RE-ORDER NO. 67-143

FINAL REPORT

THE REACTIONS PERTAINING TO ZINC-SILVER AND CADMIUM-SILVER BATTERIES

JPL 951458

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

April 1, 1967

G. Myron Arcand

Department of Chemistry

Idaho State University

Pocatello, Idaho

ABSTRACT

The use of tritium as a tracer permits an estimate of the degree of hydration of zinc and cadmium oxides when they are precipitated from solutions containing ^3H_2O. The method of precipitation makes a great difference in tritium uptake in the zinc products. Thermogravimetric analysis indicates that the zinc solids are not simple oxides, hydroxides, or hydrates.

Chemically prepared AgO is 94% converted to Ag_2O in 4.5 hours at 140°C while electrolytically prepared AgO is 94% converted in 1.1 hours. Different techniques in electrolytic preparation cause differences in the thermal behavior of the product. The diffusion of oxygen from the interior of the material during decomposition may be slow and the AgO on the surface may be more active than that in the interior.

Silver dissolved in 10 VF KOH deposits on zinc sheet immersed in the solution with the resultant oxidation of zinc. Preliminary experiments suggest that the rate of reaction in a solution initially saturated with Ag(I) averaged over about 170 hours is about 3×10^{-3} milli-equivalents/hours or 0.8 ampere-hour/year.

OBJECTIVES

The objectives of the contract are three-fold:

(1) The characterization of cadmium and zinc anodic reaction products.

(2) The thermal decomposition of silver oxide and the measurement of the rate of decomposition of AgO and Ag_2O at various temperatures between 100°C and 200°C.

(3) The deposition of silver cathode material on zinc anodes.

A. PRECIPITATION OF ZINC AND CADMIUM OXIDES

Introduction

The reaction occurring at the zinc or cadmium electrode during electrochemical oxidation in concentrated KOH is generally represented by an equation of one of the following types:

$$M_{(s)} + 2\ OH^- = MO_{(s)} + H_2O + 2\ e^- \quad (1)$$

$$M_{(s)} + 2\ OH^- = M(OH)_{2\,(s)} + 2\ e^- \quad (2)$$

The physical nature of a metal hydroxide is quite different from that of an oxide, the former being gelatinous while the latter tends to form larger crystals. Therefore, the mechanical and electrical behavior of the electrode is probably rather dependent on which of the forms is produced during the oxidation process.

In principle, at least, there should be no question concerning cadmium since the oxide is brown while the hydroxide is white.[1] However, since a small quantity of brown can mask a

large quantity of white, the appearance of a brown precipitate need not provide a reliable estimate of the relative amounts of oxide and hydroxide. Both oxide and hydroxide of zinc are white, thus no color distinction is possible. Yet another complication arises because the products may actually be hydrated oxides rather than true hydroxides. Equation (2) above would apply stoichiometrically in either case but the physical nature of the precipitate might be different.

The literature is inconsistent in characterizing zinc precipitates. Papers by Chalyi and co-workers [2,3] speak of both the oxide and the hydroxide being formed. Duval[4] presents thermogravimetric data to show the formation of different types of precipitate depending on the method of preparation. While he usually refers to all of the materials as hydroxides, he states that many metals form only oxides when precipitated by KOH.[5] Sneed[6] states that the hydroxide can be prepared only under carefully controlled conditions.

A method of identifying hydrogen in the precipitate was necessary if the formation of hydroxide was to be proved. Tritium in the system should provide that identification. If tritiated water is added to an alkaline solution, there should be a rapid exchange of the tritium between water and the hydroxide. Any metal hydroxide precipitated from that solution should contain an amount of activity proportional to the total amount of hydrogen (as hydroxide or water of hydration) present in the solid. An oxide would be inactive.

Before the electrochemical reaction was investigated, the method was checked by means of a simple, chemical precipitation in the presence of tritiated water. KOH and NH_3 were used as precipitants to determine whether the products were different. Thermogravimetry provided a check on the tracer-study results.

Experimental

Reagents

Concentrated $Zn(NO_3)_2$ stock solutions were prepared from J. T. Baker Reagent Grade materials and were standardized iodometrically.[7] Subsequent solutions were standardized polarographically.[8] Concentrated $Cd(NO_3)_2$ stock solutions were standardized initially by a gravimetric method;[9] all subsequent standardizations and analyses were made polarographically.[10] J. T. Baker Reagent Grade 45% KOH solution was standardized against HCl and stored under nitrogen. Concentrated DuPont Reagent Grade ammonia was standardized against HCl.

Liquid scintillation solutions contained 7 g/l of 2,5-diphenyloxazole (PPO), 0.3 g/l of dimethyl-2,2-p-phenylenebis (5-phenyloxazole) (dimethyl POPOP), and 100 g/l of reagent grade napthalene in J. T. Baker Reagent Grade p-dioxane stabilized with sodium diethyldithiocarbamate. The fluors (PPO and dimethyl POPOP) were obtained from the Packard Instrument Company. The solutions and the stock p-dioxane were stored under nitrogen.

Equipment

The Nuclear-Chicago Model 703 liquid scintillation counting system was calibrated at 7°C with Packard Instrument Company standard tritiated water (^3H_2O). All λ-pipets were calibrated by determining the activity of the standard ^3H_2O they contained. Stock ^3H_2O, obtained from New England Nuclear Corporation, was standardized by comparison with standard ^3H_2O.

The thermogravimetric system consisted of a Cahn Model RG Electrobalance, a Cahn "Little Gem" thermobalance attachment, an F & M Model 240M temperature controller with a Chromel-Alumel thermocouple, and a recorder. Bausch and Lomb VOM-5, Brown Electronik 1-millivolt, and Neff Instrument Corporation Model 401 PA recorders were used. The platinum sample pan, about 5 mm in diameter and 2.5 mm deep, was hung from the balance beam in an 8 mm ID Pyrex tube as shown in Figure 1. The thermocouple sensing unit was mounted through a cork stopper in the bottom of the tube so that the sensing element was about 3 mm below the center of the sample pan.

Procedures

Each group of tracer experiments consisted of three precipitations from tritiated solutions and one from an inactive solution. Sufficient stock ^3H_2O was added to the $Zn(NO_3)_2$ and $Cd(NO_3)_2$ solutions to provide accurately known activities between 10^3 and 10^4 decompositions/minute/microliter (dpm/λ). Fifty millimoles of Zn(II) or Cd(II) was precipitated with an equivalent amount of

base. In some instances, temperature was controlled throughout the precipitation while in others the mixing was done rapidly without temperature control. When an inert atmosphere was desirable, a reaction vessel of the type shown in Figure 2 was used and nitrogen was passed over the solution during the procedure.

The precipitate was separated from the mixture, washed, and usually dried in air or in vacuum over P_2O_5. The precipitate was then redissolved in 6 VF HNO_3 and the solutions diluted to exactly 25 ml with water. In most of the early experiments, washing was accomplished with pure distilled water. Later, the wash water contained ^3H_2O of a concentration comparable with that in the active salt solutions. Washing was generally continued until no test for nitrate in the washing was obtained.[11] 50-λ portions of each solution of redissolved Zn(II) were transferred to counting vials containing 15 ml of counting solution. All counting samples were prepared in triplicate.

In the early experiments, precipitates were washed by adding portions of water to the precipitate, stirring, settling, and decanting through a sintered-glass filter. The process was slow, decanting was only partially effective, and washing on the filter was not consistently effective. Later, a technique referred to as the "centrifuge method" was employed. The precipitate was transferred to a centrifuge tube of adequate size, a 15-ml portion of water added, the mixture stirred and centrifuged three times, and the supernatant decanted off. Decantation was effective and

much better contact was established between the solid and the wash liquid. The process was repeated for the number of washings deemed necessary for the removal of the contaminants.

In some cases where NH_3 was used as the precipitant, washing was continued until the washings showed a negative test for NH_3 with Nessler reagent.[12]

Inactive precipitates were prepared and treated as described above. A known quantity of stock ^3H_2O was added, the solution diluted to 25 ml, and 50-λ samples were transferred to counting vials. From the measured count rate and the known activity, the counting efficiency was calculated. The efficiency in the comparison solution was assumed to be the same as that in the sample solutions.

All scintillation samples were placed in the refrigerator chamber for at least 12 hours before counting. Counting time was adjusted to provide an optimum total count. The counter was operated automatically and data were recorded on printed tape.

In some experiments with Zn(II), excess KOH was added so that the final, calculated supernatant concentrations were 1.0 VF, 2.0 VF, and 5.0 VF KOH. No correction was attempted for zincate formation.

Rough exchange experiments were run with zinc precipitates by adding weighed amounts of dry solid to measured quantities of water in closed containers and stirring the mixtures magnetically. Where the precipitate was active initially, the

water was inactive initially; where the precipitate was inactive initially, ^3H_2O was added to the water. At intervals, 50-λ portions of the supernatant were removed for analysis. The total volume was corrected for sample removal. At the end of the run, the tritium and Zn(II) content of the precipitate was determined. No attempt was made to control temperature.

Thermograms were made of dried, inactive samples of zinc precipitates formed by precipitation with NH_3 and with KOH. Initial sample weights were generally less than 10 mg. The heating rate was controlled at approximately 5°C/min.

Zinc electrodes were prepared by electrodepositing zinc from a KOH solution saturated with ZnO onto Exmet Corporation expanded silver mesh, 5 Ag 7-4/0. The screen containing the metal was washed with water and pressed while wet in a Lucite die.

Silver oxide electrodes were prepared from chemically-prepared AgO which was lightly pressed between two pieces of silver mesh.

Preliminary electro-oxidations of zinc were carried out in KOH saturated with ZnO using the electrodes described above. A Lucite container provided inter-electrode distances of about 5 mm.

Results and Discussion

The relative amount of $Zn(OH)_2$ contained in a given precipitate was calculated from the measured activity. The proportion of ^3H to ^1H in the solid hydroxide or hydrate should be the

same as that in the total water and hydroxide in the complete system. By calculating the activity per mole of hydrogen atoms in the complete system, the activity expected in a given amount of precipitate if it is entirely $Zn(OH)_2$ can be calculated. Comparison of the measured activity with that expected gives an estimate of the relative amounts of hydroxide and oxide.

The results of precipitating zinc with NH_3 are shown in Table 1. Where no control was exercised, the maximum temperature was about 50-55°C. There is no apparent temperature effect in this system.

Washing with distilled water caused considerable loss in activity when the precipitate was formed by adding Zn(II) to NH_3. When the procedure was reversed, loss of activity was much smaller. The method of precipitation had little effect on the precipitate activity when the solid was washed with water containing tritium.

A complex zinc ammine is likely to form in the presence of excess NH_3. This complex may be coprecipitated with $Zn(OH)_2$ and thus be carried out with the solid material. On washing with water, the complex may revert to the hydroxide releasing the ammonia. The removal of NH_3 and its replacement with inactive hydroxide in the washing process would result in a precipitate activity which did not reflect the hydroxide present. On the other hand, if excess NH_3 is never permitted, then the solid would contain only oxide or hydroxide, the latter being active.

The washing procedure might carry out some of the activity through exchange, but most would be held by the precipitate. Thus, the activity would provide a better estimate of the hydroxide content in this case.

If the precipitate was formed in the presence of excess NH_3 but was washed with water containing tritium, then the conversion of the complex to the hydroxide would replace NH_3 with active hydroxide and the activity of the solid should give a reasonable estimate of the relative amount of hydroxide present. There is fair agreement between the two methods if the wash water is active. Where the NH_3 is in excess part of the time, the final activity is still low, but the observed difference may not be significant.

Table 2 shows the results of precipitating Zn(II) with KOH. In all cases, the apparent percentage of $Zn(OH)_2$ was low (less than 30%) and the high result may be spurious. The first sets of results are uncertain because washing was done with distilled water and, in the first set, washing was incomplete. There may be a significant difference between the results of the last two groups of experiments, (9-11) and (12-14). The averages of the two groups do not differ significantly, but experiment 12 gave very high results and may be in error. There were several procedural differences here, and it is not possible to isolate an effect with these data.

The use of tritiated wash water followed by careful

drying of the precipitate in vacuum over P_2O_5 seems the best way to achieve reasonably consistent results. When commercial ZnO was washed with ^3H_2O and treated as described above, no activity remained in the precipitate. While it is true that the physical nature of ZnO is different from that of the precipitates which were formed, these results provide some confidence that any occluded water is removed by the drying process. Even if active water were occluded in the precipitates, there is a significant difference in the nature of the precipitates since the measured activities are so different.

Table 3 shows the results of precipitating Cd(II) with KOH and with NH_3. Losses of cadmium were excessive when NH_3 was used, probably because significant complex formation occurs when the pH of the system is high enough to cause precipitation. In the few experiments performed thus far, washing with tritiated water indicated that the predominant species in the precipitate is $Cd(OH)_2$ when KOH is the precipitating agent. There seems to be a significant difference when the order of mixing is reversed; thus, cadmium recovery is less and the apparent percentage of $Cd(OH)_2$ is greater when Cd(II) is added to KOH than when the reverse procedure is used. These results must be verified.

Table 4 shows the results of several experiments to determine the effect of excess KOH on the precipitate. Each experimental result is the average of two or three precipitations.

The data are rough because when the experiments were performed, the crude washing procedures were still being used. Even so, the results are quite consistent. There is no real evidence that excess KOH affects the composition of the precipitate.

The results of some crude exchange experiments are given in Tables 5 and 6. The initially active material lost activity and the initially inactive material gained activity over the period of seven days. The supernatant was initially inactive if the solid was active and vice versa. It is curious that the final precipitate activities were almost the same. However, the ratio of supernatant activity to solid activity is about 70 times greater for the "ZnO" system than for the "$Zn(OH)_2$" system. This suggests that the "ZnO" contains much less $Zn(OH)_2$ than the other material. Only by assuming that the equilibrium constant for the exchange has the form, $K = A_s/A_p^2$, can the ratios be correlated with the data from the precipitation experiments.

Thermograms of the inactive precipitates formed by both procedures are shown in Figures 3 and 4. There is a significant difference between the behaviors of the two materials. A mass of information in the old literature[14] provides little help in interpretation. Various hydrate forms have been proposed with varying stabilities. Only one form, $ZnO \cdot 2H_2O$, which is not mentioned in the literature, might give curves similar to those in Figure 3. The mechanism would require that the material lose one water at the first break and be com-

pletely converted to ZnO at the second. The curve in Figure 4 suggests the possibility that the material is a mixture of $ZnO \cdot 2H_2O$, $ZnO \cdot H_2O$, and ZnO with a mole-ratio of 1:3:4 in the order shown. Unfortunately, there is poor correlation between this interpretation and the tracer data unless one assumes that only the more easily removed water is tritiated. The weight loss in the first step of the curve in Figure 3 is about 7.6 times that in the first step in Figure 4. This agrees favorably with the relative activities of the corresponding precipitates. However, it would be rash to suggest that only one of the two water molecules in the dihydrate would be tritiated so that the monohydrate formed would be inactive.

When zinc-precipitate thermograms are made and when the temperature rises above 150°C, a white residue forms inside the hangdown tube above and below the furnace where the temperature is relatively low. The amount of material is too small to analyze with equipment available and looks too small to account for the observed weight loss. No zinc compound present would be expected to vaporize at any of the temperatures attained and it is unlikely that KOH would be present in sufficient quantity to behave this way.

Cells are being fabricated in which to investigate the product formed by electrochemical oxidation of zinc. The best zinc electrodes made to date are produced by plating Zn on expanded silver screen from KOH saturated with ZnO, washing the deposit and pressing the moist material onto the screen. In

some cases, the electrodes have been dried under nitrogen and in others have been used wet. The counter electrodes have been made by pasting AgO on expanded silver screen. These have been only partially satisfactory and must be held together with layers of silver mesh on both outside surfaces. Contact with the screen has been poor so that the AgO electrode capacity has been insufficient generally. A cell which employs a minimum volume of electrolyte solution has been constructed. Although the solutions are saturated with ZnO, newly formed product either dissolves to supersaturate the solution or forms a colloidal suspension. Standard separator material will be wrapped around the zinc plate but isolated from the AgO plate to act as a retainer for the product material.

Obtaining complete oxidation of the zinc has been difficult. In most battery operations, the zinc is in excess so that some metal will remain when the battery is discharged. Here the zinc must be as completely oxidized as possible so that problems of separating the oxide from the metal will be minimized.

Conclusions

The tracer technique provides a method for distinguishing between two types of "$Zn(OH)_2$" precipitate and may also indicate the relative amounts of hydroxide contained therein. The thermograms of the materials have not yet yielded to interpretation, but they can be correlated with data from tracer precipitations to some extent. The method should be suitable

for the study of the solid product formed during electrolytic oxidation of zinc.

$Cd(OH)_2$ apparently is the predominant species formed when Cd(II) is precipitated with KOH. The order of addition seems to have a significant effect on the amount of $Cd(OH)_2$ present, the hydroxide content being higher when Cd(II) is added to KOH. Thermograms have not been made for cadmium precipitates.

Proposed Work

The activity of the precipitates formed on the electrolytic oxidation of Zn and Cd in the presence of tritiated KOH solutions should be studied in an effort to determine the effective hydration of the oxides formed. It now seems that further work is in order to determine the structure and exact chemical composition of the solids formed. The thermograms suggest that the materials are by no means simple and that there may be several forms coexisting in a given sample. Careful elemental analysis should be carried out as well as crystallographic studies, both optical and X-ray. Since the products seem to be quite sensitive to the method of formation, it is probably advisable to investigate the effect, if any, of different techniques of electrode formation on the character of the product. Pressing zinc metal onto the grid causes the formation of a very hard central layer which is oxidized with relative difficulty. It is quite possible that this material will form a different product than the softer outer layers.

B. THERMAL DECOMPOSITION OF AgO

Introduction

Argentic oxide decomposes at high temperatures as described by the equations:

$$2\ AgO = Ag_2O + 1/2\ O_2 \qquad (3)$$

$$Ag_2O = 2\ Ag + 1/2\ O_2 \qquad (4)$$

Reaction (3) is significant at 120°C and becomes relatively rapid at 140-150°C. Work reported recently[15] has shown that, under certain conditions, reaction (3) is 50% complete after 80 hours at 100°C. Allen[16] reports several discontinuities in thermograms made in vacuum below 200°C.

Crude experiments done at JPL showed that both reactions (3) and (4) occur to some extent in the vicinity of 135°C. The rate of reaction (3) seemed dependent on very slight exposure to light or very small variations in oxygen pressure or both. This work was done by heating samples in crucibles in a drying oven. It was necessary to cool the samples in a desiccator before weighing; drastic, periodic temperature changes occurred throughout each experiment and the samples were disturbed during transfer. Use of a thermobalance permits control of exposure to light, control of the atmosphere over the solid, and continuous recording of weight changes at any given temperature. The balance has made possible runs extending over several days with intermittent or continuous recording of data. Equipment recently acquired will allow the direct determination of time derivatives of the weight-loss.

Experimental

Procedures:

AgO was prepared by a modification of the method described by Bailar.[17] The washed precipitate was dried over P_2O_5 at about 35 torr for several hours. The weighed material was analyzed by heating it to 600°C for 20 minutes, cooling, and weighing. The precipitate was considered dry if the observed loss in weight agreed with that calculated for decomposition of AgO. In later experiments, this analysis was accomplished with the thermobalance.

AgO was prepared electrolytically by a modification of the method of Jolly.[18] Material was obtained using both platinum-screen and platinum-foil anodes.

The arrangement of the thermogravimetric equipment has been described in Part A of this report. The system was modified for long-term, constant-temperature runs by lengthening the hangdown tube to 56 cm and attaching it to the balance through a hole in the balance table. The thermocouple was mounted inside the furnace but outside the hangdown tube about 9 cm from the bottom of the tube and directly opposite the sample. The tube was sprayed with anti-static material and was directly grounded at the balance case and at a point just above the furnace about 19 cm above the bottom of the tube. An aluminum-foil heat radiator about 10 cm long was wrapped around the tube just above the table.

Thermograms were made at a constant $140^{\circ} \pm 2^{\circ}C$ over periods ranging from 6 hours to 10 days. Where runs extended beyond a few hours, recording was intermittent because changes were slight.

Thermograms were made with the temperature increasing at about $5^{\circ}C$/min. In these cases, shorter hangdown tubes were generally used and the thermocouple was mounted as shown in Figure 2. The tube was directly grounded at the balance case and below the furnace. No heat radiator was needed.

Results and Discussion

Figure 5 shows a typical rising-temperature thermogram for chemically prepared AgO. The results are normalized so that the total weight loss is represented as 1.000. Half of the weight loss occurred almost exactly half way between the step portions of the curve.

Figure 6 shows the composite thermogram for two runs made with material prepared electrochemically on a Pt-foil anode. The midpoint of the plateau occurs at about 0.51 which suggests that the samples contained a volatile impurity which did not show up at the heating rate employed. The total weight loss for pure AgO on heating should be 12.91% of the original sample weight; the loss for this material was 13.30%. A small amount of moisture, for example, could account for this difference and for the upward shift of the plateau midpoint. Alternatively, a small amount of Ag_2O_3 could also account for the change.

Figure 7 shows a thermogram for a run made with electrolytically prepared AgO in which the anode was platinum mesh. The loss in weight amounts to 18.62% of the total, much more than the theoretical. The midpoint of the plateau is at about 0.27 which suggests a relatively small amount of AgO. A large amount of Ag_2O should cause a smaller total weight loss. Moisture in the sample could account for the greater loss, but should have occurred before the plateau causing the midpoint to be above 0.5.

The second break shows an unusual form in that the beginning of the rise is more gradual than in the previous examples and there is a discontinuity at about 420°C. Just before this discontinuity, the curve bends over as one would expect. If this curve is extrapolated to conform with those in other examples, it would level off at about 0.75. This corresponds to a total loss of about 14%--high, but much closer to the expected value. The break suggests that another substance is being decomposed in this temperature range. The possibility of a sub-oxide has been mentioned[15], but no convincing proof of its existence is available. It still would not account for the high loss.

There is the possibility that some nitrate still is present in the material since an intermediate in this method of preparation is a nitrate. However, if the nitrate is not completely decomposed during the procedure, the product usually explodes at a temperature lower than the decomposition temperature of AgO. No such catastrophic event was observed with this material.

Figure 8 shows a constant-temperature thermogram of chemically prepared AgO extending over a period of almost 220 hours. The region of rapid change occurs in the first four or five hours. Beyond that, change is very gradual. At 4.5 hours, the weight loss corresponds to 47% of the total loss. If this is entirely oxygen loss, it corresponds to a 94% conversion to Ag_2O in that period of time. The curve also shows that, after a long period, Ag_2O is converted to Ag. This point is borne out by the appearance of a surface layer of metallic-looking material. However, this surface layer often appears before the 50% point is reached. That depends on the gross mass of sample, probably because the inner portions of the sample are not as quickly reduced if the sample is large so that silver metal will form on the surface before all of the internal AgO is converted to Ag_2O.

There is an interesting discontinuity in the curve after about a half-hour of heating. The initial rate of change is relatively high, decreases slightly, then increases and continues to follow what might be considered a normal curve. The discontinuity has been observed in all runs made with this sample batch. The phenomenon might be caused by the presence of some higher oxidation state of silver or by the presence of moisture. However, one would expect moisture to be driven off more quickly at this temperature and one would not expect an increase in rate after the removal of the water.

A more attractive explanation is that oxygen from the surface layers is removed as soon as it is formed while oxygen in the body of the material must have time to diffuse to the surface before it can escape. Thus, there would be a high initial loss of weight which would decrease as the surface layer became depleted. Then, as oxygen from the interior reached the surface, it would be lost and the rate would increase until an equilibrium between the rate of formation within the solid and the rate of removal from the surface was obtained. Nagy et al[15] mention the existence of "trapped" oxygen during thermal decomposition at lower temperatures.

Figure 9 shows a constant-temperature thermogram for AgO prepared electrolytically on Pt-foil anodes. The decomposition of AgO is much more rapid in this case, being 94% converted to Ag_2O in 1.1 hours. Also, apparent complete conversion occurs at less than 20 hours as compared with about 50 hours for the chemically prepared material.

Only a hint of a discontinuity similar to that observed in Figure 8 is seen here. This appears as a slow start in the first few minutes of the decomposition. It is not safe to say that this is anything other than a slow beginning of decomposition as the temperature of the sample approaches 140°C.

This particular material gave the rising-temperature thermogram of Figure 6 which compares quite favorably with that in Figure 5 for chemically prepared material. Particle size may be a factor, but no measurements are available for these

samples. Qualitative observations suggest that there is not much difference in particle size in the two samples. Both monoclinic[19] and tetragonal[20] forms of AgO have been reported. Possibly, different crystal forms are producing the observed difference in behavior.

Conclusions

It is evident that AgO is converted almost entirely to Ag_2O in less than twelve hours when heated in air and light at 140°C. There is evidence that the material used is not pure AgO but may contain water; some higher oxide of silver, or both.

There is strong evidence that electrochemically prepared AgO is different from the chemically prepared material. Furthermore, the physical structure of the anode on which AgO is formed appears to have a significant effect on the behavior of the product. It is reasonable to assume that this effect might be traced to differences in true current density. The physical or chemical differences in the materials have not been determined.

Proposed Work

The effect of method of preparation on the thermal stability of the AgO should be studied further. Differences in crystal size, shape, and aggregation should be sought. Existence of possible chemical species other than Ag_2O and AgO should be considered.

The effect of atmospheric conditions and of light

radiation on the rate of decomposition should be studied. It is possible that control of the oxygen content in the atmosphere could decrease the rate of thermal decomposition. If this were so, then the possibility of heat sterilization of dry, charged silver electrodes would be worth considering again.

C. DEPOSITION OF SILVER ON ZINC

Introduction

When silver dissolved in KOH solution comes in contact with zinc metal, silver is reduced with concurrent oxidation of zinc. Self-discharge is said to take place if this occurs in a charged electrochemical cell. Great pains are taken to prevent this phenomenon with the result that the current-carrying capacity of the cell is severely limited.

Dirkse[21] suggests that the deposition of silver does not inhibit the performance of the zinc electrode. Thus it may be possible to modify the separator system to permit more efficient cell operation.

The rate of corrosion of the zinc electrode through reaction with silver will depend on the rate of solution of AgO and/or Ag_2O and on the rate of transport of Ag(I) through the solution.

Experimental

10.00 VF KOH was stirred with a small quantity of Ag_2O for one week. A weighed 1-cm^2 piece of pure zinc was placed in a portion of the solution while a similar piece was placed in pure

10.00 VF KOH. Periodically, the zinc sheets were removed, washed, dried, and reweighed. They were then replaced in their respective solutions and the process repeated.

Results

The weight changes are shown in Table 7. A black coating, probably finely divided silver, was seen to form on the surface of the zinc in the solution containing silver. This coating did not adhere well and was mostly washed off the sheet when it was being prepared for weighing. Thus, the weight loss is caused by the oxidation of zinc and the loss of most of the reaction products. The weight loss was considerably greater when silver was present than when it was absent, as would be expected. The data are quite erratic and about all that can be said at this point is that the silver does have a significant effect.

The rate of loss for the sheets used here is about 9×10^{-3} ampere-hour/hour. Doubtless this rate would be affected by the nature of the electrode surface. At the rate shown, 1.3 years would be required to cause a capacity loss in these electrodes of 1 ampere-hour.

Proposed Work

The rate of solution of silver should be determined in alkaline solutions. The solid phase should be both powdered AgO and AgO plaques.

The rate of deposition of Ag on Zn should be determined accurately.

The rate of deposition of Ag on Zn should be studied as a function of the anodic potential and current density during discharge of an experimental cell.

The effect of silver deposition on the electrochemical characteristics and the capacity of smooth and porous zinc electrodes should be studied.

Expt Number	Temp (°C)	Number of Washings	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Remarks
1	25	6	72.5	37.1	Zn(II) added to NH_3 solution.
2	"	"	55.0	7.5	
3	"	"	75.0	29.8	
4	55	11	81.6	(101)	NH_3 added to Zn(II) solution.
5	"	"	87.5	96.2	
6	"	"	84.5	97.3	
7	--	12	80.0	1.2	Zn(II) added to NH_3 solution. Washing by centrifuge method.
8	--	"	80.0	17.5	No temperature control.
9	--	"	82.5	12.1	
10	--	9	95.7	83.0	Zn(II) added to NH_3 solution. Wash water contained tritium.
11	--	"	91.6	90.2	Washing by centrifuge method.
12	--	"	90.0	99.3	

Table 1

Precipitation of ZnO with NH_3

Expt Number	Temp (°C)	Number of Washings	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Remarks
13	20-25	9	90.0	87.5	NH_3 added to Zn(II) solution. Wash water contained tritium.
14	"	"	90.0	86.3	Washing by centrifuge method.
15	"	"	88.3	101	
16	"	"	91.3	70.0	Zn(II) added to NH_3 solution. Wash water contained tritium.
17	"	"	88.3	79.2	Washing by centrifuge method.
18	"	"	91.5	76.4	
19	--	9	88.0	85.4	NH_3 added to Zn(II) solution. Wash water contained tritium.
20	--	"	88.0	89.7	Washing by centrifuge method.
21	--	"	90.8	87.7	

Table 1
(continued)

Expt Number	Temp. (°C)	Number of Washings	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Remarks
1	55	6	100	11.1	Zn(II) added to KOH solution.
2	"	"	100	18.0	
3	"	"	98	21.9	
4	25	10	94.5	1.4	KOH added to Zn(II) solution.
5	"	"	92.5	21.8	
6	"	11	100	0.7	"
7	"	"	96.3	8.9	
8	"	"	95.0	13.8	
9	--	5	92.0	14.3	KOH added to Zn(II) solution. Wash water contained tritium.
10	--	"	92.5	19.9	Washing by centrifuge method.
11	--	"	94.5	19.9	
12	20-25	9	86.3	27.7	Zn(II) added to KOH solution. Wash water contained tritium.
13	"	"	84.8	9.1	Washed by centrifuge method.
14	"	"	85.0	7.0	

Table 2

Precipitation of ZnO with NH_3

Expt Number	Temp (°C)	Number of Washings	Cd (II) Recovered (meq)	Apparent % $Cd(OH)_2$	Remarks
1	25	11	88.8	40.4	Cd(II) added to KOH solution.
2	"	"	87.5	34.3	
3	"	"	86.3	45.2	
4	"	9	25.0	16.9	Cd(II) added to NH_3 solution.
5	"	"	30.4	42.1	
6	"	"	26.3	14.7	
7	--	8	78.8	95.1	Cd(II) added to KOH solution. Wash water contained tritium.
8	--	"	79.3	92.4	Washed by centrifuge method.
9	--	"	85.5	86.9	KOH added to Cd(II) solution. Wash water contained tritium.
10	--	"	85.5	81.3	Washed by centrifuge method.
11	--	"	85.5	82.8	

Table 3

Precipitation of Cadmium with KOH and NH_3

Expt Number	n (1)	Temp (°C)	Concentration KOH (VF)	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Standard Deviation (%)
1 (2)	3	54	1.0	99	7.3	0.7
2 (2)	2	54	2.0	89	6.6	---
3 (2)	3	50	5.0	50	4.5	0.3
4 (2)	3	25	1.0	96	4.1	2.4
5	3	25	2.0	89	2.5	0.5
6	2	25	5.0	42	3.8	--

(1) Number of runs, each consisting of three precipitations, in each experiment.

(2) Recovery based on one analysis in each set of runs.

Table 4

Effect of Final Hydroxide Concentration

Table 5

Exchange of Tritium Between Water and "ZnO"

Precipitate formed with KOH

Time (days)	Supernatant Activity (dpm x 10^{-8})	Precipitate Activity (dpm/meq)
0	1.1	0
0.17	1.1	---
1.2	1.1	---
2.2	1.1	---
6	1.1	---
7	1.1	3.6×10^{3}

Table 6

Exchange of Tritium Between Water and "$Zn(OH)_2$"

Precipitate formed with NH_3

Time (days)	Supernatant Activity (dpm x 10^{-6})	Precipitate Activity (dpm/meq)
0	0	3.7×10^4
0[1]	0.55	---
0.17	1.1	---
1.2	1.4	---
2.2	1.4	---
6	1.5	---
7	1.5	3.4×10^3

(1) Sample taken immediately after mixing water with precipitate.

Table 7

Weight Loss of Zinc in Reaction with Ag (I)

Time (hours)	Weight Loss in KOH-Ag (I) (g)	Rate (g/hr)	Weight Loss in KOH (g)	Rate (g/hr)
		4.2×10^{-4}		8.6×10^{-6}
28	0.01172		0.00024	
		9.3×10^{-5}		2.3×10^{-5}
47	0.01348		0.00067	
		4.4×10^{-5}		9.1×10^{-6}
70	0.01450		0.00088	
		1.3×10^{-5}		5.4×10^{-6}
167	0.01580		0.00140	
		1.4×10^{-4}		3.1×10^{-5}
24	0.00328		0.00075	
		9.5×10^{-5}		2.6×10^{-5}
48	0.00556		0.00137	
		8.3×10^{-5}		1.5×10^{-5}
72	0.00755		0.00174	
		1.4×10^{-4}		1.3×10^{-5}
168	0.02107		0.00294	
		8.4×10^{-5}		9×10^{-6}
216	0.02511		0.00337	

The second column above shows the total weight loss in the Ag (I)-KOH solution and is the combined effect of oxidation by silver and oxidation by the KOH solution. Two sets of runs are shown.

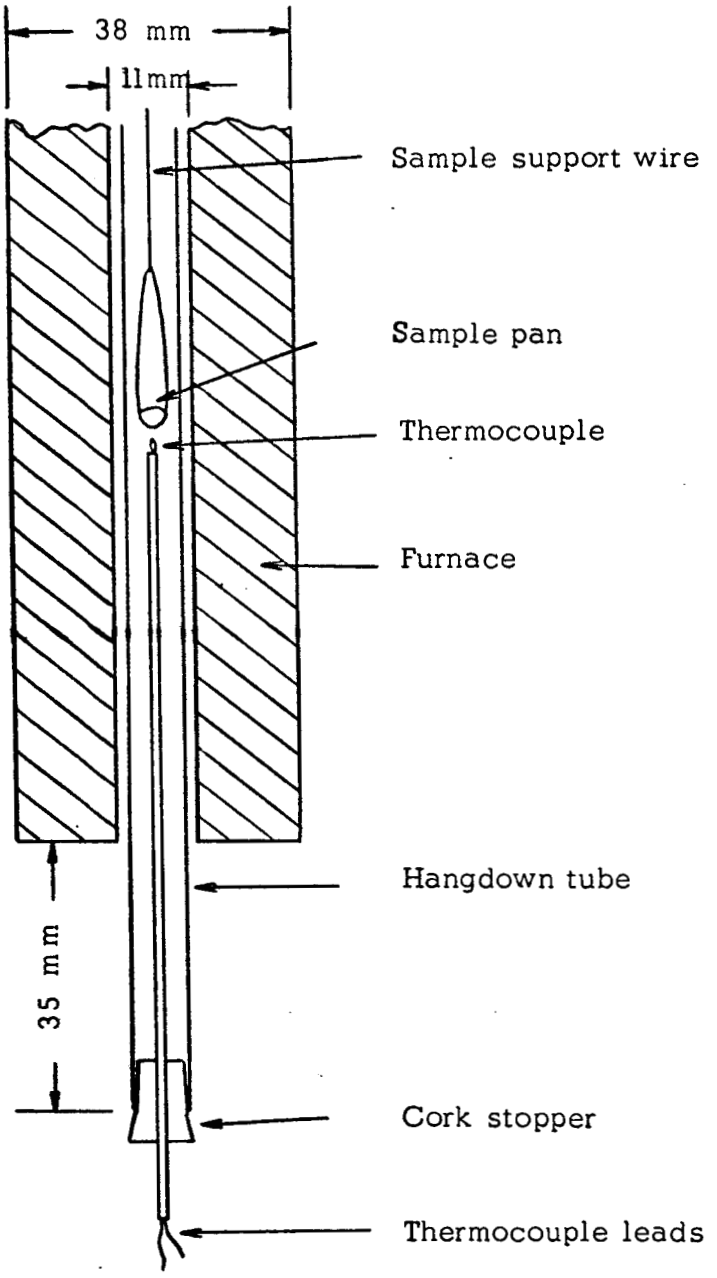

Figure 1. Configuration of Thermogravimetric Heater.

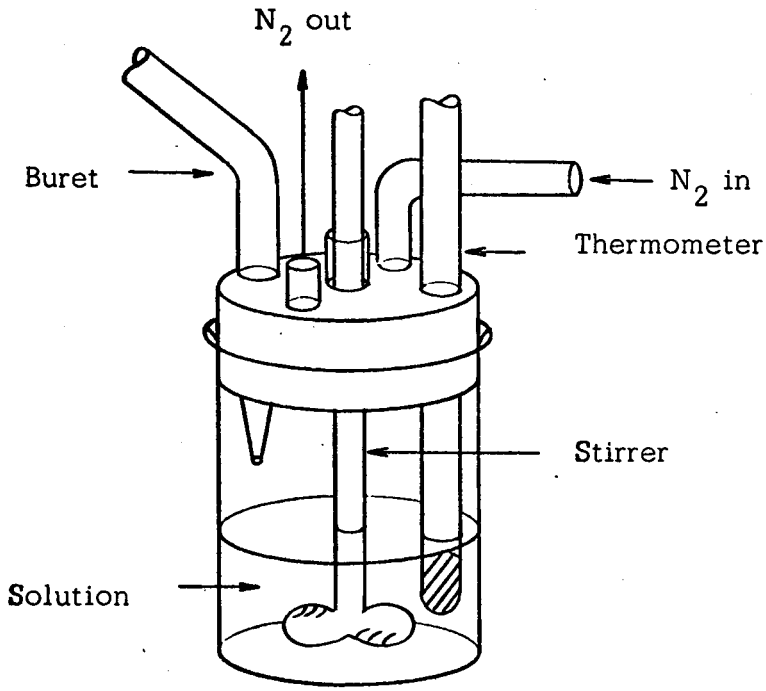

Figure 2. Precipitation Vessel

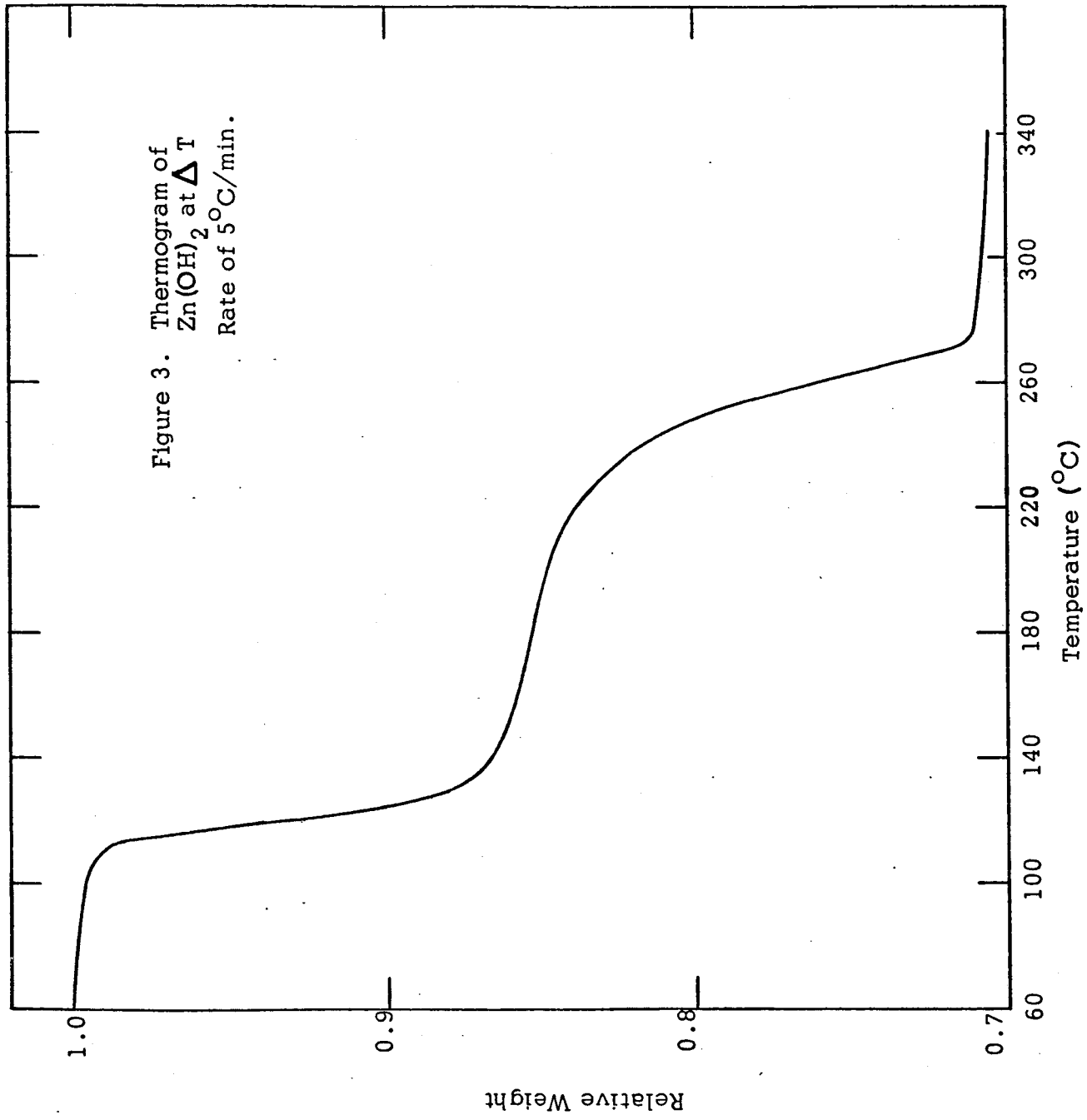

Figure 3. Thermogram of $Zn(OH)_2$ at ΔT Rate of 5°C/min.

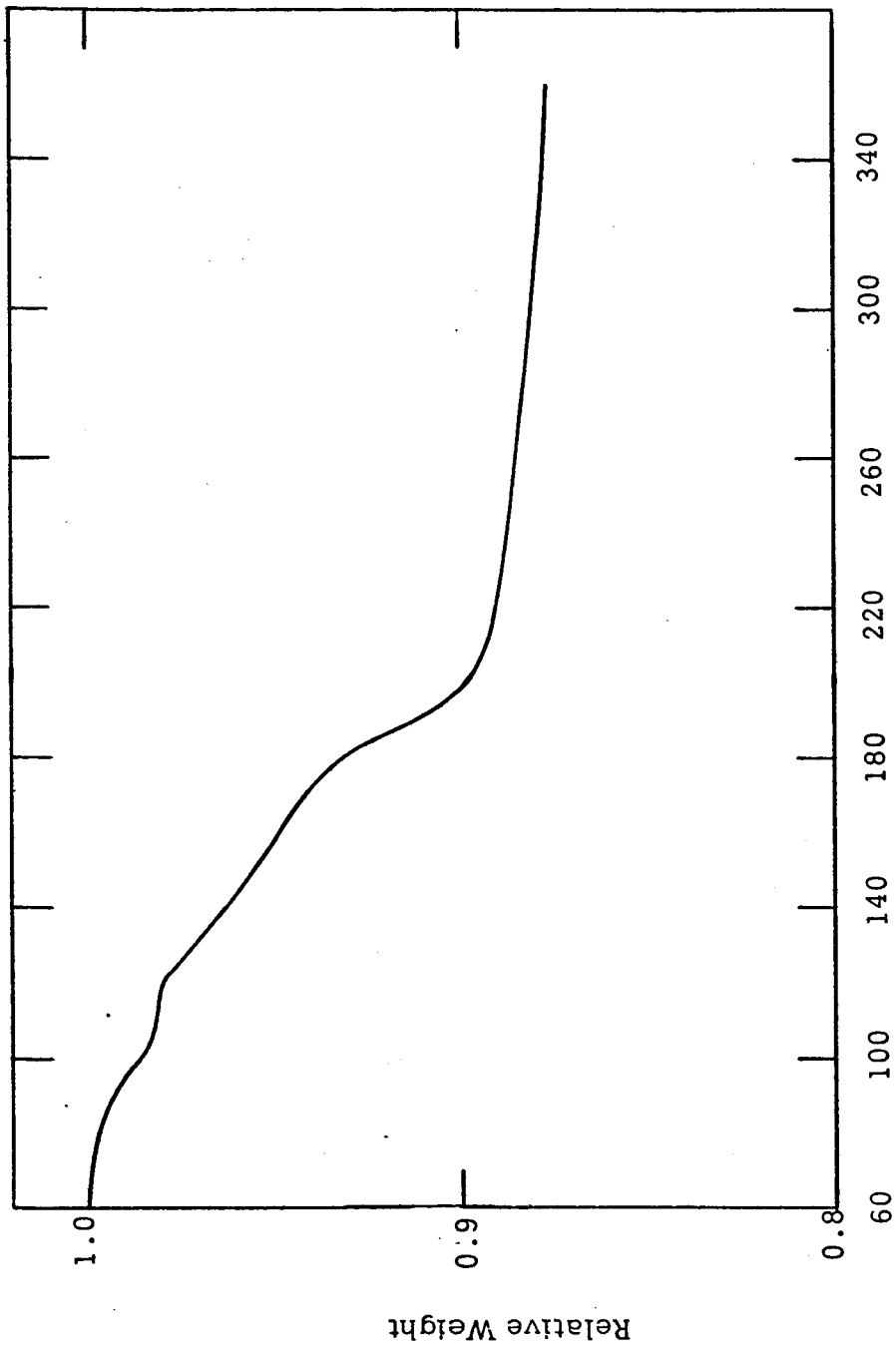

Figure 4. Thermogram of "ZnO" at ΔT Rate of 5°C/min.

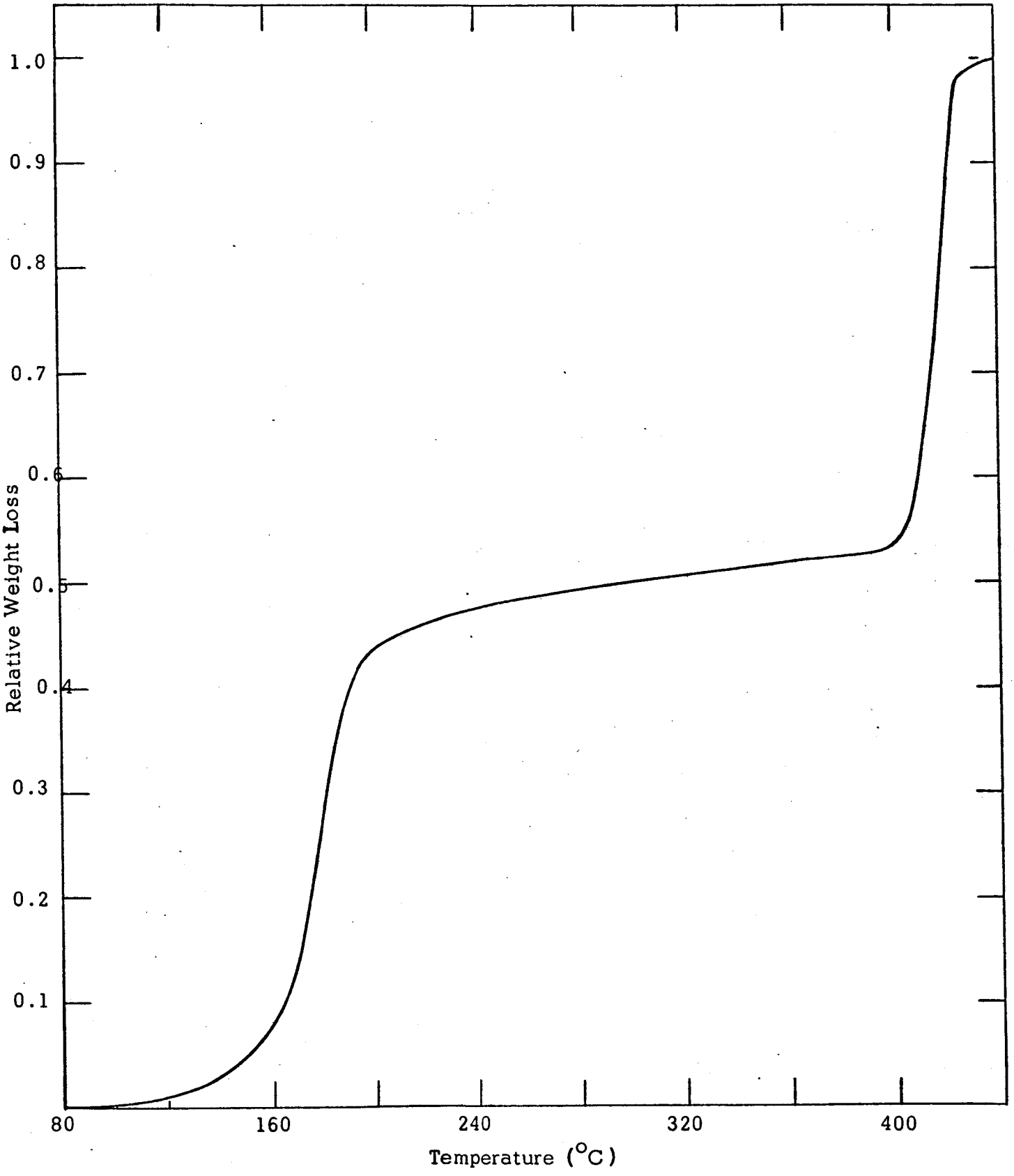

Figure 5. Thermogram of Chemically Prepared AgO at ΔT Rate of 5°C/min.

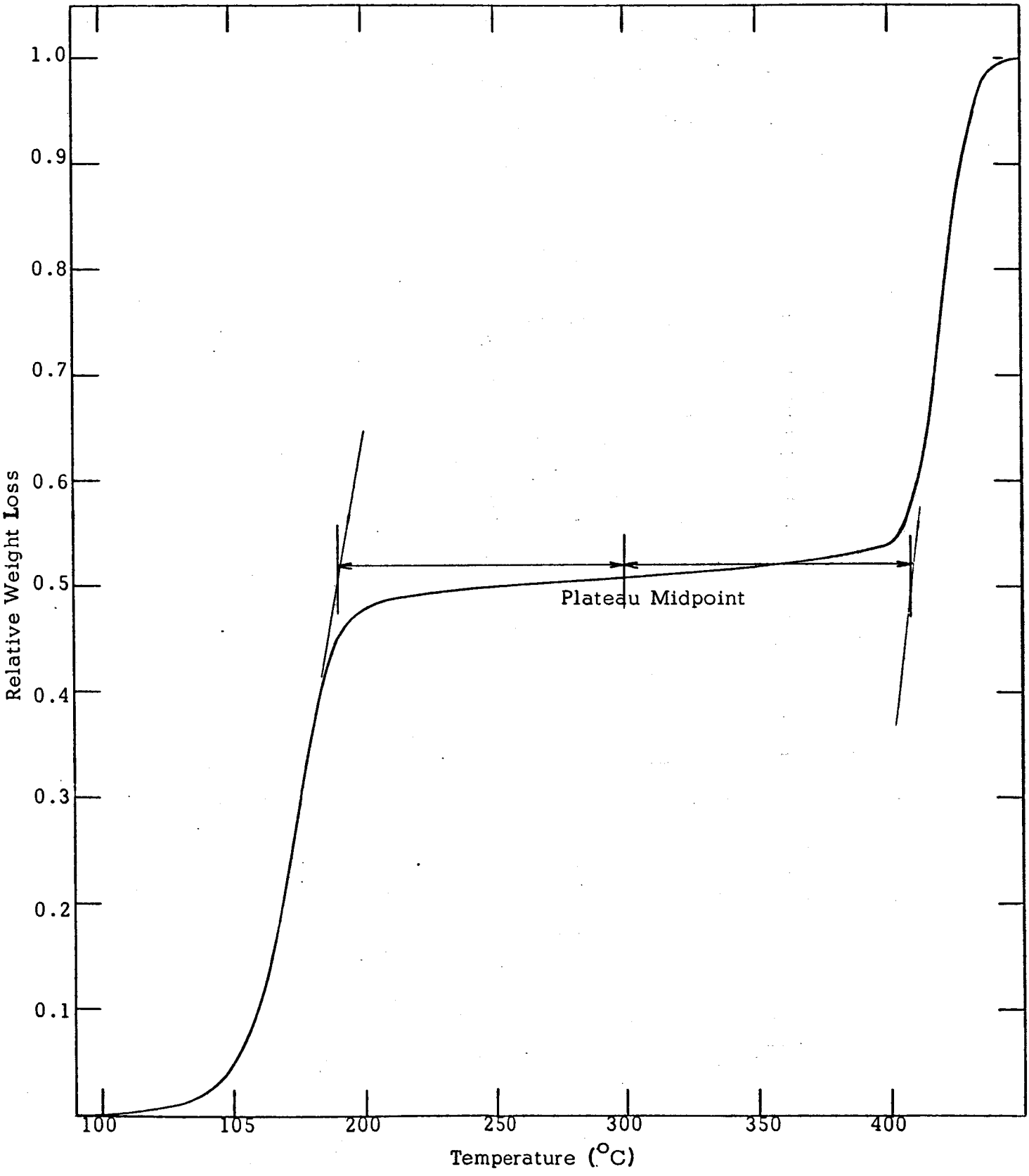

Figure 6. Thermogram of Electrochemically Prepared AgO at ΔT Rate of 5°C/min. AgO prepared on Ag-foil Anode.

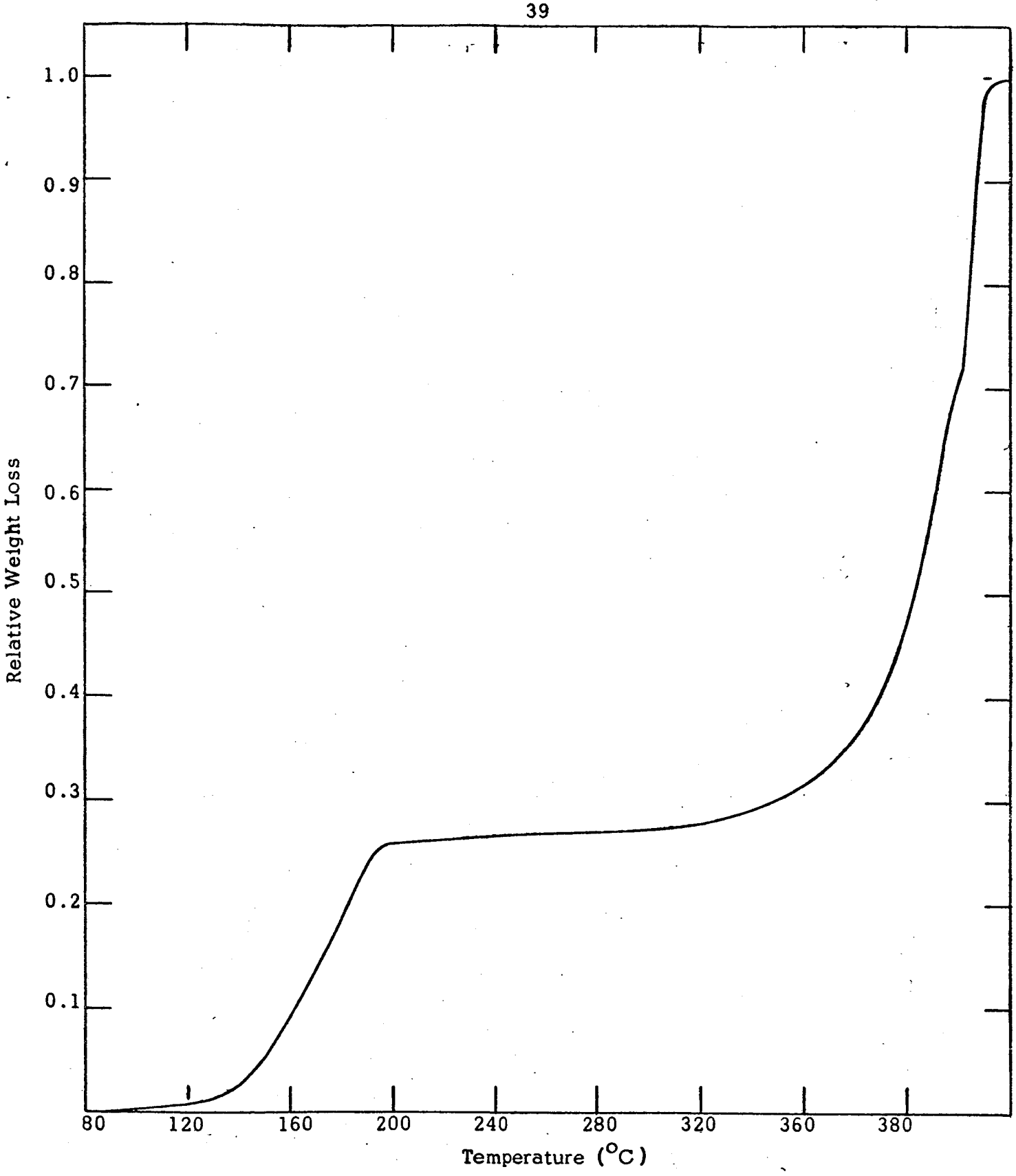

Figure 7. Thermogram of Electrochemically Prepared AgO at ΔT Rate of 5°C/min. AgO Prepared on Ag-mesh Anode.

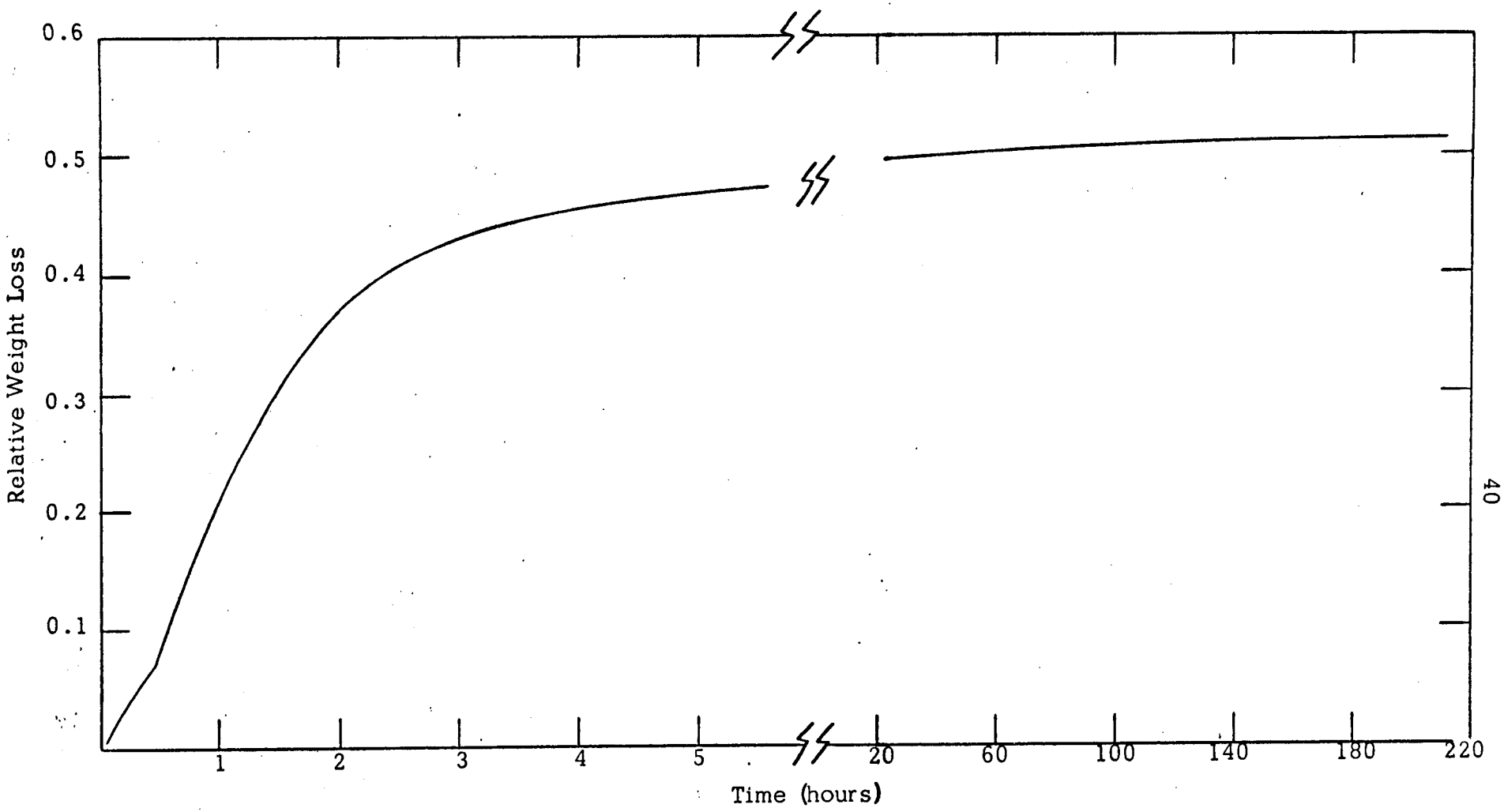

Figure 8. Constant-Temperature Thermogram of Chemically Prepared AgO at 140°C.

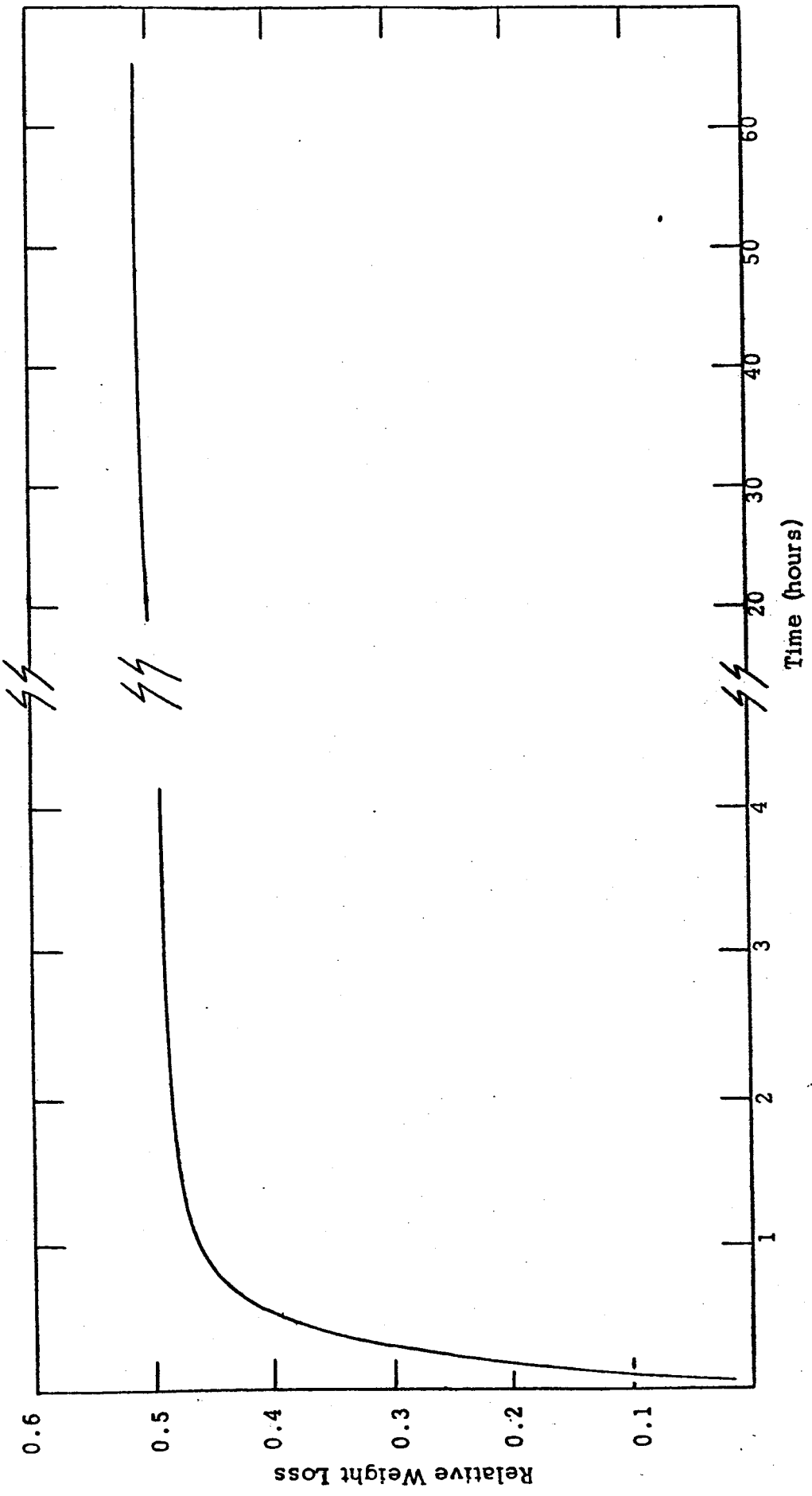

Figure 9. Constant-Temperature Thermogram of Electrochemically Prepared AgO at 140°C.

REFERENCES

[1]N. V. Sidgwick, "The Chemical Elements and Their Compounds", Vol. 1, Oxford University Press, London, 1950, p. 269.

[2]V. P. Chalyi, V. T. Zorya, and Z. Ya. Makarova, Zh. Neorgan. Khim. 10, 265(1965).

[3]S. P. Rozhenko and V. P. Chalyi, Ukr. Khim. Zh. 30, 900(1964).

[4]C. Duval, "Inorganic Thermogravimetric Analysis", Elsevier Publishing Co., New York, N.Y., 1953, pp. 275-6.

[5]Ibid., p. 238.

[6]M. C. Sneed, J. L. Maynard, and R. C. Brasted, "Comprehensive **Inorganic Chemistry**", Vol. 4, D. van Nostrand Co., Inc., New York, N.Y., 1955, p.54.

[7]E. K. Maun and E. H. Swift, Anal. Chem. 21, 798(1949).

[8]I. M. Kolthoff and P. J. Elving, "Treatise of Analytical Chemistry", Part II, Vol. 3, Interscience Publishers, New York, N. Y., 1961, p. 158.

[9]Ibid., p. 215.

[10]Ibid., p. 208.

[11]F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., New York, N.Y., 1958, p. 326.

[12]R. A. Day, Jr. and A. L. Underwood, "Quantitative Analysis, Laboratory Manual", Prentice-Hall, Inc., Englewood Cliffs, N.J. 1958,p.146.

[13]"Handbook of Chemistry and Physics", 13th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1954, pp. 1869, 1871, 1913.

[14]J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry",Vol. 4, Longmans, Green and Co., New York, N.Y., 1940, pp. 521-30.

[15]G. D. Nagy, W. J. Moroz, and E.J. Casey, Proc. Ann. Power Scources Conf., 19, 80(1965).

REFERENCES

[16]J. A. Allen, Proc. Australian Conf. Electrochem., 1st, Sydney, Hobart, Australia 1963, 72(Pub. 1965).

[17]J. O. Bailar, Jr., "Inorganic Synthesis", Vol. 4, McGraw-Hill Book Co., New York, N.Y., 1953, p. 12.

[18]W. L. Jolly, "Synthetic Inorganic Chemistry", Prentice-Hall, Inc. Englewood Cliffs, N.J., 1960, pp. 148-9.

[19]V. Scatturin, P. Bellon, and A. J. Salkind, J. Electrochem. Soc. 108, 819(1961).

[20]A. S. McKie and D. Clark, Proc. Third International Battery Symposium, Pergamon Press Ltd., Oxford, 1962, p. 171.

[21]T. P. Dirkse, "Transport and Reaction Processes in Silver Oxide-Zinc Batteries," APL-TR-66-5, March 1966, final report on contract AF 33(615)-2297.