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ANOLYTE STUDIES OF THE MAGNESIUM ELECTRODE IN MOLTEN MIXTURES OF LITHIUM CHLORIDE, POTASSIUM CHLORIDE, AND MAGNESIUM CHLORIDE

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16. Abstract

A continuation of work on the $Mg-LiCl-KCl - Cu_2O-CuO$ thermal cell at 450° C is presented and is concerned with mass transport within the cell and its effect on performance. X-ray studies on discharged cells showed that magnesium ions and oxide ions do not rapidly diffuse away from the electrodes. This produces a $MgCl_2$ rich anolyte with a resulting decrease in cell voltage and an increase in the electrolyte freezing point. Quantitative studies of these effects were made using LiCl-KCl mixtures to which $MgCl_2$ was added. The emf and polarization of magnesium anodes in these electrolytes and the freezing points of the salt mixtures were studied. The poor operating characteristics of the magnesium anode under certain conditions could be explained from the results.

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ANOLYTE STUDIES OF THE MAGNESIUM ELECTRODE IN MOLTEN MIXTURES OF LITHIUM CHLORIDE, POTASSIUM CHLORIDE, AND MAGNESIUM CHLORIDE

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SUMMARY

The present investigation is a continuation of the study of the performance of copper oxide - magnesium thermal cells operating at 450° C. It was undertaken in order to explain earlier findings which indicated that magnesium ion concentrations greater than about 20 mole percent in the anolyte resulted in premature cell failure (low electrode utilization).

The investigation consisted of three parts:
(1) The determination of the influence of temperature and electrolyte composition on the emf of the magnesium-magnesium ion half-cell potential
(2) The determination of the phase diagram of the magnesium chloride ($MgCl_2$)-potassium chloride (KCl)-lithium chloride (LiCl) system by using cooling curves over the composition range of $MgCl_2$ from 0 to 42 mole percent, KCl from 41 to 58 mole percent, and LiCl from 50 to 0 mole percent over a temperature range of 550° to 300° C
(3) The determination of the influence of temperature, electrolyte composition, and current density on the polarization characteristics of the magnesium anode in a series of electrolytes chosen to represent the changing anolyte composition in a discharging thermal cell

The open-circuit potentials of the magnesium-magnesium ion electrode in comparison with a silver-silver ion reference electrode in the various electrolytes at temperatures from 375° to 500° C showed no deviation from Nernstian behavior up to a magnesium ion concentration of about 2 molar.

The cooling curve results demonstrated that initial freezing points increase from 380° to 475° C as the $MgCl_2$ content increases from 22 to 42 mole percent.

The polarization characteristics of the magnesium anode were very dependent on the operating temperature, the magnesium ion concentration, and the current density. The results showed, that in electrolytes containing more than 20 mole percent $MgCl_2$, it is probable that in the vicinity of the anode localized freezing of the electrolyte can occur at sufficiently high current densities.

INTRODUCTION

For several years, the NASA Lewis Research Center has been engaged in research on high-temperature primary electrochemical cells. The objective of the program is to identify and characterize cells for use in high-temperature environments. As part of this effort, cells with magnesium anodes, copper oxide (80 percent CuO, 20 percent Cu_2O) cathodes, and a lithium chloride (LiCl)-potassium chloride (KCl) eutectic as the electrolyte have been constructed and tested. Operation at 450° C for times in excess of 1 week has been demonstrated.

The first studies (ref. 1) were concerned with the overall chemical reactions associated with the discharge of complete hermetically sealed cells. It was found that magnesium was oxidized to the +2 state and that both cupric and cuprous oxide were reduced finally to metallic copper. The oper-circuit voltage during approximately the first half of the discharge (based on rated capacity) resulted from the following half-cell reactions:

$$At the anode, \quad Mg \rightarrow Mg^{+2} + 2e^-$$

$$At the cathode, \quad Cu^{+1} + e^- \rightarrow Cu$$
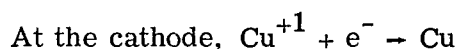
The second phase of the work (ref. 2) dealt with the effect of electrolyte type and cell configuration on the average rate of self-discharge. The results showed that the rate of self-discharge was controlled by the transport of copper ions from the cathode to the anode. This transport of copper ions, in turn, was affected by electrolyte composition and electrode configuration. However, the factors that produced a lower rate of self-discharge (wider electrode separation, different electrolyte, and thicker separator) also led to increased internal cell resistance.

The third phase of the work (ref. 3) examined the effect of mass transport processes on the overall cell performance. The results suggested that cell failure was ultimately caused by freezing of the electrolyte somewhere in the cell. X-ray analyses of discharged cells provided evidence that the composition of the electrolyte changed during the discharge.

In this report, it is shown that failure of the copper oxide - magnesium thermal cell is related to the composition of the anolyte. This was done by studying the influence of temperature on the open-circuit potentials and the influence of temperature and current density on the polarization characteristics of the magnesium anode. Twelve different electrolyte mixtures were chosen to represent the anolyte compositions in a working cell at different stages of discharge. The selected compositions covered the following range: magnesium chloride ($MgCl_2$) 0 to 42 mole percent; lithum chloride (LiCl), 59 to 0 mole percent; and potassium chloride (KCl), 41 to 58 mole percent.

In addition, the freezing points and cooling curves of 18 different mixtures of these same components were obtained, which permitted the construction of a partial ternary phase diagram for the system LiCl-KCl-MgCl$_2$. From these data, it was possible to estimate under what conditions freezing of the anolyte would occur and relate this to the appearance of severe polarization of the magnesium electrode under certain circumstances of temperature and current density.

EXPERIMENT

All measurements and manipulations were carried out in a glove box purged with dry nitrogen and equipped with an analytical balance, temperature-controlled furnaces, and appropriate electrical feedthroughs. Reagent grade KCl, LiCl, and MgCl$_2$, which had been vacuum dried at 120° C for several weeks, transferred to the glove box, and stored in capped bottles, were used to prepare the electrolytes. Compositions were formulated to maintain the total chloride ion concentration constant in all the mixtures by compensating the amount of MgCl$_2$ added with reduced amounts of LiCl. This is explained in the next section. The weights of these electrolyte samples ranged from 1.778 grams for the mixture that contained no MgCl$_2$ to 1.933 grams for the mixture that contained no LiCl.

Magnesium Half-Cell Tests

Magnesium test cells were constructed as shown in figure 1. A 12- by 75-millimeter pyrex test tube was used as the container. The magnesium anodes and cathodes were constructed from magnesium ribbon (99.8 percent Mg, 0.17- by 2.95-mm, ~1.20 cm^2, immersed area) that had been bent lengthwise at a 90° angle to increase the rigidity. They were etched in dilute hydrochloric acid to remove the oxide film, rinsed in distilled water and alcohol, and then dried. The reference electrode (ref. 4) consisted of a piece of pure silver wire (99.99 percent Ag) immersed in a eutectic mixture of LiCl-KCl that was 0.13 molar in silver chloride (AgCl). This solution was contained inside a pyrex melting point tube that acted as a lithium ion conducting membrane between the test electrolyte and the reference electrolyte. Each experiment required a new reference electrode because the tube fractured on freezing. The temperature was measured with a 28-gage Chromel-Alumel thermocouple placed inside a second pyrex melting point tube to prevent reaction with the electrolyte.

After the top of the cell had been put in place and the leads were connected, the cell was placed in a small furnace, brought to the test temperature, and allowed to equili-
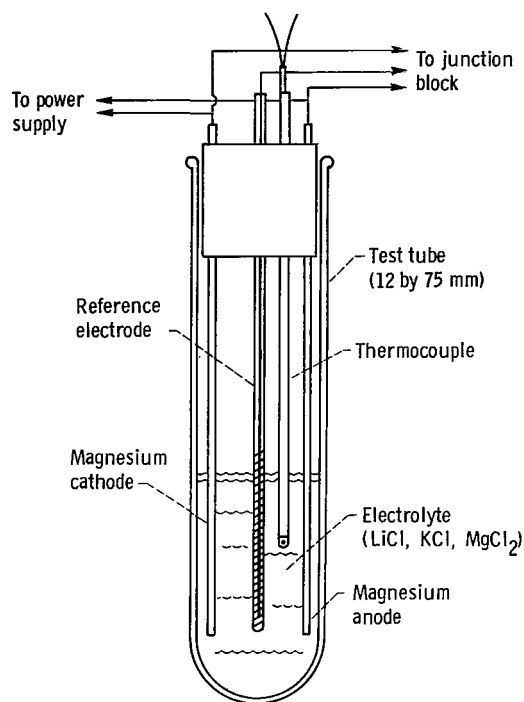
Figure 1. - Cell used for half-cell and polarization studies.

brate for 1/2 hour before measurements were started. The instrumentation shown in figure 2 was used to obtain the test data.

Open-circuit voltages were measured at temperatures of 500°, 475°, 450°, 425°, 400°, and 375° C with a battery-operated, floating-input electrometer (accuracy $\pm 1/2$ percent full scale, input impedance, $>10^{14}$ Ω). At each temperature of interest, ample time was allowed for the establishment of equilibrium conditions between the magnesium electrode and the melt. The output of the electrometer was connected to a strip-chart recorder that was used to record the voltage between the reference electrode and each magnesium electrode as a function of time. Twelve different electrolyte compositions were investigated.

Following the open-circuit measurements, polarization studies were performed on the same samples of electrolyte using the battery-operated power supply shown in figure 2. Moderate amounts of current were forced through the cells (20 to 100 mA/cm^2) by adjustment of the variable resistor in the circuit. This current density was based on the geometric area of the immersed electrode. The resistance was fixed for each measurement. The anode polarization, cathode polarization, and current were recorded as a function of time using a four-pen recorder. The measured polarization included all forms of polarization.
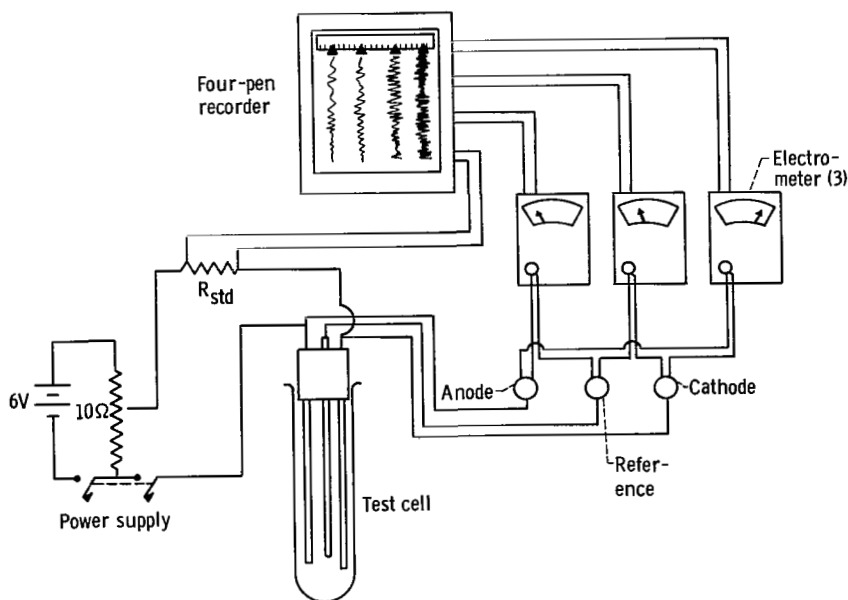
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Figure 2. - Experimental setup for half-cell and polarization studies.

Cooling Curve Studies

Cooling curves were determined for 18 electrolyte compositions. The determinations were made in 15- by 125-millimeter pyrex test tubes. The furnace used for these studies was lined with a hollow copper cylinder to minimize temperature gradients in the cooling mixtures. The thermocouple (28-gage Chromel-Alumel) was placed in the center of the sample and was used with an ice-bath reference junction. After the samples were heated to 550° C and allowed to equilibrate for 1/2 hour, the furnace was turned off and the temperature was recorded as a function of time. Initial freezing points were indicated by abrupt changes in the slope of the curve of temperature against time, while formation of an additional solid phase was made evident by thermal arrests. It should be noted that, in a ternary system which is known to have solid compounds ($MgCl_2 \cdot KCl$), more than one thermal arrest is to be expected.

RESULTS AND DISCUSSION

When the equilibrium within a copper oxide - magnesium thermal cell is displaced because of the generation of magensium ions at the anode and the consumption of copper ions at the cathode, ion transport occurs in order to counteract the charge imbalance. The nature of the transport processes will be governed in part by the mobility of the ions

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in the melt and by the number and types of electrostatic and chemical equilibria that must be satisfied.

Previous results (ref. 2) of an analysis of a deeply discharged copper oxide - magnesium thermal cell with the anode above the cathode showed

(1) The presence of magnesium oxide (MgO) in the top layers of the catholyte, which presumably resulted from the overall cell reaction

$$CuO + Mg \rightarrow Cu + MgO$$

(2) The presence of lithium oxide (Li_2O) in the lower layers of the catholyte, which presumably resulted from the overall cell reaction
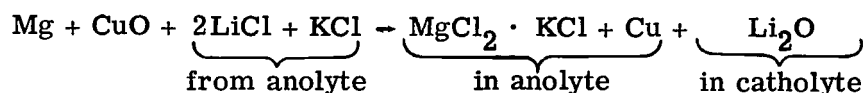
$$CuO + Mg + 2LiCl \rightarrow Cu + MgCl_2 + Li_2O$$
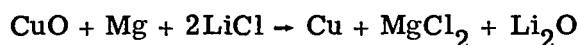
(3) The presence of large amounts of the one-to-one associated compound between magnesium chloride and potassium chloride in the anolyte ($MgCl_2 \cdot KCl$)

Since the cathode discharges from the top down in these horizontal cells, it can be concluded that, during the initial stages of discharge (0 to 40 percent depth of discharge), the magnesium ions formed at the anode surface moved to the catholyte, where they were precipitated as magnesium oxide. During the latter stages of discharge (beyond about 50 percent depth of discharge), the lithium ions moved to the catholyte, and the magnesium ions remained in the anolyte. The presence of the one-to-one associated magnesium chloride - potassium chloride compound ($MgCl_2 \cdot KCl$) in the anolyte is consistent with the evidence that a complex ion equilibrium exists between magnesium ions and chloride ions (ref. 5). This is further supported by noting that an exothermic reaction occurs in melting mixtures of the chlorides of magnesium, lithium, and potassium. Simple melting (i. e., no complex formation) is an endothermic process. Complex formation can modify ionic mobilities and, hence, can possibly play a major role in the behavior of these cells.

If the charge neutralization transport is due to the movement of magnesium ions exclusively, the composition of the anolyte and the catholyte would remain fixed during the entire discharge, and the only products of reaction would be insoluble magnesium oxide and copper. On the other hand, if the transport is due to the movement of lithium ions exclusively, the composition of the anolyte and catholyte would continuously change, and the solid reaction products would be copper and lithium oxide, once its solubility limit is exceeded. From some of the unpublished work done at Lewis, it is estimated that in the eutectic at this temperature the solubility of lithium oxide is about 8 mole percent (~1.5 molality). The estimate was made by noting the freezing point depression caused by additions of lithium oxide to the lithium chloride-potassium chloride eutectic.

For the purpose of considering the causes of cell failure at the end of discharge, the charge neutralization transport will be assumed to be due to lithium ions exclusively, since lithium oxide was found to be the major reaction product during the second half of the discharge (ref. 2). The following equation describes the overall cell reaction under these conditions:

$$Mg + CuO + \underbrace{2LiCl + KCl}_{from\ anolyte} \rightarrow \underbrace{MgCl_2 \cdot KCl + Cu}_{in\ anolyte} + \underbrace{Li_2O}_{in\ catholyte}$$

The changes in the anolyte composition during discharge would then be described by the following stoichiometric relations, if 1 mole of the KCl-LiCl electrolyte is considered to be initially present:

$$LiCl - (0.59\ to\ 1.00X)\ moles$$

$$KCl - 0.41\ moles$$

$$MgCl_2 - 0.50X\ moles$$

where X is equal to the equivalents of Mg discharged.

Based on the foregoing relations, a series of 18 electrolyte mixtures was prepared over the range of X = 0 to 0.59. These mixtures were used in the studies of the magnesium half-cell potentials (12 of the 18), the determination of the electrolyte phase diagram (all 18 mixtures), and the anode polarization studies (12 mixtures).

Effect of Magnesium Chloride Content on Potential of Mg-Mg^{+2} Electrode

The observed variation of open-circuit voltage of the Mg-Mg^{+2} - Ag^{+1}-Ag cells as a function of temperature and magnesium ion content is shown in figure 3. As expected from the Nernst equation,

$$E = E^O_{Mg} - \frac{RT}{2F} \ln(Mg^{+2}) - E_{ref}$$

the magnesium half-cell potential becomes less anodic with increasing temperature and magnesium ion content. The data in figure 3 have been corrected for residual magnesium ion concentrations resulting from the reaction of the magnesium electrodes with
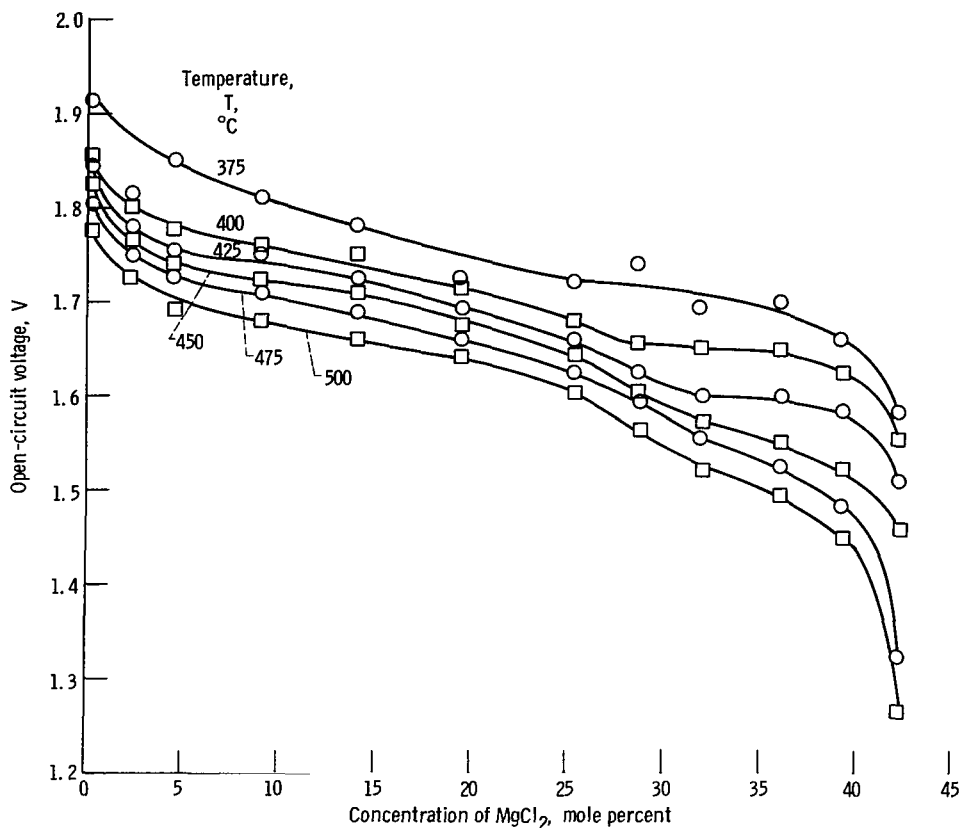
Figure 3. – Electromotive force of Mg - Mg^{+2} - Ag^{+1} - Ag cells as function of $MgCl_2$ concentration.

traces of water contained in the dried salts. This concentration was estimated to be 0.05 molal from the potential observed in the pure KCl-LiCl eutectic and from the equilibrium potential reported by Laitinen and Liu (ref. 6). The present results agree to within 10 millivolts with the Nernst equation based on Laitinen's data at magnesium ion concentrations below 2 molal (~14 mole % $MgCl_2$) at 450° C (fig. 4). The deviation of the half-cell potential (below Nerstian behavior) at magnesium ion concentrations greater than about 2 molal is related to the difference in lithium ion concentration between the electrolyte of the magnesium half-cell and the KCl-LiCl electrolyte of the silver-silver ion reference half-cell. At high magnesium ion concentrations, that is, low lithium ion concentrations, the concentration potential due to the lithium ion (membrane potential) across the glass membrane contributes significantly to the observed emf. The recommended correction of Bockris et al. (ref. 4) is equal to

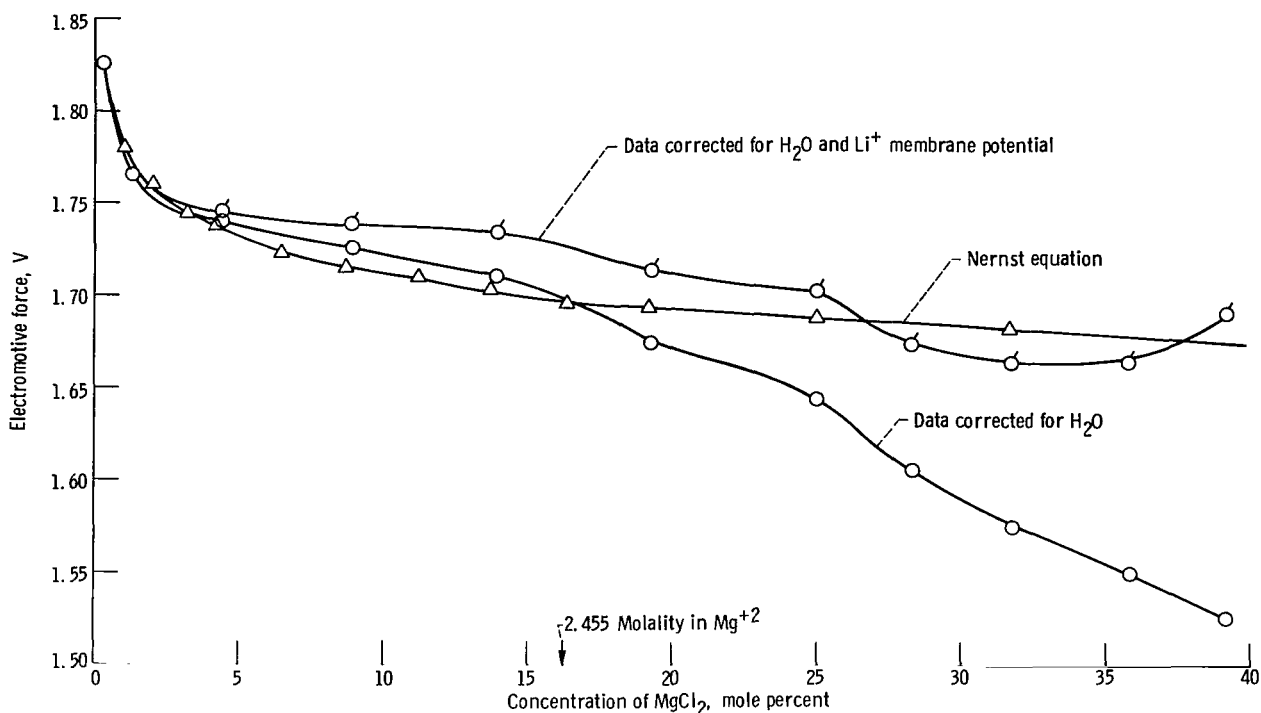$$\frac{RT}{F} \ln \frac{Li^+_{ref}}{Li^+_{sol}}$$

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Figure 4. – Comparison of Mg-Mg^{+2} – Ag^{+1}-Ag electromotive forces with different corrections applied.

This correction is also plotted in figure 4 for the 450° C data and appears to be inappropriate. Therefore, the voltages at the extreme right of figure 3 contain a large membrane potential that remains uncorrected.

Cooling Curve Studies

The freezing points and thermal arrest data for the 18 electrolyte compositions are shown in figure 5. The data points are connected by lines to form a partial phase diagram for the ternary system. More than one thermal arrest is to be expected from a ternary system where compound formation is known to be present (ref. 7). The main point to be noted in this figure is the rapid rise of the initial freezing point of the mixtures as the magnesium chloride content increases beyond about 22 mole percent. It must be remembered that between the line of initial freezing points and the lowermost thermal arrest, there is some liquid present in these mixtures.
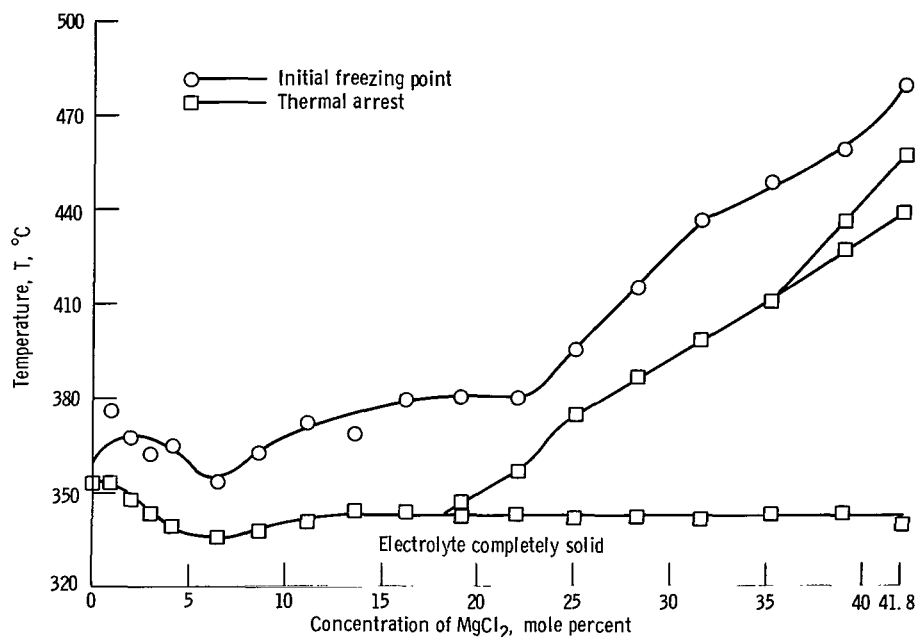
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Figure 5. - Phase diagram of (0.59 X) LiCl, 41 KCl, X/2 MgCl$_2$ system.

Effect of Magnesium Chloride on Polarization of Magnesium Anodes

The performance of the magnesium anodes in the various melts was investigated by recording anodic polarization, by means of the reference electrode already described, as a function of time after current had been applied to the cell. In order to maintain a constant overall electrolyte composition in these experiments, a magnesium cathode as well as a magnesium anode were used.

Before discussing the experimental results, it is helpful to consider the limiting conditions that may be expected to occur in the half-cell study depending on whether the electrolyte is liquid or solid. First, if the electrolyte is frozen, the polarization (ohmic plus concentration) is effectively infinite and the current flow essentially zero. On the contrary, if the electrolyte is completely molten, than a short time after the beginning of current flow, a steady-state condition will prevail in which the flow of ions into the bulk electrolyte will be just equal to the rate of generation of ions at the anode, and the polarization will reach a constant value. Between these two extremes, a continuous series of intermediate conditions of partial freezing can be envisioned, and a polarization level will be associated with each condition. It is important to note that at a working electrode at a constant temperature the state of the electrolyte (liquid or partially frozen) adjacent to the magnesium electrode is determined by the local concentration of magnesium ion which, in turn, is determined by the anodic current density and the dif-
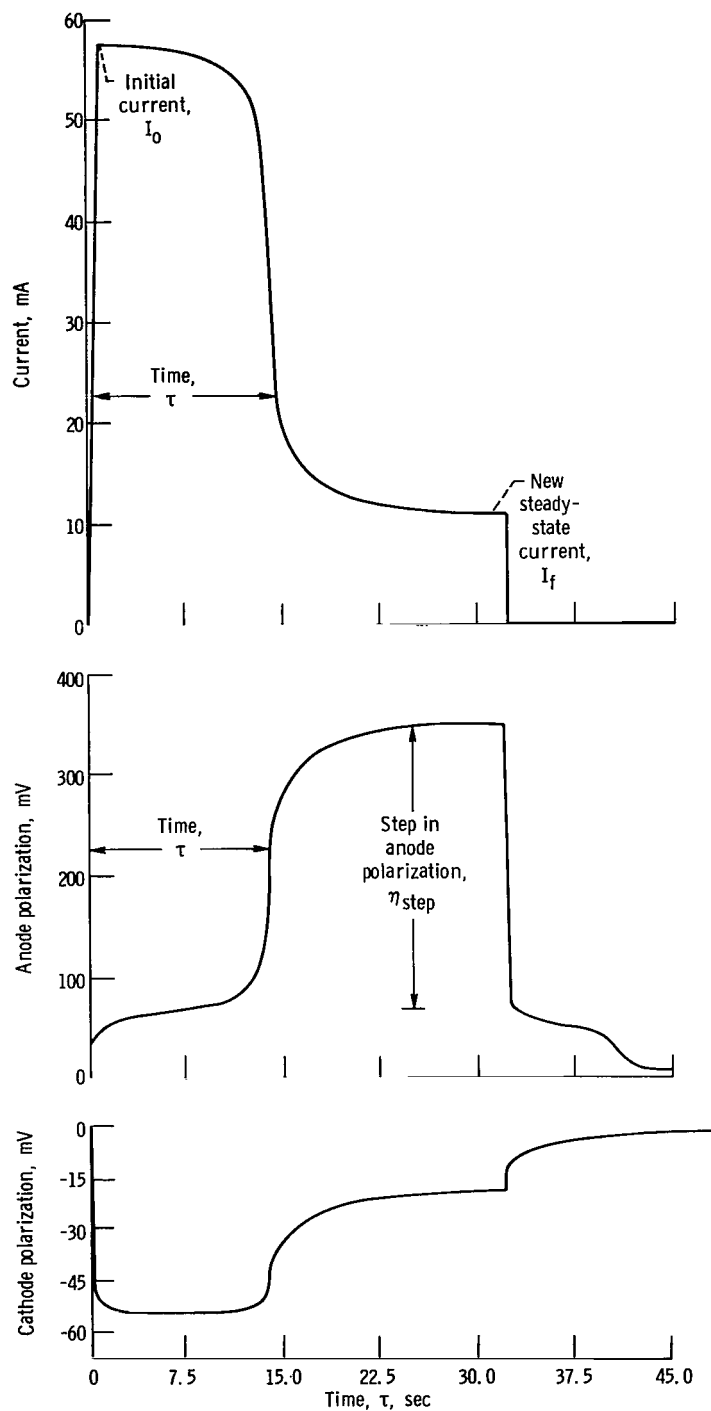
Figure 6. - Experimental results for typical polarization experiment in which current, anode polarization, and cathode polarization are measured as function of time. Temperature, 425° C; electrolyte composition: LiCl, 19.2 mole percent; KCl, 52.6 mole percent, $MgCl_2$, 28.2 mole percent.

fusivity of the magnesium ion in the bulk electrolyte. In view of this, current density, temperature, and electrolyte composition were the variables of interest with regard to their influence on electrode polarization.

The experimental results for a typical polarization experiment are shown in figure 6. In this example, the power supply was adjusted to cause an initial current I_0 of about 58 milliamperes to flow. The initial polarization at the anode was about 30 millivolts and at the cathode about 53 millivolts. These initial polarizations are presumably due to ohmic and activation polarization. After a period of time τ, which, in this example, was about 14 seconds, a large increase in the anode polarization was noted. The net effect was to lower the current flow drastically and also to reduce the cathodic polarization. A new steady-state condition was reached in about 15 more seconds. This step in the anode polarization is denoted as η_{step} and the new steady-state current I_f. After about 32 seconds, the current was cut off and on returning to equilibrium, the anode-to-reference voltage showed another discontinuity. This discontinuity is a consequence of concentration polarization only and is presumably caused by the melting of a partially frozen electrolyte near the anode; η_{step} is therefore the sum of two factors. The first is the increase in the concentration polarization caused by the buildup of the magnesium ion concentration adjacent to the anode, and the second is caused by the lower conductivity of the "slush" in the vicinity of the anode. In this particular example, the total resistance at the anode increased 27 fold when the step occurred.

The influence of temperature, current density, and composition on τ, η_{step}, and I_f help to substantiate this interpretation. Table I summarizes the results obtained

TABLE I. - RESULTS OF POLARIZATION STUDIES

[Electrolyte composition: LiCl, 14.5 mole percent; KCl, 54.0 mole percent; $MgCl_2$, 31.5 mole percent; initial freezing point, 437° C; immersed area, 1.2 cm^2.]

Temperature, T, $^\circ$C	Initial current, I_0, mA	Time, τ, sec	New steady-state current, I_f, mA	Coulombs passed up to time τ, $\int_0^\tau I\,dt$, C	Step in anode polarization, η_{step}, mV
450	48	>60	42	>2.88	---
450	60	>60	55	>3.60	---
450	82	>60	77	>4.92	---
450	106	17	55	1.80	275
440	28	62	9.2	1.74	25
440	36	18	10	.65	70
440	46	11	10	.51	140
440	56	7.0	10	.39	220
440	68	3.5	10	.24	350
440	97	2.0	13	.19	530
420	14	>60	9.0	>.84	---
420	27	11	5.0	.30	45
420	30	2.0	5.5	.06	120

using an electrolyte composition of 31.5 mole percent $MgCl_2$, 14.5 mole percent LiCl, and 54.0 mole percent KCl at three temperatures near the initial freezing point of the mixture (437° C from fig. 5). Values of I_0, I_f, τ, η_{step}, and the number of coulombs passed up to the time $\tau \left(\int_0^\tau I \, dt \right)$ are listed. It can be seen that τ becomes greater and η_{step} becomes smaller as the current density is decreased and the temperature is increased. (In these measurements, values of $\tau > 60$ sec were not determined.) Further, the data indicate that this polarization phenomenon is not directly related to the number of coulombs of charge passed but must be related to a mass transport phenomenon associated with the magnesium ion.

Table II summarizes an additional set of experiments in which the initial current density was about the same but the concentration of magnesium chloride was varied.

TABLE II. - TEMPERATURE AT AND BELOW WHICH

POLARIZATION STEPS OCCURRED - EFFECT

OF $MgCl_2$ CONCENTRATION

[Initial current in all cases, 80 to 90 mA.]

Concentration of $MgCl_2$, mole %	Temperature for step in anode polarization, T, ^{o}C	Initial freezing point (fig. 5), T, ^{o}C	$T_{step} - T_{ifp}$, ^{o}C
19.0	≤375	380	-5
25.0	≤400	395	+5
28.2	≤425	415	+10
31.6	≤450	435	+15
35.1	≤475	448	+27

The temperature below which η_{step} was measureable (i.e., $\tau < 60$ sec) is listed together with the initial freezing point of the electrolyte and the difference in these two temperatures. These data show that at a higher magnesium ion concentration the electrolytes are more prone to this partial freezing phenomenon (i.e., freezing occurs in melts that are farther away from their initial freezing points).

The data collected in this investigation can now be combined to yield a description of the processes associated with the discharge of a magnesium anode in these melts. As the anode is discharged, the magnesium ion content of the electrolyte adjacent to it is increased. If the melt was initially near its freezing point, this could result in the formation of small crystals adjacent to the anode, or if there were already small crystals

present, their number density and/or size would be increased. Just how this alteration of crystal concentration adjacent to the anode would affect the anodic polarization would depend on how rapidly mass transport phenomena could alleviate this situation. If these crystals could be carried away and redissolved in the bulk electrolyte as rapidly as they are formed, there would be no drastic change in the concentration or ohmic polarization. On the other hand, if mass transport rates were inadequate, the concentration polarization as well as the ohmic polarization would increase. This would in turn lead to a reduction in the current flow. As current flow is reduced, the rate at which mass transport processes are required to dissipate dissolved magnesium ion and crystalline material into the electrolyte is also reduced. When the rate of anodic dissolution is equal to the rate of dissipation of the products of reaction, a new steady-state situation is established.

From the results of table I, it is evident that, at high current densities, electrolytes that are above their initial freezing points can be made to exhibit what is conjectured to be crystallization adjacent to the anode that cannot be dissipated (step occurs). However, at temperatures below the initial freezing points of the melts, smaller currents can be passed through the cell without causing the severe anode polarization. This indicates that additional freezing will not occur if the current density is sufficiently low to allow adequate diffusion to occur. The reasons for the lithium ion taking part in charge neutralization are twofold. First, the lithium ion is very small and mobile compared with the magnesium ion, and, second, the magnesium ion is most likely present as a negatively charged complex ion (ref. 5). The negative charge on this large specie impedes the diffusion to the catholyte, where subsequent reaction takes place according to the reaction

$$MgCl_4^= + O^= \rightarrow MgO \downarrow + 4Cl^-$$
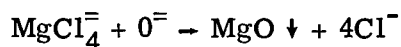
SUMMARY OF RESULTS

Based on the assumption that charge neutralization is due to lithium ion transport in copper oxide - magnesium thermal cells with a eutectic mixture of lithium chloride and potassium chloride as the electrolyte, a number of mixtures of magnesium chloride, potassium chloride, and lithium chloride were formulated which represented the anolytes of such cells at different stages of discharge.

Open-circuit voltage measurements in cells of the type $Mg-Mg^{+2} - Ag^{+1}-Ag$ revealed no unusual behavior of the magnesium-magnesium ion half-cell voltage in 12 different electrolyte mixtures. At magnesium ion concentrations below 2 molal, the Nernst relation was followed for a two-electron reaction.

Cooling curves of 18 electrolyte compositions revealed that the initial freezing points increase rapidly when the magnesium chloride content exceeds 22 mole percent.

Polarization studies of magnesium anodes in 12 different electrolyte mixtures were conducted by flowing moderate amounts of current (20 to 100 mA/cm^2) through cells with magnesium anodes and magnesium cathodes, which were equipped with silver-silver ion reference electrodes. When the initial freezing points of the electrolytes were within a few degrees of the operating temperatures of the electrochemical cells, severe anodic polarization sometimes occurred a few seconds after the application of the current. The lower the operating temperature of the cell, the higher the current density of the anode; and the higher the magnesium ion content of the melt, the shorter the time span between the application of the current to the cell and the onset of the massive anodic polarization. Not every polarization experiment resulted in a large increase in the anodic polarization during the time periods that were studied.

This behavior suggested that, in electrolytes containing magnesium ions, the mass transport processes are not always able to dissipate the magnesium ions resulting from anodic discharge, and the anolyte freezes adjacent to the anode. In an operating battery, this situation could result in premature failure. The use of more electrolyte per unit of cell capacity or adjustment of the mass transport characteristics of the cell to allow for better mixing of the anolyte and catholyte will tend to overcome this type of difficulty.

These results emphasize the importance of the electrolyte in an electrochemical cell, not only as an ionic conductor but also as a sink for the reaction products. For optimum utilization, this latter role must be understood and taken into account in the final cell design.

These findings may now be related to the premature failures observed previously (ref. 2) in the 12 ampere-hour cells. To review, the X-ray analyses showed that the anolytes of discharged cells contained large amounts of magnesium chloride (ref. 2). The discharge curves of these cells showed that the electrolytes apparently were freezing (ref. 3). The present magnesium half-cell polarization studies in conjunction with the phase diagram studies showed why the anode polarization would increase drastically as the magnesium chloride content of the electrolytes were increased.

The results of this magnesium half-cell study in combination with our previous findings (ref. 3) concerning the mass transport aspects of the copper oxide - magnesium thermal cell may now be related to cell design. Although larger amounts of electrolytes per unit of cell capacity are indicated (>2.0 g/A-hr), there is still no way of selecting the minimum amounts. If the final electrolyte composition were to be fixed at 35 mole percent magnesium chloride (initial freezing point $\cong 450^{\circ}$ C), it can be calculated that if the worst-case mass transport situation (charge neutralization due to lithium ion transport) were present exclusively, the critical electrolyte composition (35 mole % $MgCl_2$) would be reached at about 20 percent depth of discharge (i.e., 2.8 A-hr). Since some

of these cells delivered as many as 11 ampere-hours, the transport number of the lithium ion is obviously less than 1.0. It can be stated, however, that the transport number of the magnesium ion is also less than 1.0. Electrode configuration, type of separator, and other properties that affect the mass transport characteristics will all play a part in dictating the amount of electrolyte to be used.

Lewis Research Center,
  National Aeronautics and Space Administration,
    Cleveland, Ohio, November 25, 1969,
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