0.92	41.4	169	-55	
1136	26.7	10	57	125	0.03	0.13	X	68.9	75	0.030" steel heat sinks & 453 cal/ in ² heat disks
1137	25.6	202	451	648	0.52	1.02	X	198	-55	
1138	25.7	84	278	669	0.21	0.60	X	189	75	0.030" steel heat sinks & 435 cal/ in ² heat disks
1139	26.4	109	385	579	0.29	0.87	X	129	-55	
1140	26.6	302	651	901	0.78	1.49	7.77	42.8	75	same as S/N 1138 & 1139 except 0.004" nickel disks shield the 0.030" heat sinks
1141	27.1	58	374	536	0.16	0.83	12.3	108	-55	

In the next two batteries the salt heat sink/thermal buffers were replaced with 0.030" steel heat sinks. The salt heat sinks were used to keep down the weight. They were abandoned for steel heat sinks to increase the ease of construction. It is understood that the battery weight can be significantly reduced and the energy density increased just by using salt heat sinks instead of steel heat sinks.



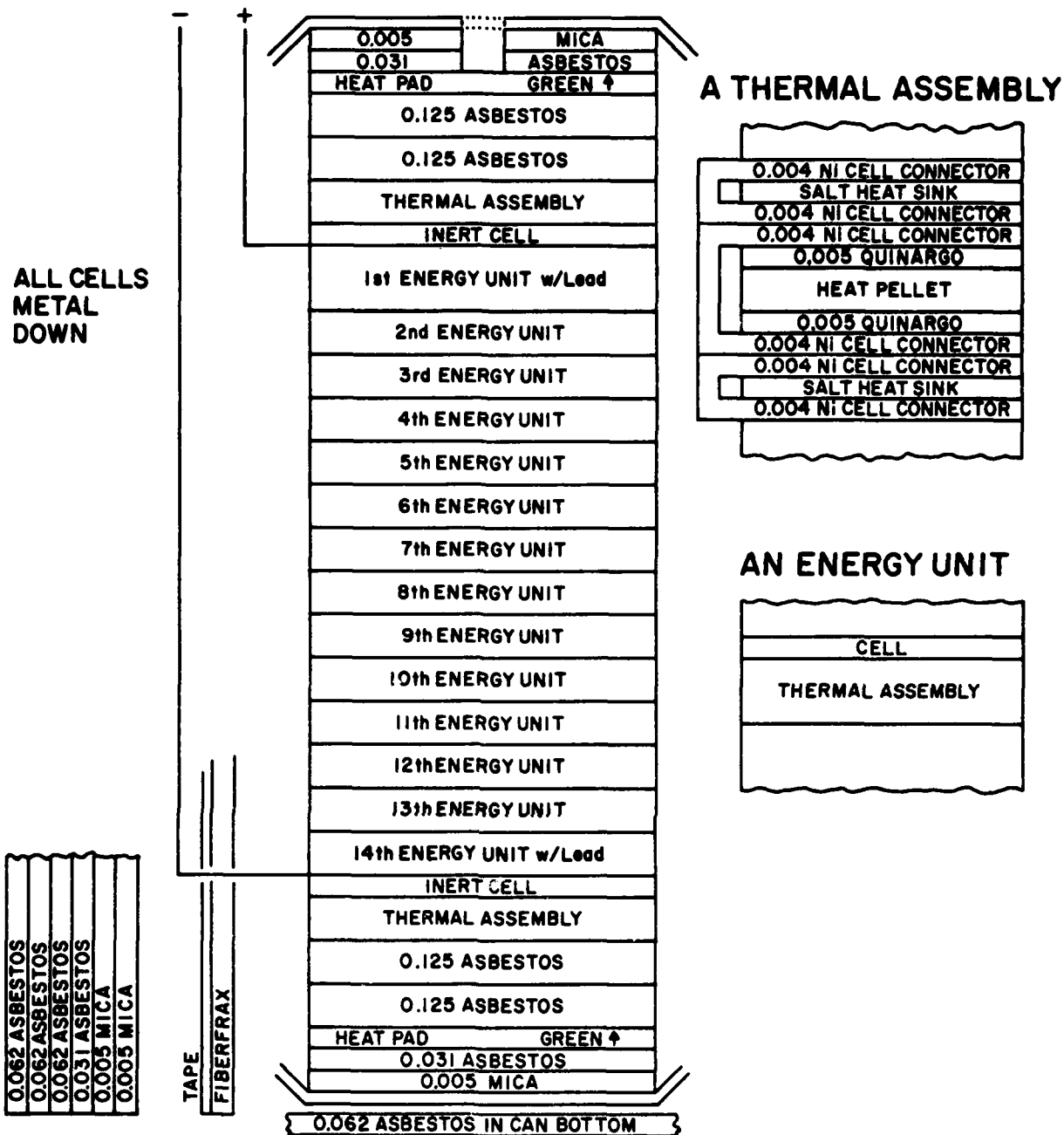
Figure 61. An x-ray photograph
of battery S/N 1134

Another change in these batteries was the use of a hotter heat source, 453 cal/in² heat disks. The hot test (see S/N 1136) showed a significant spike and so the battery was declared overheated. The next set of batteries (S/N 1138 & 1139) were made with 435 cal/in². These tests were better but there was still

a bad spike. To improve upon this a further thermal buffer of 0.004" nickel was inserted on both sides of the steel heat sinks. The entire heat sink/thermal buffer was composed of a 0.004" nickel disk, followed by a 0.030" steel disk, and followed by a final 0.004" nickel disk. These batteries (S/N 1140 & 1141) produced the best hot tests of the series, with no spike, but the cold tests were a little too short. This final design will be considered the final design for this program and shall be used for all final testing. Figure 62 diagrams the construction of these batteries.

A series of twelve of the final design batteries were constructed to be tested at various loads. There were six pairs of batteries. Each pair was tested across a different resistive load. Of each pair, one battery was tested at 75°C and one was tested at -55°C. The measured current densities were varied from 12.8 mA/cm² to 634 mA/cm². Table 105 contains the test data for these batteries. All the batteries in this series were stored for at least four hours at the test temperature before testing. The batteries were taken out of storage and were tested within about five minutes to insure that the stack would still be at the desired test temperature. Batteries with serial numbers 1148, 1149, 1150, and 1151 were made with cells that were made from a newly mixed anolyte. With only the previously mentioned exception the twelve batteries were made identically.

Figures 63, 64, 65, and 66 illustrate some of the most significant data in Table 105. Figure 63 illustrates how battery life increased as the current density became smaller. The exception was t_{90} which did not follow the trend because of a bad spike which became quite significant at the lower current densities. This was very disappointing because the entire heat sink/thermal



WRIGHT PATTERSON FINAL BATTERY DESIGN

Figure 62. A diagram of the final battery design

TABLE 105 BATTERY TEST RESULTS FOR BATTERIES MADE TO DETERMINE THE OPERATING CHARACTERISTICS OF THE FINAL BATTERY DESIGN

S/N	TEST	C.D.	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	ED ₇₀	PD ₈₀	Act.
	TEMP	Peak					Actual				
	°C	ma/cm ²	volts	seconds	seconds	seconds	Wh/kg	Wh/kg	Wh/kg	Wh/dm ³	seconds
1142	75	12.9	28.3	38	784	1230	0.06	0.88	1.26	2.30	1.20
1143	-55	12.8	28.0	19	513	698	0.03	0.51	0.67	1.33	2.60
1140	75	25.6	26.6	302	651	901	0.16	0.83	1.10	3.92	1.46
1141	-55	26.1	27.1	58	374	536	0.05	0.88	1.26	2.18	2.70
1144	75	50.0	27.3	57	236	403	0.30	1.04	1.57	2.71	1.76
1145	-55	49.2	26.9	23	149	252	0.12	0.63	0.96	1.64	3.03
1150	75	93	25.4	84	188	295	0.76	1.51	2.11	3.93	1.87
1151	-55	86	23.5	48	94	143	0.37	0.65	0.88	1.70	X
1146	75	179	24.5	33	78	135	0.59	1.20	1.79	3.08	1.94
1147	-55	174	23.8	12	29	66	0.21	0.42	0.79	1.10	3.43
1148	75	634	20.8	7.4	13.8	22.6	0.43	0.69	0.96	1.80	2.20
1149	-55	497	16.3	5.8	11.0	17	0.23	0.36	0.47	0.93	3.80

buffer design was included in the battery just to combat this spike. Furthermore, the heat sink/thermal buffers were included at a great expense of weight and volume. This greatly reduced the energy density and greatly increased the activation times. Only data from the hot tests are illustrated in Figure 63 but if the cold tests were included the data would be similar. The spike was not as bad for the cold tests.

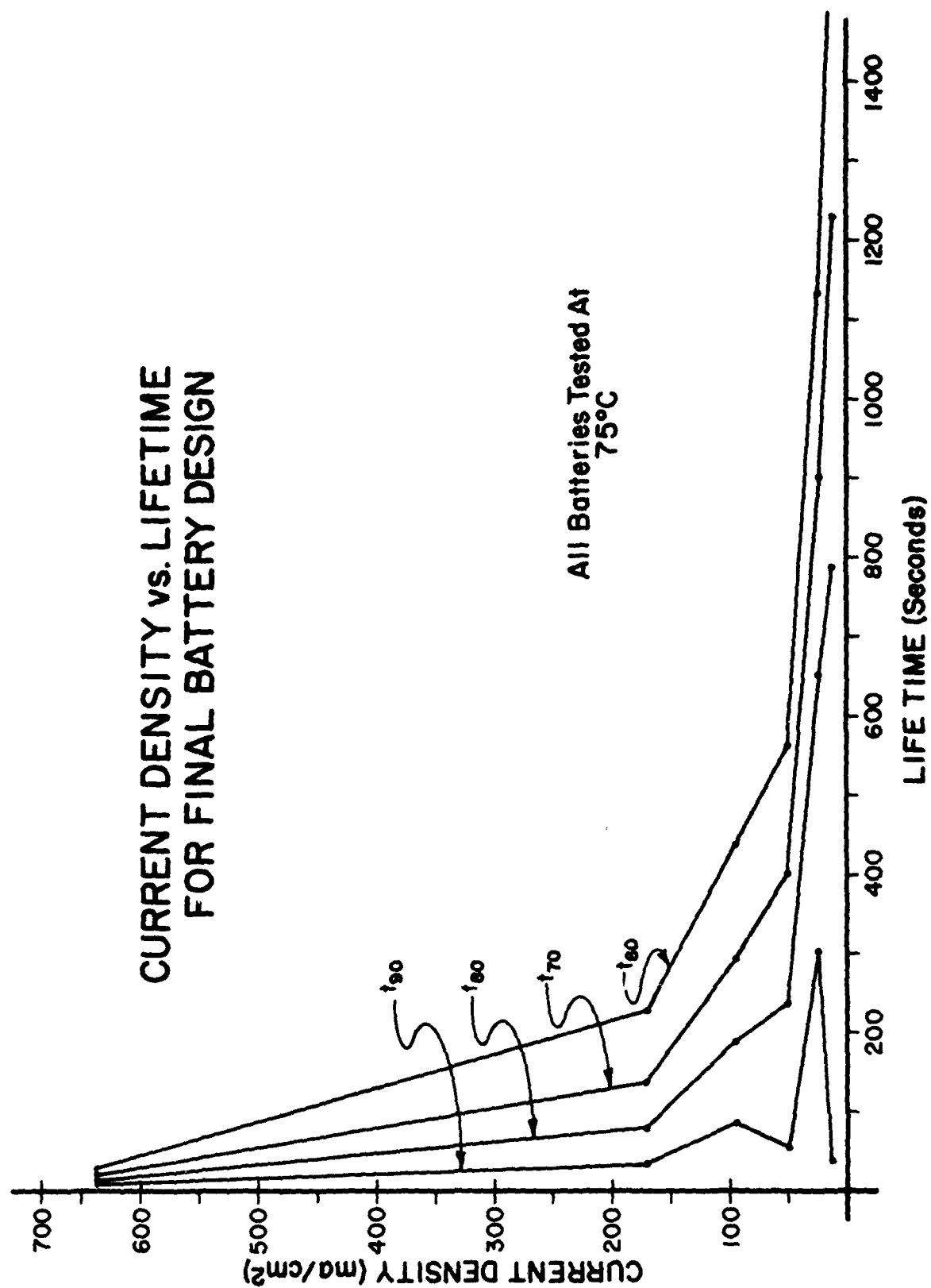


Figure 63. Current Density vs. Lifetime For The Final Battery Design. Only Data From Batteries Tested at 75°C Are Included Here

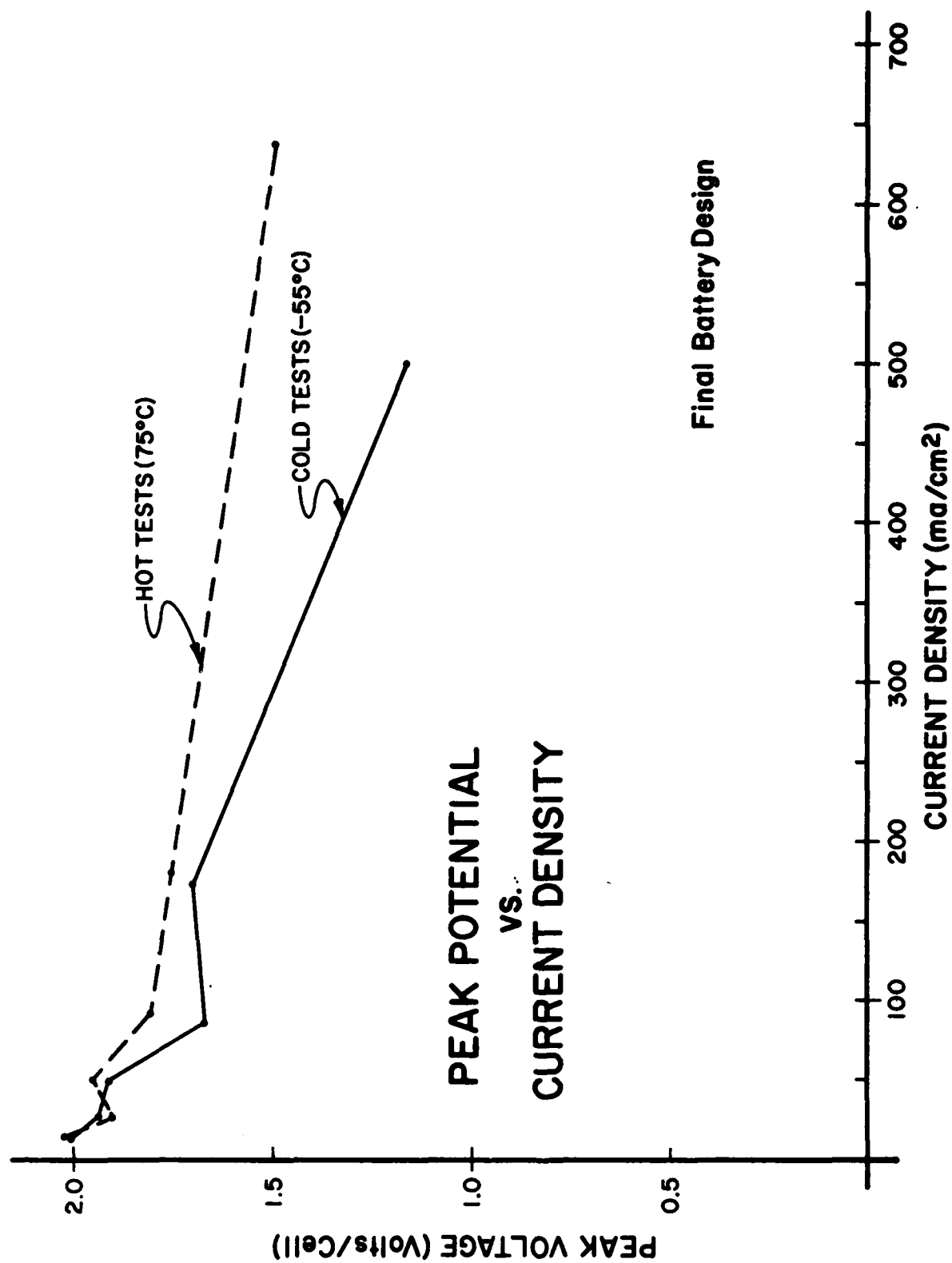


Figure 64. Peak Voltage vs. Current Density For The Final Battery Design

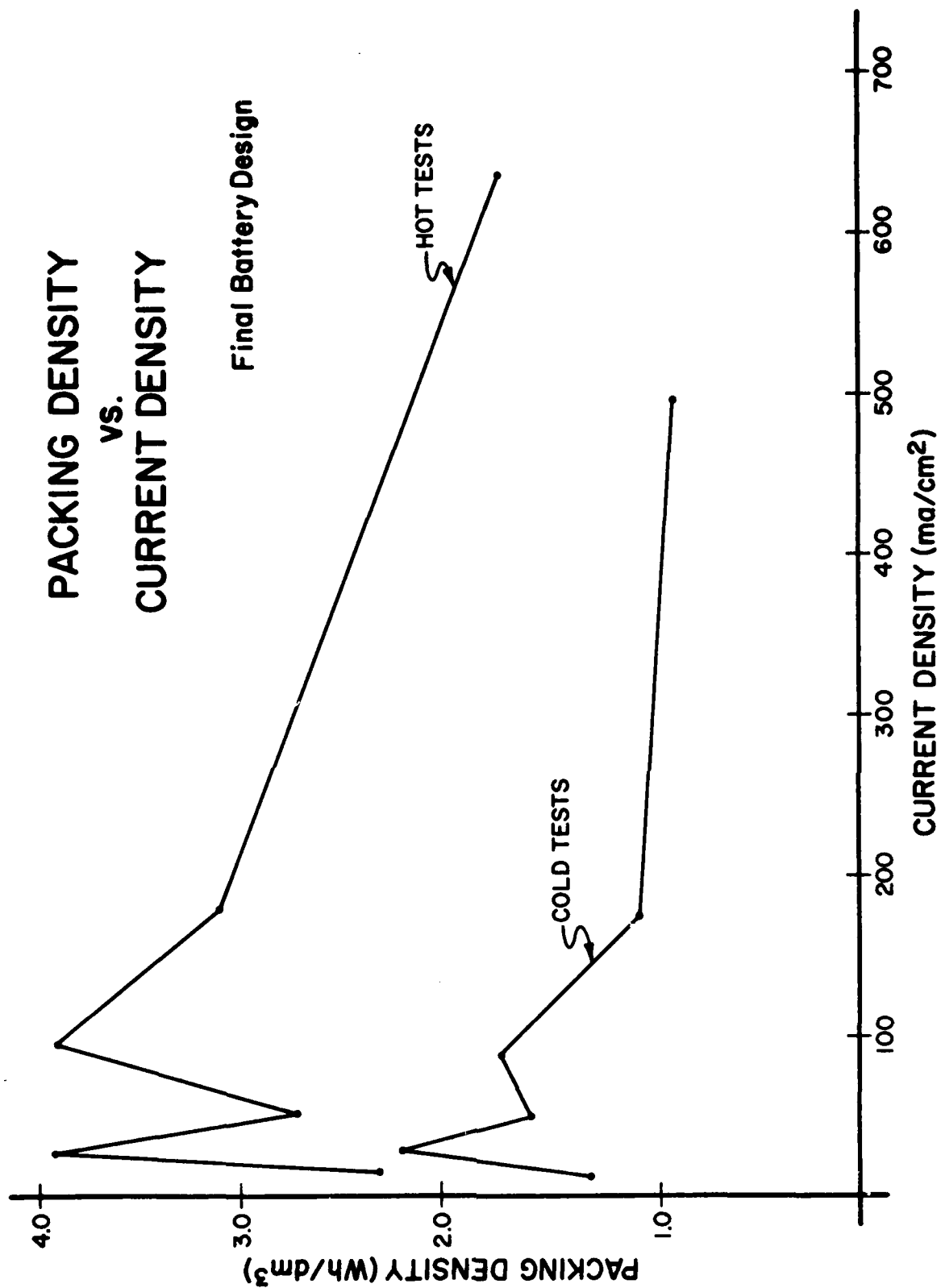


Figure 65. Packing Density vs. Current Density For The Final Battery Design

AD-A125 581

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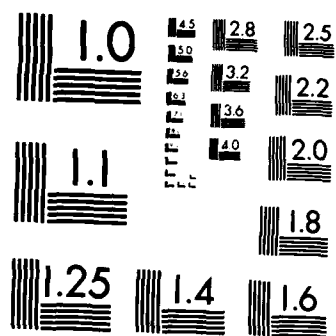


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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

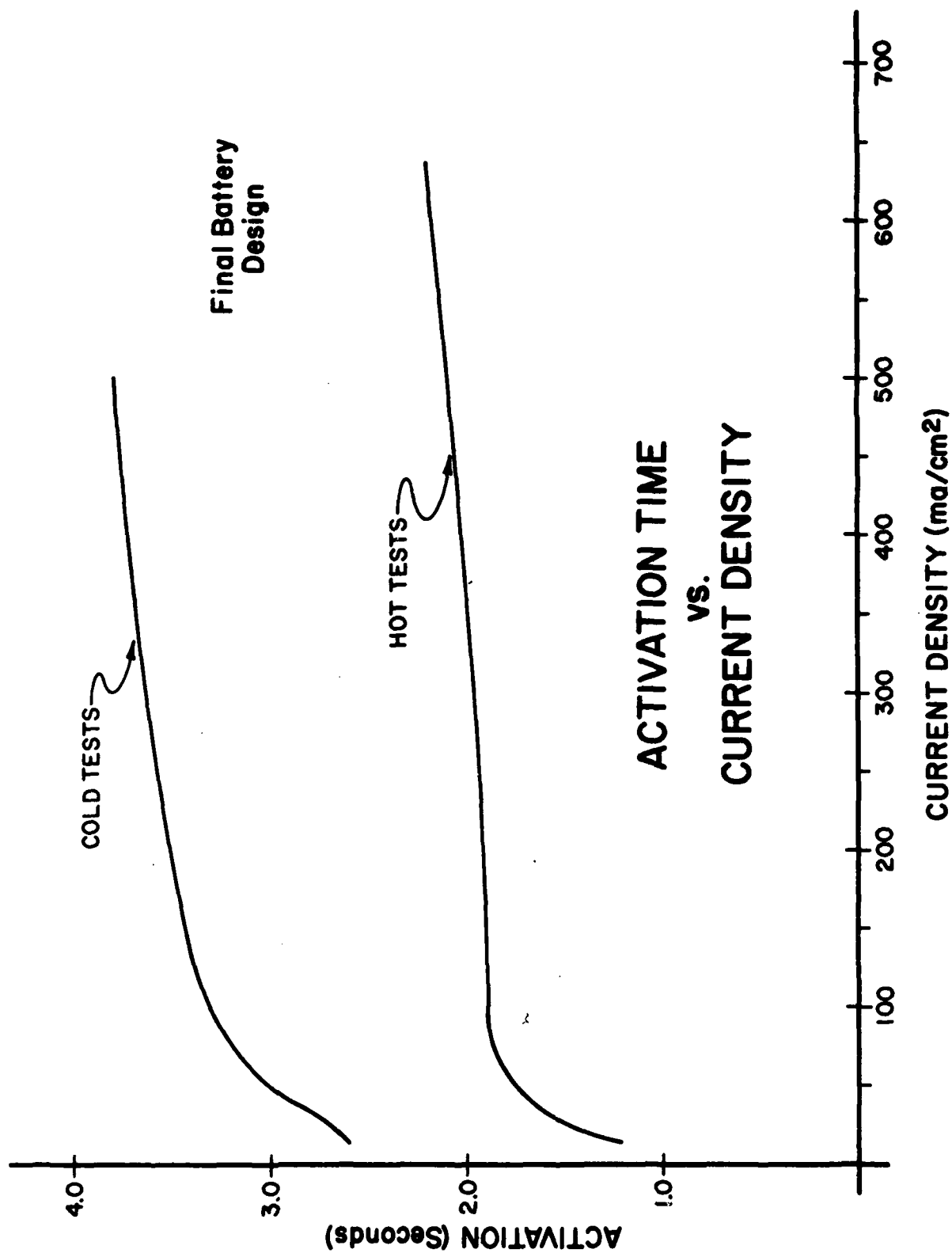


Figure 66. Activation Time vs. Current Density For The Final Battery Design

Figure 64 illustrates how the peak potential drops as the current density increases. It is interesting to compare Figure 64 (CuCl_2 battery tests) with Figure 21 (CuCl_2 single cell tests). The polarization curves for both, the hot and cold tests, were better than the data for the single cell tests. In fact, the polarization curves for these battery tests had slopes which approached the slope of the "ideal" $\text{Mg/V}_2\text{O}_5$ system. One of the reasons for this was that the single cell data was taken before such cell improvements as the use of Mg in the anode, the use of LiAlCl_4 as anolyte, or the use of acidic NaAlCl_4 in the catholyte.

Figure 65 illustrates how the packing density ($^{\text{Wh}}/\text{dm}^3$) changed with current density. It is believed that the third data points from the origin, at about $50 \text{ ma}/\text{cm}^2$, were anomolous points. A close inspection of the data in Table 105 shows that there was a significant spike for these battery tests and there was not for either the preceeding or the immediately following tests. This causes the peaking density to be much lower than it would have been if there had been no spike. For this reason it is believed that the curves in Figure 64 should show a maximum at about 25 to $30 \text{ ma}/\text{cm}^2$.

Figure 65 illustrates how the activation times slow as the current density increases. The hot tests activated about twice as fast as the cold tests. In every case the activation was much slower than previous battery designs. The large volume of the heat sink/thermal buffer assembly accounted for the slow activation.

In summary, the batteries performed about as well as might be expected for similar single cell tests. The final battery design included a massive and voluminous heat sink/thermal buffer heat source assembly which was supposed to

eliminate the spike and increase the life. While the t_{90} 's were indeed increased the t_{80} 's and t_{70} 's were not and the overall effect of the heat sink/thermal buffer design was to slow down activation and lower the energy density.

VIBRATION AND ACCELERATION TESTING:

Four batteries of the final design, were tested on the vibrator and four were tested on the centrifuge. The vibration tests were conducted on a Unimode Suspension vibrator, made by MB Electronics, a division of Textron Electronics. Two batteries were tested at 20g's and two batteries were tested at 40g's. For each set, one battery was tested at 75°C and one battery was tested at -55°C. For all four vibration tests the batteries were vibrated at a frequency of 10Hz up to 2000Hz and then back to 10Hz. It took three minutes to make one complete cycle from 10Hz to 10Hz again. All of the vibration tests were vibrated on a lateral axis. That is, all vibration tests were done with the battery on its side. Table 106 contains the data from the four vibration tests and the four acceleration tests. For every test the battery was vibrated continually during the entire test. All of these batteries were tested across a 50 ohm resistor.

The data in Table 106 can be compared to the data in Table 105, particularly batteries S/N 1144/1145 (these had similar loads and temperatures as the data in Table 106). The data are all so similar that it can be concluded that the vibration did not change the battery performance. Furthermore, there was no electrical noise noted in any of the vibration tests. The smallest noise resolvable is about 50mv.

TABLE 106 BATTERY TEST RESULTS FOR BATTERIES TESTED WHILE BEING VIBRATED OR ACCELERATED.
ALL BATTERIES TESTED ACROSS A 50 OHM RESISTOR. EXCITATION WAS CONTINUOUS DURING THE
ENTIRE BATTERY TEST

S/N	Mode of Excite.	Axis	g level g's	Test Temp °C	V _p volts	C.D. ma/cm ²	t ₉₀ seconds	t ₈₀ seconds	t ₇₀ seconds	ACTUAL			PD ₈₀ Wh/dm ³	Act. seconds	Noise volts
										ED ₉₀ Wh/kg	ED ₈₀ Wh/kg	ED ₇₀ Wh/kg			
1152	Vib	lat.	20	75	25.5	46.7	138	292	388	0.62	1.18	1.45	3.08	2.03	None
1153	Vib	lat.	20	-55	26.1	47.8	52	140	272	0.25	0.58	0.97	1.52	3.20	None
1154	Vib	lat.	40	75	25.3	46.3	160	333	463	0.76	1.33	1.68	3.48	1.90	None
1155	Vib	lat.	40	-55	25.9	47.4	59	135	240	0.28	0.56	0.86	1.47	3.40	None
1156	Acc	vert.	30	75	26.8	49.0	52	150	249	0.26	0.65	0.96	1.70	1.80	None
1157	Acc	vert.	30	-55	26.1	47.8	59	153	243	0.28	0.63	0.89	1.67	2.80	None
1158	Acc	lat.	50	75	26.2	47.9	88	218	322	0.42	0.90	1.22	2.39	1.80	.05 to 0.1
1159	Acc	lat.	30	-55	26.2	47.9	55	187	271	0.27	0.77	1.02	2.01	2.90	None

The batteries tested during acceleration were activated while mounted on a moving centrifuge arm. For two of the batteries the batteries were mounted with their vertical axis parallel to the centrifuge arm and with the header pointed toward the center of the turning radius. Thus the 30g acceleration was toward the bottom of the battery. One battery was tested at 75°C and one at -55°C. The batteries were brought up to 30g's before the battery was activated. The 30g acceleration was maintained for the entire battery test (to about t_{50}). There was no noise noted during either of the vertical axis tests. The lower limit of noise resolution was about 50mv.

The last two batteries to be accelerated were mounted with their vertical axis at a right angle to the centrifuge arm and with the header pointed in the direction of travel. Thus the 30g acceleration was toward the side of the battery. One battery was tested at -55°C and this battery displayed no electrical noise. The other battery was tested at 75°C. It too was tested at at least 30g's. At about t_{75} the acceleration was slowly increased up to 50g's. At about t_{70} the battery was accelerating at 40g's and noise of 50 to 100mv was noted. The increase in acceleration was continued up to 50g. The noise did not increase. As with the vibration testing no noticable change in performance can be attributed to the acceleration.

In summary, four batteries were tested for the effects of vibration on performance and four batteries were tested for the effects of sustained acceleration. The vibration had no noticable effect. The batteries were vibrated laterally from 10Hz to 2000Hz and back to 10Hz at a level of 40g during the entire test. There was no noticable effect. Batteries were accelerated both laterally and longitudinally up to 50g. The lateral test showed 50 to 100mv noise at about 40g. There was no

noise for the longitudinal tests. Noise could be resolved to a lower limit of about 50mv. There were no other noticable effects in performance due to either mode of excitation.

SECTION XXII

CONCLUSION

The object of this program was to develop technology for an advanced long life, compact, lightweight thermal battery for missile and air delivered weapon applications. This objective has been achieved. The effort built upon electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories and exploratory development of the LiAl alloy anode, NaAlCl_4 electrolyte, and MoCl_5 cathode battery under Contract F33615-76-C-2080. The work done under the previously mentioned contract demonstrated the feasibility of the system but was so limited in scope that a new contract was issued to provide further development and optimization of an advanced thermal battery system.

Among the results of this contract was a better understanding of the activation high voltage spike and its subsequent control. Also accomplished was the establishment of a source of high purity electrolyte sufficient for thermal battery use. Techniques for fabricating and handling the electrolyte cells were developed.

Alternate material investigations were performed which led to greatly improved cells. These investigations led to the improved anode which contained 35% Mg and 65% LiAl. Also included in these investigations were alternate electrolyte and cathode active materials which led to the improved optimum cell design with a LiAlCl_4 anolyte and $\text{CuCl}_2/\text{NaAlCl}_4$ cathode.

After the most promising material combination and fabrication techniques were discovered, optimization experiments were performed to maximize the cell and battery performance. This improved final design included optimum design cells, heat source selection, and thermal balancing. A sufficiently large number of

batteries were tested to demonstrate the performance levels achieved. While not all of the performance goals were met the potential of meeting those goals has been explored completely and no ambiguity remains.

The electrical requirements of the goal battery were:

- a) Voltage, 28 volts nominal, 30 volts maximum, and 24 volts minimum;
- b) Current, 2 amps across a resistive load;
- c) Activation time, less than 1 second;
- d) Operating life, 45 minutes continuous
- e) Electrical noise, 1/2 volt peak to peak

The voltage and current can be achieved by stacking enough cells in series (about 1.85v/cell) and making the total cell area large enough (the optimum current density was about 25 ma/cm^2). Electrical noise was never a problem and the final design was at least five times better than specification. Activation was never a problem until the heat sink/thermal buffers were included into the final design. It should be noted that the activation of the system was well within specification even though the batteries of the final design were not. It is therefore possible to change the design and the activation would be within specification.

The physical requirements of the goal battery were:

- a) volume, 6 in^3 or less;
- b) weight, 1 pound or less.

These requirements were sacrificed to achieve the electrical requirements. This was necessary because of the relatively low optimum current density. Also the weight was sacrificed by the relatively massive heat sink/thermal buffer system

which was used to increase the active life by decreasing the high voltage activation spike.

To test battery performance under various environmental conditions the batteries were tested while undergoing continuous vibrational stress and also continuous acceleration stress. The batteries performed quite well under these conditions.

Almost all battery testing was done with pairs of batteries. One battery was always tested hot (after at least 3 hours storage at 75°C) and one battery was tested cold (after at least 3 hours storage at -55°C).

The biggest problem area which occurred was that of shelf life. The initial cell design contained MoCl_5 which proved to make a volatile catholyte which caused rapid autodischarge. This problem was solved by substituting CuCl_2 for the MoCl_5 in the catholyte. In addition it was found that the uninitiated cells made with AlCl_4^- electrolytes were 10,000 times more conductive than more conventional thermal cells. It is believed that thermal batteries made with this system could have significant shelf lives if care is taken to keep exposure to moisture during cell fabrication and battery assembly to a minimum.

Further development of this system must include some method of activation high voltage spike control which does not require the massive heat sink/thermal buffer system. Also a more economical source of the LiAl alloy is needed. It is also believed by this author that this system requires an extraordinarily dry environment during component and battery fabrication. If these three major areas of development were carried through to a successful conclusion the result would be a safe, reliable, economical thermal battery with a significant shelf life and a relatively cool skin temperature which could be manufactured profitably.

APPENDIX
PRELIMINARY HAZARD ANALYSIS
DI-H-3278/M

A thermal battery is a self-contained reserve energy unit which is inert until activated. An inert thermal battery offers very little hazard. An activated thermal battery generally develops an elevated skin temperature which could cause human injury or could cause thermal injury to its immediate environment. Thermal batteries which have some kinds of internal faults, or good batteries which are not being used as their design intended, can be explosion hazards. Where a battery explodes it generally exposes its environment to noxious gases and burning heat source and anode materials.

Thermal batteries are generally constructed with an outer case material which has high mechanical strength. However, should the case of thermal battery be breached the inside of the battery would be exposed to water and moist air. The electrolyte salts of the battery often attract moisture and sometimes reacts with moisture to form HCl or some other gas. Heat is also evolved. If the breach is small, gas pressure can build up causing an explosion hazard. The anode active materials are also usually reactive with moisture and this can create an explosion hazard. Should the breach be great the explosion hazard is lessened but excessive moisture can accelerate the reactions with the cell materials to such an extent that the anode active material could ignite and burst into open flame. Should the heat source inside a thermal battery be exposed it is a fire hazard while dry. This means that it is hazardous to expose the inside of a thermal battery, inert, activated, or expended, under any circumstances. The fact requires care for safe manufacture, storage, and disposal of all thermal batteries.

Special attention should be given to thermal battery manufacture. The dust from the fabrication of cell components, heat sources, insulation, cell stacks, and finished batteries is always an employee safety and health hazard. Inflammable metals such as powdered anode materials and heat source materials (LiAl, LiSi, Sr, Mg, etc.) are fire hazards and local irritants. In the case of the anode active materials exposure to moisture must be prevented. In the case of powdered zirconium the proper levels of moisture must be maintained. Insulation materials often contain asbestos or other dangerous fibers. Reaction of electrolyte salts and cathode active materials to moisture can often lead to the generation of noxious and hazardous gases.

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