



NASA TN D-2915

FACILITY FORM 808

N65-27818

(ACCESSION NUMBER)	(THRU)
18	1
(PAGES)	(CODE)
(NASA CR OR TMX OR AD NUMBER)	03
	(CATEGORY)

GPO PRICE \$ _____
 CPSTI
 GTS PRICE(S) \$ 1.00

Hard copy (HC) _____
 Microfiche (MF) .50

A LONG-LIFE THERMAL CELL

by Lawrence H. Thaller
Lewis Research Center
Cleveland, Ohio

UK

A LONG-LIFE THERMAL CELL

By Lawrence H. Thaller

**Lewis Research Center
Cleveland, Ohio**

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 - Price \$1.00

A LONG-LIFE THERMAL CELL

by Lawrence H. Thaller

Lewis Research Center

SUMMARY

27818

Primary thermal cells using molten salt electrolytes were constructed that had service lives measured in days, and seven research cells were discharged at elevated temperatures of 800° to 1000° F. These cells consisted of magnesium anodes, mixed copper oxide cathodes, and an electrolyte of the eutectic mixture of lithium chloride and potassium chloride. During discharge, the cathodes were reduced to metallic copper and oxide ions while the anodes were oxidized to magnesium ions. Solid magnesium oxide was formed nonelectrochemically in both the anolyte and catholyte. A heat-resistant glass, U-shaped cell was used to determine the regions where the magnesium oxide was formed. The solubility of magnesium oxide in the electrolyte was found to be 2.68×10^{-3} gram magnesium oxide per gram of eutectic at 800° F. Both chemical and X-ray diffraction analyses of the spent cell contents were used to ascertain the course of the chemical and the electrochemical reactions that took place within the cell during discharge. Comparison of the amount of current delivered during discharge with the quantities of materials found in the analyses showed the electrode efficiencies varied from 73 percent for a cell that was discharged over a period of 6 days to 93 percent for a cell that was discharged over a period of 1 day. The open circuit voltage of these cells (1.55 V) was about 1/2 volt less than expected from thermodynamic considerations. Current-voltage characteristics of one of these cells showed a total internal resistance of about 0.5 ohm at 800° F. The time dependence of the concentration polarization for the glass cell was also measured. For these nonoptimized research cells, energy densities of 28 watt-hour per pound of total battery were shown.

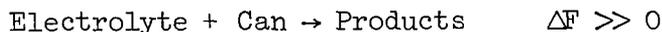
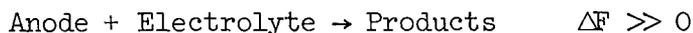
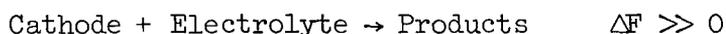
INTRODUCTION

Thermal cells, which usually have solid electrolytes, become activated when these solids are melted. Such cells have been described by several authors including Vinal (ref. 1), Goodrich and Evans (ref. 2), and McKee (ref. 3). These cells are generally employed when very high currents and voltages up to 3 volts are desired for very short periods of time. Once activated, a lifetime measured in minutes is the rule. In general, the anode reacts with the electrolyte, and the soluble cathode reacts with the anode. These undesirable side reactions are only of minor significance during the short-term operation of these short-life thermal cells.

An investigation was conducted of electrochemical systems that would be able to last for days in the activated condition and still maintain some of the desirable characteristics of these thermal cells, such as high current capabilities and high operating temperatures. No separators, no membranes, or any diffusion hindrances were built into these cells. A potential need for a high temperature, long-life battery can be seen for some future applications.

The general criteria established for a long-life thermal cell were the following:

(1) Thermodynamically, all the constituents should exhibit interface compatibility:



(2) The anode and the cathode should be insoluble in the electrolyte. Solubility would lead to self discharge. The rates would depend on the speed of solution and reaction.

(3) The products of the electrochemical and chemical reactions should be insoluble in the electrolyte. Solubility might adversely affect the physical characteristics of the electrolyte.

Two facts should be realized about these three criteria: (1) no cell would rigorously meet all three, and (2) the open circuit voltage of any cell partially meeting these requirements will be lower than that of the short-life cells.

The eutectic mixture of lithium chloride (LiCl) and potassium chloride (KCl) (59 mole percent LiCl) was chosen for the molten salt electrolyte. This mixture has a rather low melting point (665° F), a low viscosity, and the individual compounds have large free energies of formation ΔF_f° . Magnesium was chosen for the anode material. It is lightweight, has a rather high melting point (1204° F), will not replace lithium (Li) or potassium (K) from the molten salt (as does calcium), and is relatively insoluble in the molten salt. Although the alkali metals (Li, Na, and K) possess high electrode potentials, they are liquid at the temperatures where the electrolyte is molten. A study of liquid electrodes was not desired. Any number of likely cathode materials could have been tested. In general, the halides could be ruled out because of their solubility in the halide electrolyte (ref. 4). The oxides would not as a rule be very soluble, and thus they represent a source of potential cathode materials (ref. 5). Calculation of free energy changes of some metal oxides that react with magnesium makes it possible to find a number of oxides that might form cells with high energy densities. From this latter group, mixed copper oxides (Cu₂O, CuO) were chosen for investigation because this system possesses good electronic conductivity and thus would serve as the current collector.

EXPERIMENT

Cells

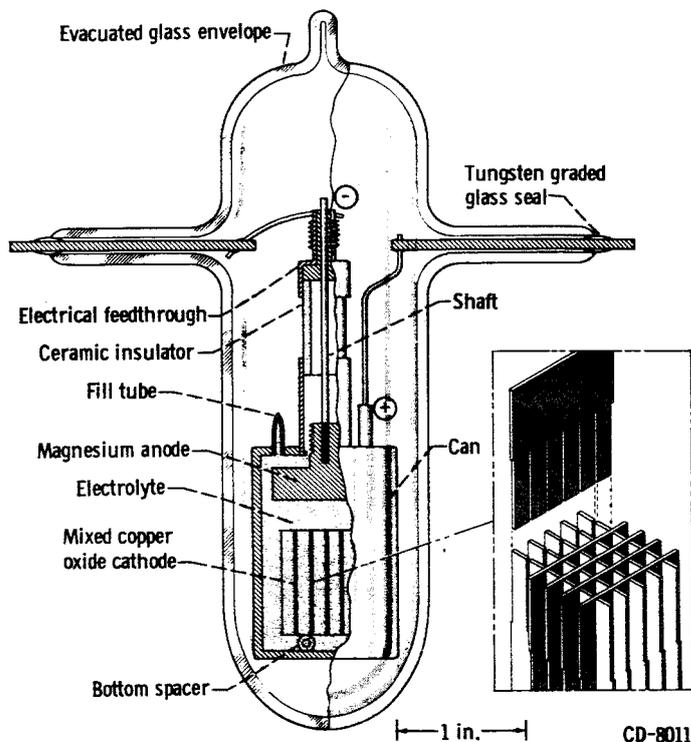


Figure 1. - Cutaway view of typical cell.

Figure 1 shows the general construction of the cells used in these studies. The can was constructed of commercially pure copper (Cu) or nickel (Ni). The nominal composition of commercially pure copper is 99.9 percent Cu with the remainder of phosphorus (P) and sulfur (S); commercially pure nickel is 99.4 percent Ni and about 0.1 percent Cu, 0.15 percent iron (Fe), and 0.25 percent manganese (Mn). On the top of the can were three small tubes used for adding electrolyte, venting the cell during the addition of electrolyte, and affixing the positive lead to the cell. An electrical feedthrough, consisting of a ceramic insulator brazed between two metal tubes, was also affixed to the top of the can.

A stainless-steel rod, which was screwed into the shank end of the anode and was silver soldered to the upper part of the ceramic feedthrough, served as the negative terminal of the cell. The cathode of copper oxides rested on a small piece of coiled copper tubing, which, in turn, rested upon the bottom of the can. The cathode of copper oxides was raised above the floor of the cell to prevent solid products of reaction from possibly clogging the passages of the checkerwork cathode. Another stainless-steel rod was silver soldered into one of the small tubes. This rod was the positive lead of the cell.

The lid assembly consisted of the lid, the three small tubes, the feedthrough, the shaft, and the anode. The can assembly consisted of the can, the copper spacer, and the cathode. The cell was completed by heliarc welding the lid assembly to the can assembly. This welding was performed in a dry box filled with argon. These cells were ready to be filled with the electrolyte of the eutectic mixture of lithium chloride and potassium chloride.

When the copper can cells were run, the entire cell was enclosed in an evacuated glass envelope to prevent the oxidation of the copper cans. One cell was constructed using only an anode, a cathode, and a glass envelope to permit visual observation of the discharging cell. Copper wires were used to connect the electrodes to the tungsten feedthroughs. This cell will be referred to as the glass cell.

The anodes were of primary magnesium (99.8 percent Mg, 0.15 percent Mn, 0.02 percent Cu), while the cathodes were a mixture of Cu_2O and CuO . The anodes were made in the form of thick round disks with a shank on one end. The

TABLE I. - WEIGHT BREAKDOWN
OF TYPICAL CELL

Component	Weight, g
Anode	5.6
Can	39.8
Cathode	16.8
Electrolyte	22.8
Total	85.0 (0.187 lb)

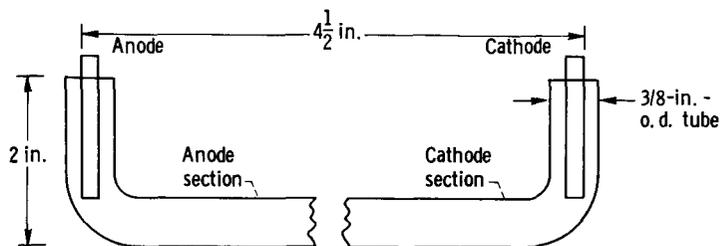
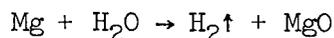


Figure 2. - Pyrex U-shaped cell.

cathodes were made by oxidizing a checkerwork of oxygen-free high conductivity (OFHC) copper plates, which had been slotted and fitted together. This checkerwork was placed in a furnace and oxidized in air for 6 hours at 1832° F followed by a 1-day oxidation at 1112° F. The cathodes were analyzed to be nominally 16 mole percent CuO and the remainder Cu₂O.

Although some effort was made to have an anhydrous melt, there were always some hydrolysis products in the melt. The salts were dried in an oven for several days at about 300° F, weighed in the proper proportion, and melted. To the melt were added some magnesium chips, which reacted at least partially with the water present in the melt according to the reaction



After all evidence of reaction had disappeared, the melt was filtered through quartz wool. The electrolyte in effect was the eutectic of LiCl and KCl with some dissolved MgO plus some unwanted hydrolysis products.

The cells were then filled as needed by the addition of the electrolyte. The small tubes were then pinched off and silver soldered. The nickel cells were ready to remain in the furnace and begin the discharge program. The copper cells were cooled and placed in an evacuated glass envelope. The weights of the individual components are given in table I.

The overall heat capacity was estimated to be about 13 calories per gram.

A U-shaped cell (fig. 2) was discharged at 800° F. Folded magnesium ribbon served as the anode, while oxidized copper wires were used at the cathode. The cell was constructed of heat-resistant glass, which permitted visual observation of the cathode and anode regions separately. The ampere hours withdrawn were noted and then the cell was broken into two portions. These sections were then analyzed for total magnesium.

Experimental Setup

Most of the experiments were carried out at 800° F (table II) using a setup as shown in figure 3. The cell undergoing discharge was wired to a load resistor and the switching relay. The value of load resistance (1, 5, 10, and 20 ohms) depended upon the duration the cell was expected to last. For example,

TABLE II. - DETERMINATION OF CELL LIFE, OUTPUT, AND EFFICIENCY
FOR CELLS OF DIFFERENT CAN MATERIAL

Cell		Temperature, °F	Life, hr	Cell output, A-hr	Anode efficiency, percent	Cause of failure
Can material	Number					
Copper	1	800	46	1.04	----	Cell leaked
	2	800	28	2.55	----	Disconnection of anode
	3	800	52	1.73	64.3	Cell leaked
Glass		800	140	5.82	73.4	Disconnection of anode
Nickel	1	800	35	2.48	92.5	Internal short
	2	800	22	5.29	97.8	Disconnection of anode
	3	800 - 1000	5	3.04	90.5	Disconnection of anode

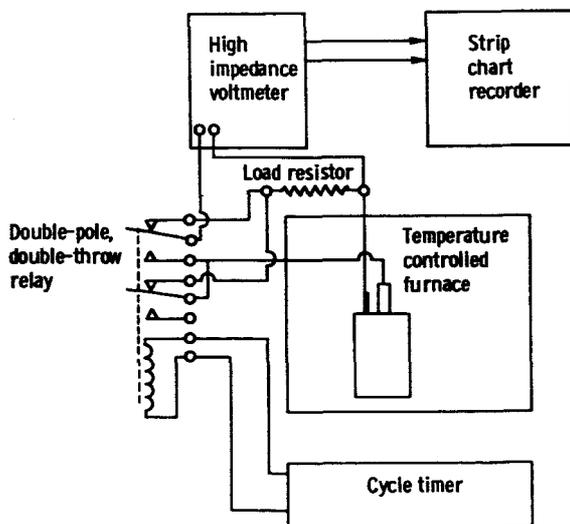


Figure 3. - Schematic diagram of apparatus.

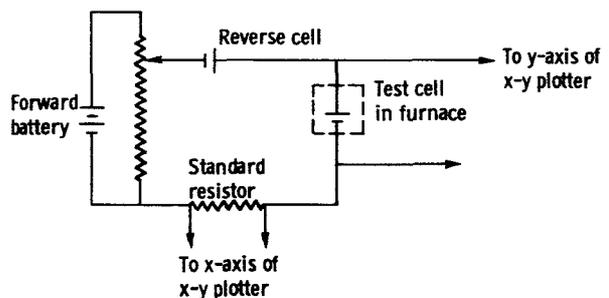


Figure 4. - Wiring diagram of power supply used in making plots of voltage against current.

a 20-ohm resistor was the load for the glass cell that ran for about 6 days while a 1-ohm resistor was used for the 5-hour run of nickel cell 3. The voltage across this load resistor, which represented a measure of the current flowing through the system, was fed into a high impedance voltmeter. A recording potentiometer was connected to the output of the voltmeter. A cycle timer was employed during several runs. It would alternately place the cell under load for 15 minutes, followed by 2 minutes in the no-load condition. The system was connected so the voltmeter would read the voltage across the load resistor during one portion of the cycle and the no-load voltage during the other. The ampere-hours delivered during discharge were calculated from the recorded voltage across the load resistor.

Figure 4 shows the wiring diagram used to investigate the current-voltage characteristics of a nickel cell. Plots of voltage against current (E-I) were made at 800°, 900°, and 1000° F.

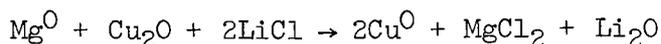
Analysis Techniques

The discharged cells were analyzed in an attempt to follow the course and extent of the chemical and electrochemical reactions that took place within the cells. Three nickel cells were assembled with known amounts of Mg, Cu₂O, and CuO. After these cells had been discharged, they were analyzed quantitatively for reaction products and unused electrode components. The three copper cells and the one glass cell on the other hand were analyzed qualitatively.

The magnesium and copper oxides were expected to react to form magnesium oxide and metallic copper. Selis, et al. (ref. 6), however, found in the analysis of the molten salt cell, Mg/KCl-LiCl/Fe₂O₃, Ni, that the oxidized magnesium in the spent cells was water soluble magnesium chloride (MgCl₂). The oxide ion from the discharging iron oxide cathode was taken up in the form of non-soluble Li₂O · (FeO)_x.

The exact course of the electrochemical and chemical reactions were not known, so an analysis routine (fig. 5) had to be made up, which would try to take into account all possible courses of reaction. The resultant routine allowed for analyses of the following constituents as they would appear after a spent cell had been opened and the contents dissolved if possible in water: magnesium metal, water soluble magnesium compounds, magnesium oxide, magnesium hydroxide, water soluble copper salts, cuprous oxide, cupric oxide, copper metal, acid or water soluble compounds of nickel, and finally any alkali metal hydroxides. The pH of this initial wash solution was also measured. If any MgCl₂ was present in the spent cells formed during these studies, it would react with the corresponding amount of alkali metal oxide to form, in the presence of water, Mg(OH)₂ according to the following reactions:

In cell,



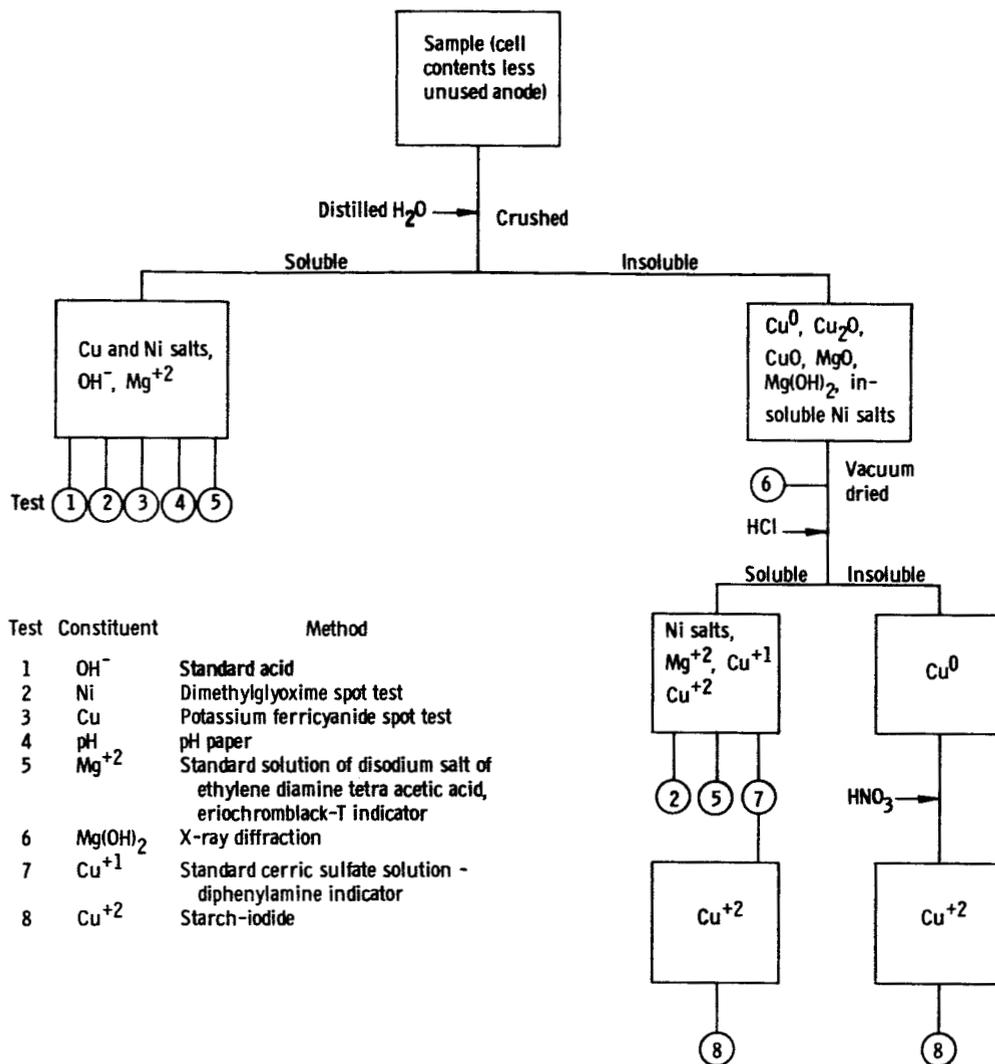
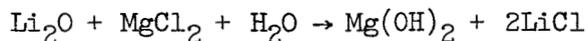


Figure 5. - Flow sheet of analysis.

In wash solution,

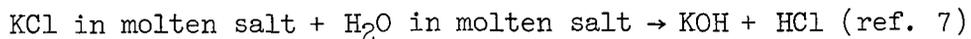


Therefore, the presence of Mg(OH)₂ in the residue had to be considered, although it was later found to be absent. The analyses of the spent cells for unused reactants would permit calculation of the electrode efficiencies, while analyses for products of reaction would allow some conclusions to be made concerning the course of the reaction.

Routine for Spent Cells

The discharged cells were opened, and the entire contents except for the unused anode were placed in distilled water. The unused anode was cleaned and weighed on an analytical balance. The remaining contents (products of reaction,

electrolyte, and unused cathode) were crushed and allowed to stand in the wash water. After all the solubles had time to dissolve, this wash solution was filtered. This solution would contain the water soluble copper and nickel salts (if present), some magnesium ion from the slight solubility of MgO and Mg(OH)₂, and any excess alkali hydroxide, which will be reported as KOH. A proposed hydrolysis product of the molten salt is KOH:



Aliquots were taken and spot tested for the presence of copper and nickel ions. Another was taken for the determination of pH followed by neutralization with standard acid to yield total equivalents of base. Another aliquot was analyzed for Mg⁺². The method employed a standard solution of the disodium salt of ethylene diamine tetra acetic acid (EDTA). This Mg⁺² analysis was performed in the standard way (ref. 8). The difference between equivalents of Mg⁺² and total base is the amount of OH⁻ due to excess KOH.

The insoluble material from the wash solution filtration contained Cu⁰, unused Cu₂O and CuO (from cathode), MgO, and Mg(OH)₂ if present, and any water insoluble nickel salts. This mixture was vacuum dried, crushed, and a small sample was placed in a 0.3-millimeter capillary and was analyzed for Mg(OH)₂ by means of X-ray diffraction techniques. The remaining solids were then treated with a concentrated HCl solution in an inert atmosphere; this was an attempt to retard the air oxidation of cuprous ions to cupric ions and the copper fines to copper ions. Acid soluble nickel salts, MgO, Mg(OH)₂, Cu₂O, and CuO would go into solution while the Cu⁰ would remain undissolved. After filtering, the solution was analyzed for Cu⁺¹ by oxidizing the Cu⁺¹ to Cu⁺² with standardized ceric sulfate solution. When the end point for the conversion of all the Cu⁺¹ to Cu⁺² was reached, the solution, after being neutralized, was subsequently titrated with standard thiosulfate solution to yield total copper ions. This coupled with the ceric determination of cuprous ions enabled the determination of the amount of cupric ion present in the initial solution. A fresh aliquot was taken for the determination of Mg⁺². The solution was first neutralized, and the copper ions complexed with cyanide to prevent interference with the Mg⁺² determination. In a fresh aliquot a spot test was made for acid soluble nickel salts.

The Cu⁰ remaining from the HCl treatment was dissolved in HNO₃ and, after this solution had been neutralized, was titrated with standard thiosulfate solution.

RESULTS AND DISCUSSION

General Characteristics of the Cell

The cells with the electrodes as they are presently arranged have total internal resistance of about 0.5 ohm at 800° F. The accumulation of solid products of reaction in the cells caused no major increase in the internal resistance of the cell. The electrolyte of the molten salt mixture presented no corrosion problem in the sealed cells. The initial open circuit voltage of 1.55 volts dropped to about 1.48 volts after the withdrawal of a fraction of an

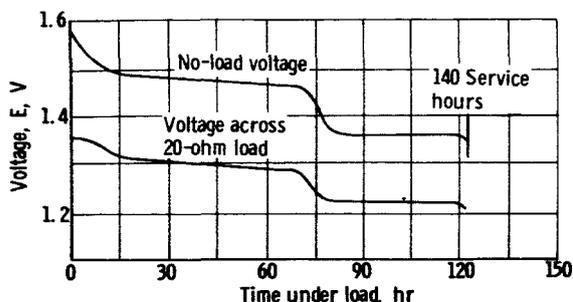


Figure 6. - Discharge characteristics of glass cell. Duty cycle: 15-minute load, 2-minute open circuit.

ampere-hour of electricity. It then decreased slightly over the life of the cell (fig. 6). Cell failure was caused primarily by disconnection of the anode material. Electrochemical action at the base of the shank of the anode caused this portion to be consumed before the main body of the anode. At higher drain rates, this consumption was more significant.

The U-shaped cell experiment (fig. 2, p. 4) was performed to gather more information than available from chemical analysis concerning the physical state and region of origin of the MgO. It was already suspected from the discharge curves of the copper and nickel cells that a tightly bound, electrochemically formed layer of MgO at either of the electrodes was not present. The existence of such an insulating layer would probably have not permitted further electrochemical reaction. Oxidized copper wires were used for the cathode while a folded magnesium ribbon served an anode. The ampere-hour output of the cell was followed as the cell discharged. The progress of the reaction was observed from time to time through the heat-resistant glass wall of the cell. A white flocculent cloud of material was formed at both the anode and cathode regions and grew towards the center of the cell. Before the clouds overlapped, the reaction was stopped, the cell was frozen and was broken into the two portions as indicated, and then each of these portions was analyzed for Mg^{+2} . The presence of Mg^{+2} (MgO) was found in both compartments. About 60 percent of the MgO was formed in the anode half of the cell and 40 percent in the cathode half.

After the nickel cells had been discharged across a known load, the ampere-hours withdrawn were determined, and the cells were opened and analyzed. Table III(a) shows a set of typical results. The weights of the magnesium and copper compounds are always reported in terms of the weight of the particular element. That is to say, 1 equivalent or 0.5 mole of MgO (20.15 g) would be reported as 12.16 grams of Mg^{+2} . This form was convenient in that the weights of the electrodes could be more easily followed as they underwent oxidation or reduction. The ampere-hour equivalent of these materials is also given as an aid in determining the electrode efficiencies.

The calculated electrode efficiencies (table III(b)) are affected by sources of error in the chemical analysis, by the inherent self-discharge characteristics of the cell itself, and by small amounts of water present in the LiCl and KCl used for the electrolyte. Both massive bright shiny copper and micron size dull red copper were formed concurrently during the discharge of the cells. The very fine particles most likely underwent some oxidation during the handling procedure even though precautions were taken to prevent it. Consequently, a high value for CuO in the spent cell appears in table III(a). Otherwise, the results of the analytical routine are accurate to within 4 percent. The self discharge of the cell due to the slight solubility of the copper oxides caused both the anode and cathode efficiencies to be low. Once the electrode material is in solution, it can migrate to the other electrode and there react chemically.

TABLE III. - ANALYSIS OF NICKEL CELL 3

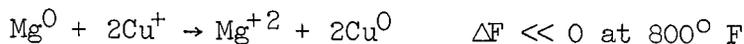
[Test for nickel salts, negative; pH of 1.0 liter of wash solution, 8 ± 0.3 .]

(a) Analysis

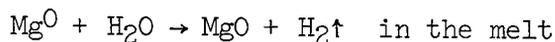
Material		Weight		
In fresh cell	In spent cell	g	milli equivalents	A-hr
	Mg ⁰	5.661	466	12.48
	Mg ⁰	4.165	343	9.20
	Mg ⁺² (MgO)	<u>1.548</u>	<u>131</u>	<u>3.41</u>
	Total	<u>5.713</u>	<u>474</u>	<u>12.61</u>
	Cu ⁺² (CuO)	1.49	46.8	1.25
	Cu ⁺¹ (Cu ₂ O)	<u>13.36</u>	<u>210.0</u>	<u>5.63</u>
	Total	<u>14.85</u>	<u>256.8</u>	<u>6.88</u>
	Cu ⁺² (CuO)	0.48	15.2	0.41
	Cu ⁺¹ (Cu ₂ O)	8.50	133.7	3.57
	Cu ⁰	<u>5.79</u>	-----	----
	Total	<u>14.77</u>	-----	----

(b) Electrode efficiencies (A-hr delivered, 3.04)

Electrode	Efficiency, percent
Anode (from Mg ⁰ lost)	92.7
Anode (from Mg ⁺² gained)	89.2
Cathode (from Cu ₂ O and CuO lost)	104.8



The effect of water in the electrolyte is to lower the anode efficiency while not affecting the cathode efficiency.



Since most of the water was removed from the electrolyte prior to use by this same reaction, the magnesium results could have been high because of the presence of this soluble MgO. Solubility studies for MgO in the electrolyte at 800° F were made to determine the magnitude of this error, and they were found to be negligible.

Determination of Electrochemical and Chemical Reactions Within Cell

The results of chemical analyses, the observations of the open circuit voltage as a function of depth of discharge, and thermodynamic considerations all helped in deducing the course of reaction in these cells. From thermodynamic considerations, the open circuit voltage of an electrochemical cell

TABLE IV. - FREE ENERGY CHANGES AND THEORETICAL

ELECTRODE POTENTIALS AT 800° F

Reaction	Free energy change, $\Delta F_{800^\circ F}^\circ$, kcal	Theoretical open-circuit voltage, $E_{800^\circ F}^\circ$, V
$\text{CuO} + \text{Mg}^\circ \rightarrow \text{Cu}^\circ + \text{MgO}$	-103.2	2.24
$2\text{CuO} + \text{Mg}^\circ \rightarrow \text{Cu}_2\text{O} + \text{MgO}$	-109.5	2.37
$\text{Cu}_2\text{O} + \text{Mg}^\circ \rightarrow 2\text{Cu}^\circ + \text{MgO}$	-96.4	2.09
$\text{CuO} + \text{Mg}^\circ + 2\text{KCl} \rightarrow \text{K}_2\text{O} + \text{MgCl}_2 + \text{Cu}^\circ$	+18.0	1.11
$\text{CuO} + \text{Mg}^\circ + 2\text{LiCl} \rightarrow \text{Li}_2\text{O} + \text{MgCl}_2 + \text{Cu}^\circ$	-44.6	.97
$2\text{CuO} + \text{Mg}^\circ + 2\text{KCl} \rightarrow \text{Cu}_2\text{O} + \text{MgCl}_2 + \text{K}_2\text{O}$	+11.4	.83
$2\text{CuO} + \text{Mg}^\circ + 2\text{LiCl} \rightarrow \text{Cu}_2\text{O} + \text{MgCl}_2 + \text{Li}_2\text{O}$	-51.2	----
$\text{Cu}_2\text{O} + \text{Mg}^\circ + 2\text{KCl} \rightarrow 2\text{Cu}^\circ + \text{MgCl}_2 + \text{K}_2\text{O}$	+24.5	----
$\text{Cu}_2\text{O} + \text{Mg}^\circ + 2\text{LiCl} \rightarrow 2\text{Cu}^\circ + \text{MgCl}_2 + \text{Li}_2\text{O}$	-38.1	----
$\text{Li}_2\text{O} + \text{MgCl}_2 \rightarrow \text{MgO} + 2\text{LiCl}$	-57.3	----
$\text{K}_2\text{O} + \text{MgCl}_2 \rightarrow \text{MgO} + 2\text{KCl}$	-120.9	----
$\text{Mg} + 2\text{KCl} \rightarrow \text{MgCl}_2 + 2\text{K}$	+56.5	----
$\text{Mg} + 2\text{LiCl} \rightarrow \text{MgCl}_2 + 2\text{Li}$	+50.5	----
$\text{CuO} + 2\text{LiCl} \rightarrow \text{CuCl}_2 + \text{Li}_2\text{O}$	+42.3	----
$\text{Cu}_2\text{O} + 2\text{LiCl} \rightarrow 2\text{CuCl} + \text{Li}_2\text{O}$	+43.5	----

can be estimated. These estimates are exact if the following criteria are met.

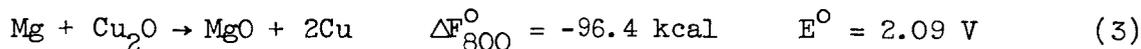
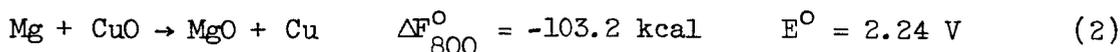
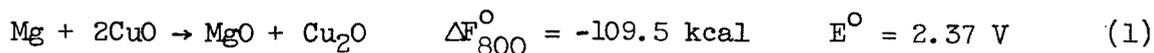
(1) The electrochemical reaction that takes place at the electrodes is the same as the one for which the free energy change ΔF is being calculated.

(2) The necessary free energy and heat capacity data needed are available and accurate.

(3) The electrodes are reversible.

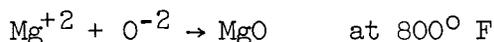
For the system Mg, MgO, CuO, Cu₂O, Cu, KCl, and LiCl at 800° F, there are a limited number of reactions that are thermodynamically feasible (table IV).

Three possibilities of the electrochemical reaction are the following:



As mentioned in General Characteristics of the Cell, an effort was made to determine the solubility of MgO in the eutectic melt at 800° F. The results of these experiments showed that 2.68×10^{-3} gram of MgO per gram of eutectic was the limit of solubility of MgO. Once this number was known, an estimate of the

free energy change of the following reaction could be arrived at.



$$\Delta F^{\circ} = -RT \ln K$$

where

ΔF° standard state free energy change

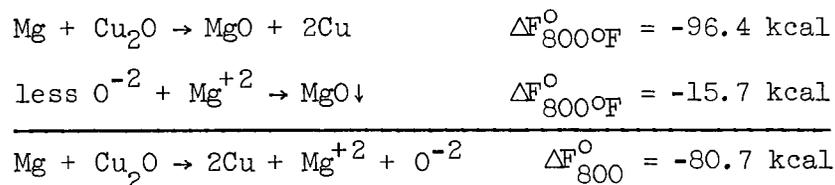
R universal gas constant

T absolute temperature, $^{\circ}\text{K}$

K equilibrium constant

$$K = \frac{(a_{\text{Mg}^{+2}})(a_{\text{O}^{-2}})}{a_{\text{MgO}}}$$

Since dilute solutions were employed, the activities a of the ions were assumed to be equal to the mole fractions, and the activity of the solid a_{MgO} was taken to be unity. The ΔF° of the reaction was calculated to be -15.7 kilocalories and theoretical open circuit voltage E° equivalent to this was 0.34 volt. Reactions (1), (2), and (3) assume that MgO is formed electrochemically. However, by subtracting the reaction for the chemical formation of MgO, the following type of reaction will result:



This correction can be applied to the other two reactions, and the following theoretical open circuit voltages will result:

Reaction (1):

$$2.37 - 0.34 = 2.03 \text{ V}$$

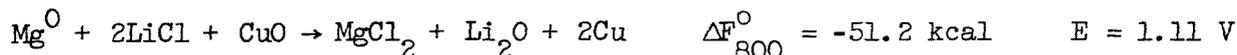
Reaction (2):

$$2.24 - 0.34 = 1.90 \text{ V}$$

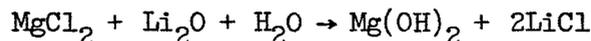
Reaction (3):

$$2.09 - 0.34 = 1.75 \text{ V}$$

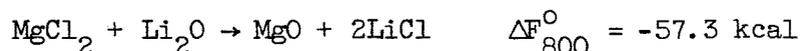
A possible side reaction of the type



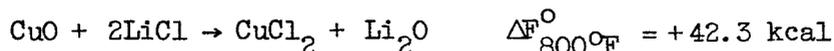
was not considered very likely considering the ΔF° 's of the reactions 1, 2, and 3. If the reaction products underwent no further reaction, $\text{Mg}(\text{OH})_2$ would have been present in the analysis sample:



Although $\text{Mg}(\text{OH})_2$ was found not to be present (X-ray analysis), this side reaction in the cell cannot be completely discounted. There could have been a further chemical reaction, which would have removed these initial products of reaction



Other possible side reactions involving the electrodes or electrode reaction products with the electrolyte all have large positive free energy changes (table IV, p. 11).



They were not considered significant in these cells.

The results of the chemical analysis showed that the oxidized magnesium in the spent cells was present as MgO , and the cathodes were reduced finally to copper metal. The analysis did not indicate, however, whether cupric oxide was reduced directly to copper or intermedially to cuprous oxide, which was further reduced. The U-shaped-cell experiment showed that MgO was formed both in the anolyte and catholyte, that is, both magnesium ion and oxide ion were mobile in the electrolyte.

From the previous information, the following statements were postulated concerning the principal electrochemical and chemical reactions that took place within the cells. At the anode, the magnesium was oxidized to magnesium ions. In the anolyte some of the magnesium ions were precipitated by oxide ions. At the cathode, the mixed oxides were reduced finally to copper metal and oxide ions. In the catholyte some of the oxide ions were precipitated by magnesium ions.

Reactions 1 to 3 corrected for the nonelectrochemical formation of MgO predict open circuit voltages of 2.03, 1.90, and 1.75 volts, respectively. These voltages are greater than found in these studies. This difference is large and no obvious explanation of it can be seen.

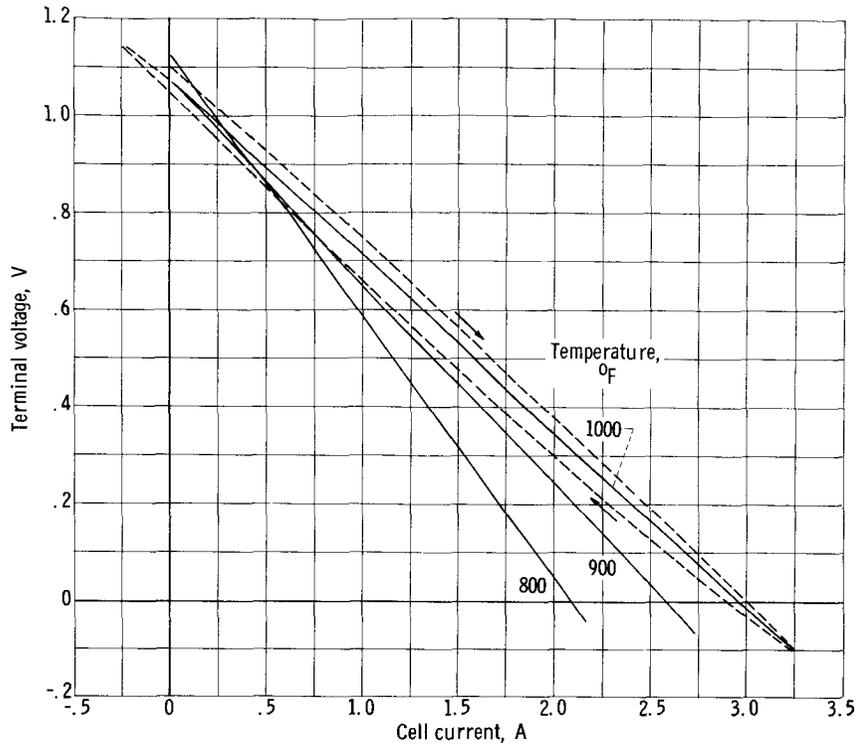


Figure 7. - Plot of terminal voltage against current for nickel cell 3. Dashed lines show lines generated on x-y plotter for 1000° F.

Dynamic Characteristics

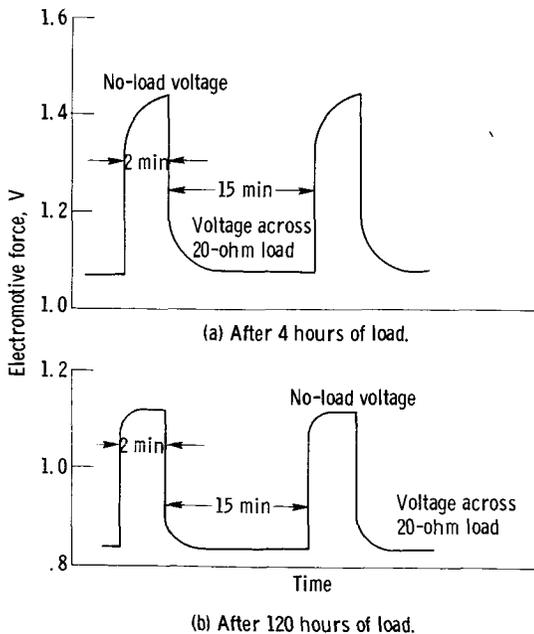


Figure 8. - Load and no-load voltage traces of intermittently operated glass cell.

Some dynamic characteristics of these cells were obtained to gain some insight not only into the electrode characteristics, but also into the internal resistance of these cells. Voltage current (E-I) plots (fig. 7) were made of these characteristics on nickel cell 3 using an x-y plotter in conjunction with an electrical circuit as depicted in figure 4 (p. 5). The terminal voltage of the cell is plotted in the y-direction concurrently with a measure of the currents passing through the cell in the x-direction. The no-load voltage of the cell is the point along the y-axis at a condition of zero current passage. The straight lines of figure 7 are actually averages of the line made on the upswing and the line made on the downswing. The lines made going from no-load voltage to short circuit current were a maximum of about 0.2 ampere higher (dotted lines) than the return line going

from short circuit current back down to no-load conditions. The actual data for the E-I plot at 1000° F is shown in figure 7. The slope of this line has the units of ohms and is a measure of the total internal resistance of the cell. The position of the line near where it crosses the x-axis depends upon the length of time needed to generate the line. If a cell is allowed to discharge at a high rate, the concentration polarization effects will cause the line to drop towards lower currents. An attempt was made to take a uniform amount of time to construct these E-I plots (about 10 sec). The total resistance of this cell decreased from a value of 0.52 ohm at 800° F to 0.37 ohm at 1000° F. This fact was to be expected in that the higher temperatures lead to higher values of the ion mobilities.

Reproductions of the actual time-voltage traces of the glass cell appear in figure 8. The polarization caused by ion depletions is measured by the length of time needed for the cell voltage to adjust once the load has either been switched on or off. Concentration polarization is more pronounced in a fresh cell than in the cell filled with products of reaction (deeply discharged).

CONCLUSIONS

A long-life thermal cell was built following certain guidelines. One of the cells that was discharged over a period of 6 days failed when the anode became disconnected. This type of failure was prevalent during this investigation and in no way reflects the ultimate periods of usefulness of this type of cell. A different anode design would enable more of the useful energy to be withdrawn from the cell. The self-discharge characteristics of the cell are what limits the period of usefulness. The cell that was discharged over a period of 6 days had an anode efficiency of 73 percent, which shows that 27 percent of the anode either flaked off, was consumed by internal discharge reactions, or reacted with the impure electrolyte during the 6 days of operation. It is felt that better salt drying techniques will improve this number. The wide operating temperature range of from about 670° to about 1200° F would make it a useful cell for some anticipated space applications. The open circuit voltage of 1.55 volts was lower than expected from thermodynamic considerations. It was concluded that the following reactions took place at the electrodes. At the cathode, the copper oxides were reduced to metallic copper with oxide ions being liberated into the electrolyte. At the anode, the magnesium was oxidized to soluble magnesium ions. Insoluble magnesium oxide was found to form in the region of both the cathode and anode. The excess magnesium ions near the anode and the excess oxide ions near the cathode exceeded the solubility limit of the slightly soluble magnesium oxide.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 16, 1965.

REFERENCES

1. Vinal, G. W.: Primary Batteries. John Wiley & Sons, Inc., 1950, pp. 324-329.
2. Goodrich, R. B.; and Evans, R. C.: Thermal Batteries. Electrochem. Soc., vol. 99, no. 8, Aug. 1952, pp. 207-208.
3. McKee, E.: Thermal Cells. Proc. Tenth Annual Battery Res. and Dev. Conf., Power Sources Div., Signal Corps Eng. Labs., Fort Monmouth (N. J.), 1956, pp. 26-28.
4. Laitinen, H. A.; and Liu, C. H.: An Electromotive-Force Series in Molten Lithium Chloride-Potassium Chloride Eutectic. J. Am. Chem. Soc., vol. 80, 1958, pp. 1015-1020.
5. Laitinen, H. A.; and Bhatia, B. B.: Electrochemical Study of Metallic Oxides in Fused Lithium Chloride-Potassium Chloride Eutectic. J. Electrochem. Soc., vol. 107, 1960, pp. 705-710.
6. Selis, Sidney M.; McGinnis, Laurence P.; McKee, Elmer S.; and Smith, James T.: Electrode Reactions and Iron Oxide Selection for the Thermal Cell Mg/LiCl-KCl/FeO_x/Ni. J. Electrochem. Soc., vol. 110, no. 6, June 1963, pp. 469-476.
7. Laitinen, H. A.; Ferguson, W. S.; and Osteryoung, R. A.: Preparation of Pure Fused Lithium Chloride-Potassium Chloride Eutectic Solvent. J. Electrochem. Soc., vol. 104, no. 8, Aug. 1957, pp. 516-520.
8. Schwarzenbach, G.: Complexometric Titrations. Intersci. Pub. 1957, p. 62.