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DISCHARGE CHARACTERISTICS OF LIAL/NAALCL SUB 4/FECL SUB 3 THERM--ETC(U)
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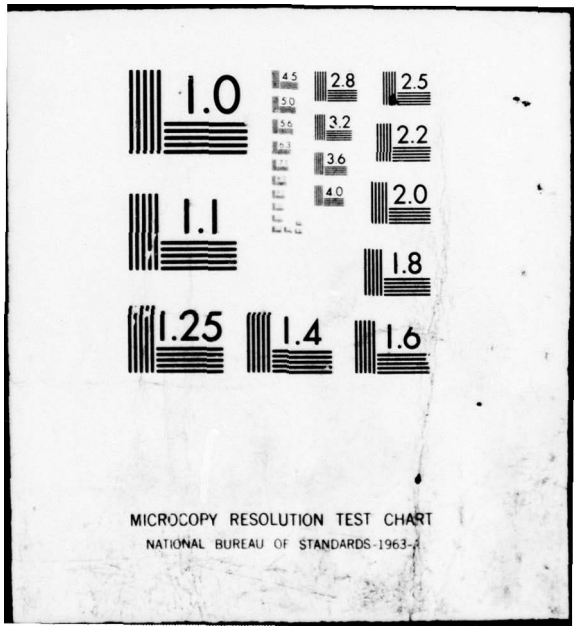
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FJSRL TECHNICAL REPORT - 79-0001

FEBRUARY 1979

DISCHARGE CHARACTERISTICS OF LiAl/NaAlCl$_4$/FeCl$_3$ THERMAL CELLS

CAPT ROBERT L. VAUGHN
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PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-79-0001

This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F2-07, "Pelletized Thermal Batteries". Captain Robert L. Vaughn was the Project Scientist in charge of the work.

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: FJSRL-TR-79-0001	2. GOVT ACCESSION NO.: ADA
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): Discharge Characteristics of LiAl/$NaAlCl_4$/$FeCl_3$ Thermal Cells.	5. TYPE OF REPORT & PERIOD COVERED: Technical rept.
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Robert L. Vaughn, Lowell A. King	8. CONTRACT OR GRANT NUMBER(s):
9. PERFORMING ORGANIZATION NAME AND ADDRESS: F. J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102F/2303/F2/07
11. CONTROLLING OFFICE NAME AND ADDRESS: F. J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840	12. REPORT DATE: February 1979 13. NUMBER OF PAGES: 33
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermal Battery
Aluminum Chloride
Tetrachloroaluminate
Lithium-Aluminum alloys
Reserve Battery
Single Cells
Iron(III) Chloride

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Pelletized thermal battery single cell experiments are described for the lithium-aluminum/sodium tetrachloroaluminate/iron(III) chloride electrochemical system. The cells were optimized for anode, electrolyte, and cathode composition. The cell discharge behavior was characterized, defining optimum conditions of temperature and discharge rate to produce maximum energy output. The best cell produced 50.6 Wh/kg (to 80% initial closed circuit voltage) at 175°C and 15 mA/cm^2. The iron(III) chloride cells were compared to molybdenum pentachloride and copper(II) chloride cells for the operating conditions 165°C to

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250°C and 15 mA/cm^2 to 100 mA/cm^2. Iron(III) chloride cells were comparable to or superior to the molybdenum pentachloride and copper(II) chloride cells for these operating ranges.

FJSRL-TR-79-0001

DISCHARGE CHARACTERISTICS OF $LiAl/NaAlCl_4/FeCl_3$ THERMAL CELLS

By

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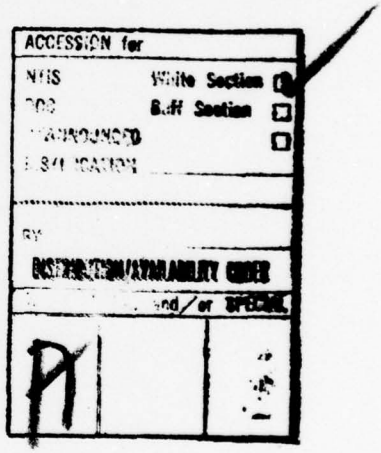
TECHNICAL REPORT FJSRL-TR-79-0001

February 1979

Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840

PREFACE

This report documents work done under Work Unit 2303-F2-07, Pelletized Thermal Batteries, between 30 March and 15 October 1978. The authors thank Donald Bush, Sandia Laboratories, for his help in designing the single cell tester used in this work.



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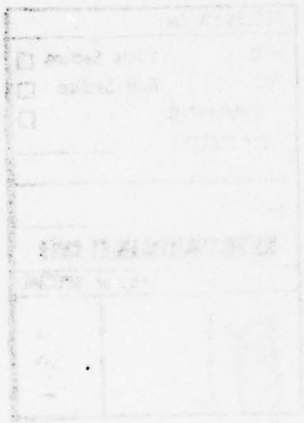

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INTRODUCTION

In previous studies we investigated the sodium tetrachloroaluminate ($NaAlCl_4$) electrolyte for use in thermally activated reserve cells (thermal cells). Lithium-aluminum alloys were used as anodes and $MoCl_5$ and $CuCl_2$ were used as cathode materials (1,2). A cathode screening study of 40 inorganic compounds indicated that $FeCl_3$ might exhibit performance superior to either $MoCl_5$ or $CuCl_2$ over a wider temperature range (3).

The electrochemistry of iron in equimolar $AlCl_3$-NaCl was studied by Boxall et al. (4), who reported the Fe(III)/Fe(II) system to be reversible. The $E°$ value for the Fe(III)/Fe(II) couple was 1.44 $\pm$ 0.03V and for the Fe(II)/Fe(0) couple, 0.63 $\pm$ 0.03V. They also reported $FeCl_3$ to be quite soluble and $FeCl_2$ to be very insoluble in $NaAlCl_4$ melt.

The purpose of the present study was to investigate the discharge characteristics of the LiAl/$FeCl_3$ couple in the $NaAlCl_4$ electrolyte and to compare the performance of $FeCl_3$ cells to $MoCl_5$ and $CuCl_2$ cells.

The first task was to optimize the anode, separator, and catholyte compositions. Single cell tests of the optimum cell configuration were made at current densities of 15, 50, and 100 mA/cm^2 and at temperatures of 165, 175, 200, 225, and 250°C. Cell tests were also made at initial cell pressures from 560 to 7200 kg/m^2.

EXPERIMENTAL

Electrolyte preparation, pellet fabrication, and single cell discharge experiments were conducted in an argon-filled glove box (Vacuum/

Atmospheres Co., Model HE 243-2 Dri-Lab/HE 193-2 Dri-Train) according to procedures given previously (1).

Iron(III) chloride (99.999%) was obtained in powdered form from Atomergic Chemetals Corp. and was used as received. The $FeCl_3$ particle size was roughly uniform (70 - 100 ASTM mesh) as determined using U.S.A. Standard Testing Sieves (W. S. Tyler, Inc.). Graphite (Grade 38 powder) was obtained from Fisher Scientific Co. and used as received.

Molybdenum foil (t3N) 0.25 mm thick was obtained from Alfa-Ventron, Inc. and used as current collectors. The foil was cut into 2.9 cm diameter circles with tab. The current collectors were burnished with 400 grit wet and dry sandpaper, washed with methanol and distilled water, and dried with acetone. The collectors were again lightly burnished immediately before use.

The single cell platen press used previously (1) was modified to incorporate a force transducer (Sensotec Inc., Model 20). The lower platen (see Fig. 1) was attached to a moveable base which rested on the force transducer. The upper platen was attached to a moveable piston. After the desired weight was placed on the piston, it was locked in position, giving a known initial stack pressure. The actual pressure encountered during heat up and discharge of the cell would then vary with time and extent of discharge. The pressure was monitored by an SCA 7-DI-3 amplifier (Sensotec Inc.), the output of which went to an HP 7100B recorder (Hewlett Packard, Inc.) through a digital multimeter (Honeywell Model 333).

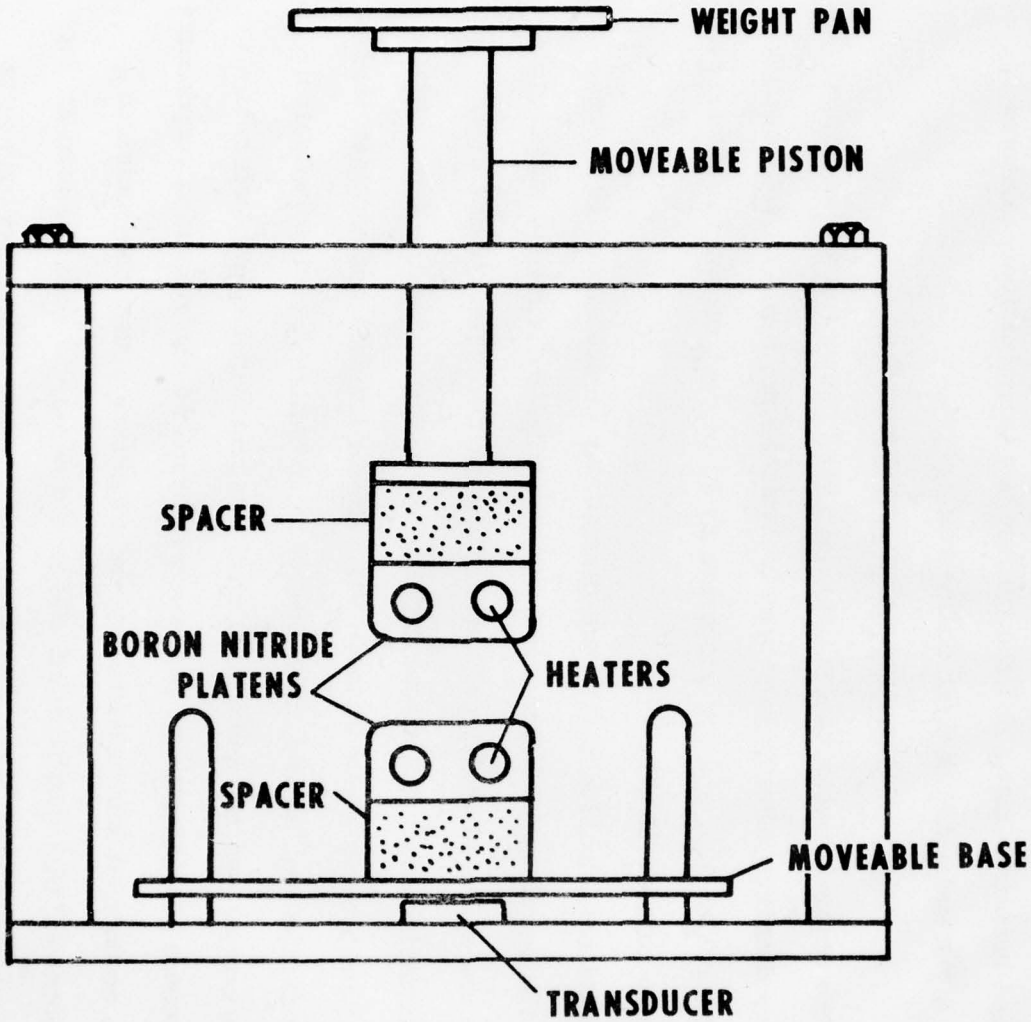

Figure 1. Simplified diagram of single cell tester.

The single cells were placed between the platens, the desired pressure applied, the platens heated to the desired temperature, and cell discharge initiated when the cell voltage stabilized. Constant current was maintained by a PAR Model 173 potentiostat/galvanostat (Princeton Applied Research Corp.) and the current was quantitatively measured with a PAR Model 179 digital coulometer.

RESULTS AND DISCUSSION

The criterion used to evaluate cell performance was the delivered energy density. Energy density calculations were based on the total mass of the pellet (1), and for discharge to 80 percent of initial closed circuit voltage (ICCV).

Cell optimization tests were carried out at 200° C and 15 mA/cm^2.

The weight of each component was otpimized individually starting from the optimized $MoCl_5$ cell configuration (1). The results of the optimization study are summarized in Tables I - VI and the final optimum configuration is given in Table VII. The individual optimization studies were carried out in the order presented in Tables I - VI. Implicit in this process was the assumption that the configuration of each cell component was independent of the composition of the remaining components. This assumption was supported by the observation that the optimized weights of LiAl, graphite and EBM in the catholyte were the same as for the optimized $MoCl_5$ cell configuration. Still, the assumption may or may not be wholly valid, and certainly would need to be more carefully considered in any battery development study.

Electrolyte-binder mixture (EBM*) was added to the LiAl to facilitate fabrication of the anode layer. The desire was to add as little EBM as possible in order not to adversely effect the delivered energy density, yet still increase the ease of fabrication. As seen in Table VI, there was no significant difference in perforance for added EBM weights from about 0.11g to about 0.14g. The value 0.12g was chosen to best facilitate anode fabrication without degrading cell performance.

The composition of the electrolyte and the amount of binder present in the electrolyte were not variables in the optimization process and therefore not necessarily the best values. They were, however, identical to those used in our previous studies.

*EBM 90 w/o electrolyte (49.85 m/o $AlCl_3$, 50.15 m/o NaCl) and 10 w/o SiO_2 binder

TABLE I. Optimization of $FeCl_3$ weight[a].

$FeCl_3$ weight (g)	Energy Density[b] (Wh/kg)
1.402	31.2
1.458	33.0
1.512	35.3
1.559	37.6
1.608	28.1

a. Cell configuration:

Anode	0.27g LiAl
Separator	0.78g EBM
Catholyte	0.64g EBM
	$FeCl_3$ as indicated
	0.23g graphite

b. To 80% ICCV.

TABLE II. Optimization of separator weight[a].

Separator Weight (g)	Energy Density[b] (Wh/kg)
0.779	37.6
0.852	39.3
0.921	46.2
0.990	50.6
1.060	44.2

a. Cell configuration:

Anode	0.27g LiAl
Separator	EBM as indicated
Catholyte	0.64g EBM 1.56g $FeCl_3$ 0.23g graphite

b. To 80% ICCV

TABLE III. Optimization of LiAl Weight[a].

LiAl Weight (g)	Energy Density[b] (Wh/kg)
0.240	35.5
0.270	50.6
0.298	48.3
0.302	32.4

a. Cell configuration:

Anode	LiAl as indicated
Separator	0.99 g EBM
Catholyte	0.64g EBM 1.56g $FeCl_3$ 0.23g graphite

b. To 80% ICCV.

TABLE IV. Optimization of graphite weight in catholyte[a].

Graphite Weight (g)	Energy Density[b] (Wh/kg)
0.200	45.1
0.229	50.6
0.256	43.9

a. Cell configuration:

Anode	0.27 g LiAl
Separator	0.99 g EBM
Catholyte	0.64 g EBM 1.56 g $FeCl_3$ graphite as indicated

b. To 80% ICCV

TABLE V. Optimization of EBM in cathclyte[a].

EBM Weight (g)	Energy Density[b] (Wh/kg)
0.583	41.9
0.638	50.6
0.700	47.7

a. Cell configuration:

Anode	0.27g LiAl
Separator	0.99g EBM
Catholyte	EBM as indicated 1.56g $FeCl_3$ 0.23g graphite

b. To 80% ICCV.

TABLE VI. Weight of EBM added to anode[a].

EBM Weight (g)	Energy Density[b] (Wh/kg)
0.110	46.1
0.113	46.4
0.132	46.0
0.146	47.3

a. Cell configuration:

Anode	0.27g LiAl EBM as indicated
Separator	0.99g EBM
Catholyte	0.64g EBM 1.56g $FeCl_3$ 0.23g graphite

b. To 80% ICCV.

TABLE VII. Optimum cell configuration

Anode	0.27 g LiAl (60 a/o Li)
	0.12 g EBM
Separator	0.99 g EBM
Catholyte	0.64 g EBM
	1.56 g $FeCl_3$
	0.23 g graphite

Cell Characteristics

The open circuit voltage (OCV) of the $FeCl_3$ cells was 2.36 to 2.38V at temperatures of 175°C and above. At 165°C, the OCV was 2.32V. The internal resistance was determined by measuring initial closed circuit voltage under various loads on a series of cells. Fig. 2 shows that cell resistances at different current densities vary between about 0.73 Ω to about 0.36 Ω at 175°C. The internal cell resistance then is of the order of 0.5 Ω. This value was relatively constant over the temperature range studied.

A yellow color was observed throughout the separator layer after every cell was discharged, indicating that the cathode reaction was a single electron reduction of Fe(III) to Fe(II).

The cell resistance as a function of extent of discharge also supports the Fe(III) to Fe(II) cell reaction. The cell resistance as a function of extent of discharge was determined using the method described in a previous study (5), and the results are graphed in Fig. 3. The rapidly increasing resistance at about 70% of discharge indicates a single insoluble product.

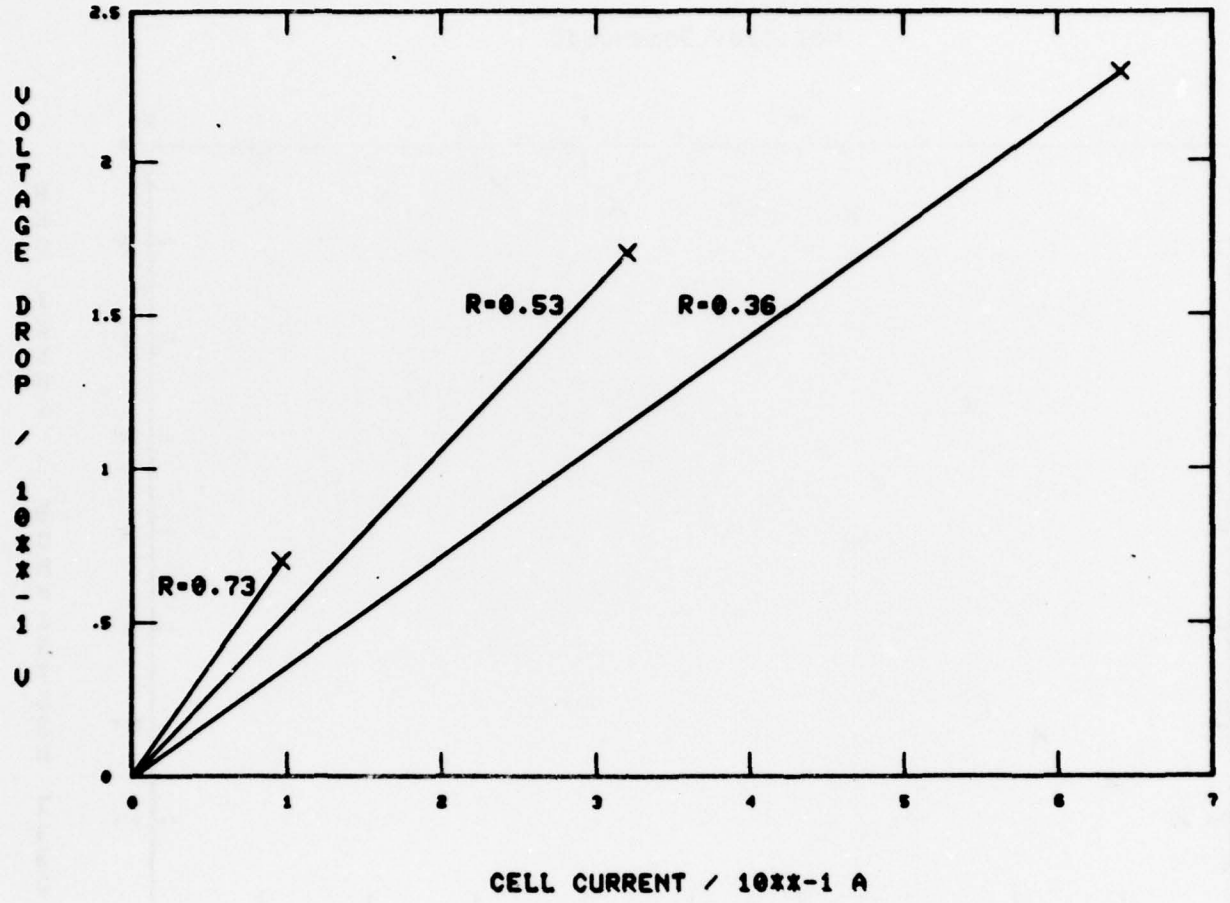

Figure 2. Internal resistance of FeCl3 cells (175 C and 15 mA/cm2)

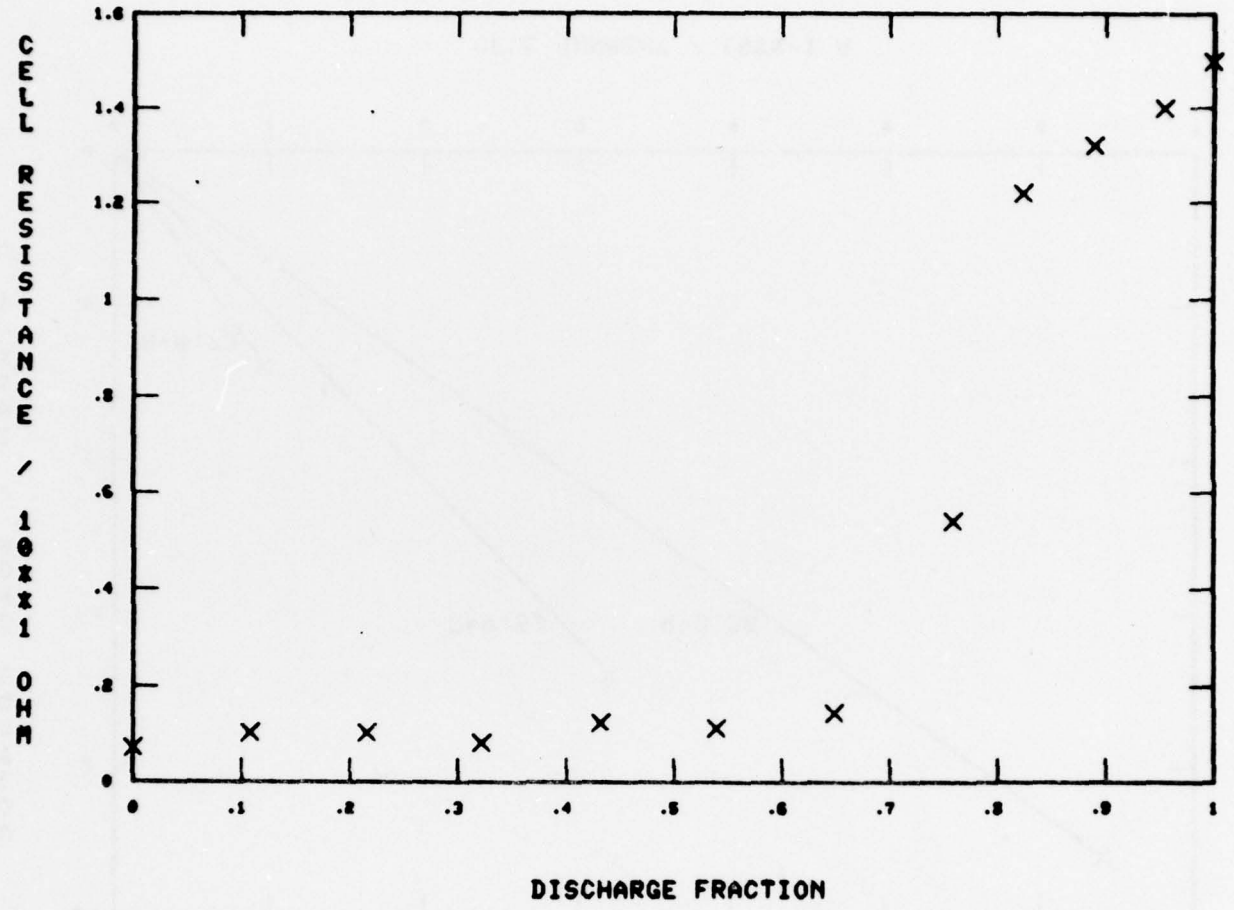

Figure 3. Cell resistance of FeCl3 cells as a function of extent of discharge (175 C and 15 mA/cm2).

Cell Discharge Behavior

Cell discharge experiments were performed to study the effects of stack pressure, temperature, and discharge rates on cell performance. Initial stack pressure was varied from 560 to 7200 kg/m^2, the temperature range was 165 to 250°C, and discharge rates were 15, 50, and 100 mA/cm^2.

Our results of varying stack pressure using the $NaAlCl_4$ electrolyte (Fig. 4) were similar to the results obtained by Bush with the LiCl-KCl electrolyte (6). At initial pressures greater than about 1400 kg/m^2, there appeared to be little dependence upon pressure of the energy densities obtained. Pressure varied in a roughly reproducible manner during cell discharge for all combinations of temperature, current density, and initial stack pressure (above ca. 1400 kg/m^2). A maximum of 3 to 4 times the initial stack pressure was reached early in the discharge, followed by a relative minimum at about 80% of ICCV, then another maximum occurred, and finally the pressure decayed to approximately the initial value at 0.0V. We have made no attempt to relate the pressure changes to specific cell processes; however, there appeared to be a noticeable correlation between the pressure/discharge profile of a given cell and whether or not that cell delivered its full expected energy.

Typical discharge curves for various temperatures and discharge rates are shown in Fig. 5 and Fig. 6 respectively, and the corresponding energy densities are given in Table VIII.

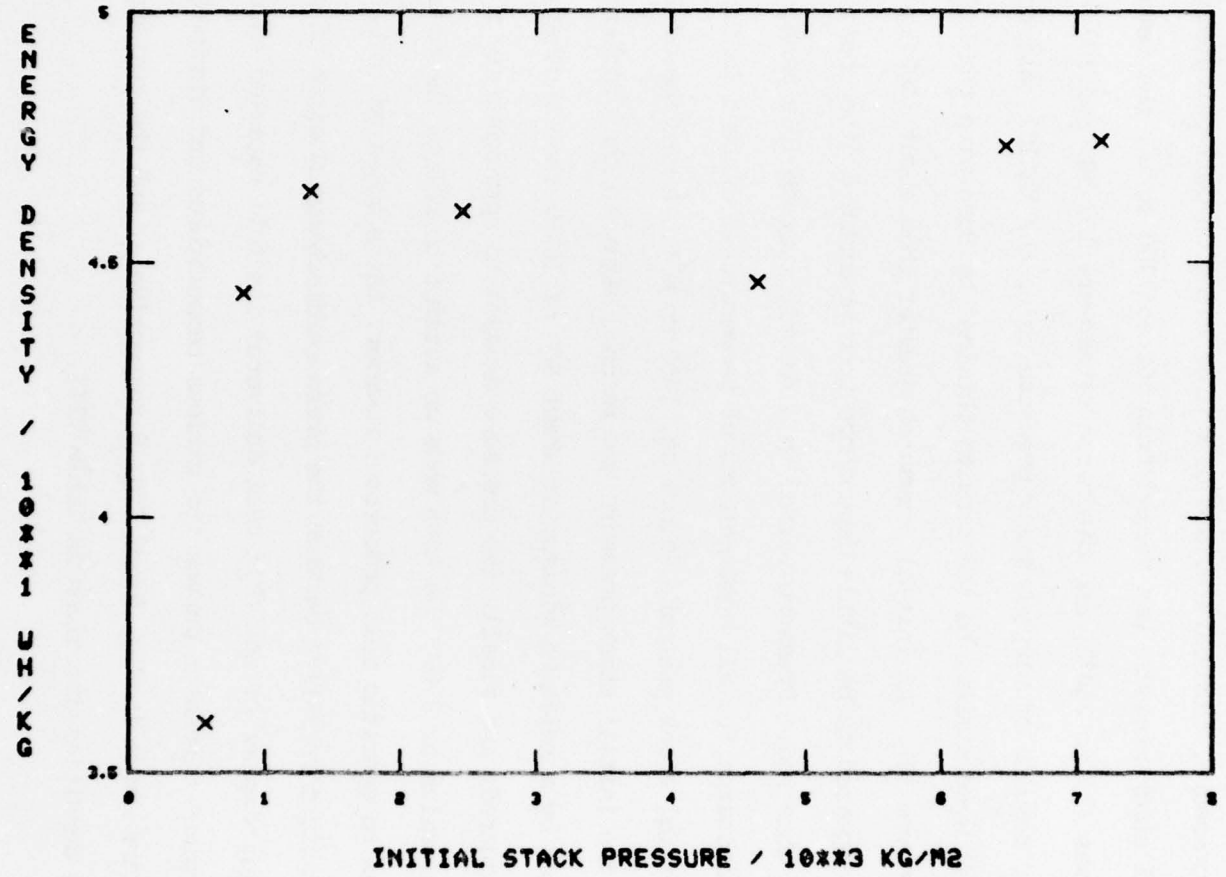

Figure 4. Dependence of energy density on initial stack pressure.

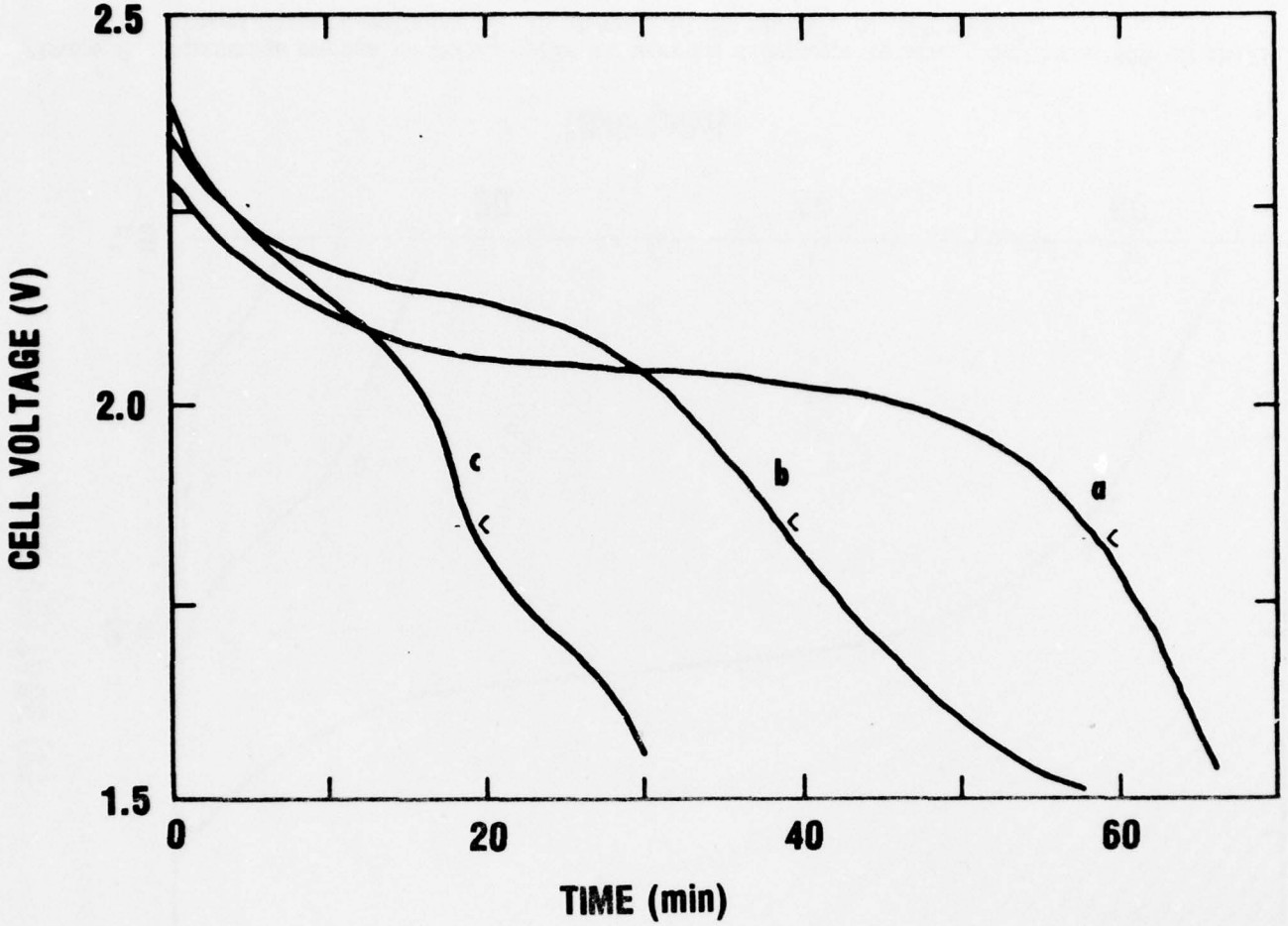

Figure 5. Discharge curves of $FeCl_3$ cells at various temperatures (15 mA/cm^2). < indicates 80% of initial closed circuit voltage; a) 175°C, b) 225°C, c) 250°C.

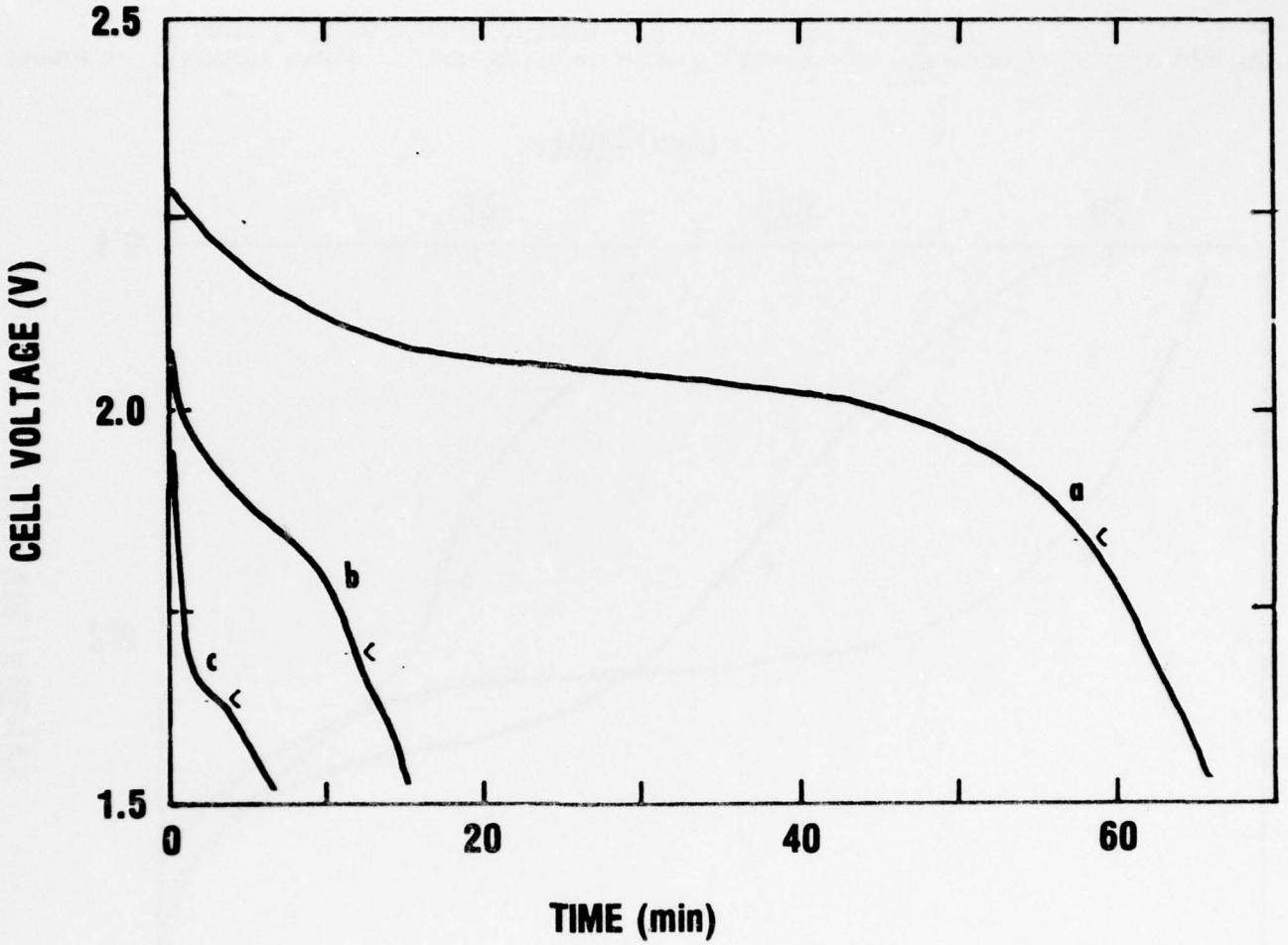

Figure 6. Discharge curves of $FeCl_3$ cells at various discharge rates. < indicates 80% of initial closed circuit voltage; a) 15 mA/cm^2, b) 50 mA/cm^2, c) 100 mA/cm^2.

TABLE VIII. Energy densities obtained for $FeCl_3$ cells at different current densities and temperatures.

Current Density (mA/cm^2)	Energy Density[a] (Wh/kg)				
	165°C	175°C	200°C	225°C	250°C
15	42.1	50.6	46.4	38.1	17.2
50	36.1	31.7	31.9	44.4	34.9
100	12.1	14.9	32.2	36.7	33.4

a. 80% ICCV

Cell lifetimes are considerably shortened with increased temperature and increased current density; however, delivered energy density remained high in most cases. Those conditions for which cell performance was significantly reduced were the low temperature-high current density and the high temperature-low current density conditions, as seen in Table VIII, and in Fig. 7. These performance losses may be due to diffusional limitations or to the increased cell resistance as Fe(II) formation progresses during cell discharge. The optimum operating temperatures were 200-250°C where, as seen in Fig. 7, cell performance was relatively stable for the current density range studied.

Comparison of $FeCl_3$ cells with $MoCl_5$ and $CuCl_2$ cells.

The parameter used to compare the different types of cells was the percent change in performance defined by the following relation:

$$\% \text{ Change} = \frac{\text{Maximum Energy Density} - \text{Minimum Energy Density}}{\text{Maximum Energy Density}} \times 100$$

This parameter relates the relative performance of cells at constant current density with varying temperature, and at constant temperature

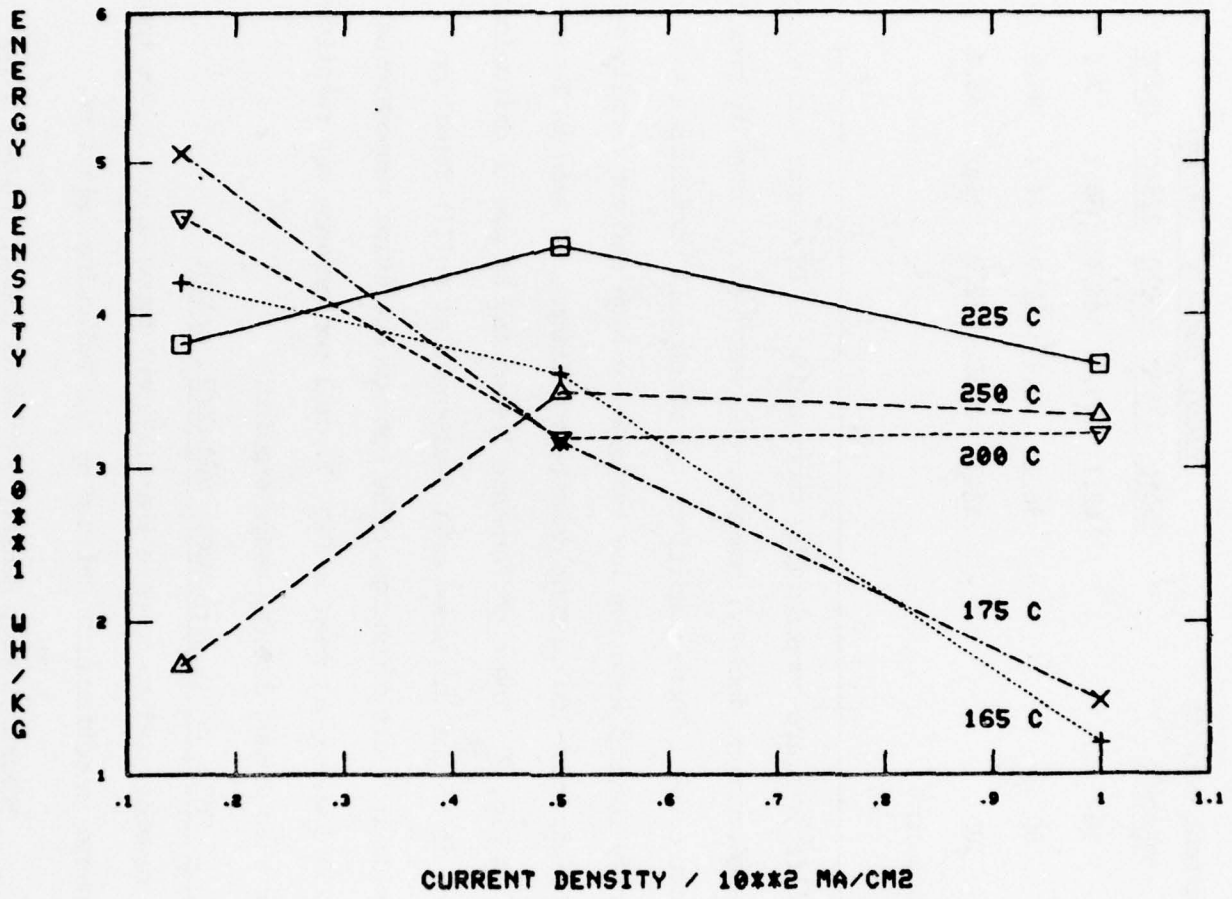

Figure 7. Energy densities of FeCl3 cells at various temperatures as a function of current density.

with varying current density. The smaller the value of the parameter, the more tolerant the cell is toward the changing operating conditions. Percent changes for cells discharged at constant current densities are tabulated in Table IX.

TABLE IX. Comparison of $FeCl_3$, $MoCl_5$, and $CuCl_2$ cells over the temperature range 165°C to 250°C at constant current densities.

Current Density (mA/cm^2)	Cell Type	Energy Density[a] (Wh/kg) 165°C	175°C	200°C	225°C	250°C	Percent Change[b]
15	$CuCl_2$	-	19.8	25.3	12.3	4.8	81.0
	$MoCl_5$	29.7	36.3	26.4	20.4	15.0	58.7
	$FeCl_3$	42.1	50.6	46.4	38.1	17.2	66.0
50	$MoCl_5$	12.3	17.6	27.7	24.4	21.8	55.6
	$FeCl_3$	36.1	31.7	31.9	44.4	34.9	28.6
100	$MoCl_5$	-	-	36.1	14.3	21.1	60.4
	$FeCl_3$	12.1	14.9	32.2	36.7	33.4	67.0
							(12.3)[c]

a. To 80% ICCV

b. Percent change is defined as

$$\frac{\text{Maximum Energy Density} - \text{Minimum Energy Density}}{\text{Maximum Energy Density}} \times 100$$

c. Value in parentheses is for the same temperature range as $MoCl_5$ data.

The $FeCl_3$ cell performance was substantially better than $MoCl_5$ and $CuCl_2$ cells at 15 mA/cm^2 discharge rate at each temperature studied, and the percent change in performance for $FeCl_3$ cells was comparable to or

better than $MoCl_5$ and $CuCl_2$ calls at that discharge rate. At higher discharge rates, $FeCl_3$ cells were definitely superior to $MoCl_5$ cells. Data for $CuCl_2$ cells at temperatures other than 175°C were not available at 50 and 100 mA/cm^2, therefore, no valid comparison could be made between $CuCl_2$ and $FeCl_3$ cells at the higher discharge rates.

Table X compares the percent change in performance for $FeCl_3$ and $MoCl_5$ cells under varying discharge rates at each temperature studied.

TABLE X. Percent change in performance for $FeCl_3$ and $MoCl_5$ cells for the current density range 15 to 100 mA/cm^2

	Percent Change	
Temperature (°C)	$MoCl_5$	$FeCl_3$
165	55.6[a]	71.3 (14.3)[b]
175	51.6[a]	70.6 (37.4)[b]
200	26.9	31.3
225	41.4	17.3
250	31.2	50.7

a. $MoCl_5$ data is over the current density range 15 to 50 mA/cm^2.

b. Values in parentheses is for the same current density ranges as $MoCl_5$ data.

At temperatures below 250°C, $FeCl_3$ cell performance is superior to $MoCl_5$ cell performance for the same current density ranges.

CONCLUSIONS

Iron(III) chloride was an excellent cathode material for thermal cells using a $NaAlCl_4$ electrolyte. The optimum operating temperature of

$FeCl_3$ cells based on percent change in performance was 200-250°C where the delivered energy density (to 80% ICCV) varied from 31.9 to 46.4 Wh/kg over the full current density range studied. The best energy density (50.6 Wh/kg) was obtained at 175°C and 15 mA/cm^2.

Iron(III) chloride cell performance was compared to $MoCl_5$ cell performance. At a given current density, $FeCl_3$ cells suffered less performance loss over the temperature range 165°C to 250°C than cells containing $MoCl_5$. At a given temperature, $FeCl_3$ cell performance was usually superior to $MoCl_5$ cells when compared over the same current density range.

Several areas need to be investigated further. The compaction pressures used during cell fabrication need to be studied to determine if cell performance is effected. The effects, if any, of $FeCl_3$ purity need to be studied. The $FeCl_3$ used in this study was 99.999 percent pure and cost $175 for 100 g. However, the same supplier offers $FeCl_3$ that is 96% pure for $12.50 for 250 g. This was the first study done in this laboratory in which the pressure changes could be observed during cell discharge. The results obtained indicate that further study and data are needed in this area.

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