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EFFECT OF AMOUNT OF ELECTROLYTE, DRAIN RATE AND ELECTRODE GEOMETRY ON PERFORMANCE OF COPPER OXIDE-MAGNESIUM THERMAL CELLS

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ABSTRACT

This is a continuation of the studies of the performance of $Mg/LiCl-KCl/Cu_2O-CuO$ thermal cells operating at 450° C. The measure of performance used in the present study is the parameter X, the depth of discharge at which the approximate 0.25-V drop in open circuit voltage occurs. This parameter was evaluated as a function of three factors which influence mass transport, namely, the amount of electrolyte, the rate of discharge, and the electrode shape and spacing. The amount of electrolyte per unit of cell capacity had little effect on X. In tests on horizontal- and vertical-type cells, X was inversely related to current density, with a stronger dependence on current density for cells with poorer mass transport characteristics. An increase in current density and decrease in operating temperature promoted premature failure (low cathode utilization).

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SUMMARY

This work is a continuation of the studies of the performance of copper oxide-magnesium thermal cells.

The measure of performance used in the present study is the parameter X, the depth of discharge at which the approximate 0.25-volt drop in open circuit voltage occurs. This parameter was evaluated as a function of three factors which influence mass transport, namely, the amount of electrolyte, the rate of discharge, and the electrode shape and spacing. Also reported herein are the results of a test on the relation of cell end-of-life failure to current density, electrolyte temperature, and composition.

Discharge tests were made on horizontal- and vertical-type thermal cells containing the eutectic mixture of potassium chloride-lithium chloride at 450° C as the electrolyte. In tests on five cathode limited vertical cells, the amount of electrolyte per unit of cell capacity was observed to have little effect on X. Tests of five horizontal- and four vertical-type cells indicated that X was inversely related to current density, with a stronger dependence on current density for cells with poorer mass transport characteristics (i.e., horizontal-type). Three horizontal-type cells were tested to determine the effect on X of the amount and direction of cathode expansion. For a given cathode thickness, the cell with the cathode that was allowed to expand away from the anode gave a higher value of X than either the cell with the cathode that expanded toward the anode or the cell with the constrained cathode.

The cause of end-of-life failure was investigated by varying the operating temperature and current density of a deeply discharged horizontal-type cell. An increase in

current density and decrease in operating temperature promoted premature failure (low cathode utilization). This behavior, taken together with reported compositional changes in the electrolyte, suggest that the cause of failure is freezing of the electrolyte.

INTRODUCTION

Earlier studies (refs. 1 and 2) at this laboratory were 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 were magnesium; the cathodes were mixed copper oxide ($CuO + Cu_2O$); and the electrolyte was the eutectic mixture of lithium chloride and potassium chloride. This type of thermal cell might find application in Venusian and solar probe missions. The first phase (ref. 1) of these studies was concerned with the overall chemical reactions associated with the discharge of hermetically sealed cells. The open circuit voltage of these cells at the early stages of discharge was found to be due to the following half-cell reactions:

$$Mg \rightarrow Mg^{+2} + 2e^{-} \text{ at anode}$$
$$Cu^{+1} + e^{-} \rightarrow Cu \text{ at cathode}$$

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

$$Cu^{+2} + Cu \rightarrow 2Cu^{+1}$$

In the second phase of the earlier studies of the copper oxide-magnesium thermal cell (ref. 2) investigations were made of ways to reduce the self-discharge rates of these cells. It was determined that the rate of transport of copper ions from the cathode to the anode controlled the overall rate of self-discharge.

Although copper oxide-magnesium thermal cells have demonstrated satisfactory operating times (> 1 week) and reasonably low rates of self-discharge (less than 10 percent of total rate), several undesirable features are still evident. One such feature is the approximately 0.25-volt drop in the open circuit voltage (OCV) which occurs during the latter stages of discharge. A second undesirable feature is the incomplete usage of the electrode materials. Both undesirable features are believed to be related in part to adverse mass transport conditions within the cells. In this study cell performance, particularly the 0.25-volt drop in OCV, is evaluated as a function of three factors which influence mass transport, namely, the amount of electrolyte, the rate of discharge, and the electrode spacing and shape. Finally, end-of-life failure is related to current density and electrolyte temperature and composition.

EXPERIMENT

Materials

The electrolyte used was the eutectic mixture of lithium chloride and potassium chloride. This material, purified according to a modified Laitinen process (ref. 3), was ground to a suitable particle size and stored in a nitrogen filled double drybox. The anode material was primary grade magnesium (99.8 percent Mg, 0.15 percent Mn, and 0.02 percent Cu). The cathode material was the wire form of cupric oxide. This material is a mixture of cupric and cuprous oxide (73±2 percent by weight cupric oxide). Although the specific gravity of cupric oxide is 6.4 and cuprous oxide is 6.0, the specific gravity of these wires was only 5.6 and the apparent specific gravity of the packed wire cathode was about 2.6. The individual copper oxide wires must, therefore, contain about 12 percent voids and the bulk cathode structure about 53 percent voids.

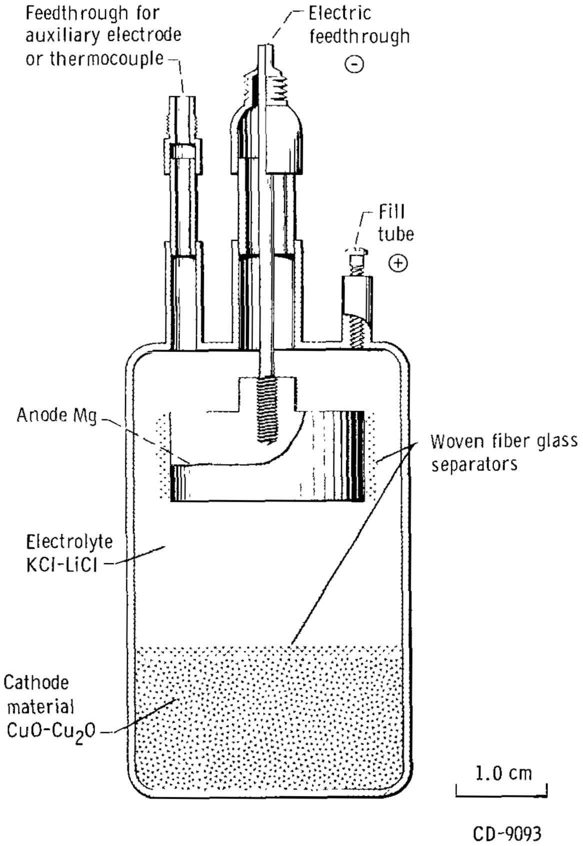

Figure 1. - Horizontal-type cell.

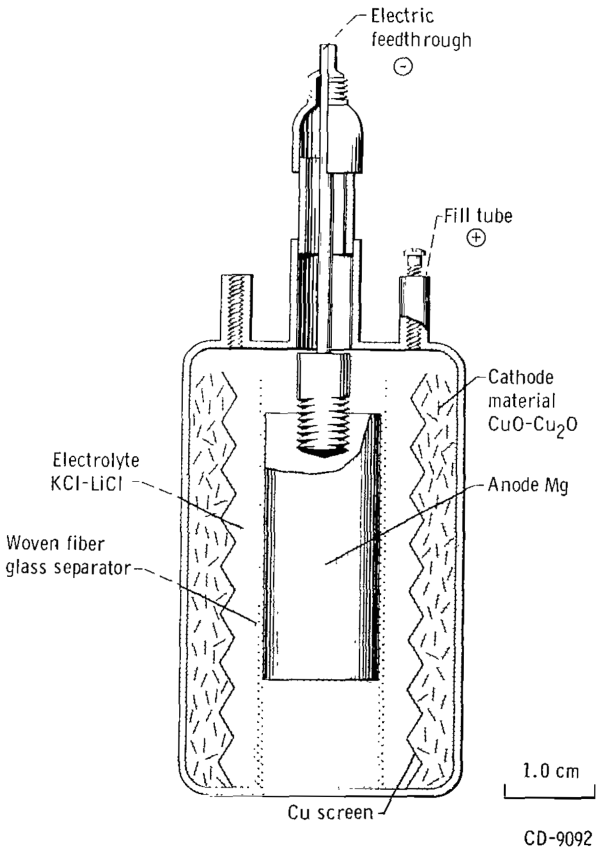

Figure 2. - Vertical-type cell.

The separators were tightly woven glass fabric about 1 millimeter thick. This material was heated in a furnace to 500° C to decompose the resin coating that had been applied during its manufacture.

The cells tested were of two types. The first type were sealed horizontal and vertical cells as shown in figures 1 and 2, respectively. The second type were open top horizontal and vertical cells. These cells were like those shown in figures 1 and 2 except they had no welded tops.

Procedure

The open top cells were discharged in a small electrically heated temperature controlled furnace that was located inside a continuous flow nitrogen double drybox.

Sealed cells were discharged in a nitrogen filled furnace described in reference 2. All cells were discharged in 2-hour cycles that were divided as follows:

(1) 100 minutes - fixed external resistance = R_1
(2) Followed by 10 minutes - fixed external resistance = $R_1 + R_2$
(3) Followed by 10 minutes - no load

The cycle was repeated to 0.5-volt cutoff.

The voltage of the cell as well as the current flowing through the discharge circuit was recorded continuously. Complete details of the discharge circuit are given in reference 2.

RESULTS AND DISCUSSION

Treatment of Data

After a cell had failed (i.e., reached the 0.5-V cutoff), the average rate of electrochemical discharge and self-discharge were calculated as described in reference 2. By way of example, figure 3 presents a typical discharge curve for a horizontal cell. Shown are the open circuit voltage OCV (value at end of 10-min no load period), cell operating voltage V, cell current I, and total equivalent internal resistance $R = (OCV - V)/I$ plotted as a function of time t.

For the purposes of the following discussion, it is meaningful to describe the position of the OCV step as it appears on the discharge curve in terms of the depth of discharge of the cathode. The discharge factor used, designated the step placement fraction X, is the ratio of the ampere-hours of products of reaction at the time of the step to the ampere-hours inherent to the cathode. Included in the numerator are those reaction products that are a consequence of self-discharge reactions. This minor

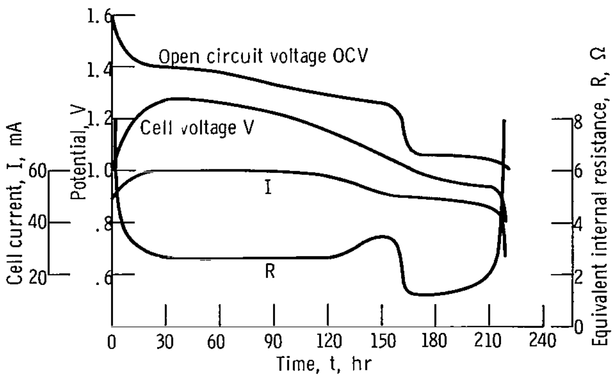

Figure 3. - Characteristic discharge of typical horizontal cell.

contribution is estimated by multiplying the average rate of self-discharge (as defined in ref. 2) by the number of hours of discharge prior to the appearance of the step. The ampere-hours of products of reaction that are due to electrochemical reaction are calculated from the area under the current-time curve.

Cathode utilization is also calculated for some of the cathodes. As defined here, it is the ratio of ampere-hours of cathodic products of reaction at the end of discharge divided by the initial cathodic coulombic capacity. This term is a measure of the acessibility of the cathode material to reaction at the rates of discharge investigated.

The results are presented in four sections. The first three sections present the effect on cell performance of the variation of the following mass transport factors:

(1) The amount of electrolyte
(2) The electrode configuration and rate of discharge
(3) The amount and direction of cathode expansion

In the final section, the failure of deeply discharged cells is related to current density and electrolyte temperature and composition.

Effect of Amount of Electrolyte on Cell Performance

The object of this set of experiments was to determine the effect of the amount of electrolyte on the cathode utilization and the step placement fraction. Five cathode limited, vertical, open top cells (as in fig. 2, but without a top), containing about 6.5 ampere-hours (23 400 C) of cathode material and 13 ampere-hours (46 800 C) of anode material, were discharged. As shown in table I, in all cases the cathode utilization was 93 percent or greater and the step placement fraction was not dependent upon the amount of electrolyte used.

TABLE I. - EFFECT OF AMOUNT OF ELECTROLYTE ON CELL PERFORMANCE

Cell	Electrolyte, g/A-h	Step placement fraction, X	Cathode utilization, percent
1	2.0	0.72	98
2	2.5	.72	93
3	3.0	.68	93
4	3.0	.60	98
5	3.5	.66	94

The step in the open circuit voltage has been postulated (ref. 2) to be caused by a change in one of the half-cell reactions during the latter part of the discharge. The results presented in table I show that the use of more electrolyte does not prevent the occurrence of the step nor does it have much effect on its position on the discharge curve.

The use of more electrolyte only allows a larger average current flow for a fixed external resistance. This is to be expected since the use of more electrolyte maintains a more constant electrolyte composition and thus reduces the concentration polarization. As more electrolyte is added, however, the cell weight increases and thereby lowers the energy density. Therefore, a compromise must be made between current drain rate and cell weight.

Effect of Rate of Discharge and Electrode Configuration on the Cell Performance

Although it is difficult to quantitatively rate the mass transport performance for different cell configurations and operating conditions, a qualitative rating can be readily made. Cells that are constructed as in figure 1 (horizontal type) will have poorer mass transport characteristics than those shown in figure 2 (vertical type). First, the horizontal cathodes have less frontal area exposed to the electrolyte than the vertical type. Second, the horizontal cathodes are thicker than the vertical cathodes and this thickness will hinder mass transport processes as the reaction zone moves from that closest to the anode to that farther away from the anode. Third, under operating conditions of high current density, the diffusion and migration of products of reaction into the bulk electrolyte will be more difficult.

TABLE II. - STEP PLACEMENT FRACTION AS A FUNCTION OF CELL CONFIGURATION AND CURRENT DENSITY

Cell	Cell type	Current density	Step placement fraction, X
1	Horizontal	Low	0.69
2	↓	High	.59
3	↓	↓	.50
4	↓	↓	.48
5	↓	↓	.47
6	Vertical	Low	.75
7	↓	High	.72
8	↓	↓	.71
9	↓	↓	.70

Table II lists results from five horizontal and four vertical cells that had been discharged in an earlier work (ref. 2). All cells contained about 2.0 grams of electrolyte per ampere-hour of capacity. It is seen that the step placement fraction is larger for cells designed to enhance mass transport. The step placement fraction appears to be dependent on cell configuration. With the horizontal type cell, X is noticeably dependent on the current density. A much weaker dependence of X on current density was indicated for the vertical-type cells. The cells in table II are listed in the order of increasing current densities.

It was shown in reference 2 that, as the mass transport conditions improve, the self-discharge becomes larger. In the design of a practical cell then, a compromise must be made to achieve optimization of overall cell performance.

Effect of Cathode Expansion on the Cell Performance

As the wire form of cupric oxide discharges, it is converted to micron-size particles of copper. Also, the magnesium oxide is precipitated among the copper particles as very small crystals. These very low bulk density products of reaction tend to fill any volume available, in this case, the volume occupied by electrolyte. Copper oxide cathodes have been reported (ref. 4) to expand as much as 300 percent if not restrained.

Three horizontal cells containing 2.5 grams of electrolyte per ampere-hour of capacity were tested using the same fixed external resistor as the load. The first cell had no restraints on the cathode expansion other than the anode itself; that is, the cathode, with two layers of separators above it, could expand 100 percent in the upward direction.

The second cell was constructed so the top of the cathode was separated from the anode by two thicknesses of separator material and a screen. The screen was spot welded to the cell case to prevent any upward movement of the cathode. This cell was constructed with a collapsible bottom on the cathode compartment. The allowable expansion in the downward direction was 100 percent. This cell would be expected to have better mass transport characteristics than the first one because of the closeness of the cathode to the anode. A third cell was constructed with the cathode on the bottom of the cell (as in the first type). A wire screen was affixed to the inside of the cell above the two layers of separator so there could be no expansion of the cathode. It must be remembered, however, that the porosity of these packed oxide wires is about 53 percent, thus providing internal space for electrolyte and products of reaction. On a qualitative basis, this configuration would be expected to have the poorest mass transport characteristics of the three configurations listed.

From the results shown in table III, it is seen that the cathode that was not allowed to expand at all (cell 3) had the same X value as the cathode that expanded toward the anode (cell 1). The cathode that expanded away from the anode gave the highest X value (cell 2). It appears from these limited number of tests that, if some cathode expansion is allowable, expansion away from the anode is preferable since the cell will operate longer at the higher voltage. Also, for a minimum volume cell, the cathode may be completely constrained without serious loss of cell performance.

TABLE III. - STEP PLACEMENT FRACTION AS A FUNCTION

OF CATHODE EXPANSION

Cell[a]	Cathode expansion	Step placement fraction, X	Average electrochemical current, mA
1	100 percent upward	0.48	190
2	100 percent downward	.58	165
3	No expansion	.47	150

[a] All cells were filled with 2.5 g of electrolyte/A-h of capacity and had the same external load.

The high value for the current in cell 1 is believed to be due to the absence of a stainless-steel screen. Cells 2 and 3 had screens welded to the cell to prevent expansion in the upward direction. The presence of the screen would interfere with ionic movement from the anolyte to the catholyte.

In terms of cathode expansion, optimization of cell performance will depend on balancing cell size against the X value.

Cause of Cell Failure

The fourth area of investigation was the cause of failure of cells that dropped below the 0.5-volt cutoff during discharge. The single cell tested was a sealed horizontal cell with matched electrode capacities (13 A-h) and was filled with 2.0 grams of electrolyte per ampere-hour of cell capacity. Shown in figure 3 is a discharge curve typical of this type of cell. To be noted is the sharp cutoff at the end of cell service life, as evidenced by the sharp increase of the overall internal resistance or conversely the sharp drop in the cell operating voltage. Discharged cells of this type that were opened for analysis (ref. 2) contained unused anode and cathode material. There was always at least 1 ampere-hour of active material remaining that had not been consumed either chemically or electrochemically. When cells were discharged that were either anode limited or cathode limited, it was found that no more than a few tenths of an ampere-hour of the limiting electrode remained unused.

The cell tested in this investigation was discharged in a somewhat different manner than normally. Figure 4 shows the end-of-life portion of the discharge curve for this cell. The test was not terminated when the cell reached the 0.5-volt cutoff but was continued. Near the estimated end-of-life, the cell was placed under a different load which about doubled the current drain from about 40 to about 70 milliamperes. This

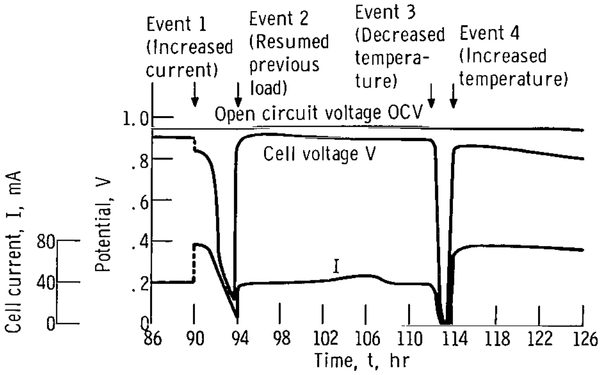

Figure 4. - End-of-life cell discharge.

change in fixed external resistance occurred at about the 90-hour mark (event 1, in fig. 4). It is seen from this figure that the cell was unable to maintain the 70-milliampere drain and the current and cell operating voltage dropped quite sharply. By switching back to the previous load (event 2), the cell recovered during the 10-minute open circuit period and resumed operating as before. On the basis of previous experience with these cells, this type of behavior resembled that of freezing and remelting of the electrolyte. This possibility was checked further by lowering the cell operating temperature from 450° to 445° C at about the 112-hour mark (event 3). Figure 4 shows that again the cell current and operating voltage dropped abruptly. The cell operating temperature was next increased from 445° to 455° C; the figure shows (event 4) that the cell not only recovered, but was able to maintain a 70-milliampere drain for some time.

Since the freezing point of the electrolyte at the start of discharge is 352° C, a significant change in composition would have to take place during discharge to produce an increase in the freezing point of almost 100° C. This possibility is supported by results of electrolyte composition changes reported in reference 2. A number of discharged cells were cut in half vertically and X-ray diffraction patterns were obtained from powdered samples taken from different areas within the cell. The portion of the electrolyte above the separator is referred to as the anolyte and the portion below the separator as the catholyte. The following is a summary of the analysis given in reference 2:

(1) Magnesium ions present in large amounts in the anolyte
(2) Magnesium oxide present only in the upper two layers of catholyte
(3) Lithium oxide present only in the lower two layers of the catholyte
(4) The ratio of lithium chloride to potassium chloride in the catholyte about equal to that of the pure eutectic

These facts lead to the following picture of the mass transport processes in the cells:

(1) During the initial stages of discharge, magnesium ions move to the catholyte where they are precipitated by the oxide ions.

(2) During the latter stages of discharge, the magnesium ions do not move away from the anolyte, but lithium ions do.

A consequence of the first statement is that the electrolyte as a whole (both anolyte and catholyte) remains fixed in composition during the initial stage of discharge; that is, if viewed overall, the electrolyte is nonparticipating. A consequence of the second statement is that there is a progressive change in the composition of the anolyte and the catholyte during the latter stages of discharge. The composition changes could conceivably raise the melting point of the anolyte or catholyte so that freezing could take place. Unfortunately, pertinent ternary phase diagrams (e.g., $LiCl-KCl-MgCl_2$ and $LiCl-KCl-Li_2O$) are not available to confirm this.

SUMMARY OF RESULTS

This is a continuation of the program to evaluate the performance of copper oxide-magnesium thermal cells operating at 450° C. The measure of performance used in the present study is the parameter X, the depth of discharge at which the approximate 0.25-volt drop in open circuit voltage occurs. This parameter was evaluated as a function of three factors which influence mass transport, namely, the amount of elecrolyte, the rate of discharge, and the electrode shape and spacing. The following is a summary of the findings of this study:

1. The results of tests on five cathode limited vertical cells indicated that the amount of electrolyte per unit of cell capacity had little effect on the parameter X, the depth of discharge at which the step in open circuit voltage occurs.
2. Five horizontal- and four vertical-type cells were evaluated for the effect of electrode configuration and current density on X. It was found that X was inversely related to the current density for the cells with poorer mass transport characteristics (i.e., horizontal type).
3. Three horizontal-type cells were tested to study the effect of the amount and direction of cathode expansion on X. Cell 1 was allowed 100 percent upward (toward the anode) cathode expansion; cell 2 was allowed 100 percent downward cathode expansion; cell 3 was allowed no cathode expansion. The X values for cells 1 and 3 were the same, while for cell 2 the value of X was significantly higher than for cells 1 and 3.
4. The cause of end-of-life failure was investigated by varying the operating temperature and current density of a deeply discharged horizontal-type cell. An increase in current density and a decrease in operating temperature promoted premature cell failure (low cathode utilization). This behavior, taken with the previously reported compositional changes in the electrolyte during the latter stages of discharge, suggest that the cause of failure is freezing of the electrolyte.

Lewis Research Center,
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