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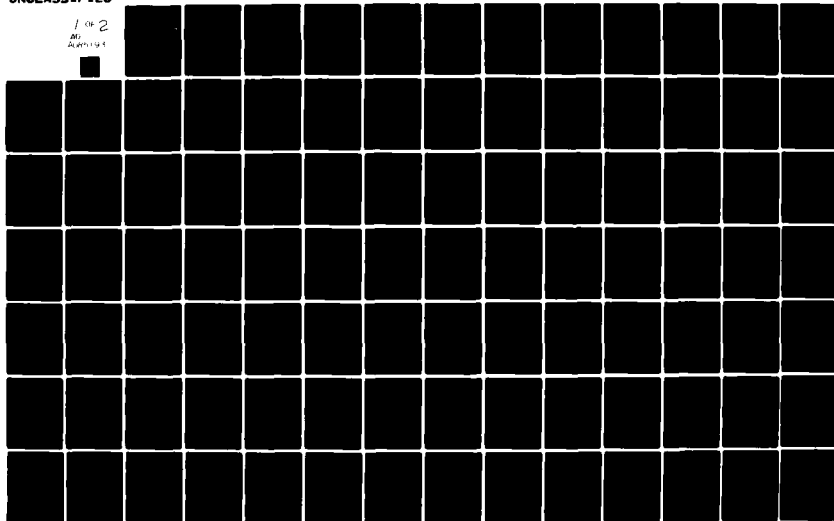
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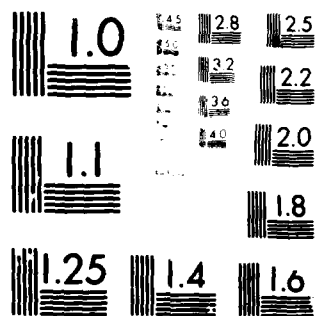
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ADVANCE SCIENCE DIVISION ✓
1201 E. BELL STREET
BLOOMINGTON, ILLINOIS 61701

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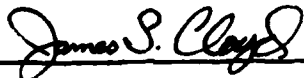
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This technical report has been reviewed and is approved for publication.



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The feasibility of building thermal batteries with cells composed of an anode of LiAl alloy, a cathode of a heavy metal chloride, and a NaAlCl₄ electrolyte has been demonstrated. During the further investigation of this system some interesting problems have developed and had to be studied. The particle size growth of the catholyte developed into a major storage problem. MoCl₅ was found to form a volatile catholyte which is not			

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suited for thermal battery use. As a result of this problem other catholyte materials were experimented with. CuCl_2 is the most successful alternate to MoCl_5 .

Some alternate binder materials have been investigated - kaolin clay, Illinois Mineral Amorphous Silica, and magnesia.

Some alternate electrolytes have been investigated including NaAlCl_4 (containing 52 m/o AlCl_3), LiAlCl_4 and KCl-LiCl . This work indicates that each material has unique properties which lend themselves to a particular application.

Among the alternate cathode materials experimented with are CrCl_3 , a number of heavy metal oxides, fluorocarbon, TiS_2 , TiS_3 , and sulfur.

Some alternate processes investigated have been freon blending, adding materials to the anode, cell and battery desiccation and filling batteries with an inert atmosphere.

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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 December 1979, covering effort completed during the interval 15 September 1978 thru 15 September 1979.

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 and Dr. Joseph Malloy of the project officers organization was very beneficial and greatly appreciated. The consultation and technical support of Lt Col Lowell King and Capt Larry Vaughn of the Air Force Academy, Colorado 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.

This report is for the second year of work. The first year of work was reported December 1978 in:

"Advanced Thermal Batteries"
AFAPL-TR-78-114

Air Force Aero Propulsion Laboratory
Air Force Wright Aeronautical Laboratories
Air Force System Command
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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 has a general and specific objective. The general objective is to develop technology for an advanced, long life, compact, lightweight thermal battery for missile and air delivered ordnance applications. This effort will be built upon electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories and engineering research and development done by the Eureka 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., should be eliminated or at least controlled. Alternate materials should be investigated to optimize the cell/battery performance. These investigations shall 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 is to design and develop a battery which will 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 for the second year of work. The first year of work was reported December 1978 in:

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Air Force Aero Propulsion Laboratory
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Wright-Patterson Air Force Base, Ohio 45433

SECTION II

NaAlCl_4 ANALYSIS

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 % 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 may be the inexpensive, fast and easy acid-base indicator that has been needed.

SECTION III

PARTICLE SIZE GROWTH IN CATHOLYTES

Most of the cathode materials used with this thermal system have been chlorides. FeS_2 was also tested and found to be suitable only for high temperature application. A second nonchloride, MoO_3 has been tested. An MoO_3 catholyte, (C #1117), 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 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 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 catholyte #1117. These 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 similar to a 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-gray 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.

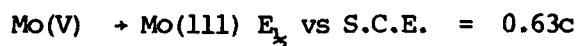
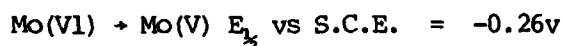
DSC spectra were generated for these yellow crystals. There is a distinct endotherm at about 160°C . An infrared spectrum of the compound in Nujol mull was recorded over the range 4000 to 500 cm^{-1} , but showed no significant absorption bands except those representative of traces of water.

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 suggests 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 % LiAl, 1/2 inch of basic or acidic anolyte, and MoCl_5 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°F but a few of the samples were maintained at room temperature. One sample with MoCl_5 catholyte was made with the alloy on the top and the catholyte on the bottom so the LiAl could be removed and examined. One MoCl_5 sample was made with the layers of materials separated with disks of quinargo.

Similar samples were prepared for CuCl_2 catholytes and for MoO_3 catholytes (Table #1).

Most of the these samples were stored in an oven at 160°F . After just one day storage all of the MoCl_5 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 CuCl_2 samples. There was not any apparent reaction in any of the MoO_3 samples, even the acidic samples.

TABLE 1 SCHEME FOR ORGANIZING COMPATIBILITY SAMPLES

MoO_3 CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Not Exposed	
	BASIC CATHOLYTE	Basic Catholyte	X
			X
		Acidic Catholyte	X
		Not Exposed	
CuCl_2 CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Not Exposed	
	BASIC ANOLYTE	Basic Catholyte	X
		Not Exposed	
		Acidic Catholyte	X
		Not Exposed	
MoCl_5 CATHOLYTES	ACIDIC ANOLYTE	Acidic Catholyte	X
		Not Exposed	
	BASIC ANOLYTE	Basic Catholyte	X
		Not Exposed	
		Acidic Catholyte	X
		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 is compatible with the NaAlCl₄ system.

The LiSi turned black within days after the samples were prepared. It is concluded that 58 ^W/o LiSi is more sensitive than 20 ^W/o 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 "blueing" of the anode in the LiAl/KCl·LiCl/V₂O₅.

After about 5 weeks the samples had to be removed from the vacuum oven. The MoCl₅ 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 sample was a fine black ring which formed on the inside of the glass sample tube just above the anode/fibrefrax 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 blueing 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 MoO_3 and the CuCl_2 samples showed no signs of volatility. Samples #5 & #7, the MoO_3 catholyte samples, had a few square, dark colored crystals condense onto the cooler upper portions of the sample tube. Sample #4, the MoCl_5 sample produced a large number of square crystals on the cooler 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.

CONCLUSION:

- 1) 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;
- 2) the double peaks of the no load single cell 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;
- 3) the presence of the yellow crystals, which are so similar to the white yellow crystals reported previously, 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;

- 4) the Mo species in a MoO_3 catholyte apparently diffuse thru the cell even faster than the species in the normal basic MoCl_5 catholyte;
- 5) the LiAl alloy anode must be protected from excessive air and moisture contamination;
- 6) the LiAl alloy appears to stop reacting after just a short time;
- 7) the MoCl_5 catholytes appears to form volatile oxychlorides upon storage. The mechanism for this reaction is unknown. A suggested reaction path is MoCl_5 could form molybdic acid which can then form the oxychlorides;
- 8) there is no indication that the catholyte degradation will slow down or stop during storage;
- 9) the volatile component in the MoCl_5 catholyte is somewhat independent of the active nature of the atmosphere in the storage containers;
- 10) CuCl_2 catholytes do not contain a volatile component;
- 11) neither MoCl_5 or WCl_6 are suitable for thermal battery use. CuCl_2 is quite suitable for thermal battery use.

SECTION IV

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 antflow agent is included in the electrolyte powders. This material is often referred to as a binder. The two binders which are most often used are kaolin and Cab-O-Sil. 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.

The 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 % w/o). In order to prevent flow only about 8 % w/o Cab-O-Sil is necessary and only about 35 % w/o 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 % w/o) 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 into molten NaAlCl_4 . It required 130 gms to immobilize the liquid (56.5 % w/o). 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 4 is a tabulation of test results taken at constant temperature and varying load resistance. Table 5 is a tabulation of test results run at constant load and varying temperatures.

TABLE 4 SINGLE CELL TEST RESULTS OF 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 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 4 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 littler 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 MoCl_5 cells.

There is another feature about these cell tests which does not show in Table 4. 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.

TABLE 5 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	

The results in Table 5 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.

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 been 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

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

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

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

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 NaAlCl₄ (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 NaAlCl₄.

The Cab-O-Sil anolyte was also fused and reground. Again a CuCl₂ 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 6 for all of these cell tests).

TABLE 6 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	

CONCLUSIONS:

These conclusions can be made about the use of Illinois Mineral amorphous silica and J. T. Baker magnesite as an antiflow agent for NaAlCl_4 thermal cells.

- 1) Imsil A-25 does prevent molten electrolyte flow;
- 2) approximately 4 or 5 times as much Imsil A-25 as Cab-O-Sil is needed to prevent flow of the molten electrolyte;
- 3) no dramatic increase in internal resistance can be expected as it is with kaolin;
- 4) no cold voltage is observed as it is with Cab-O-Sil;
- 5) the Imsil A-25 increases the tendency to form a spike with the CuCl_2 system which shortens life times and decreases energy densities;
- 6) the Imsil A-25 is significantly cheaper and easier to use than Cab-O-Sil;
- 7) it is not necessary to fuse Imsil A-25 into the NaAlCl_4 to act as an antiflow agent;
- 8) it has not been possible to wet the MgO with molten NaAlCl_4 . MgO does not appear to be a good antiflow agent for this system.

SECTION V

ACID-BASE PROPERTIES OF THE ELECTROLYTE

In the first Interim Report, covering the period September 1977 through September 1978, the use of acidic (69 m/o AlCl_3) NaAlCl_4 was reported. A large volume of single cell tests were used to demonstrate that acidic electrolytes could be expected to make superior cells. At that time no batteries had been made with these cells. However, this experiment has now been done and the results will now be reported. Batteries #1019 & #1020 were made to test the acidic CuCl_2 electrolytes.

TABLE 7 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 shows 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 or 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 may be possible to use V_2O_5 as an acid-base indicator. The light green observed in the MoO_3 samples exactly match the color observed in the anolyte layer of the MoO_3 cells which were examined post-mortem.

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 $NaAlCl_4$ has been 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 8.

TABLE 8 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 & 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 best cells tested during this contract (Figure 1).

It is predicted that a superior cell can 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".

CONCLUSIONS:

In almost every case cells made with acidic electrolytes have been superior cells and are surely candidates for an optimized system.

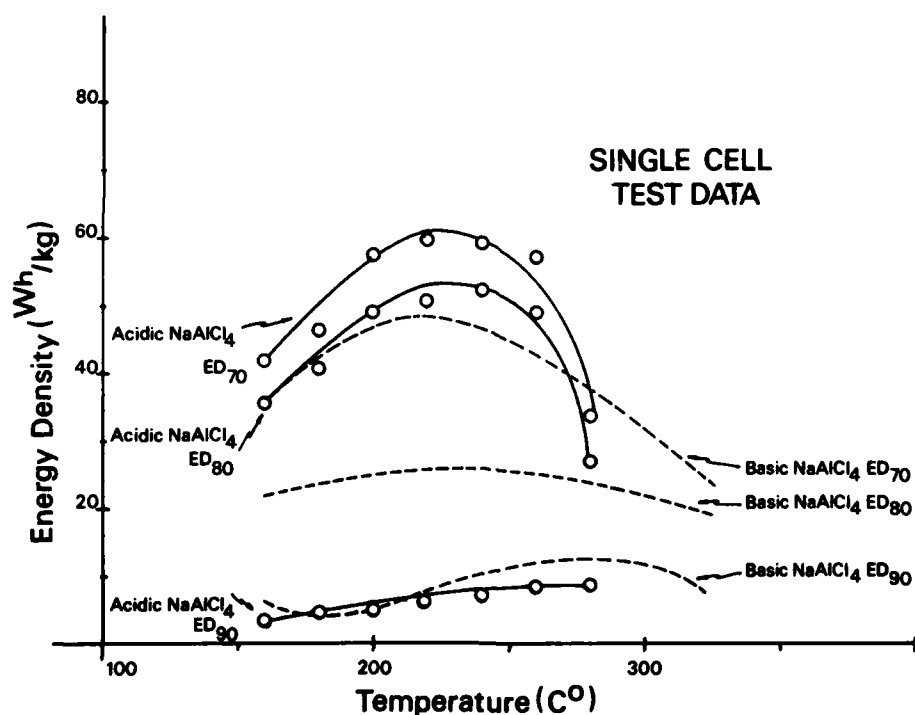


Figure 1. Single Cell Test Data. Basic $NaAlCl_4$ vs. Acidic $NaAlCl_4$

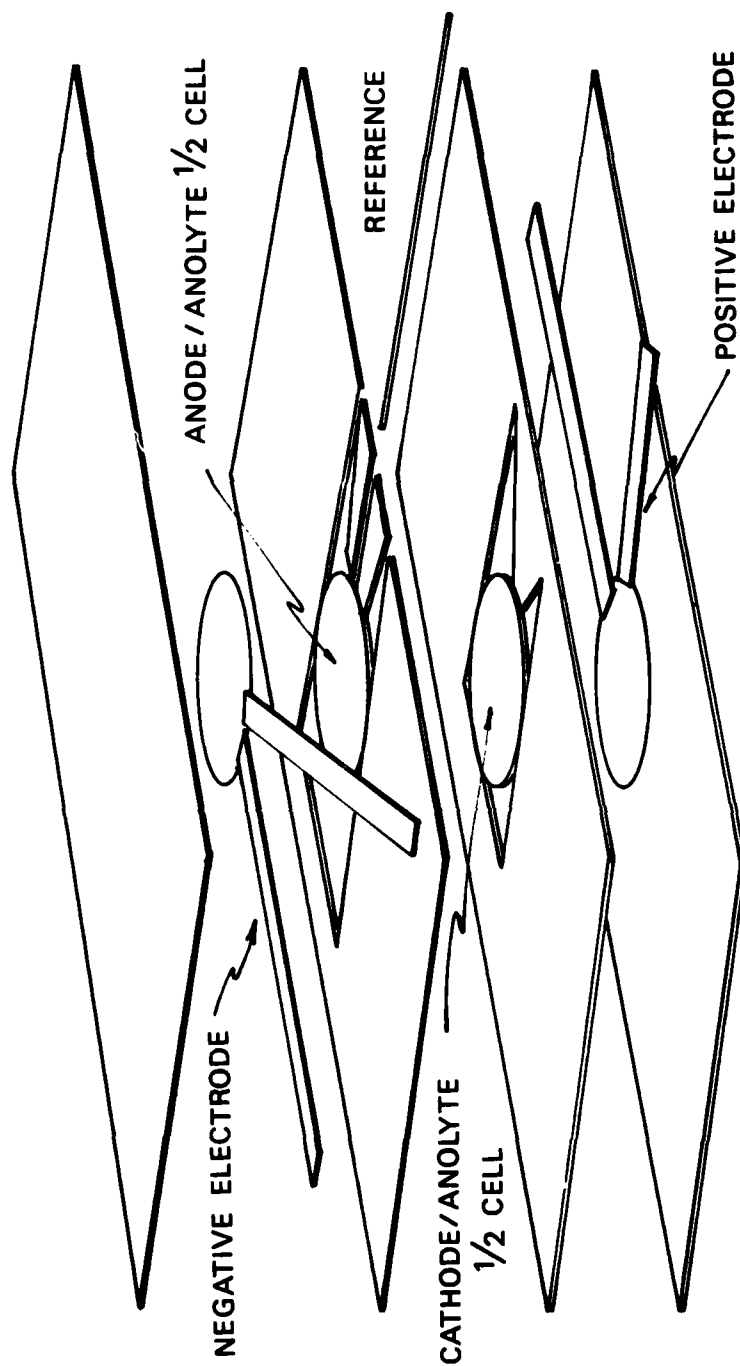


Figure 2. Reference Electrode Test Apparatus

SECTION VI

ALTERNATE CATHODE CHLORIDES

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 will 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 2).

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 ^W/o anode. There was no load on the cell.

The first twenty seconds of the test were 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 9 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 9 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_+ to -	R_{INT} + to -	V_+ to R	R_{INT} + R	V_- 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	0.08	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 1.5 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 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 by an anode reaction (Figure 3).

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 were marred by the presence of excessive electrical noise at the cell activation. This noise hindered "spike" formation observation. It was felt that this condition could 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 is a great improvement. Included in this report are several reproductions of activation portions of three of these new RET's (Figures 4, 5, and 6).

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 7 and 8 are reproductions of the activation portions of two MoCl_5 RET's. The spike is well developed in Figure 7 but there is no spike in Figure 8. It can also be seen in Figure 8 that there is no spike in the anode contribution to the cell.

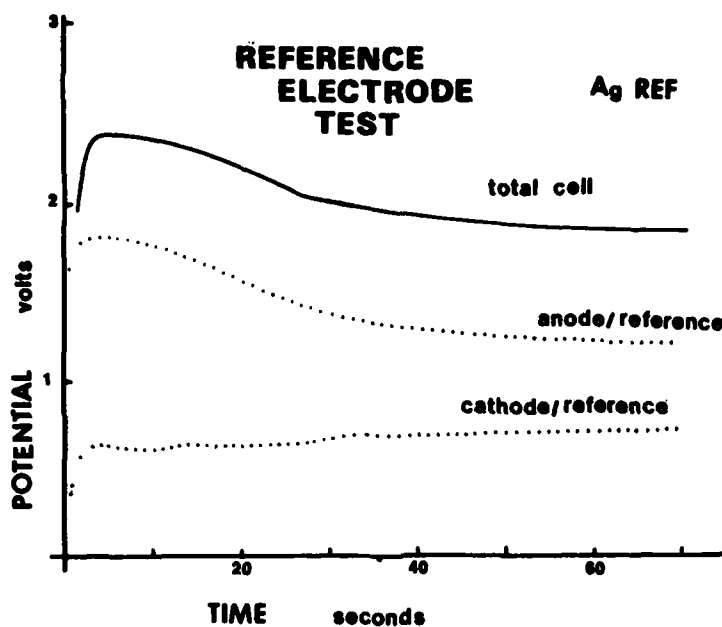


Figure 3. A Typical Reference Electrode Test

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 10) 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 is 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.

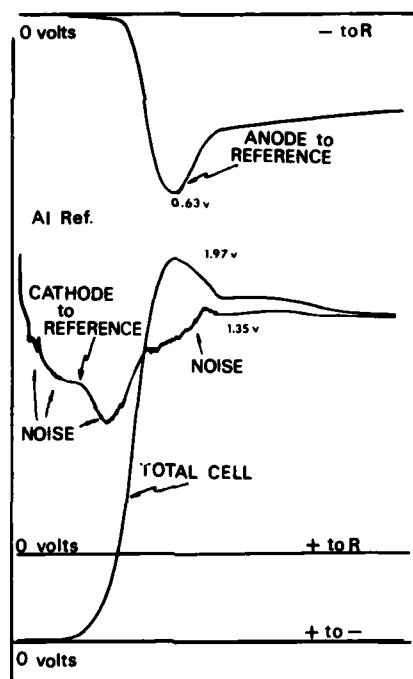


Figure 4. A Reference Electrode Test With An Aluminum Reference Wire

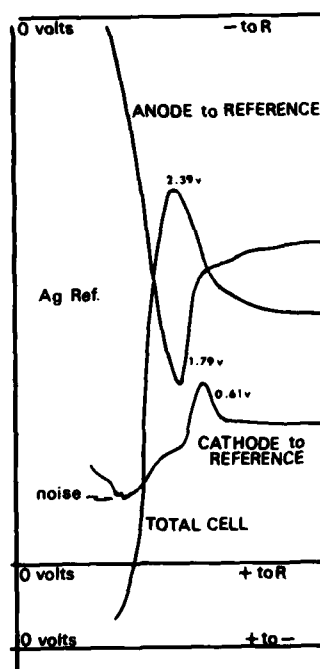


Figure 5. A Reference Electrode Test With A Silver Reference Wire

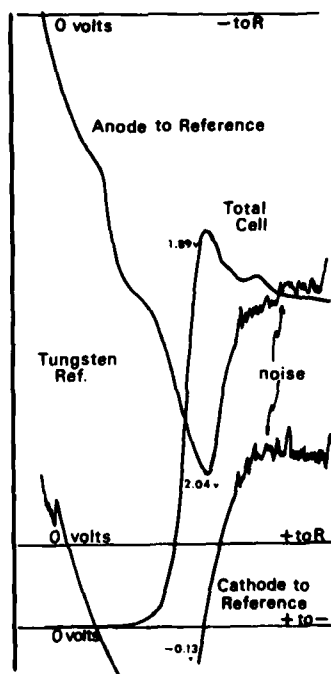


Figure 6. A Reference Electrode Test With A Tungsten Reference Wire

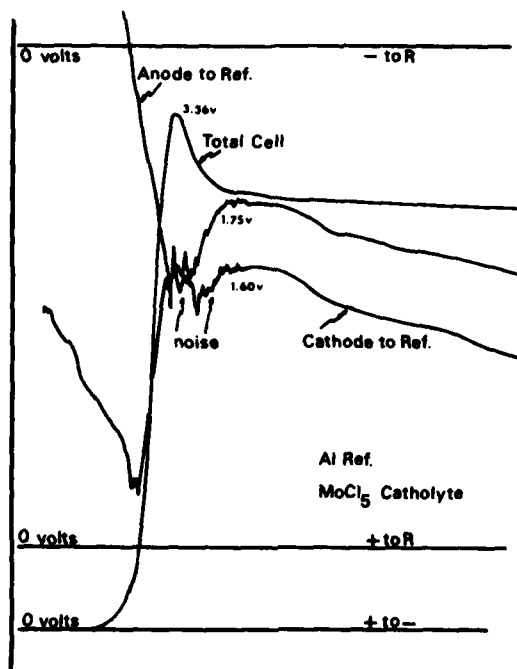


Figure 7. A MoCl_5 Cell Tested With An Aluminum Reference Wire Showing A Spike

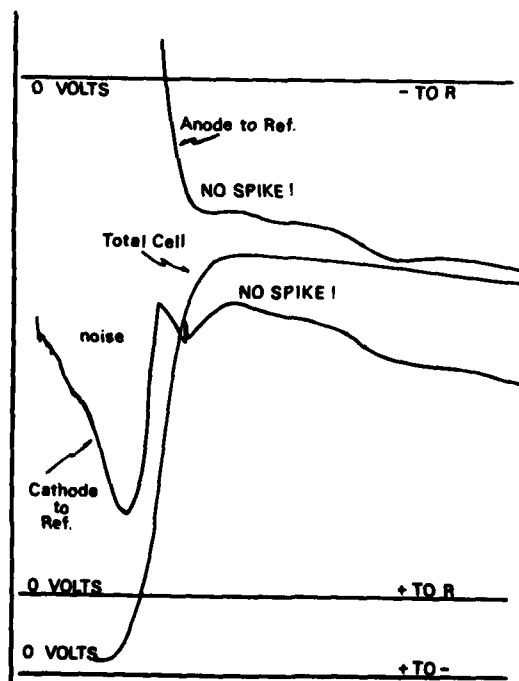


Figure 8. A Reference Electrode Test Showing No Spike

TABLE 10 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 Rev.	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. These were two split pellet type cells. The reference wire was Ag. The test temperature was 200°C . One cell each was tested across 0.4, 1.5, 5.0, and 12.6 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 9 is a sketch of a typical discharge curve for a CuCl_2 RET type cell. On the same set of axes is 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.

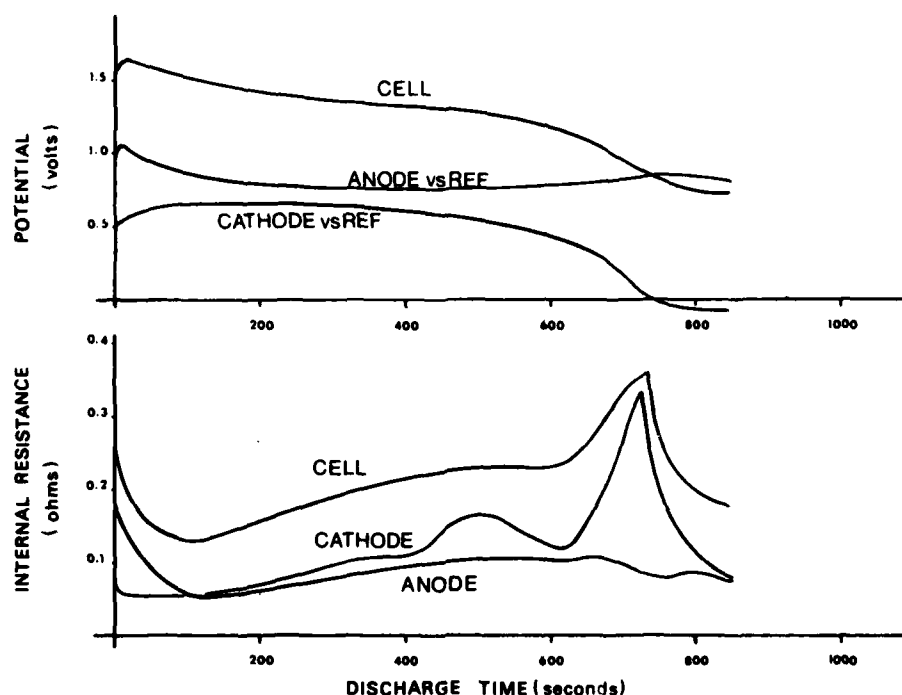


Figure 9. An R.E.T. With A CuCl_2 Cell Showing Potential And Internal Resistance Varying With Time

SUMMARY OF REFERENCE ELECTRODE TESTS:

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.

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 has been 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. This catholyte was not as dense as the regular CuCl_2 catholyte. This material was used to prepare cells for testing. Table 11 contains the results of these tests.

TABLE 11 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	°C	ohms	
1558	1.66	74.5	53	79	1.63	2.16	200	0.81	LiAl/NaAlCl ₄ / CrCl ₃ ,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 12 is a tabulation of this test data.

Figure 10 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 13 is a tabulation of these cell results.

TABLE 12 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 13 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	

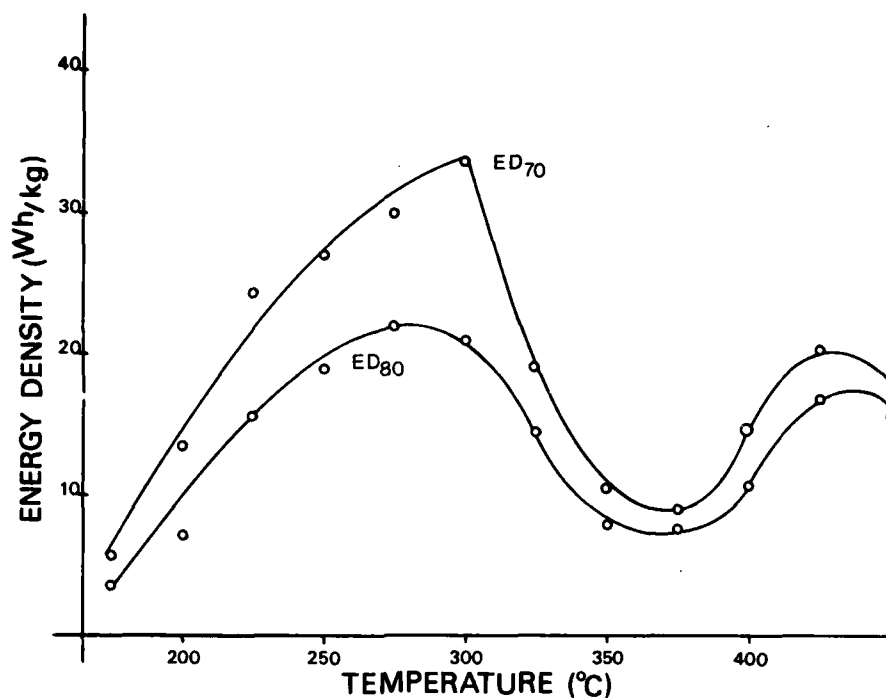


Figure 10. Energy Density vs. Test Temperature
For CrCl_3 Type Cells

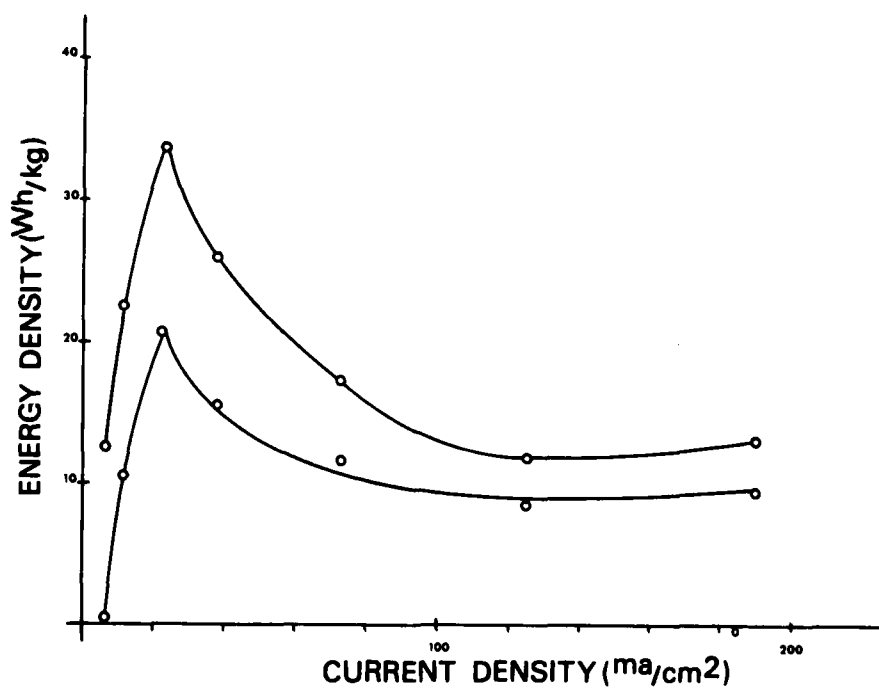


Figure 11. Energy Density vs. Current Density
For CrCl_3 Type Cells

Figure 11 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). This material has been reported in previous Progress Reports.

Cells were made from the 69 m/o AlCl_3 acidic catholyte and the old 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 LiCl-KCl eutectic. Table 14 shows the results of some cell tests with LiCl-KCl electrolyte and a catholyte of $2/3 \text{ CrCl}_3$ and $1/3 \text{ LiCl-KCl}$. The anode was 20 w/o LiAl .

TABLE 14 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 14 is compared to Tables 11 and 12 it can be seen that the LiCl-KCl was indeed a superior electrolyte for this application. The last four test results in Table 14 indicate a possible high temperature problem.

The next step was to try these powders with a magnesium anode. The results were interesting (Table 15).

TABLE 15 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 15 with Tables 11, 12, and 14), 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 12 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.

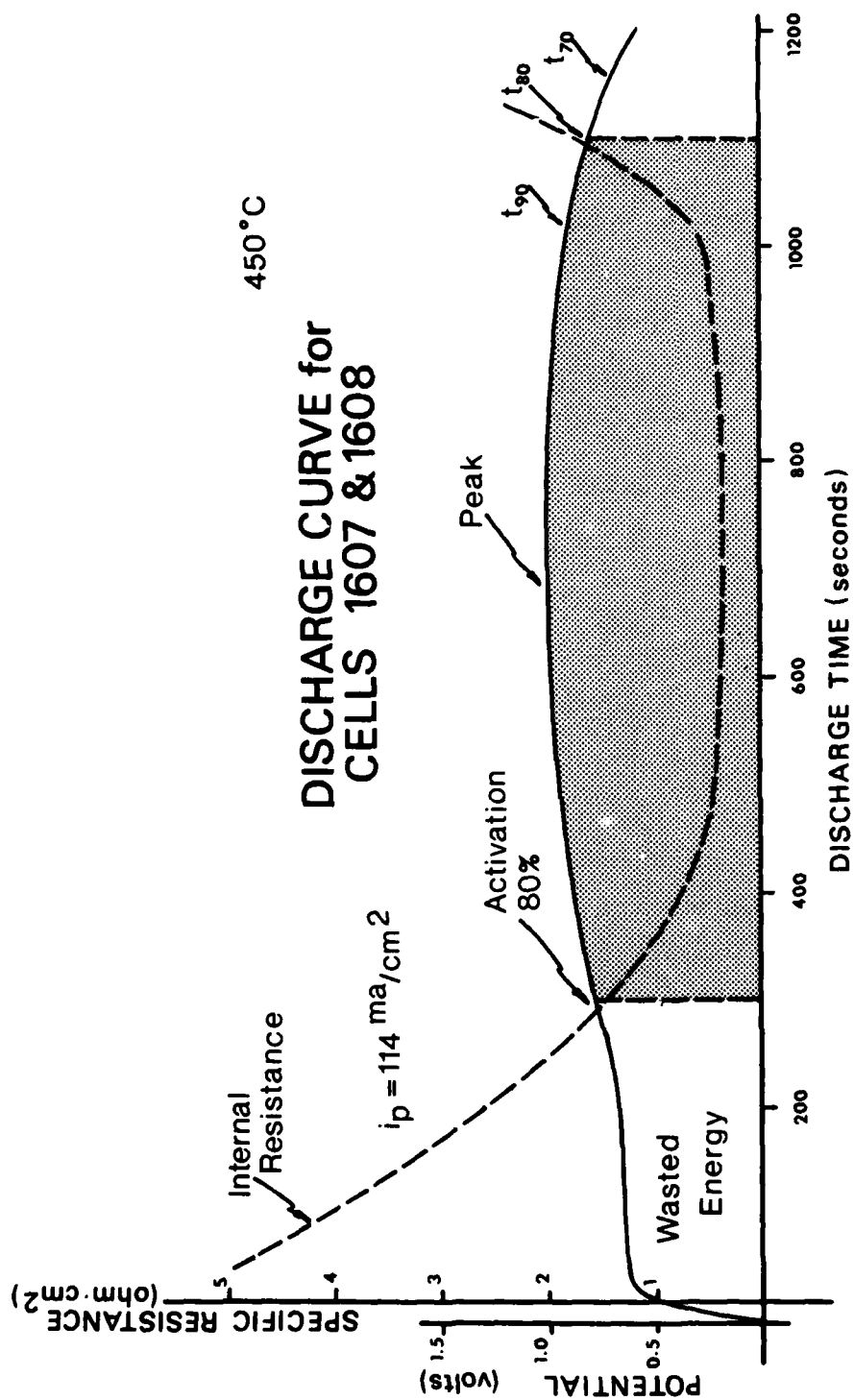


Figure 12. A Discharge Curve Of A CrCl_3 Type Cell
Showing Internal Resistance

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 (see Progress Report, October, 1976, High Energy Density Pelletized Aluminum Chlorine Thermal Batteries, Contract F33615-76-C-2080, Project No. 3145).

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

$$\begin{aligned}x_1 &= \frac{\text{anode weight}}{\text{anolyte weight}} \\x_2 &= \frac{\text{cathode weight}}{\text{anolyte weight}} \\x_3 &= \frac{\% \text{ CuCl}_2 \text{ in the catholyte}}{\% \text{ anolyte in the catholyte}} \\x_4 &= \frac{\% \text{ graphite in the catholyte}}{\% \text{ anolyte in the catholyte}}\end{aligned}$$

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:

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

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

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

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

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

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

LL $\equiv$ 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 w/o
graphite 11.54 w/o
anolyte 38.46 w/o

CuCl_2 at maximum and graphite at minimum

HL $\equiv$ CuCl_2 69.77 w/o
graphite 6.98 w/o
anolyte 23.26 w/o

CuCl₂ at minimum with maximum graphite

LH $\equiv$ CuCl₂ 42.62 %
graphite 24.59 %
anolyte 32.79 %

Both CuCl₂ and graphite at maximum

HH $\equiv$ CuCl₂ 63.16 %
graphite 15.79 %
anolyte 21.05 %

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_2 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 CuCl₂ 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. 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 16 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 16.

TABLE 16 SINGLE CELL TEST RESULTS FOR THE CELLS
TESTED FOR THE FACTORIAL DESIGN STUDY DONE TO
OPTIMIZE THE $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2/\text{C}$ 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 _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	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 _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	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 _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	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	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	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 _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 _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 L _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	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 _H	1.89	201	661	758	7.32	20.7	22.9	36.2	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	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 17 tabulates the relative position of each cell type with respect to the others. For example, notice that under the column marked V_p cell HHHL is listed as #1. This means that the HHHL 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 HHHL 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 17 the larger the actual value of the measured variable.

TABLE 17 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 17, 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 17 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 was much greater than the effect of the internal resistance.

Notice also from Table 17 that the last four cell types had the best performances. An exception was the 70% 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 18 is a tabulation of all nine of the linear models generated from this data.

TABLE 18 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 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 16 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} was almost 50% of the constant β_0 . However, for t_{70} the most significant factor (β_0) 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_0 , 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 70% 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 thought 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:

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

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). 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 lifetime 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 can be developed the spike must be controlled.

CONCLUSION TO THE ALTERNATE CATHODE CHLORIDE STUDY:

The reference electrode tests taught that the spike was in the anode. It was also learned that the cells were anode limited at initiation and cathode limited at end-of-life.

The CrCl_3 experiments demonstrate that CrCl_3 is a high temperature cathode material unsuitable for low temperature thermal batteries.

The factorial design study for LiAl/CuCl_2 led to an optimum cell formula and optimum catholyte formula but because of the spike there is an inherent doubt about these results.

SECTION VII

ALTERNATE CATHODE MATERIALS

Most of the cathode materials used with this cathode system have been chlorides. It was mentioned earlier in this report that MoO_3 was also tried. The preparation of the catholyte was described under "Particle Size Growth in the Catholyte". Cells were made with these materials and they were tested.

The catholyte was used with 28 % LiAl and A #1050 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.

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

- 1) MoO_3 catholytes produce at least as great a 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 in February, 1978 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.

WO₃, Fe₂O₃, CuO

Some more cathodic oxides have been tested. The first was WO₃. The results were not very dramatic. Also tested this report period was CuO and Fe₂O₃. MoO₃ has been tested before but not with basic electrolyte materials. Table 19 shows how each type of cell performed over a similar density range at 200°C.

TABLE 19 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	WO 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 19 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 at 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. WO₃ 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 20). The Fe results were no better than those reported in Table 19.

TABLE 20 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 20 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 W_3O_3 at higher temperatures but the 80% energy density did not. This is because of a bad "spike" with the W_3O_3 system which was not as much in evidence with the CuO and MoO_3 cathodes. The Cu cathode was clearly superior in these tests even though the voltage was less.

SUMMARY:

- 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 ^{w/o} 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 75 Ω 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 12.6 Ω 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 12.6 Ω 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.

In an attempt to make a catholyte which was more readily usable a third catholyte was mixed (with the same formula as #1203) and prefused at 180°C for 10 minutes. This material was allowed to cool, was ground and sieved. This was catholyte C #1025. However, it was still not possible to make cells with this catholyte.

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^{w/o} 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 21 shows the results of the tests.

It can be seen from Table 21 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 TiS_3

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 TiS_3 is not a good cathode material for this application.

TABLE 21 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	160	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_3 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	

SECTION VIII

ALTERNATE GRAPHITES

One pint samples of eight different graphites have been 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 sources. Asbury Mills sent data sheets with each sample. The following Table (Table 22) is a condensed tabulation of the sample characteristics.

TABLE 22 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

These graphites were used to prepare regular test CuCl₂ catholytes. These catholytes were used to make regular test cells with 28 ^w/o 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.

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 13 and 14 illustrate this point well.

Figure 13 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 noticable about the data in Figure 13 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 13 - 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 14 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

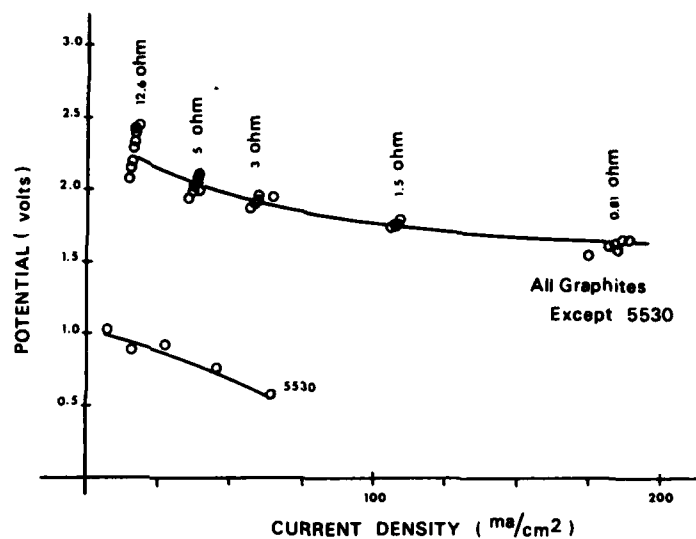


Figure 13. Potential vs. Current Density Comparing Different Graphites

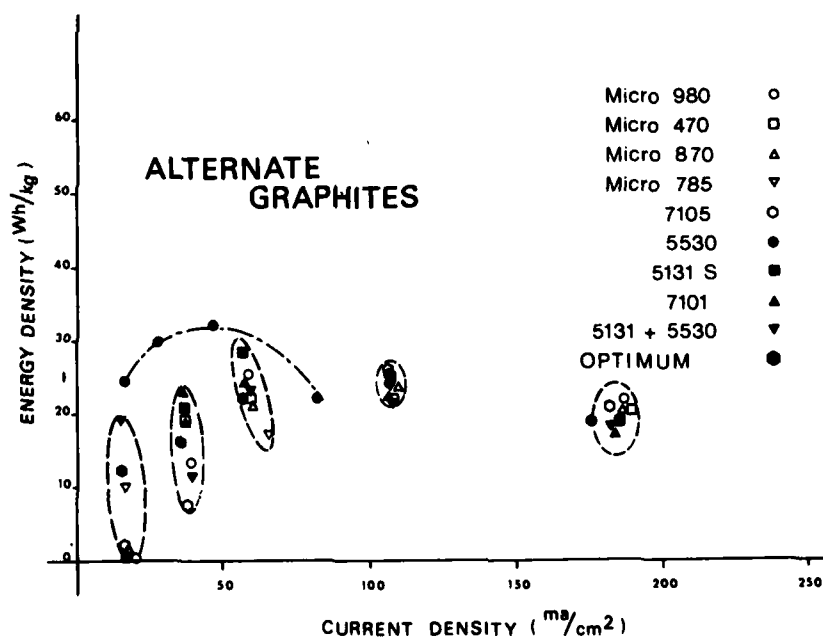


Figure 14. Energy Density vs. Current Density Curves Comparing Different Graphites

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 degassed for an additional two hours. Once again the three types of cells performed 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 IX

SULFUR

The first sulfur cells 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 23 shows typical test results.

TABLE 23 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	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	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

As can be seen from Table 23 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 3.15 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. 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.

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.

TABLE 24 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	ohm·cm ²	ohm·cm ²	°C and ohms	
1881	0.40	45.2	X	X	0.61	2.04	1.86	160°	Cells Not Charged
1882	1.09	19.9	0.66	2.13	4.09	0.26	0.35	0.81Ω 160°	
1883	1.16	8.4	X	2.92	4.80	X	X	5Ω 160° 12.6Ω	
1884	1.88	34.4	25.5	29.9	32.7	X	6.71	160° 5Ω	This cell was charged, tested, and recharged and tested
	1.94	35.5	10.5	14.1	19.5	7.3	8.66	160° 5Ω	
1885	1.83	33.5	23.5	26.6	29.0	7.92	15.5	150° 5Ω	Discharged Cool
1886	1.78	32.6	26.0	28.0	30.8	8.81	8.74	150° 5Ω	Discharged Hot
1887	2.05	14.9	22.9	27.6	29.1	9.97	7.20	160° 12.6Ω	Discharged Hot
1888	1.63	29.8	21.8	26.3	28.3	10.9	14.1	150° 5Ω	These cells charged for 1 hr. at 4.6v
1889	1.76	32.2	15.2	19.5	24.1	X	9.47	150° 5Ω	
1890	1.73	31.7	17.9	22.7	26.4	10.9	9.47	150° 5Ω	Charged to 3.25v
1891	1.61	29.5	17.4	19.5	21.4	20.2	13.1	140° 5Ω	Charged to 4.60v
1892	1.94	35.5	26.8	30.7	32.2	5.77	5.47	150° 5Ω	Cooled at 4.5v
1893	2.01	36.8	25.1	30.7	32.5	4.05	5.92	150° 5Ω	Cooled at 4.2v
1894	1.84	33.7	21.0	23.7	25.3	6.25	11.9	160° 5Ω	Stored 1 Day
1895	1.82	33.3	16.8	18.8	20.4	5.86	17.1	160° 5Ω	Stored 3 Days

These tests showed that there was at 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 so far has been;

- 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 25 contains the results of these cells.

TABLE 25 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 ED_{90} might be expected to be from 20 to 25 Wh/kg. However, after adding the kaolin the expected value of the ED_{90} went to 30 to 35 Wh/kg and ED_{80} 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 26 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 reported 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).

Cells #1913 - 1915 were the first of these cells to be tested. The results were not particularly good. Cell #1916 was charged for 3 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 fuse, reground, and sieved. It seemed to work. There was a small increase in capacity and voltage. However, these cells still were not particularly good either.

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 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 acid 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.

The sulfur experiment can be considered completed until some acidic LiAlCl_4 is obtained. 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, and of not being volatile. 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 X

ALTERNATE ELECTROLYTES

In view of some of the storage problems incurred during storage testing some new cell material combinations were tried. FeS_2 is a very stable material but it has previously been determined that it only functions well at temperatures too high for NaAlCl_4 . So cells were made with $\text{LiCl}\cdot\text{KCl}$ eutectic anolyte.

Two catholytes were used with these cells - FeS_2 and a mixture of FeS_2 and graphite. Two anodes were used - LiAl and Mg . Some cells were also made with V_2O_5 catholytes.

An FeS_2 catholyte was prepared by mixing 66 W/o FeS_2 with 33 W/o $\text{LiCl}\cdot\text{KCl}$ 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 $\pm$.1
Anolyte	1.20 gm $\pm$.1
Catholyte	1.30 gm $\pm$.1
Total Wt.	3.00 gm $\pm$.1

A similar catholyte was made with graphite with this formula:

3 parts $\text{LiCl}\cdot\text{KCl}$ eutectic anolyte
6 parts FeS_2
1 part graphite

While the cell without graphite produced an energy density greater than any NaAlCl_4 cell yet tested the cells with carbon in the catholyte produced even more (Table 28).

Another set of cells was made with Mg anodes (Table 27). Once again the cells with FeS_2 /carbon mixture were superior.

TABLE 27 SINGLE CELL TEST RESULTS FOR CELLS USING $\text{LiCl} \cdot \text{KCl}$ ELECTROLYTES, AND FeS_2 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 27 above 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·KCl, FeS_2 , 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 NaAlCl_4 electrolytes do not function well with oxide cathodes. However, for this series of cells the electrolyte was $\text{LiCl} \cdot \text{KCl}$. This electrolyte works well with oxides. Therefore, V_2O_5 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.

In addition to these tests there were the CrCl_3 cells (which were previously reported under Alternate Cathode Chlorides) which were also made with CrCl_3 . Once again these cells had a superior output but require higher operating temperatures.

CONCLUSION:

From these tests it can be concluded that FeS_2 is a good cathode material but only at the relatively high temperature of 400° to 450° and then with the $\text{LiCl} \cdot \text{KCl}$ electrolyte. As good as they were none of these cells were of an optimum configuration.

LiAlCl_4 :

Some LiCl saturated LiAlCl_4 was received from Alcoa. To test this material the LiAlCl_4 was mixed with 10 ^W/o Cab-O-Sil, fused, ground, and sieved like a regular NaAlCl_4 anolyte. This anolyte was mixed with CuCl_2 and graphite to make a LiAlCl_4 catholyte. Some cells were made with both LiAlCl_4 electrolytes, some with LiAlCl_4 anolyte and NaAlCl_4 catholyte and visé versa. Table 29 shows some single cell test results.

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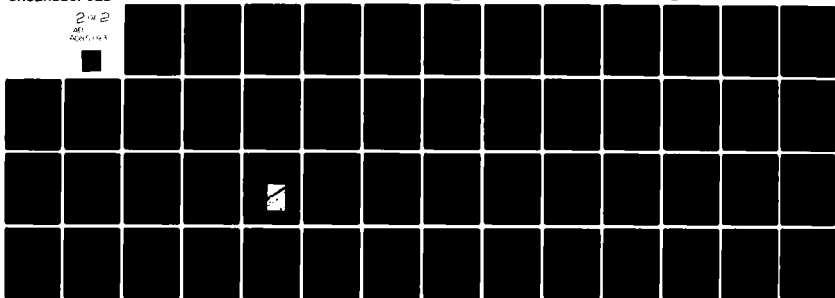
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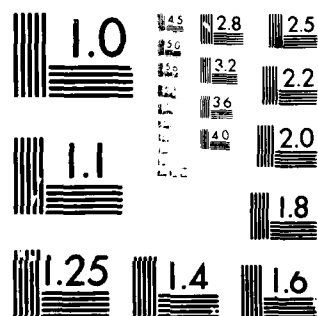
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TABLE 28 SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH LiAlCl_4 ELECTROLYTE POWDERS

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	
1756	1.61	182	11.5	19.8	22.5	X	1.1	1.2	1.2	0.8	Li ⁺ anolyte and Li ⁺ catholyte
1750	1.89	35	37.7	53.3	54.3	0.3	X	X	X	5	
1758	1.93	14	27.3	42.7	43.4	0.7	1.5	0.2	0.3	12.6	
1759	1.60	181	4.4	16.2	22.1	2.1	1.5	1.8	X	0.8	Na ⁺ anolyte and Li ⁺ catholyte
1760	2.22	41	2.4	9.5	34.2	1.7	3.8	1.8	3.0	5	
1761	2.27	17	1.4	8.8	43.2	2.4	5.2	1.5	4.2	12.6	
1762	1.42	160	6.9	13.7	20.7	2.3	2.1	2.6	3.1	0.8	Li ⁺ anolyte and Na ⁺ catholyte
1763	1.90	35	4.8	14.4	22.1	3.2	3.0	3.3	2.7	5	
1764	1.94	14	3.1	4.0	22.5	2.8	X	0.8	0.9	12.6	

It can be seen that the data in Table 28 are divided into three horizontal ranks. The three cells represented in the top rank were made with both electrolytes, anolyte and catholyte, made with LiAlCl_4 . With the middle rank, only the catholyte contained LiAlCl_4 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 ED₈₀'s and ED₇₀'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 ED₉₀ (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 29 is a tabulation of these test results.

TABLE 29 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_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	NOTES
	volts	mA/cm ²	Wh/kg	Wh/kg	Wh/kg	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	°C	
1745	0.31	6	0.14	0.20	X	437	X	X	X	100	LiAlCl_4 anolyte & LiAlCl_4 catholyte
1746	1.00	18	0.88	1.2	2.1	33	35	37	38	120	
1747	1.81	33	7.6	25.1	32.5	3.7	2.6	2.9	4.1	140	
1748	1.86	34	27.8	42.8	45.2	1.7	0.6	X	0.4	160	
1749	1.91	35	17.5	51.1	53.3	0.6	0.3	0.4	0.4	180	
1750	1.89	35	37.7	53.3	54.3	0.3	X	X	X	200	CuCl_2 & 28 w/o LiAl
1751	1.88	34	33.8	43.2	44.2	0.6	0.9	0.4	0.4	220	
1752	1.88	34	32.7	X	X	0.3	1.3	X	X	240	
1753	1.88	34	27.0	32.8	34.8	0.3	0.9	0.7	X	260	
1754	1.88	34	13.2	18.0	19.1	0.3	0.9	X	X	280	
1755	1.89	35	14.1	17.3	18.2	0.3	X	1.3	1.6	300	

These data are further illustrated by Figure 15. Figure 15 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 line

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 15. 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} .

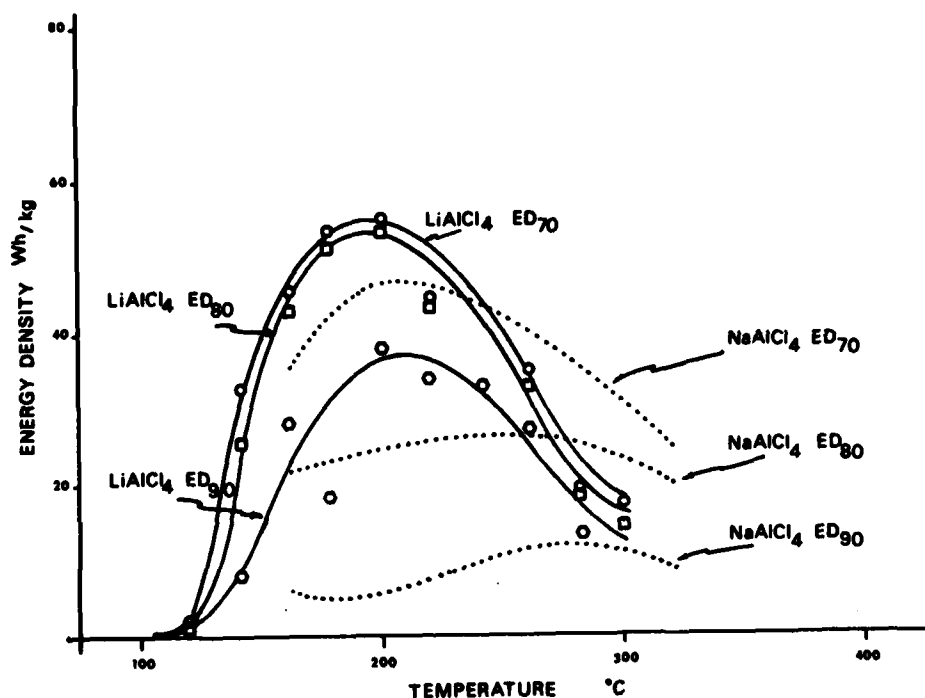


Figure 15. Energy Density vs. Temperature Curves Comparing LiAlCl_4 And NaAlCl_4 Type Cells

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, by mixing LiAlCl_4 and NaAlCl_4 it may 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. 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 is 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. This anolyte was used to mix a catholyte with CuCl_2 and graphite.

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.

Another excellent electrolyte material was the slightly acidic NaAlCl_4 (52 m /o AlCl_3). 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 cells were made with a larger than normal anode.

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 earlier.

CONCLUSION:

The initial cell tests with cells prepared with LiAlCl_4 were quite good. The cells had excellent voltage, current carrying ability and lifetime. There was an indication that mixing NaAlCl_4 and LiAlCl_4 could produce a superior cell. However, the cells made by mixing LiAlCl_4 and NaAlCl_4 did not perform as well as expected. They did not perform as well as cells made with just LiAlCl_4 . There was a possibility the anodes had been deteriorated by overnight storage in a vacuum oven at 165°C . These tests were repeated with fresh cells.

Because of symptoms of electrolyte flow with the LiAlCl_4 powders a new anolyte was made with 12 w /o Cab-O-Sil. The cells did not perform well but the tests will be repeated because there is a possibility the anode had been deteriorated by hot storage.

While cells made with mixed electrolytes (LiAlCl_4 mixed with NaAlCl_4) have shown no improvement over previous cells they have confirmed that cells made with LiAlCl_4 based anolytes and NaAlCl_4 based catholytes are superior cells. There is a strong indication that these cells can stand higher temperatures than cells made with either all NaAlCl_4 or LiAlCl_4 .

SECTION XI

FREON BLENDING

The first 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 as 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 thru 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 (0.076" 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 III, Alternate Binders.

SUMMARY AND CONCLUSION:

The first freon blended powders have been made. These include freon blended anolytes and catholytes with both 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.

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 XII

ALTERNATE ALLOYS AND ANODES

Two new anode materials, 40 % w/o LiAl and some 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. This material was finer than the previous lot. When a small sample 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 there 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 was made after a recent visit to Sandia Laboratory. Don Bush reported 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 over abundance of Li, it was decided to try this approach.

This first anode experimented with was 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 30 contains the results of these cell tests.

TABLE 30 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	0.70	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 30 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 31 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 31 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 32.

TABLE 3. 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 32 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 12.6 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 32. The experiment did not work. The cells were worse instead of better.

CONCLUSION AND 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.

SECTION XIII

SALT IN THE ANODE

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 in 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.

CONCLUSION:

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.
- 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 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 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 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.

An alloy/salt mixture containing 25 % NaAlCl₄ was fused and reground. 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 to fusing NaAlCl₄ with the alloy and so this procedure will not be 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 was prepared which had anodes made with $\frac{1}{2}$ anolyte and $\frac{1}{2}$ LiAl alloy (28 %). 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 33). The noise was not eliminated.

TABLE 33 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	62.6	Anodes: $\frac{1}{2}$ A #1066 & $\frac{1}{2}$ LiAl (28 %)
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 slower when salt is mixed into the anode. There are no dramatic effects observed when salt is added to the anode and, so, the procedure will not be further pursued.

SECTION XIV
CELL PROCESSING & FABRICATION

DESICCATION OF GRAPHITE
& CALCINATION OF CAB-O-SIL

It was believed that perhaps the moisture content of the Cab-O-Sil was causing compatibility problems. Some Cab-O-Sil was baked in a vacuum oven at 160°F for eight days before it was fused with NaAlCl₄. This was anolyte #1060.

Cells were made from 28 w/o LiAl, anolyte A #1060, and a MoCl₅ 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.

It is believed that perhaps excessive moisture is contained in two electrolyte materials - Cab-O-Sil and graphite. The first attempt to correct this was to desiccate the Cab-O-Sil in a vacuum oven held at 165°F and 2 mm Hg. However, there was no apparent difference in cell performance with cells made with electrolyte powders made with this desiccated 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 room 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°F 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 now on all regular test anolytes and catholytes will contain 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 34 contains the battery test results.

TABLE 34 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.

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 noted 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 XIII, "Salt in the Anode", of 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} & t_{80} which correspondence with the low ED_{90} and ED_{80} . The internal resistances were unusually 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 blueing 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.

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 re-tested there was a reduced spike (Figure 16).

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 17).

When freon blending began many of these cells displayed bad spikes and, once again, these were removed by vacuum desiccation (Figure 18).

Finally, a set of cells was made and tested specifically to observe this process (Figure 19).

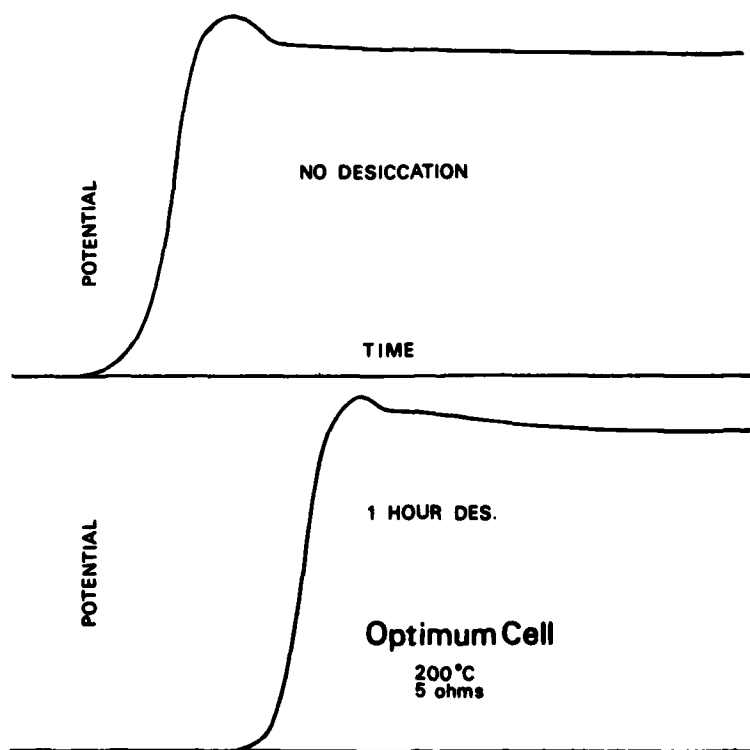


Figure 16. Discharge Curves Comparing "Wet" And Dry Cells

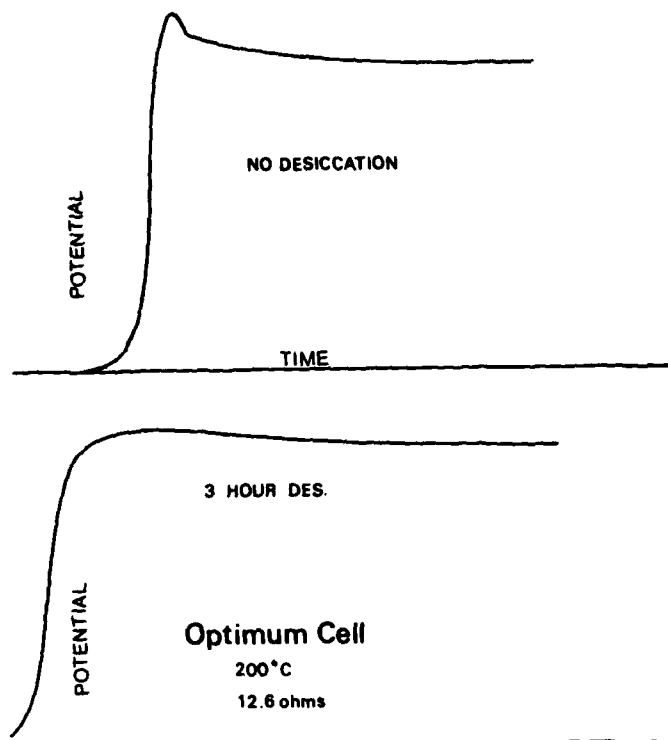


Figure 17. Discharge Curves

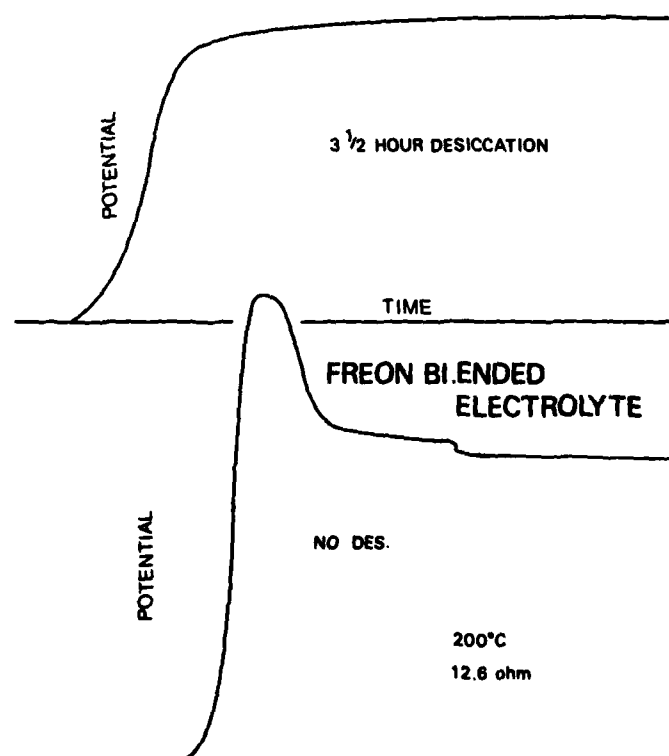


Figure 18. Discharge Curves For Freon Blended Cells Showing The Effect Of Desiccation On Spike Formation

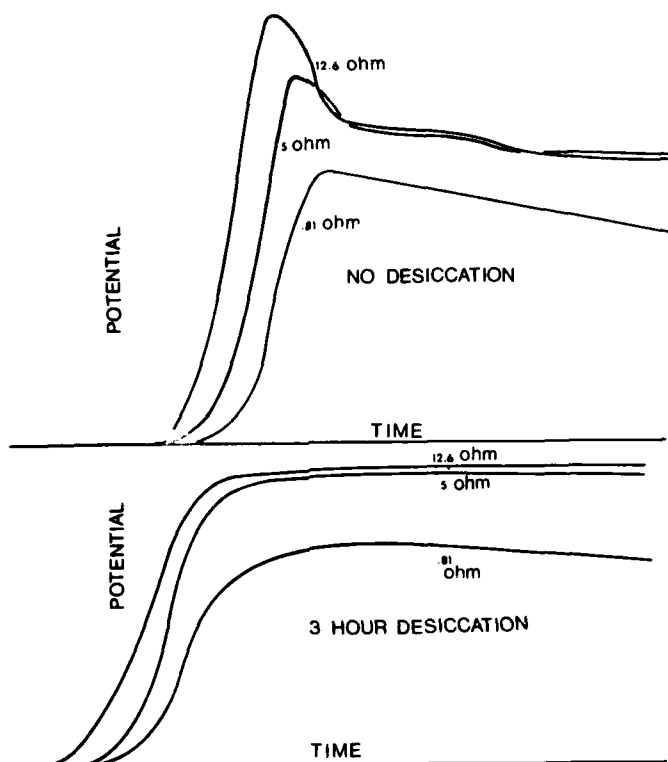


Figure 19. Discharge Curves Demonstrating The Effect Of Desiccation Upon Spike Formation

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 this "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.

SECTION XV

BATTERY FABRICATION

Batteries S/N 1051, S/N 1052, and S/N 1053 were the first batteries backfilled with argon. These batteries had a hole drilled in the header which was later soldered shut. However, the soldering process was difficult and some of the first batteries were spoiled by over heating. One battery was initiated during soldering.

Batteries 1051, 1052, and 1053 all displayed cold voltage at about 40 volts. These batteries contained only 14 cells. When activated these batteries showed a spike well in excess of 40 volts. The 50% lifetimes were all under one second. It is believed that the heat of soldering initiated the batteries without igniting the heat paper.

Some more batteries were backfilled with argon but were closed with epoxy instead of soldering. These were S/N 1054 and S/N 1055. Since two batteries would not make a very complete storage series these batteries were tested for internal resistance and polarization.

These batteries were activated across a 260 ohm load for the first 30 seconds of life. At 30 seconds the load was switched to 5.4 ohms. At 60 seconds the load was switched back to 260 ohms. Under the 260 ohm load the battery produced about 325 mA/cm^2 . The voltage dropped from 26.0v to 19.4v when the load was switched. That is, when the current density increased 27 times the voltage dropped 25%. The voltage at the end of 60 seconds was 15.9v and this jumped to about 23.6 when the 5.4 ohm load was switched back to the 260 ohm load. The battery produced 8.75 Wh/kg ideally and 1.58 Wh/kg actually during the 60 second test. This battery was tested at -65°F .

Battery S/N 1055 was tested at 165°F. The voltage dropped from 26.5 to 23.3 when the load was switched and increased from 18.4 to 22.2 when the 260 ohm load was switched back. That is, when the current density increased 30 times the voltage dropped about 15%. This was an improvement over the cold test. This battery produced about 12.1 Wh/kg ideally and about 2.19 Wh/kg actually during the first 60 seconds of life.

Both batteries had large spikes ($V_{p-65^{\circ}\text{F}} = 34.2$ volts and $V_{p-165^{\circ}\text{F}} = 36.2$).

SECTION XVI

BATTERY COMPATIBILITY

A number of MoCl_5 and CuCl_2 batteries were made and saved for storage testing. These batteries were stored at both room temperature and at 165°F . The MoCl_5 batteries were found to be completely unstorable. The CuCl_2 batteries were much better. Table 35 contains the test results for batteries made with CuCl_2 catholytes and stored in an oven held at 165°F .

TABLE 35 HOT STORAGE DATA FOR CuCl_2 BATTERIES

S/N	Storage Time	V_p	t_{90}	t_{80}	t_{70}	$\frac{ED_{80}}{IDEAL}$	T_{Peak}	Specific Resistance	NOISE
		volts	seconds	seconds	seconds	Wh/kg	$^\circ\text{C}$	$\text{ohm}\cdot\text{cm}^2$	
1027	Control	19.3	62	183	333	14.5	120	12.6	-
1038	1 day	20.1	66	153	303	13.5	104	32.9	-
1037	1 wk	19.7	65	150	231	12.6	110	42.3	slight noise at act.
1036	2 wks	19.5	62	138	247	11.5	109	40.5	slight noise at act.
1033	1 mth	18.0	50	105	186	7.47	102	82.2	slight noise at act. heavy noise at 90%
1035	3 mths	13.8	25	52	86	2.18	97	225	heavy noise

These batteries have displayed deterioration. The principle problem is the presence of considerable electrical noise. The noise began to appear after only one week of storage. The noise was heavy after one month. After three months storage the noise was so great the battery could be considered a total failure. The remaining batteries of this series have been dissected and examined pre-mortem. The only visible deterioration is a blackened layer in the cell at the alloy/anolyte interface. The anolyte and catholyte layers looked completely unchanged.

It is concluded that the LiAl alloy is deteriorating upon hot storage. The darkened color suggests the deterioration is caused by exposure while the batteries and cells are being fabricated and gradual reaction with the internal atmosphere of the battery. There is no apparent deterioration of the catholyte or anolyte.

The compatibility samples indicated that the Mo species in the catholyte could migrate through the anolyte even while the cell is uninitiated. To try to prevent this, a battery was constructed with the cells fabricated from two pellets (similar to the two pellet type cells used in the reference electrode tests) with an asbestos separator between the two halves of the cell.

However, after three weeks of hot storage this battery was opened and examined. The two cell halves had grown together right through the separator. In the anolyte portion of the cathode, half of the cell had turned brick red just like the anolyte portion of the compatibility samples. Figure 20 is a photomicrograph of one of the cells which was broken in half and examined in section. In this photo the anode/anolyte is toward the top and the cathode/anolyte is toward the bottom. The thin separator between the "white" anolyte and "red" anolyte can just barely be seen. This cell was about 0.080 inches thick.

The CuCl_2 batteries stored at room ambient temperature showed only a small deterioration after the first day. It is believed that the LiAl alloy reacted to any atmosphere inside the battery very quickly and then there was no more deterioration (see Table 36).

TABLE 36 CuCl_2 STORAGE BATTERY TEST RESULTS.
THESE BATTERIES WERE STORED AT ROOM AMBIENT
TEMPERATURE

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	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	
1027	Control	19.3	62	183	333	14.5	2.75	120	12.6	Regular CuCl_2 Room Ambient 25 Ω
1028	1 week	20.3	15	108	282	9.0	1.71	115	15.2	
1029	1 mth.	19.7	45	111	215	9.5	1.80	115	15.8	
1050	3 mth.	19.7	38	115	311	9.5	1.81	110	17.5	
1070	6 mth.	19.1	34	110	287	8.6	1.61	103	12.0	

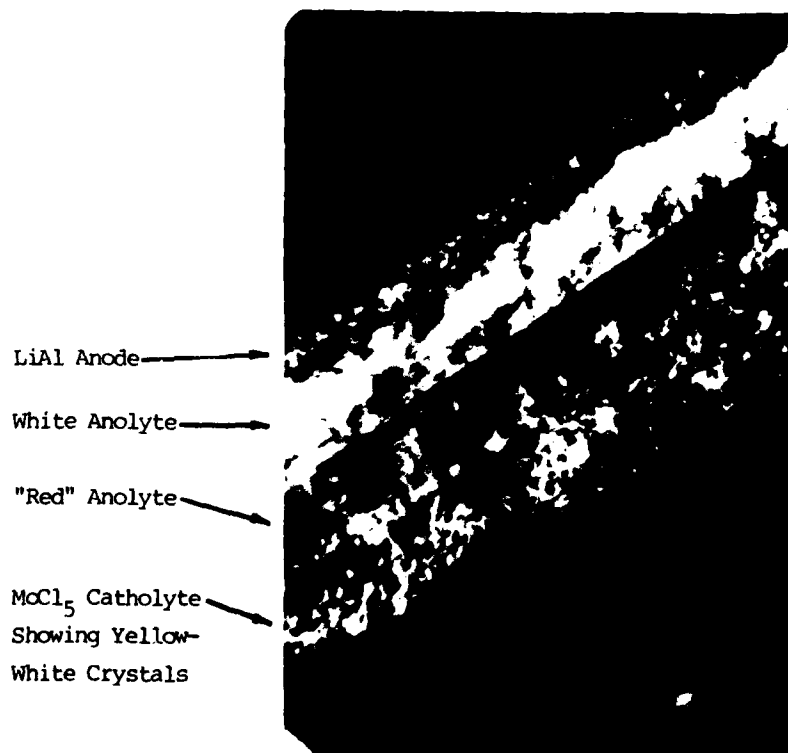


Figure 20. A photomicrograph of a sectional view of a split cell. The LiAl anode layer is toward the top of this photo.

When the MoCl_5 storage problem first arose, a number of batteries were made which were backfilled with argon in an attempt to remove any possible moisture from the atmosphere inside the battery. These batteries were stored at 165°F . The test results are in Table 37. Obviously the backfilling process did not help the storability of these batteries at all.

TABLE 37 MoCl_5 STORAGE BATTERY TEST RESULTS

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	$^\circ\text{C}$	ohm-cm ²	
1056	Control	28.3	56	190	275	26.8	4.88	135	4.84	Stored at 165°F MoCl_5 Catholyte
1057	1 week	25.9	20	158	272	18.0	2.88	105	14.6	
1058	2 week	25.3	26	144	256	15.8	2.52	X	14.9	
1059	1 mth.	23.9	35	121	194	12.2	1.96	108	17.2	
1071	3 mth.	6.8	25	37	55	0.39	0.06	84	17.7	Argon Backfilled

Another series of batteries were made and backfilled with argon. These were CuCl_2 batteries and they were stored at 165°F (Table 38).

As was true with previous CuCl_2 test results, the most deterioration was after the first day of storage. However, where the room temperature tests showed no further deterioration, these hot storage tests did show further deterioration. The internal resistance has been steadily climbing. The peak voltage and the capacity also showed a gradual but steady decrease. There also may have been a degradation of the peak skin temperature.

TABLE 38 TEST DATA FOR STORAGE BATTERIES MADE BY BACKFILLING THE BATTERY WITH ARGON. THE ENERGY DENSITIES ARE EXPRESSED AS Wh/kg.

S/N	Storage	V _p	t ₉₀	t ₈₀	t ₇₀	ED ₈₀	ED ₈₀	T _{Peak}	R _{INT} t ₈₀	NOTES
	Time	volts	seconds	seconds	seconds	IDEAL	ACTUAL	°C	ohm·cm ²	
1060	Control	24.7	73	203	380	19.0	3.46	109	26.2	Stored at 165°F CuCl ₂ Catholyte Argon Backfilled
1061	1 day	25.2	61	252	574	23.8	4.32	107	21.7	
1062	1 week	23.2	41	127	454	10.4	1.90	101	57.9	
1063	2 wks	23.7	32	130	390	10.9	1.97	103	49.2	
1072	3 mths	21.9	22	112	376	7.9	1.45	102	75.4	
1075	6 mths	20.3	20	110	348	6.6	1.20	99	94.0	

CONCLUSION:

The MoCl₅ system has been abandoned because it forms a volatile catholyte which cannot be successfully stored in a sealed thermal battery. CuCl₂ does not form a volatile catholyte. However, it appears that there is an initial degradation of the LiAl anode which is independent of the nature of the catholyte. The anode deterioration appears to be dependent upon moisture conditions around the battery (and cell) construction areas. There is also evidence of some self-discharge at elevated temperatures due to the relatively high conductivity of the solid electrolyte.

SECTION XVII

BATTERY THERMAL MANAGEMENT

Battery #1027 is also the control unit for another series of batteries. These batteries are made similar to the other series. They will be stored in an oven at 160°F.

Three batteries were made similar to #1002. The anolyte was acidic. The catholyte was an acidic CuCl_2 catholyte. The anode was 40 w/o LiAl. The heat paper was only 85 cal/in². These batteries were constructed because the CuCl_2 batteries showed a tendency to form a spike when overheated.

The experiment was a failure. The heat pads did not ignite. Only the fuze strips burned. This type of heat source cannot produce such "cool" heat paper and still burn reliably.

A new battery case has been received. The new case will produce batteries with a final volume of 156 cm³, 2.25" dia. and 2.5" tall. A minor adjustment had to be made in the end asbestos to fit the cell stack into the new can. Batteries #1039, #1040, and #1041 were made to test these changes. The batteries were made with 28 w/o anodes, basic CuCl_2 catholyte, and 100 cal/in² heat paper. Table 39 contains the result of these tests. These batteries contain 14 cells.

TABLE 39 BATTERY TEST RESULTS ACROSS A 25 OHM RESISTOR

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	°F	ohm·cm ²
1039	27.4	100.3	0.78	41	165	405	19.4	3.38	120	165	13.9
1040	27.1	99.0	1.54	55	147	426	16.9	2.95	95	R.A.	22.9
1041	18.3	67.0	0.99	6.5	9.3	13.2	0.49	.085	56	-65	733

There is no explanation for the poor performance of #1041. The cooled battery was examined post mortem. The entire ignition and thermal system functioned. There was the correct number of cells and none were facing the wrong direction. There was some unusual discoloration near the edges of the cells where the glass tape held the fuze strips. There was no evidence of internal shorting.

Two more batteries were made with hotter heat paper, 120 cal/in² (Table 40).

TABLE 40 BATTERY TEST RESULTS FOR BATTERY
MADE WITH 120 CAL/IN² HEAT PAPER

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	°F	ohm.cm ²
1042	29.4	108	0.66	3.7	82.3	276	11.2	1.93	132	165	10.3
1043	26.4	96.6	1.60	69.4	139	220	15.2	2.66	87	-65	58.6

The bad spike in the hot test indicates that 120 cal/in² is too hot for this battery design.

Three more batteries were made with 115 cal/in² paper. In addition to this, the battery can was only 2.397" tall instead of 2.50" tall. These batteries were tested at room ambient temperature but with different load resistance.

TABLE 41 BATTERY TEST RESULTS AT ROOM AMBIENT
TEMPERATURE AND VARIOUS LOAD RESISTANCES

S/N	V_p	i_p	Act.	t_{90}	t_{80}	t_{70}	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T_p	Load	Spec. r at 80%
	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	ohms	ohm·cm ²
1044	24.8	221	1.78	10.2	27	63	6.39	1.15	171	10.25	19.9
1045	23.9	336	1.86	8.8	22.7	50	7.87	1.39	183	6.5	16.7
1046	22.8	448	2.03	7.0	17	35	7.49	1.33	194	4.66	14.0

The single cell tester was originally constructed with independent temperature controls on each platen. Taking advantage of this capability a series of cells have been 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 would be tested with the anode up (anode hot) and the second cell would be tested anode down (cathode hot). Some of the cells were loaded 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 42 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 42 that the cells with hot anode produced a greater peak voltage than the cells with hot cathodes (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.

TABLE 42 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°	C°	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} /kg
J	350	200	2.12	Fast	20%	Cab-O-Sil 5 ohm load, ED ₉₀ =0.33 ^{Wh} /kg
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

Accordingly the lower platen temperature was raised to 150°C. The upper platen temperature was maintained at 200°C. From Table 42 (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.

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 cells 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 one 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 the shape of the discharge curve is similar to the cathode to reference discharge curve.

CONCLUSION:

As a result of this work it was learned that even CuCl_2 batteries could form a spike 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. These batteries were only partially successful and further experimentation will be done at another time. It is still believed that the CuCl_2 cathode should be protected from the heat paper flash.

SECTION XVIII

CONCLUSION

The problem which was originally referred to as the particle size growth problem has mushroomed into a serious storage problem. MoCl_5 forms volatile products in the catholyte. These materials are quickly distributed throughout the interior of a battery and the battery quickly self discharges. At this time the best alternative to the MoCl_5 catholyte has been the CuCl_2 catholyte.

Some alternate binder materials have been investigated. The first, Illinois Mineral Amorphous Silica, was found to prevent electrolyte flow. However, four or five times as much silica would be needed as the present amount of Cab-O-Sil. It is interesting to note that the cells made with electrolytes composed of this amorphous silica did not display either cold voltage or high internal resistance. Furthermore, the amorphous silica does not need to be fused with the salt as does Cab-O-Sil. Some magnesia was also tried as an antiflow agent but was abandoned because it was not wetted by the molten salt.

Some slightly acidic NaAlCl_4 (52 ^m/o AlCl_3) has been tested as an alternate electrolyte. Cells made with this material were superior and this material should be considered for an optimized system.

To study the high voltage initiation spike some cells were tested with reference electrodes positioned in the anolyte layer. From these tests it was learned that the activation spike originated in a high voltage anode reaction. It was also learned that this reaction is quite sensitive to exposure and it is quite temperature sensitive. Even though a number of ways have been found to control or cure the spike, no way has been found to eliminate it. Also found in the reference electrode testing was the fact that the capacity of the cell was anode limited.

Chromium chloride, CrCl_3 , has been tested as an alternate cathode chloride. This was a good cathode material but only at relatively high temperatures.

A factorial design study was done upon the CuCl_2 cells to optimize the cell. However, the presence of a spike has cast doubt about whether the thus arrived at formula is really optimum.

A variety of alternate cathode materials were investigated. There were first some heavy metal oxides (MoO_3 , WO_3 , CuO). It now appears that these materials will not be suitable for use with this system. It furthermore appears that oxides, as a class of compounds, can be eliminated from further consideration for use with this system. Second, the materials TiS_2 and TiS_3 were tested. These materials did not work any better than the oxides. Third, a fluorocarbon was tested. This material did not work well either.

Finally, elemental sulfur was tried. It was soon learned that elemental sulfur was not a good cathode material but the cells made with it could be "charged" like a secondary cell. The charged sulfur cells performed at least as well as some of the earlier MoCl_5 cells. There is no evidence of how long the cell could hold a charge or how well the uninitiated battery could be stored. As good as they were the sulfur cells were still quite short of the program goals.

LiAlCl_4 was tested as an alternate electrolyte. Cells made with this material were exceptionally good and must be considered for an optimum system.

It was found that a superior anode could be prepared by mixing Mg into the LiAl powder. This anode is much cheaper to fabricate and is mechanically much stronger. NaAlCl_4 anolyte was also added to the anode but the practice was abandoned because there appears to be no positive results.

It was found that vacuum desiccation of both cells and cell stacks could be beneficial to removal of the activation spike but that it could also be detrimental and should only be used with caution.

A number of batteries were made with inert internal atmospheres (argon). The practice was abandoned because there appeared to be no benefit to the process.

The MoCl_5 cells were found to be completely unstorable. However, the CuCl_2 cells are quite storable. There is evidence that great care must be taken to control exposure of the anodes to moisture. There is also evidence that the increased conductivity of the tetrachloroaluminate electrolytes will cause the batteries to have a shorter storage life than batteries based on LiCl-KCl electrolytes.

It was found that the thermal shock of igniting heat paper almost always caused a spike and buffers have been used to control this. All of the battery testing to date shows that the batteries can be made quite reproducibly if the spike can be controlled.

In the last year a good alternate to the volatile MoCl_5 catholyte has been found. The capacity of the cell has been increased about 20%. It is now believed that a storable low operating temperature thermal battery can be built which will approach the goals of the program.

SECTION XIX
APPENDIX
ELECTROLYTE FORMULAS

ANOLYTES

- A 1048 - 10 ^W/o Cab-O-Sil and 90 ^W/o NaAlCl₄ (NaCl saturated)
- A 1050 - 10 ^W/o Cab-O-Sil and 90 ^W/o NaAlCl₄ (NaCl saturated)
- A 1052 - 90 gms IMSIL A-25 amorphous silica and 180 gms NaAlCl₄
(NaCl saturated)
- A 1054 - 100 gm NaAlCl₄ (NaCl saturated) and 80 gms IMSIL A-25
amorphous silica which had previously been baked for
1 1/2 hours
- A 1056 - 10 ^W/o Cab-O-Sil and 90 ^W/o NaAlCl₄ (NaCl saturated)
- A 1058 - 10 ^W/o Cab-O-Sil and 90 ^W/o NaAlCl₄ (NaCl saturated)
- A 1060 - 90 ^W/o NaAlCl₄ (NaCl saturated) and 10 ^W/o Cab-O-Sil
which had been vacuum desiccated
- A 1062 - 90 ^W/o NaAlCl₄ (NaCl saturated) and 10 ^W/o calcined
Cab-O-Sil
- A 1064 - 90 ^W/o NaAlCl₄ (NaCl saturated) and 10 ^W/o calcined
Cab-O-Sil
- A 1066 - 10 ^W/o Cab-O-Sil and 90 ^W/o NaAlCl₄ (NaCl saturated)
- A 1068 - 90 ^W/o NaAlCl₄ (NaCl saturated) and 10 ^W/o calcined
Cab-O-Sil
- A 1070 - 90 ^W/o NaAlCl₄ (NaCl saturated) (lot AC-526) and 10 ^W/o
calcined Cab-O-Sil
- A 1072 - 90 ^W/o NaAlCl₄ (NaCl saturated, lot 79004-1-KB02) and
10 ^W/o calcined Cab-O-Sil

APPENDIX - CONTINUED

ANOLYTES - CONTINUED

- A 1074 - 90 ^{w/o} NaAlCl₄ (NaCl saturated, lot 79004-1-KB02) and
10 ^{w/o} calcined Cab-O-Sil
- A 1076 - 67 ^{w/o} NaAlCl₄ (NaCl saturated) and 33 ^{w/o} calcined
kaolin
- A 1078 - 90 ^{w/o} NaAlCl₄ (69 ^{m/o} AlCl₃) and 10 ^{w/o} calcined
Cab-O-Sil
- A 1080 - 90 ^{w/o} NaAlCl₄ (NaCl saturated) with 10 ^{w/o} calcined
Cab-O-Sil; freon blended
- A 1082 - 90 ^{w/o} NaAlCl₄ (NaCl saturated) with 10 ^{w/o} calcined
Cab-O-Sil; freon blended
- A 1084 - 90 ^{w/o} NaAlCl₄ (NaCl saturated, lot 79004-1-KB02) and
10 ^{w/o} calcined Cab-O-Sil
- A 1086 - 90 ^{w/o} LiAlCl₄ (LiCl saturated) and 10 ^{w/o} calcined
Cab-O-Sil
- A 1088 - 90 ^{w/o} NaAlCl₄ (52 ^{m/o} AlCl₃) and 10 ^{w/o} calcined
Cab-O-Sil
- A 1090 - 220 gm NaAlCl₄ (NaCl saturated)
220 gm LiAlCl₄ (LiCl saturated)
60 gm calcined Cab-O-Sil
- A 1092 - 225 gm MgO
275 gm NaAlCl₄ (NaCl saturated)
- A 1094 - 90 ^{w/o} NaAlCl₄ (NaCl saturated, lot 79004-1-KB02) and
10 ^{w/o} calcined Cab-O-Sil
- A 1096 - 88 ^{w/o} LiAlCl₄ (LiCl saturated) and 12 ^{w/o} calcined
Cab-O-Sil

APPENDIX - CONTINUED

ANOLYTES - CONTINUED

- A 1098 - A freon blended $\text{NaAlCl}_4/\text{MgO}$ anolyte; not fused
- A 1100 - 10 ^{w/o} calcined Cab-O-Sil and 90 ^{w/o} NaAlCl_4 ; freon blended; not fused
- A 1102 - 90 ^{w/o} NaAlCl_4 (52 ^{m/o} AlCl_3) and 10 ^{w/o} calcined Cab-O-Sil
- A 1104 - 440 gm LiAlCl_4 (LiCl saturated) and 60 gm calcined Cab-O-Sil
- A 1106 - Equal parts of A 1102 and A 1104 fused together and ground
- A 1108 - 90 ^{w/o} NaAlCl_4 (52 ^{m/o} AlCl_3) and 10 ^{w/o} calcined Cab-O-Sil
- A 1110 - 11 ^{w/o} calcined Cab-O-Sil
45 ^{w/o} NaAlCl_4 (NaCl saturated)
44 ^{w/o} LiAlCl_4 (LiCl saturated)

CATHOLYTES

- C 1081 - A catholyte made of 56 ^{w/o} CuCl_2 , 26 ^{w/o} #1042, and 18 ^{w/o} graphite - This is an "acidic" catholyte.
- C 1083 - A test catholyte approximately 3 parts C #1081 and 1 part C #1073.
- C 1085 - 56 ^{w/o} CuCl_2
26 ^{w/o} acidic NaAlCl_4 anolyte (A 1078)
18 ^{w/o} graphite
- C 1087 - 1 part C 1083 and 6 parts C 1085

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1089 - 56 ^W/o MoCl_5
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite
- C 1091 - 56 ^W/o MoCl_5
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite
- C 1093 - 5 parts C 1091 mixed with 2 parts C 1089
- C 1095 - 56 ^W/o CuCl_2
26 ^W/o acidic NaAlCl_4 anolyte (A 1078)
18 ^W/o graphite
- C 1097 - 56 ^W/o CuCl_2
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite
- C 1099 - 56 ^W/o MoCl_5
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite
- C 1101 - 56 ^W/o CuCl_2
26 ^W/o acidic NaAlCl_4 anolyte (A 1078)
18 ^W/o graphite
- C 1103 - 56 ^W/o CuCl_2
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite
- C 1105 - 56 ^W/o CuCl_2
26 ^W/o NaAlCl_4 (NaCl saturated) anolyte
18 ^W/o graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1107 - 56 ^{w/o} MoCl₅
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} graphite
- C 1109 - 56 ^{w/o} CuCl₂
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} graphite
- C 1111 - A basic CuCl₂ test catholyte made with A 1052 which
contained IMSIL-25
- C 1113 - A basic CuCl₂ test catholyte made with A 1054 which
contained IMSIL-25 which had been previously baked
1 1/2 hours at 950°C
- C 1115 - 56 ^{w/o} MoCl₅
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} graphite
- C 1117 - 13 gm NaAlCl₄ (69 ^{m/o} AlCl₃) anolyte
28 gm MoO₃
9 gm graphite
- C 1119 - 12.5 gm NaAlCl₄ (69 ^{m/o} AlCl₃) anolyte
37.5 gm MoO₃
No graphite
- C 1121 - 21 gm C 1119
4 gm graphite
- C 1123 - 56 ^{w/o} MoCl₅
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1125 - 56 ^{W/o} MoCl₅
25 ^{W/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{W/o} graphite
- C 1127 - 70 gm C 1123 mixed with 100 gm C 1125
- C 1129 - 56 ^{W/o} CuCl₂
26 ^{W/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{W/o} graphite
- C 1131 - 56 ^{W/o} MoCl₅
26 ^{W/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{W/o} graphite
- C 1133 - 56 ^{W/o} CuCl₂
26 ^{W/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{W/o} graphite
- C 1135 - A MoCl₅ catholyte made with the anolyte A 1060 which
had been prepared from vacuum desiccated Cab-O-Sil
- C 1137 - 13 gm A 1058
28 gm WO₃
9 gm graphite
- C 1139 - 25 ^{W/o} A 1058
75 ^{W/o} WO₃
- C 1141 - 40 gm C 1139}
 } fused, ground and sieved
20 gm A 1058}
- C 1143 - 35 gm C 1141
5.25 gm graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1145 - 42.5 ^W/_O A 1058
42.5 ^W/_O WO₃
15 ^W/_O graphite
- C 1147 - 26 gm NaAlCl₄ (NaCl saturated) anolyte
36 gm MoO₃
18 gm graphite
- C 1149 - 56 ^W/_O Fe₂O₃
26 ^W/_O NaAlCl₄ (NaCl saturated) anolyte
18 ^W/_O graphite
- C 1151 - 56 ^W/_O CuO
26 ^W/_O NaAlCl₄ (NaCl saturated) anolyte
18 ^W/_O graphite
- C 1153 - 56 ^W/_O CuCl₂
26 ^W/_O NaAlCl₄ (NaCl saturated) anolyte
18 ^W/_O graphite
- C 1155 - 56 ^W/_O CuCl₂
26 ^W/_O NaAlCl₄ (NaCl saturated) anolyte
18 ^W/_O graphite
- C 1157 - 56 gm CuCl₂
26 gm NaAlCl₄ (NaCl saturated) anolyte vacuum
desiccated graphite
- C 1159 - 56 ^W/_O CuCl₂
26 ^W/_O NaAlCl₄ (NaCl saturated) anolyte
18 ^W/_O graphite
- C 1161 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
(NaCl saturated)

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

C 1163	-	38.5 gm A 1074	}	
			}	
		50.0 gm CuCl_2	}	the (LL) formula
			}	
		11.5 gm graphite	}	
C 1165	-	32.8 gm A 1074	}	
			}	
		42.6 gm CuCl_2	}	the (LH) formula
			}	
		24.6 gm graphite	}	
C 1167	-	23.2 gm A 1074	}	
			}	
		69.8 gm CuCl_2	}	the (HL) formula
			}	
		7.0 gm graphite	}	
C 1169	-	21.1 gm A 1074	}	
			}	
		63.1 gm CuCl_2	}	the (HH) formula
			}	
		15.8 gm graphite	}	
C 1171	-	23.2 gm A 1074	}	
			}	
		69.8 gm CuCl_2	}	the (HL) formula
			}	
		7.0 gm graphite	}	
C 1173	-	13 gm A 1074		
		28 gm CrCl_3		
		9 gm graphite		
C 1175	-	19.5 gm A 1078		
		42.0 gm CrCl_3		
		13.5 gm graphite		
C 1177	-	56 ^{w/o} CuCl_2		
		26 ^{w/o} NaAlCl_4 (NaCl saturated) anolyte		
		18 ^{w/o} MICRO 980 brand graphite		

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1179 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o MICRO 470 brand graphite
- C 1181 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o MICRO 870 brand graphite
- C 1183 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o MICRO 780 brand graphite
- C 1185 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o #7105 brand graphite
- C 1187 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o #5530 brand graphite
- C 1189 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o #S-5131 brand graphite
- C 1191 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o #7101 brand graphite
- C 1193 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
9 ^W/o #5131 brand graphite
9 ^W/o #5530 brand graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

C 1195 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte
18 ^W/o MICRO 470 brand graphite

C 1197 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte; freon blended
18 ^W/o graphite

C 1199 - 56 ^W/o CuCl₂ }
26 ^W/o NaAlCl₄ (NaCl saturated) anolyte } mixture freon blended
18 ^W/o graphite }

C 1201 - 18.6 gm CF
8.4 gm A 1084
3.0 gm graphite

C 1203 - 9.0 gm CF
18.0 gm A 1084
3.0 gm graphite

C 1205 - 9.0 gm CF
18.0 gm A 1094
3.0 gm graphite

C 1207 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
(NaCl saturated)

C 1209 - 56 ^W/o CuCl₂
26 ^W/o NaAlCl₄ (NaCl saturated)
18 ^W/o graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1211 - 56 ^{w/o} CuCl₂
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} #7101 brand graphite
- C 1213 - 56 ^{w/o} CuCl₂
26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
18 ^{w/o} #S-5131 brand graphite
- C 1215 - 56 ^{w/o} CuCl₂
26 ^{w/o} NaAlCl₄ (52 ^{m/o} AlCl₃)
18 ^{w/o} graphite
- C 1217 - 26 ^{w/o} A 1084
56 ^{w/o} sulfur
18 ^{w/o} graphite
- C 1219 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
(NaCl saturated)
- C 1221 - 56 ^{w/o} CuCl₂
26 ^{w/o} A 1090 (50 ^{w/o} NaAlCl₄ & 50 ^{w/o} LiAlCl₄)
18 ^{w/o} graphite
- C 1223 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
(NaCl saturated)
- C 1225 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
(NaCl saturated)
- C 1227 - 56 ^{w/o} CuCl₂
26 ^{w/o} A 1100 (not fused, freon blended anolyte)
18 ^{w/o} graphite

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1229 - 56 ^{w/o} CuCl₂
 26 ^{w/o} A 1098 (not fused, freon blended anolyte made
 with MgO)
 18 ^{w/o} graphite
- C 1231 - 56 ^{w/o} TiS₂
 26 ^{w/o} A 1096
 18 ^{w/o} graphite
- C 1233 - A CuCl₂ catholyte made with the new lot of NaAlCl₄
 (NaCl saturated)
- C 1235 - 56 ^{w/o} CuCl₂
 26 ^{w/o} NaAlCl₄ (52 ^{m/o} AlCl₃) anolyte
 18 ^{w/o} graphite
- C 1237 - 56 ^{w/o} TiS₃
 26 ^{w/o} NaAlCl₄ (NaCl saturated) anolyte
 18 ^{w/o} graphite
- C 1239 - 56 ^{w/o} sulfur
 26 ^{w/o} LiAlCl₄ (LiCl saturated) anolyte
 18 ^{w/o} graphite
- C 1241 - Similar to C 1239 except that the sulfur was fused with
 25 ^{v/o} kaolin prior to mixing with A 1096
- C 1243 - Similar to C 1241 except the sulfur was mixed with 33 ^{v/o}
 kaolin
- C 1245 - A sulfur catholyte with one part kaolin for every 2 parts
 sulfur and with LiAlCl₄ anolyte mixed with slightly acidic
 NaAlCl₄ anolyte

APPENDIX - CONTINUED

CATHOLYTES - CONTINUED

- C 1247 - 12.6 ^{w/o} NaAlCl₄ (69 ^{m/o} AlCl₃)
12.4 ^{w/o} LiAlCl₄ (LiCl saturated)
39.9 ^{w/o} S₈
12.0 ^{w/o} graphite
20.0 ^{w/o} kaolin
3.1 ^{w/o} Cab-O-Sil
- C 1249 - 25.1 ^{w/o} NaAlCl₄ (52 ^{m/o} AlCl₃)
40.0 ^{w/o} S₈
12.0 ^{w/o} graphite
20.0 ^{w/o} kaolin
2.8 ^{w/o} Cab-O-Sil