

NASA TECHNICAL NOTE



NASA TN D-5731

2.1

NASA TN D-5731



LOAN COPY: RETURN TO
AFWL (WL0L)
KIRTLAND AFB, N MEX

CATHOLYTE STUDIES IN COPPER OXIDE - MAGNESIUM THERMAL CELLS

by Lawrence H. Thaller
Lewis Research Center
Cleveland, Ohio



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • APRIL 1970



0132332

1. Report No. NASA TN D-5731		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle CATHOLYTE STUDIES IN COPPER OXIDE - MAGNESIUM THERMAL CELLS				5. Report Date April 1970	
				6. Performing Organization Code	
7. Author(s) Lawrence H. Thaller				8. Performing Organization Report No. E-5482	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				10. Work Unit No. 120-34	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Technical Note	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract <p>This is the conclusion of work on the Mg/LiCl-KCl/Cu₂O thermal cell at 450° C. This phase of the program is concerned with mass transport within the cells and how it affects the open-circuit voltage of single cells. During the latter stages of discharge (beyond about 50-percent depth of discharge), a large drop in the open-circuit voltage (~0.25 V) occurs. This has been found to be caused by the formation of a complex which reduces the activity of the cuprous ion by about two orders of magnitude. Potentiometric titrations of cuprous ion with lithium oxide were performed in an attempt to more accurately characterize this interaction. The changing mass-transport conditions present inside a discharging thermal cell cause this cuprous complex to be formed only during the latter stages of discharge.</p>					
17. Key Words (Suggested by Author(s)) Battery Thermal cell				18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 15	
				22. Price* \$3.00	

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

CATHOLYTE STUDIES IN COPPER OXIDE - MAGNESIUM THERMAL CELLS

by Lawrence H. Thaller

Lewis Research Center

SUMMARY

The present investigation concludes the study of the performance of copper oxide - magnesium thermal cells operating at 450°C . The objective of this present study was to investigate the cause of the 0.25-volt step drop in open-circuit voltage that occurred during the latter stages of discharge of these cells.

The investigation consisted of two parts:

(1) Cells that were equipped with a reference electrode between the anode and cathode were discharged. These tests showed that the step drop in the open-circuit voltage was due to a sudden drop in the activity of the cuprous ion in the vicinity of the cathode. This two-order-of-magnitude drop in the cuprous ion activity was attributed to the formation of a complex. Other cells were discharged which had additions of either magnesium chloride or lithium oxide in the electrolyte. Additions of lithium oxide brought about the formation of this complex, and additions of magnesium chloride retarded the formation of this complex at the expense of a much higher rate of self-discharge.

(2) Potentiometric titrations were performed to more fully investigate the stoichiometry of the complex. These titrations were performed in solutions of the lithium chloride - potassium chloride eutectic. When 1.5 moles of lithium oxide were added per mole of cuprous oxide, an end point in the titration occurred. The difference in electromotive force (emf) of a copper electrode placed in a saturated solution of cuprous oxide and one placed in a saturated solution of the cuprous complex was the same as the emf difference that occurred at the voltage step during discharge of complete cells.

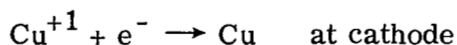
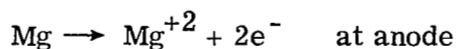
Additions of magnesium chloride to this solid complex returned the cuprous ion to solution by precipitating the oxide ion (as MgO) associated with the complex.

Based on these and our previous findings, a model is presented that explains essentially all the significant features of cell behavior during discharge. This model suggests that, during the initial stages of discharge, magnesium ions move to the catholyte, where they are precipitated as magnesium oxide. During the latter stages of discharge, lithium ion predominates in the charge neutralization process and creates conditions favorable for the formation of the cuprous complex. This lowers the open-circuit and operating voltages of these thermal cells.

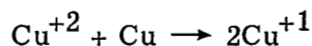
INTRODUCTION

A continuing program (refs. 1 to 4) at Lewis has been directed toward the investigation of a high-temperature primary cell having an operating time of several days at a temperature of 450° C. The anodes used are magnesium; the cathodes, mixed copper oxides; and the electrolyte, the eutectic mixture of lithium chloride and potassium chloride. One of the objectives of this program was to understand the overall electrochemical and chemical reactions that take place during the discharge of these cells and how they are influenced by mass-transport processes.

In the first phase of these studies (ref. 1), the open-circuit voltage during the early stages of discharge of complete cells was shown to be the result of the following half-cell reactions:



The cupric ion is chemically reduced to the cuprous state by reaction with copper according to the reaction



In the second phase (ref. 2), methods of reducing the self-discharge rates of these cells were investigated. It was determined that the rate of transport of copper ions from the cathode to the anode controlled the overall rate of self-discharge. In the third phase (ref. 3), the performance of two different cell designs was investigated as a function of the amount of electrolyte, discharge rate, and electrode geometry. One of the important findings of this study was that cell failure under the test conditions was probably due to freezing of the electrolyte. This must have been caused by a change in electrolyte composition during the course of the discharge; specifically, an increase in magnesium ion content.

This saturation was investigated more completely in anode half-cell studies (ref. 4) employing electrolyte compositions which simulated different stages of discharge in actual cells. It was shown that under certain conditions of temperature, composition, and current density, the electrolyte adjacent to the anode (anolyte) partially froze next to the anode and thus caused extreme concentration and IR polarization.

One of the remaining unanswered questions in the study of this thermal cell was the origin of the 0.25-volt drop in the open-circuit voltage that was observed at greater than

about 45-percent depth of discharge of complete cells (refs. 1 to 3). It had already been shown (ref. 2) that in the latter stages of discharge, lithium oxide was one of the products of reaction in the vicinity of the cathode. Also a compound of unknown composition (compound X) was located in the region of the discharged cathode (catholyte) in cases which showed the 0.25-volt drop in open-circuit voltage. It was suggested that this unknown compound may be a complex species of lithium oxide and cuprous ion or cuprous oxide, which could explain the abrupt drop in the open-circuit voltage.

This present study was undertaken in order to explore this point in more detail. It consisted of two sets of experiments:

- (1) A study of the anode and cathode polarization during the discharge of complete cells by means of a reference electrode
- (2) Potentiometric titrations to explore the complex ion chemistry of the electrolyte in the catholytes

MATERIALS

The electrolyte used was the eutectic mixture of lithium chloride and potassium chloride. This material, purified according to the modified Laitinen process (ref. 5), was ground to a suitable particle size (<3 mm). A nitrogen filled (from liquid boiloff) drybox was used to store the materials and to carry out all the experimental procedures (weighing, mixing, heating, etc.). The cathode material was the wire form of cupric oxide (a mixture of cuprous and cupric oxide), and the anodes were primary magnesium. The chemical compositions of the materials used, determined by analytical techniques already described (ref. 1), are listed in table I. In some of the experiments, reagent-

TABLE I. - COMPOSITION OF MATERIALS^a

Material	Content, wt %	Material	Content, wt %
Cuprous oxide:		Cupric oxide (wire form):	
Cu ₂ O	96.60	CuO	72.6
CuO	2.07	Cu ₂ O	27.4
H ₂ O (by difference)	1.33	Magnesium:	
Magnesium chloride:		Mg	99.8
MgCl ₂	97.4	Mn	0.15
Mg	1.4	Cu	~0.02
H ₂ O (by difference)	1.2	Lithium oxide:	
		Li ₂ O	99.9
		CaO	0.1

^aLiCl-KCl used as received from manufacturer. Silver wire had a silver content of 99.99 percent, as analyzed by manufacturer.

grade, anhydrous powders of cuprous oxide, lithium oxide, and magnesium chloride were used. It was assumed that water in the cuprous oxide and magnesium chloride accounted for the discrepancy from 100.0 percent.

The reference electrodes (ref. 6) were of the disposable type. Silver wire (99.99 percent Ag) was immersed in a 0.13-molal silver chloride solution of the lithium chloride - potassium chloride eutectic. This mixture was contained in a glass melting point tube which acted as a membrane between the reference electrolyte and the cell electrolyte.

PROCEDURE

Cell Discharge Studies

Open-top vertical cells, shown in figure 1, were discharged in a small, electrically heated, temperature-controlled furnace located inside the drybox. The cells, with reference electrodes placed between the anode and cathode, were discharged for 2 hours in a regime programmed as follows:

- (1) Fixed external resistance equal to R_1 , 100 minutes
- (2) Fixed external resistance equal to $R_1 + R_2$, 10 minutes
- (3) No load, 10 minutes

This program was repeated as necessary until the cell voltage dropped to the arbitrary cutoff voltage of 0.5 volt. The voltage of the cell, as well as the current flowing through

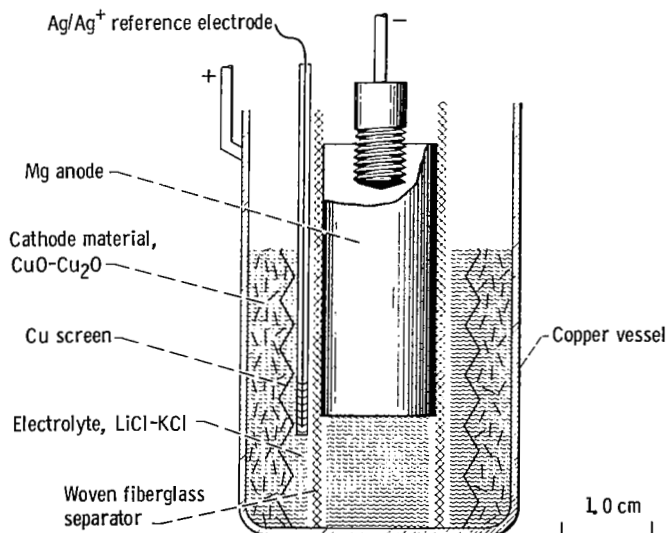


Figure 1 - Cell with reference electrode.

the discharge circuit, was recorded continuously. The details of the discharge circuit are described in reference 2. For the sake of this discussion, the term open-circuit voltage is defined as the cell voltage at the end of each 10-minute no-load period.

The cells were assembled for discharge with weighed amounts of anode and cathode material. The anode was covered with two layers of tightly woven glass fabric to reduce the possibility of internal short circuits. The cell, minus electrolyte and reference electrode, was placed in the furnace and allowed to preheat to 450°C . The desired amount of powdered electrolyte was added to the cell and melted. At this point, electrolyte additives (lithium oxide or magnesium chloride) were mixed with the molten electrolyte. After insertion of a reference electrode, the discharge was begun and was continued until the cell voltage dropped below the 0.5-volt cutoff point.

Potentiometric Titration Studies

Figure 2 shows the details of the cell used for the potentiometric titrations. The

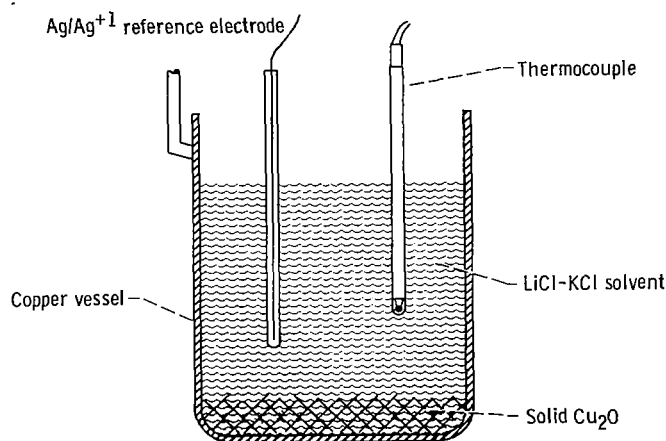


Figure 2. - Titration cell.

copper vessel (identical to those used for the discharge studies) served as the indicator electrode (Cu/Cu^{+1}) and contained the mixture to be titrated. About 30 grams of the lithium chloride - potassium chloride eutectic was the solvent. After a weighed amount of the cuprous salt had been added to the solvent, the cell was placed inside the furnace (the same as used for the discharge studies) and allowed to equilibrate for 1/2 hour after melting. Either the saturated solutions of cuprous oxide with excess solid on the bottom of the vessel or the unsaturated solutions of cuprous chloride were used as starting mixtures for the titrations.

After a silver/silver ion reference electrode was placed in the cell and the emf between the reference electrode and the copper electrode became constant within 2 millivolts, the titration was begun. Weighed additions of lithium oxide or magnesium chloride were made to the electrolyte, and the emf of the Cu/Cu^{+1} electrode was followed relative to the Ag/Ag^{+1} reference electrode. Between additions, ample time was allowed for the reestablishment of equilibrium conditions. Electromotive force was recorded continuously on a strip-chart recorder fed from a high-impedance ($>10^{14} \Omega$), battery-operated electrometer.

RESULTS AND DISCUSSION

Cell Discharge Studies

As pointed out in the INTRODUCTION, previous studies indicated that the origin of the 0.25-volt drop in open-circuit voltage was the formation of a cuprous ion complex (compound X) which would reduce the cuprous ion activity in the vicinity of the cathode. Further, it was indicated that lithium oxide was implicated in some way with the complex formation. For these reasons, cells were discharged that had a reference electrode placed between the anode and cathode so that individual electrode potentials could be obtained.

Figure 3 shows the open-circuit voltages between the anode and the reference

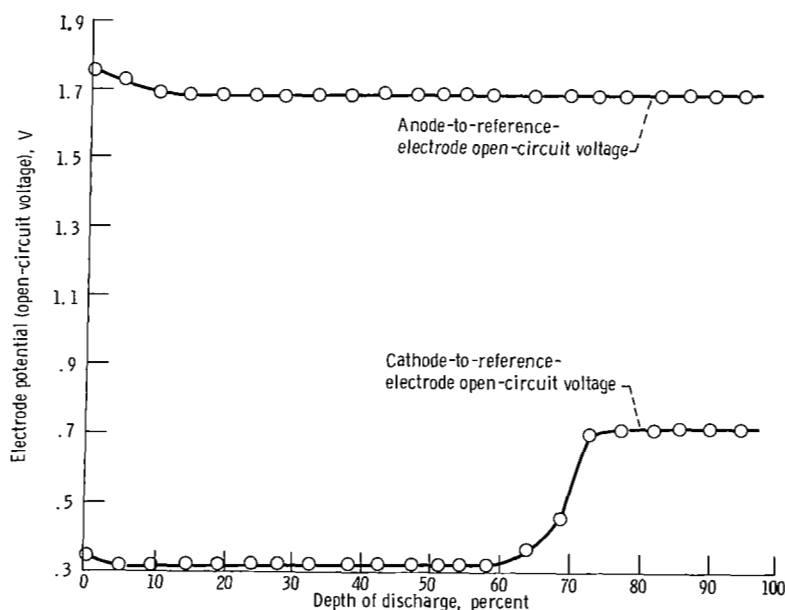


Figure 3. - Electrode potential as function of depth of discharge. Temperature, 450° C.

electrode and between the cathode and the reference electrode recorded during the discharge of a cell. Clearly evident is the 0.3-volt change in the emf of the cathode at about 70-percent depth of discharge. This change in the cathode potential, together with the gradual decline of 0.05 volt in the anode emf, leads to a net decrease in cell potential of about 0.25 volt at the step. Based on this information this potential drop is associated with decreased cuprous ion activity at the cathode.

The chemical analytical work described previously (ref. 2) had revealed that lithium oxide, as well as compound X, was present in large amounts in the catholyte during the latter stages of discharge. Based on these facts it was speculated that the lithium oxide was in some way responsible for the change in the cathode half-cell potential. To verify this hypothesis, another cell was discharged that had 1 gram of lithium oxide dissolved in the 20 grams of electrolyte prior to discharge. Figure 4 compares this discharge to

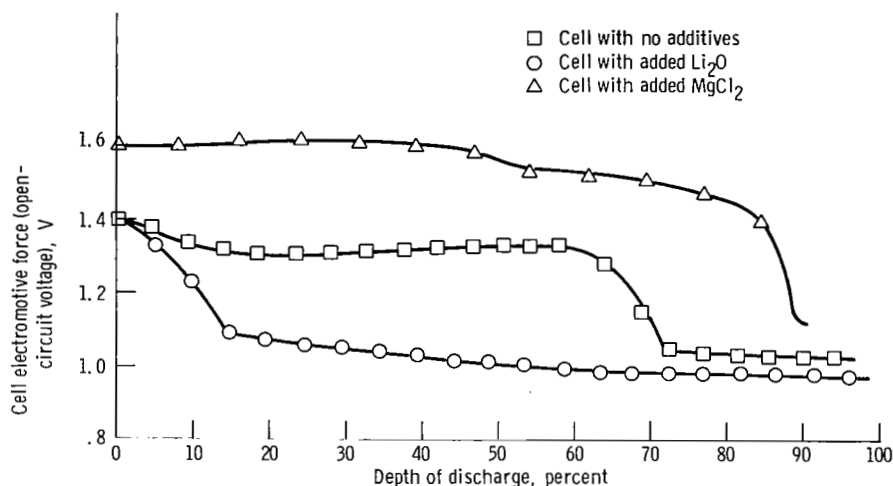


Figure 4. - Cell voltages (open-circuit voltage) as function of depth of discharge.

the previous one in which no lithium oxide was added. Only the open-circuit anode-to-cathode voltages are plotted as a function of depth of discharge. The drop in open-circuit voltage of the cell with the added oxide occurred at a much smaller depth of discharge. These two cells differed only in electrolyte composition. They contained about the same amounts of active materials, were discharged through the same fixed external resistance, and delivered essentially the same number of ampere-hours of electricity. This amounted to about 95 percent of their theoretical capacity (based on the cathode) (see table II). So, although the activity of the cuprous ion was reduced

TABLE II. - CELL OPERATING PARAMETERS

Parameter	Cell		
	1	2	3
Weight, g:			
Mg anode (initial)	5.87	6.13	6.10
CuO-Cu ₂ O cathode (initial)	10.0	10.0	10.0
LiCl-KCl	19.0	19.0	19.0
Li ₂ O	0	1.0	0
MgCl ₂	0	0	3.7
Cell life (to 0.5 V), hr	42	42	22
Cell output (to 0.5 V), A-hr	6.07	5.97	3.25
Average cell current, mA	145	142	148
Average self-discharge current, mA	3.1	15	102
Step placement factor, χ	0.68	0.10	0.87

about two orders of magnitude, as evidenced by the change in open-circuit voltage, there was no decrease in the electrochemical accessibility of this complex form of the cuprous ion.

If the addition of lithium oxide accelerates the appearance of the step in the open-circuit voltage, the addition of magnesium chloride should have the opposite effect. This can occur because soluble magnesium ion should precipitate more of the oxide ion freed by the discharge of the copper oxides than the amount of magnesium ion diffusing over from the discharging anode. Also shown in figure 4 are the open-circuit voltages of a cell discharged with 3.7 grams of magnesium chloride dissolved in the electrolyte prior to discharge. It should be noted that the predicted behavior is observed, namely, that the step in the open-circuit voltage is delayed to the end of the discharge.

In connection with these results, it is important to compare several other aspects. In table II, all the pertinent parameters are listed for the three cells. The two most important parameters to compare are (1) the step placement factor χ defined previously (ref. 3), which is the depth of discharge at which the voltage step occurs; and (2) the average rate of self-discharge. As the amount of soluble oxide in the cell is reduced, χ increases. However, the addition of the magnesium chloride leads to a 34-fold increase in the rate of self-discharge when compared with the cell that had no additives. This is caused by a shift in the copper oxide solubility equilibrium to favor dissolution as the soluble oxide ions are removed by precipitation. The resulting increase in concentration of copper ions leads to an increase in the rate of self-discharge.

Titration Studies

Although the cell discharge studies were fully adequate to detect the presence of the cuprous complex and identify lithium oxide as one of the constituents, there was no way of ascertaining the stoichiometry of the complex species. Potentiometric titration studies were undertaken to investigate this matter.

In the titrations described in this section, the emf (relative to the Ag/Ag^+ reference) of the copper indicator electrode is plotted against what is referred to as the oxide ratio. The oxide ratio is defined as the moles of oxide that are either in solution or can be forced into solution (by shifts of equilibrium) for every 2 moles of cuprous ion. When the data are plotted in this manner, inflection points in the emf at certain oxide ratios will denote the composition at which a large change in cuprous ion activity has occurred. It is presumed that this corresponds to complex formation. It must be re-emphasized here that only the cuprous ion can be in equilibrium with metallic copper. Copper in any higher oxidation state is reduced by the metal to form cuprous ion (Cu^+). Hence, only cuprous compounds were investigated.

Figure 5 shows a typical titration curve. The starting mixture was a saturated solution of cuprous oxide with excess solid on the bottom of the container. Slightly soluble cuprous oxide has an oxide ratio of 1.0 (1 mole $\text{O}^{2-}/2$ moles Cu^+) and this is the starting point of the titration curve at about 0.32 volt relative to the 0.13-molal silver - silver ion reference electrode. The circular data points represent the successive additions of lithium oxide. A very strong complex is formed at an oxide ratio of about 2.5; that is, 1.5 moles of lithium oxide and 1 mole of cuprous oxide are required for its formation. The extent of the emf shift from the solution saturated with cuprous

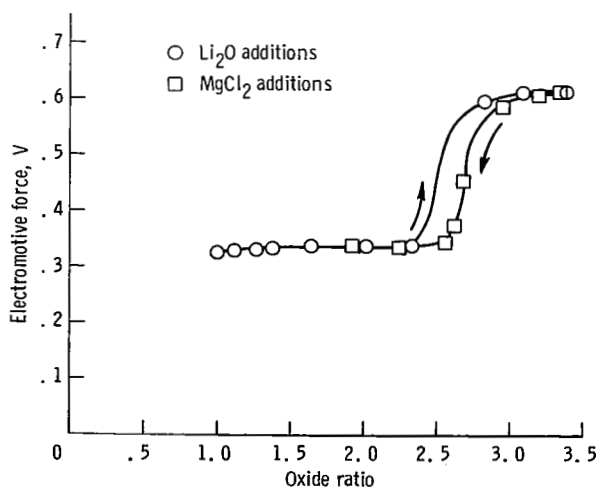
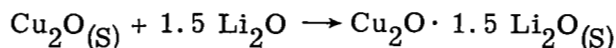


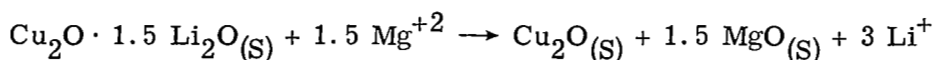
Figure 5. - Typical titration curve; lithium oxide added first, then magnesium chloride. Temperature, 450° C.

oxide to that saturated with respect to the complex is about 0.3 volt, which is identical to the magnitude of the cathode potential shift in the cell discharge studies. This complex was a light-green solid material that was partially soluble in the melt. The squares in the figure represent back-titration data points using magnesium chloride, which is very soluble. It appears that the very low solubility of magnesium oxide shifts the complex formation equilibrium so that the complex is quantitatively dissociated. During the course of this back titration, one insoluble material (MgO) is being formed at the expense of another insoluble material (stoichiometric $\text{Cu}_2\text{O} \cdot 1.5 \text{Li}_2\text{O}$). The exact composition of the cuprous complex has not been determined, but the preceding representation is convenient for the purposes of discussion. These reactions are summarized as follows:

Complex formation:



Complex dissociation:



This evidence for complex formation was by no means unexpected considering the changes that took place in the cathode potentials during cell discharge, which have already been discussed. However, further studies of this cuprous complex did lead to some unexplainable results. Figure 6 shows another titration that started with excess cuprous

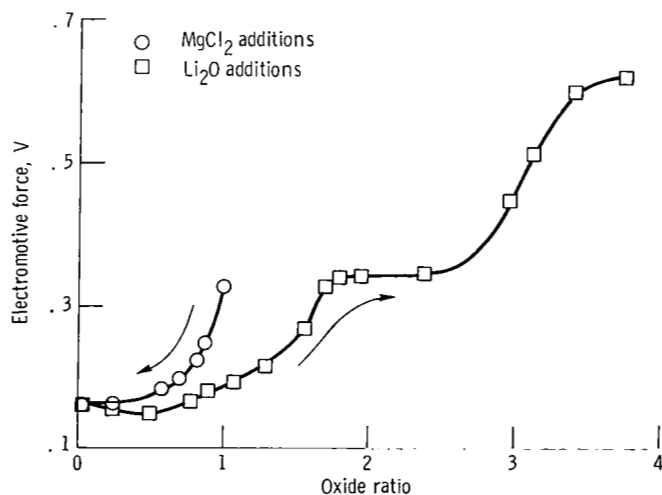
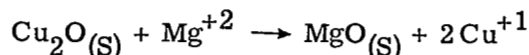


Figure 6. - Further titration study; magnesium chloride added first, then lithium oxide. Temperature, 450° C.

oxide as before. Magnesium chloride was added first to force the cuprous ions into solution as magnesium oxide was precipitated, that is,



Note here that oxide in the form of magnesium oxide does not contribute to the oxide ratio since it is too insoluble. Enough magnesium chloride was added to reduce the oxide ratio from 1.0 to almost zero (0.012). Starting from this point, lithium oxide was added. The emf from an oxide ratio of about zero to 1.0 was not retraced, but two inflection points were obtained; one at an oxide ratio of about 1.5 and the other at about 3.0. A simple precipitation of cuprous ion $2\text{Cu}^{+1} + \text{O}^{=2} \rightarrow \text{Cu}_2\text{O}_{(s)}$ would have resulted in an inflection point at an oxide ratio of 1.0. Clearly, cuprous ion does not precipitate as the oxide in a simple manner, but forms at least two different species as lithium oxide is added to the solution.

From the values of emf at an oxide ratio of 1.0 in the two titration curves, namely 0.18 volt (fig. 6) and 0.32 volt (fig. 5), it can be noted that the activity of cuprous ion is greater when lithium oxide is added to cuprous ion alone than when cuprous oxide itself is placed in the melt. This indicates that the solution process of cuprous ion is itself coupled with complex formation involving lithium ions from the melt.

In contrast to the differences noted at oxide ratios of 1.0, at ratios of 2.0 both titration curves show a rather constant emf of about 0.34 volt. Also, both titrations show the final formation of a complex that has an emf of about 0.62 volt.

This information on the complex forms of the cuprous ions may now be added to the information obtained from the discharge of complete cells to form a more accurate concept of the overall chemical and electrochemical reactions that take place inside an operating thermal cell. Figure 7 depicts the overall reactions as they are now understood. There are essentially two limiting cases, depending on whether the magnesium ion or the lithium ion carries the current (i.e., has a transport number of 1.0). In actual cell operation, there will, of course, be a combination of these two processes, depending on such factors as the current drain and the depth of discharge. It is assumed here that the transport numbers of the chloride ion and oxide ion are zero. This is justified since no magnesium oxide was ever found in the anolytes of discharged cells (ref. 2). Although it will not be proven that the transport number of the chloride ion is zero at all times, the point is irrelevant to the following argument.

First, the case where the transport number of the magnesium ion is 1 is discussed. For lack of evidence to the contrary, it is assumed that cupric oxide dissolves in a simple manner at the cathode. The cupric ion then oxidizes metallic copper to form cuprous ions which are electrochemically reduced. Meanwhile in the anode compart-

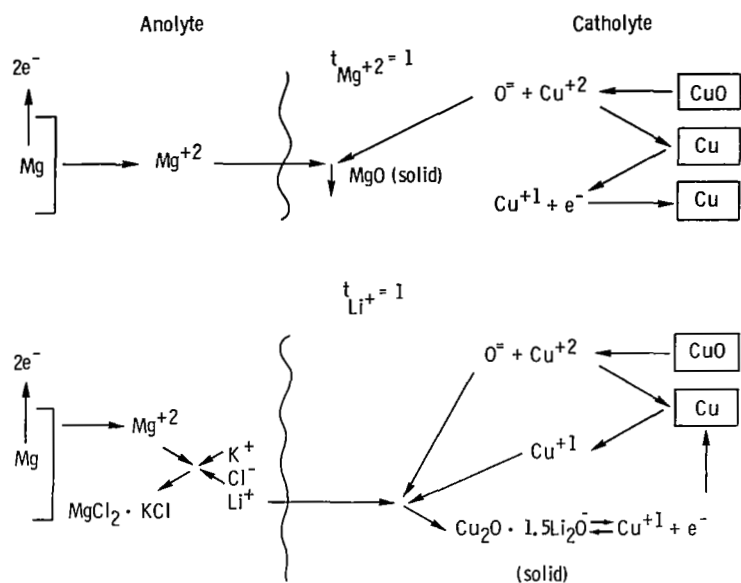


Figure 7. - Overall reactions involved during cell discharge.

ment, a magnesium ion is generated and migrates to the catholyte where it precipitates the oxide ion liberated when the cupric oxide dissolved. This overall situation would be characterized by a cell open-circuit voltage of 1.5 to 1.3 volts. The distribution of reaction products and cell emf agrees with that observed during the early stages of cell discharge (ref. 2). Since the data agree with the proposed model, the assumption that chloride ion plays little or no part in the charge neutralization process appears to be valid.

Later in the discharge, as it becomes more difficult for the magnesium ions to move through the layer of discharge products, the smaller lithium ion predominates in the charge neutralization process. As a consequence, a solid cuprous complex is formed in the catholyte. This results in a cell emf of 1.1 to 0.9 volt. It also results in a magnesium ion enrichment of the anolyte causing an increase in the melting point (ref. 4), which leads eventually to partial freezing of the electrolyte next to the discharging anode. Once again, the model is consistent with experimental facts and provides an explanation for the 0.25-volt drop in the open-circuit voltage of cells in the later stages of discharge and the sharp cutoff at the end of their service lives which occurs before all the active materials have been consumed.

SUMMARY OF RESULTS

This is the conclusion of a program to evaluate the performance of copper oxide - magnesium thermal cells at 450° C. The present study was conducted to verify the

presence of solid cuprous complexes in the vicinity of the cathode during the latter stages of discharge of complete cells and, further, to study these complexes using potentiometric titrations. The significant findings are as follows:

1. Cells that were discharged with a reference electrode placed between the anode and cathode revealed that the step drop in the open-circuit voltage during the latter stages of discharge was due to a change in the half-cell reaction at the cathode.

2. This change in half-cell reaction could be brought about earlier in the discharge by the addition of lithium oxide to the cell electrolyte.

3. This change in half-cell reaction could be made to occur later in the discharge by the addition of magnesium chloride to the cell electrolyte. This addition caused a very large increase in the rate of self-discharge of otherwise identical cells.

4. In the titration studies, the addition of 1.5 moles of lithium oxide per mole of cuprous oxide in a lithium chloride - potassium chloride solvent brought about the formation of an insoluble cuprous complex compound. The difference in electromotive force (emf) of a copper electrode placed in a saturated solution of cuprous oxide and one placed in a saturated solution of the cuprous complex was the same as the emf difference that occurred at the voltage step during discharge of complete cells.

5. Cuprous ions that were precipitated by lithium oxide in the lithium chloride - potassium chloride solvent formed two different complexes, indicating that cuprous oxide does not dissolve in a simple manner.

6. Finally, based on this and our previous studies, a model is presented that explains essentially all the significant features of cell behavior during discharge.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 16, 1970,
120-34.

REFERENCES

1. Thaller, Lawrence H.: A Long-Life Thermal Cell. NASA TN D-2915, 1965.
2. Thaller, Lawrence H.: Discharge Characteristics of Some Copper Oxide-Magnesium Thermal Cells. NASA TN D-4306, 1968.
3. Thaller, Lawrence H.: Effect of Amount of Electrolyte, Drain Rate and Electrode Geometry on Performance of Copper Oxide-Magnesium Thermal Cells. NASA TN D-4790, 1968.

4. Thaller, Lawrence H.: Anolyte Studies of the Magnesium Electrode in Molten Mixtures of Lithium Chloride, Potassium Chloride, and Magnesium Chloride. NASA TN D-5657, 1969.
5. 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.
6. Bockris, J. O'M.; Hill, G. J.; Inman, D.; and Young, L.: An All-Glass Reference Electrode for Molten Salt Systems. J. Sci. Instr., vol. 33, no. 11, Nov. 1956, pp. 438-439.