FIRST QUARTERLY REPORT

INVESTIGATION OF ELECTRODE MATERIALS FOR ALKALINE BATTERIES

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NOTICE

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ABSTRACT

Greatest reduction of Ag(I) from a 10 VF KOH solution saturated with Ag_2O occurs within the first 24 hours with little subsequent change. Chronopotentiograms, at 147 mA/cm^2, of zinc plates upon which silver has been deposited show transition times of 24 to 50 seconds as compared with 69 seconds for untreated plates. The results suggest that silver is deposited first as a strongly adherent layer followed by weakly held layers.

AgO decomposes rapidly at first at 160° and then only slowly over a period of several hours. Decomposition of Ag_2O is considerable at 290°, but is insignificant below that temperature. Rough calculations show the activation energy for the thermal decomposition of AgO to be 26.2 kcal/mole and that of Ag_2O to be 43 kcal/mole.

Amalgam electrodes with lithium, sodium, potassium, magnesium, calcium, barium, aluminum, copper, lead, zinc, and cadmium as active metals have been considered. The zinc-amalgam electrode gives good performance at high current-densities; its open-circuit potential is about -1.4 V *vs* Hg/HgO. The potassium-amalgam electrode also shows good discharge behavior; its open-circuit potential is about -1.8 V *vs* Hg/HgO. The "cadmium-amalgam" electrode is poorly defined and actually may be a potassium-amalgam electrode.

Hydrogen polarization studies on zinc electrodes have not yielded definitive information yet. Preliminary data indicate extrapolated exchange current-densities (i_o) around 10 $\mu A/cm^2$ in 0.10 VF KOH and about 35 $\mu A/cm^2$ in 1 VF KOH. A rough experiment in 10 VF KOH suggested an i_o of about 140 $\mu A/cm^2$ in that system.

The objectives of the contract are four-fold:

(1) Study of the reduction of Ag(I) by zinc.

(2) Study of the thermal decomposition of AgO and Ag_2O.

(3) Study of amalgam electrodes.

(4) Study of the evolution of gas at electrodes.

Each of the above topics will be taken in order. However, the first two areas of study have been plagued with equipment malfunctions and will, necessarily, be quite short.

A. DEPOSITION OF SILVER ON ZINC FROM KOH SOLUTIONS.

Experimental

A tracer method was used to determine the silver concentration in the electrolyte solutions. The stock solution was 0.0252 VF* in silver and contained an appropriate amount of $^{110}Ag^m$. Usually, the initial silver activity was about 1×10^5 cpm/μ eq. of silver as determined with the Nuclear-Chicago Model 703 liquid scintillation counter. No attempt was made to determine the absolute activity because the only requirement was a relationship between the observed count rate and the amount of silver present. The stock was recalibrated frequently because the half-life of $^{110}Ag^m$ is only 260 days.

The temperature was controlled at $25^\circ \pm 0.1^\circ$ in all experiments. One ml of silver stock was pipetted into about 50 ml of 10 VF KOH in a polyethylene bottle. A piece of zinc sheet was hung in the solution on a glass hook, the bottle was capped, and the system was stirred with a magnetic spin-bar. Portions (usually 50 λ) were withdrawn periodically. Several methods were used to remove the solid particles; none were completely satisfying. In some cases, the solution was drawn through a medium-porosity glass frit, in some, the solution was centrifuged, and in some, the

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*VF signifies that the solution contains the designated number of formula-weights of solute per liter of solution.

solution was both filtered and centrifuged. Results seemed much the same in all cases. Consequently, centrifugation was used in later experiments because it is easier and there is less danger of excessive adsorption of silver. The samples were added to 15 ml of scintillator cocktail and counted.

The composition of the scintillator cocktail was 7g/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 naphthalene in J. T. Baker Reagent Grade p-dioxane stabilized with sodium diethyl-dithiocarbamate. The fluors (PPO and dimethyl-POPOP) were obtained from the Packard Instrument Co.

Chronopotentiograms were run using a Model C629CMK Electronics Measurements constant-current power supply and a Dohrmann Model RSC1100 multirange recorder. Transition times were measured with a Labline electric timer accurate to 0.1 sec. The cell consisted of a zinc sheet disc cut to fit the cap of a 20 ml polyethylene vial. The screw threads were dipped in hot paraffin and the zinc was mounted and fastened in place by screwing down the vial cap. Electrical connection was made through the cap. The bottom of the vial was cut out to allow addition of the electrolyte solution and access for the platinum auxiliary electrode and the salt bridge. The auxiliary electrode was placed inside a tube with a fritted-glass end in order to minimize turbulance in the main body of solution. The salt bridge was not fitted with a Luggin capillary and no attempt was made to bring the tip close to the zinc plate because only the transition time was sought and the transition voltage-rise was both large and abrupt. The reference electrode was Hg/HgO in 10 VF KOH.

Results and Discussion

The results of the deposition experiments are quite erratic as can be seen in Table 1. In most cases, the major concentration decrease occurs in the first 24 hours. The rate is a maximum initially (around -1.8×10^{-5} VF/hour) and decreases, as expected, to average around 9×10^{-6} VF/hour in the next 24 hours. After 24 hours, the concentration seems to remain fairly constant around 2-4 x 10^{-6} VF.

These data are quantitatively suspect although they present a reasonable qualitative trend. Probably the most disturbing aspect is the scatter in the first measured concentrations. These should approach the solubility concentrations of silver yet are considerably lower and vary by as much as 90%. Such error cannot be traced to pipet errors because nothing of this magnitude has been observed when calibrating stock solutions where a variation of 5% is considered poor. However, the total amount of silver added to the KOH solutions was not much greater than that necessary to saturate the solution. Therefore, excessive losses may be occurring through adsorption on the container walls. New solubility experiments are being made in which the amount of silver added is at least five times that required for saturation. This should provide a check on the polarographic solubility measurements previously reported[1] and, if these prove reproducible, will provide another attack on the rate of deposition.

Chronopotentiometric experiments were begun to determine some of the electrochemical effects of a deposit of silver on the solid zinc anode. Comparisons will be made with the results previously obtained in this lab on zinc which was not exposed to silver[2]. Only two sets of experiments were successful. The results are shown in Table 2.

The transition time for a horizontal zinc plate anode in 10 VF KOH operating at 147 mA/cm^2 was found to be 69.0 sec^2. This value was reproducible whether multiple runs were made on the same plate or fresh plates were used for each run. The transition times where silver has been deposited are considerably shorter and increase with successive runs. One can calculate that about 0.02 meq of silver is deposited on the zinc in the first 24 hours of deposition. This deposit will mask a portion of the zinc working surface so that the effective surface is less than in the case of the untreated plate. At the same time, an equivalent amount of ZnO would be formed, although this probably dissolves quickly to produce zincate in these solutions. Even so, this amount is only about 10% of that required to passivate the electrode. Beyond the transition time the voltage rises to that required to evolve oxygen and, unless the current is stopped, oxygen continues to form rather vigorously. In so doing, the gas will sweep away any loosely adhering material. Thus, the higher transition times for successive runs should be expected since more of the zinc area is exposed.

In both experiments shown here, the transition times were roughly doubled in the second run indicating considerable removal of interfering material. The increase in the third run was not more than 2.5%, yet the transition times were still much less than the 69 seconds of the comparison system. Evidently, the <u>loosely held</u> silver was almost all swept away in the first run and only a small residue remained in the second run or a relatively adherent material was swept off with difficulty.

Data are not sufficiently complete to explain the differences or lack of differences between the two runs. In the first case, 23 hours were allowed for deposition while in the second, only 4 hours were allowed, yet the transition times for the first runs were very nearly the same and shorter times were found for the 4 hour case in subsequent runs. This suggests that only an initial layer of silver adheres to the zinc while subsequent layers are sloughed off and do not cause further passivating effects. This interpretation is supported by the appearance of a dark precipitate in the Ag(I)-KOH solutions when the zinc metal is added.

Proposed Work

The solubility of Ag(I) in 10 <u>VF</u> KOH will be re-examined by the tracer technique and, depending on the results of these experiments, deposition procedures will be changed. Further chronopotentiograms will be run to see if transition times will approach those made without prior deposition of silver. If the solubility experiments give results significantly different from those previously reported, a third method of analysis will be considered to verify one of the techniques.

B. THE THERMAL DECOMPOSITION OF AgO AND Ag_2O

Experimental

The principal experimental arrangement of the thermobalance and accessories has been described previously[1]. Recently, the balance was mounted in a Cahn #2005 Glass Vacuum Bottle accessory. The hangdown tube was attached to the bottle by means of a T/S 40/35 joint. The inner thermocouple was attached at the bottom of the tube through a T/S 10/30 joint. The control thermocouple was attached to the outside of the tube with glass hooks. Ports were made available in the bottle to permit control of the atmosphere near the sample.

Most experiments were performed as described previously. In some cases, the rising-temperature thermograms were arrested for several hours at temperatures between 250° and 300° and then continued to complete decomposition. No attempt was made to shield the samples from light in those runs made with the balance in the bottle.

Results and Discussion

In order to determine the energies of activation for the decomposition of AgO and Ag_2O, it is necessary to know how much of the particular species is present initially. This has posed a major problem since the Ag_2O plateau in all of the rising-temperature thermograms has had a considerable negative slope. One was forced to conclude that the decomposition of Ag_2O probably began before the decomposition of AgO was completed. Consequently, no accurate estimate of the total amount of either AgO or Ag_2O could be made. An attempt was made to alleviate this problem by arresting the thermograms in the region between 250° and 300° for several hours. The results are shown in Figures 1 and 2. Both are thermograms of Ames AgO made with a temperature increase of 5°/min. The sample represented in Figure 1 was run before the balance was mounted in the bottle. The temperature was arrested and held at 270° for 2.8 hours whereupon the rising-temperature regime was continued. The sample represented in Figure 2 was run with the balance in the bottle. Here, the temperature was arrested and held at 290° for 2.5 hours. There is an obvious difference in the thermograms in the vicinity of and beyond the hold-point. Before the hold-point, the two thermograms are quite similar, although the sample represented in Figure 2 seems to decompose somewhat more rapidly. Beyond the hold-point, the differences are marked. In Figure 2, the relative loss at the end of the hold is about 0.51, indicating definite onset of Ag_2O decomposition; in Figure 1, the relative loss <u>at the same temperature</u> is about 0.48. These differences are significant. Further along, the shape of the curve differs with that in Figure 2 bending over fairly smoothly while that in Figure 1 bends down abruptly. This latter behavior has been characteristic of the Ames material. Neither of these thermograms has been repeated; some behavior in either could be spurious.

Figure 3 shows a thermogram of Ames AgO made at two different constant temperatures. The decomposition of AgO at 160° follows a path similar to those observed previously. After about 5-1/2 hours, the temperature was quickly brought to 287° and held there for the remainder of the experiment. Two points are obvious: the material continues to lose weight over the whole period and the rate of loss appears to increase with time. Both points are surprising. In Figures 1 and 2, there is no positive appearance of Ag_2O decomposition until the temperature reaches about 330°. In Figure 3, there is an initial, fairly rapid decrease, then a leveling off, and, finally, an increase in the rate of loss. This increase is difficult to explain. One would normally expect the rate to decrease as the amount of active material decreased. The tendency in these decompositions is for the silver metal to form on the surface of the material and work in as the decomposition proceeds. One would expect this to inhibit the loss-rate.

In order to determine whether the above phenomenon was a peculiar characteristic of the Ames AgO, a sample of K & K Ag_2O was run starting at 200° and progressing stepwise up to 290° as shown in Figure 4. The first drop, which is shown on the plot as a negative region, is assumed to be loss of moisture. Here, again, the material decomposes at 290° and the rate of decomposition increases with time. In fact, the effect is somewhat greater than in the case of the Ames sample. Below 290°, no significant decomposition seems to occur, although something might appear if the material were left longer at these temperatures. The rapid decrease which appeared in Figure 3 on raising the temperature to 289° is probably the decomposition of the last residue of AgO.

There is still much to learn about these systems at the higher temperatures and the experiments reported here must be repeated. It is still not known that the new experimental configuration has no effect on the results. It seems, however, that complete decomposition of AgO can be accomplished at 250° without significant decomposition of Ag_2O, at least for a period of several hours.

Data similar to that shown in Figure 1 were used to estimate the activation energies for the decomposition of Ames AgO and its product Ag_2O. The method described by Flynn and Wall[3], along with data by Doyle[4], was used. Thermograms were run at 2°/min, 5°/min, and 10°/min. All were interrupted but not at the same temperature so the accuracy of the data is suspect. The calculations show the activation energies to be 26.2 kcal/mole for AgO and 43 kcal/mole for Ag_2O. This work must be repeated in light of more recent information and supporting methods should be used to check the values obtained.

Proposed Work

Some further investigations will be made in the region between 200° and 300° in order that adequate data may be obtained for the determination of activation energies and reaction orders for both AgO and Ag_2O. The effects of changes in both illumination and atmosphere will be investigated. A new, split-tube furnace has been purchased which should allow better temperature stability and more reproducible placement of samples.

C. THE STUDY OF AMALGAM ELECTRODES

Introduction

Amalgamated zinc electrodes are used quite commonly in battery construction, largely to prevent self-discharge of the zinc. This is the case in the usual silver-zinc cell or the Ruben mercury cell. There is little indication that liquid amalgams have been used in which an active metal is completely dissolved in mercury. Exceptions are thermally regenerative systems such as those developed by Atomics International and by Allis-Chalmers and the cadmium-amalgam electrode used in the Weston standard cell. This last is not designed to deliver power. A patent has been issued to Mallory Batteries Ltd. for a regenerative cell employing a liquid zinc-amalgam cell, but no performance data are available[5]. Some crude experiments indicated that the liquid-amalgam electrode could be used as a regenerative electrode in an aqueous alkaline electrolyte system. There was evidence than an active metal dissolved in mercury could produce a remarkably high current-density with little or no apparent damage to the electrode. The results of some exploratory work done with both zinc- and calcium-amalgams have been reported[1].

Alkali-metal amalgams have been used almost exclusively for the deposition of the metals as in the Kastner-Kellner process or for controlled reduction in certain chemical reactions. The possibilities of these materials as power-producing electrodes does not seem to have been explored. The purpose of this project is to investigate a number of such systems and to make some fundamental studies of the more promising systems.

Experimental

Mercury was purified by drawing air through the liquid for several hours, pinholing the material into dilute HNO_3, and triply distilling the product. All chemicals were J. T. Baker Reagent Grade. Potassium hydroxide was obtained both as 45% solutions and as pellets; all other hydroxides were obtained in solid form.

All experiments were carried out in some form of H-cell with the working electrode in one arm and the platinum auxiliary electrode in the other. The Hg/HgO reference electrode was connected to the working electrode compartment by means of a polyethylene capillary bridge, the tip of which rested a few millimeters from the amalgam surface.

Current for both charge and discharge was supplied by a Model C629CMK Electronics Measurements constant-current power supply. Potentials were followed with either a Dohrmann Model RSC1100 multi-range recorder or with a Honeywell Model Y143X(58) 1-mV recorder coupled with a Cahn #1490 recorder controller.

In many cases, the working electrode did not fill the bottom of the half-cell compartment. Usually, a small cup was cemented into the bottom of the compartment and a platinum contact was sealed into it. The cup contained the amalgam and surface areas were controlled by controlling the diameter of the cup.

Electrolyte solutions contained the hydroxide of the metal to be amalgamated. Where the solubility of the hydroxide was low, the hydroxide concentration was raised by adding KOH. The amalgams were charged at some convenient current-density, i.e., one which did not require an excessive potential or cause immediate gassing. Charge was usually continued until the amalgam was obviously saturated as estimated by the appearance of solid material in the amalgam. Discharges were made at various current-densities, the maximum rate being determined by the voltage drop below the open-circuit electrode potential. All potentials were measured against the Hg/HgO electrode and are so reported. Discharge was considered complete when the electrode potential dropped to half the open-circuit potential.

Stand life experiments were made by charging a number of amalgam electrodes equally and allowing them to stand for varying lengths of time before discharge. The cells each contained approximately the same amount of mercury and identical electrolyte solutions. They were connected in series to the constant-current power supply and charged at a fixed rate. Generally, these amalgams were not charged to full capacity. After charging was discontinued, the amalgams were withdrawn through stopcocks in the bottoms of the cell compartments into test tubes containing KOH electrolyte solutions. These were stoppered and set aside for prescribed periods. Each was discharged at a rate which had been observed to be efficient and the relative recovery determined.

Results and Discussion

A number of possible systems was surveyed. Of the alkali-metal group, lithium, sodium, and potassium systems were considered. Magnesium, calcium, and barium were tried in the alkaline-earth group. Only aluminum was attempted in the third group. Lead was considered in Group IV, copper in Group Ib, zinc and cadmium in Group IIb. Preliminary zinc results were reported previously[1].

Of the metals used in the preliminary investigations, lithium, sodium, copper, and lead proved generally unsatisfactory, although sodium probably needs further consideration. The discharge behaviors obtained with the other metals are shown in Figures 5 through 10. Figure 5 shows the discharge of a potassium-amalgam electrode in a saturated KOH electrolyte solution. The discharge curve is quite flat over most of the range and the electrode produced almost 100% recovery of charge at the respectable current-density of 214 mA/cm^2. The potential was about 0.4 V higher than that obtained with a zinc electrode.

Figure 6 shows the discharge behavior of a magnesium-amalgam electrode in an electrolyte solution 10 <u>VF</u> in KOH and saturated with MgO. Again, almost 100%

of the charge was recovered, but at a considerably lower current-density. The voltage characteristics are not as good as for potassium amalgam.

Figure 7 shows the behavior of a calcium-amalgam electrode. This is not as good as either the magnesium- or potassium-amalgam electrodes.

Figure 8 shows the behavior of a barium-amalgam electrode. The electrolyte solution was 10 <u>VF</u> KOH saturated with $Ba(OH)_2$. The open-circuit potential was quite high, but the discharge characteristics were not as good as in the previous examples. Not only was the recovery less than 86%, but the voltage changed quite rapidly and somewhat erratically.

The aluminum-amalgam electrode characteristics are shown in Figure 9. The behavior is not very satisfactory, a low current-density being required. However, it was possible to recover 100% of the charge.

The cadmium-amalgam electrode showed promising behavior with good voltage characteristics at current-densities as high as 535 mA/cm^2. Charge recovery was not 100%, but probably would have been at more moderate discharge rates.

The behavior illustrated in Figure 10 led to considerable further investigation of the cadmium-amalgam electrode, an investigation which is still in progress. The immediate point which attracts attention is the electrode potential, both at open circuit and during discharge. This value is approximately twice that which is expected for this system. Furthermore, it has proved to be a characteristic of the electrolytic formation. Cadmium amalgams produced by dissolving the metal in mercury form electrodes with open-circuit potentials of -0.78 V while solid cadmium electrodes give open-circuit potentials of about -0.88 V. Although this information has aroused suspicion, the electrode will be referred to as "cadmium-amalgam" for the time being.

Various mercury-pool sizes were tried with different charge and discharge rates. As yet, no definite trend in behavior has been observed in the "cadmium-amalgam" system, although behavior certainly has varied. Figure 11 shows three discharge curves at different current-densities. The potentials during discharge at the highest current-density is lower as would be expected. However, the higher open-circuit potential and the lower charge recovery in Curve II is not expected. System II contained 0.047 A-hr of charge while system I contained only 0.020 A-hr. However, system II contained 0.0045 A-hr/g of Hg while system I contained 0.0047 A-hr/g of Hg, about the same concentration of active metal. System II was charged at 14.4 mA/cm^2 while system I was charged at 35.7 mA/cm^2. System III contained 0.140 A-hr of charge, but its concentration was 0.0038 A-hr/g of Hg. This system was charged at 17.4 mA/cm^2, yet the discharge characteristics at 65 mA/cm^2 are poorer than either of the others in terms of potential and poorer than system I in charge recovery. One might expect that a higher concentration of metal in the amalgam would cause a higher open-circuit potential and this is observed on comparing system III with either of the others. However, the reverse effect is observed in comparing systems I and II. One would normally expect poorer recovery of charge at the higher current-densities, yet this does not always appear.

In all of the "cadmium-amalgam" charging curves, the electrode potential rose almost immediately to values around -1.65 V or higher. Since the Cd/CdO potential should be about -0.8 V, it seemed that there should be a plateau at the less negative value. Therefore, a series of experiments was made in which the electrodes were charged for short periods and alternately left on open circuit for identical periods. In general, the charge and open-circuit intervals were one minute each. The results of one of these experiments at the very low charge rate of 1.8 mA/cm^2 are shown in Figure 12. It is seen that a low voltage-plateau does, indeed, exist on open circuit and that, finally, the open-circuit potential approaches that of the charge potential. A similar charge curve, followed by a discharge curve, is shown in Figure 13. Here, the charge rate is about ten times that in the previous case and the open-circuit potential equals the charge potential after about 15 minutes. Obviously, the difference between charge potential and open-circuit potential cannot be attributed to IR drop because the difference disappears after a time while the IR drop should remain essentially unchanged. These phenomena must be considered to be electrochemical or chemical in nature.

Before further consideration of the anomalies of the "cadmium-amalgam" electrode, the behavior of the potassium-amalgam electrode should be observed. Several plots of the discharge behavior of these electrodes are shown in Figure 14. All of these electrodes show fairly satisfactory performance with recoveries near 90% for the two lower current-densities. Here, again, there is a case in which a higher discharge current-density yielded a greater energy recovery. Furthermore, the discharge potentials for these two cases (systems I and II) were almost identical through 85% of the discharge. At 455 mA/cm^2, both the voltage and charge recovery were low.

On comparing Figures 11 and 14, one sees considerable similarity in behavior. At current-densities up to about 200 mA/cm^2, both yield reasonably flat discharge curves with voltages lying between -1.6 and -1.8 V. In general, the systems containing cadmium seem to produce potentials slightly more negative than those containing only potassium. However, data are not sufficient to determine if these differences are significant. The similarities in these figures suggest that what has been called a "cadmium-amalgam" electrode actually may be a potassium-amalgam electrode and that relatively little, if any, cadmium enters the amalgam in the alkaline system. The difference in potential between the Cd/CdO electrode and the K(Hg)/K$^+$ electrode is such that one would expect the potassium-amalgam to reduce Cd(II) to the metal. This apparently happens to form a metallic layer on the surface which does not amalgamate even slowly. The reaction is slow so that the electrode potential on open circuit is controlled by the Cd/CdO electrode initially, but, as the concentration of potassium builds up in the amalgam, the amalgam electrode ultimately controls the entire system. Thus, in Figure 12, the potassium content is not sufficient to control the open-circuit potential until the experiment has been running for about 40 minutes.

One would expect that, on discharge, the Cd/Cd0 electrode would ultimately control again. However, as is seen in Figure 13, this does not happen. There is the possibility that, in basic solution, the mercury makes poor electrical contact with the undissolved metal on the surface so that no Cd/Cd0 potential can be measured; this is contrary to the charge behavior.

If the "cadmium-amalgam" electrode is charged very slowly or by the alternate open-circuit-charge procedure and is then discharged shortly after the open-circuit and charge potentials coincide, the recovery is found to be very poor. This suggests that, under these conditions, most of the potassium is re-oxidized during the open-circuit rest periods. On the other hand, if the charge is continued considerably past the point of coincidence, then a reasonable recovery is possible. Recovery for the system shown in Figure 13 was 79%. When the electrode is charged without interruption at higher rates, the opportunity for re-oxidation is much less and good recovery is obtained.

The behavior of the cadmium-potassium system raises questions about the other systems in which K0H was used to provide the required hydroxide concentration. The magnesium-amalgam system shown in Figure 6 behaves in a manner comparable with that of the potassium system although it is not as good. Nevertheless, the predominant amalgamated species might be potassium.

A potassium-amalgam electrode was prepared and discharged in a 5 <u>VF</u> K0H solution. The results are shown in Figure 15. Evidently, the major effect is to increase the resistance of the electrolyte system. There also may be the effect of increasing the open-circuit potential. One would predict a shift in that direction from the Nernst equation though possibly not of this magnitude. No correction has been made for changes in the potential of the reference electrode when the KOH concentration is changed. In general, the KOH concentration in the reference has been the same as that in the working electrode compartment. Open-circuit potentials have been sufficiently irreproducible that no correlation can be made safely. The voltage remains reasonably steady over most of the discharge range and recovery is good.

Zinc-amalgam electrodes have been prepared and operated in 8 VF KOH and 15 VF KOH, both saturated with ZnO. The discharge performance is shown in Figure 16. The potentials during discharge at 536 mA/cm^2 are not as stable as those produced at 219 mA/cm^2 in 10 VF KOH. This is not surprising because considerable turbulence is observed in the mercury pool at high discharge rates so that the surface concentration of zinc is constant changing. Furthermore, build-up of oxidation products at the surface probably exceeds the rate of transport away from the surface at the high current-densities. In this case, the cell resistance seems to be increased by the increased KOH concentration as opposed to the effect noted with the potassium system. However, effects of concentration at 15 VF may be quite different from those at 5 VF. Both cells show quite good charge recovery at these high current-densities although the electrode potential is impractically low after about 40% discharge in the 15 VF case.

Stand life experiments were made under a variety of conditions and are still in progress. The amalgams were charged and then removed to test tubes containing solutions of various compositions. Usually, but not always, the electrodes were charged in the same solutions under which they later stood on open circuit. In all cases, no electrical contact of any kind was made with the amalgams during stand. At various times, one of the amalgams was transferred to a cell, discharged, and the recovery determined. The electrodes were charged at 1.75 mA/cm^2 and discharged at 12.5 mA/cm^2. The results of these experiments are shown in Tables 3, 4, and 5.

Table 3 shows the results for "cadmium-amalgams" under KOH solutions. The charge recovery seems to be quite good up to at least five days of stand in 10 VF KOH. In two weeks the recovery has dropped to 75% in the one trial made with this system. Stand life is poorer in 8 VF KOH.

Table 4 shows the results for "cadmium-amalgams" under 10 VF KOH saturated with CdO. Here, one would expect oxidation of the potassium in the amalgam both by water and by CdO. The results support this expectation.

Table 5 shows the results for potassium amalgams under KOH solutions. In the shorter stand periods, there is no significant difference in behavior between saturated KOH and 10 VF KOH. Longer stand times are being investigated. Recovery is poorer at the lower KOH concentrations as would be expected, since the water activity shouldl be higher resulting in more rapid oxidation of potassium. Note that results shown in Table 5 compare favorably with those in Table 3.

Stand life experiments are being continued on most of the systems reported here. Methods of modifying the electrolyte solutions to improve stand life are being considered.

A silver oxide-"cadmium-amalgam" cell was constructed by placing 45 g of mercury in the bottom of a polyethylene container and mounting a partially charged silver electrode above it. The silver electrode was wrapped in one layer of polypropylene and was placed about 5 mm from the mercury surface. About 50 ml of 10 VF KOH saturated with CdO was added along with a small excess of the CdO. The mercury surface-area was 3.12 cm^2.

The cell was initially charged at 25 mA for a total of 0.175 A-hr. It was then discharged at 300 mA, corresponding to a current-density of 96 mA/cm^2 for the amalgam electrode. The discharge behavior is shown in Figure 17. The open-circuit voltage was 2.34 V and initial discharge voltage was 1.75 V which held quite constant over the entire discharge period. The initial voltage drop is considerable in this system and probably can be attributed predominantly to the silver electrode since nothing of this magnitude has been observed for the amalgam electrodes alone. However, no measurement of individual electrode potentials was made in this experiment. The almost 90% recovery of charge is quite good considering the limitations of the cell configuration used. The early voltage increase of about 40 mV during the discharge is not explained.

Upon completion of the first discharge, the cell was re-charged at 15 mA for a total of 0.233 A-hr. It was then discharged through a resistor at 1 A which corresponds to an amalgam current-density of 322 mA/cm^2. The results are shown in Figure 18. The open-circuit voltage was 2.32 V, within 20 mV of the value at the end of the first charge. Again, the initial voltage drop is large but the change is sufficiently small that the major portion of the drop must be assigned to a non-resistive polarization phenomenon. The further drop in the early stages of discharge suggests the conversion of the silver electrode to the argentous state although this electrode was presumably re-charged with the amalgam. Beyond that point, at about 15% of discharge, the voltage stays fairly steady until the end of the discharge. Recovery is not as good as in the previous case, being only 77%. However, charge efficiency may have been poorer at the slower rate because the polypropylene separator does little to prevent migration of dissolved silver and some self-discharge may have occurred at the amalgam because of it. The cell still contained enough active material at the end of the discharge to maintain an open-circuit voltage of 1.95 V.

Evidently, large currents can be delivered at respectable voltages even by crude cells of this type. At present, the limiting electrode appears to be the cathode.

Proposed Work

Work will continue with the potassium-amalgam and "cadmium-amalgam" electrodes. The effect of rate of charge and rate of discharge on the energy recovery and stand life will be determined. Open-circuit potentials will be measured for different concentrations of metal in the amalgams. The effect of mixtures of hydroxides in the electrolyte solution will be studied. Potentiostatic investigations will be instituted to gain better understanding of the mechanisms of the charge and discharge reactions. Other amalgam systems will be investigated more closely.

D. HYDROGEN OVERVOLTAGE ON ZINC

Introduction

Hydrogen overvoltage has been studied on many metals, but most of the studies have been made in acid or neutral solutions. A few investigations such as those by Makrides[6] and Weininger and Breiter[7] have been done on nickel in dilute alkaline solutions. Nothing in the recent literature indicates any similar study on zinc or cadmium, particularly at high alkali concentrations. Since hydrogen is evolved in zinc and cadmium battery electrodes on overcharge, such studies seem important.

Experimental

Reagent grade chemicals were used without further purification. Zinc, both sheet and wire, was grade 6N. Water was triply distilled, the last distillation being from alkaline permanganate.

The cells were of a simple, multi-compartment construction. A "buffer" compartment containing a solution identical with that in the working compartment was placed between the reference electrode and the working compartment. A similar "buffer" was placed between the auxiliary and working electrodes when the auxiliary was mercury. The working compartment contained a Luggin capillary placed within a few millimeters of the working electrode and provision for gas bubbling, either nitrogen or hydrogen. The reference was a Hg/HgO electrode.

Early experiments were carried out by applying a potential to the working and auxiliary electrodes with a mercury battery and measuring the reference-working electrode potential with a potentiometer. The current was measured by determining the IR drop in a precision resistor. Later, the electrode potential was set with a Wenking Model 66 TS-1 potentiostat. A precision resistor was placed in the auxiliary electrode lead and the current determined by measuring the drop across that resistor with a Leeds and Northrup K3 potentiometer.

A cathodic current of about 5 mA was passed through the zinc electrode for at least 15 minutes before beginning measurements. The solution was generally saturated with hydrogen by slowly bubbling purified gas through the system. The gas flow was continued during the measurements to provide stirring. In a few cases, only nitrogen was present. Oxygen was excluded in all cases.

Both wire and plate electrodes were used. In general, the wire electrodes gave better results. Concentrations of KOH ranged from 0.1 VF to 10 VF.

Results and Discussion

Little, if any, useful data have been accumulated this quarter. The main effort has been directed toward developing procedures and establishing techniques that will yield reproducible results. A few of the results are reported here.

Only one fairly successful set of data was acquired with a plate electrode. The plate was a disc of 1.53 cm^2 area pressure-sealed into the top of a polyethylene bottle. The bottom was cut out of the bottle, the bottle inverted, and 0.1 VF KOH solution added. The solution was swept with nitrogen before each measurement, but was undisturbed during each measurement. The results are shown in Figure 19. In all of this discussion, the term, "polarization" will be used instead of "overvoltage" in accordance with the arguments presented by Vetter[8]. Similarly, i_o will pertain to the extrapolated exchange current as defined by Makrides[6] rather than the true exchange current. These terms are used because the zero-current electrode potential probably is not a true equilibrium potential in this case but may be a mixed potential. This is suggested by the fact that the zero-current potential is more nearly a Zn/ZnO potential than a H_2/H^+ potential. The symbol, I, will represent the measured current while the symbol, i, will represent current-density. According to Figure 19, there appears to be a region of Tafel behavior. Extrapolation of the straight section of the plot yields an i_o=4.26 μA/cm^2. This value suggests a respectable polarization as compared with those found on platinum.

A similar experiment was performed in 1 VF KOH with a wire electrode. The results are shown in Figure 20. Here, i_o=36.3 μA/cm^2, considerably higher than that observed in the previous case. It is not known whether this difference can be attributed to the different electrode configurations or the different KOH concentrations.

The behavior of a zinc wire in 0.10 VF KOH saturated with hydrogen is shown in Figure 21. Here, a long, straight Tafel line resulted which extrapolated to i_o=13.25 μA/cm^2. This is higher than that found in the previous 0.1 VF case, but the system is different in that the electrode is a wire and the system was operated saturated with hydrogen and with a slow gas flow during the measurements.

Results in 10 VF KOH have been unsatisfactory, generally. Figures 22 and 23 shows the results of two wire electrodes run under almost identical conditions except that a higher gas-flow rate was used for the system in Figure 22. Figure 23 shows no discernable Tafel region while Figure 22 shows a straight region which could be considered such. Extrapolation of the straight section yields i_o=140 μA/cm^2, a very high value. This number must be considered suspect. However, there does appear to be a decrease in polarization with increasing KOH concentration. There is also a probable increase in side reactions which may be responsible for the erratic results.

Proposed Work

Efforts along the lines described will be continued. Since reasonable results are obtained at low KOH concentrations, experiments will be performed in increasingly concentrated solutions until erratic results appear in hopes that valid extrapolations will be possible. At the same time, attempts will be made to attain reproducible results with the high-concentration alkali systems. Cell configurations are being changed to keep hydrogen bubbles from the gas stream from adhering to the electrode; this has been something of a problem.

Table 1

Removal of Silver from K0H Solution by Deposition on Zinc

Weight of Zn (g)	Deposition Time (hours)	Silver Concentration (VF x 10^6)
0.3720	0.25	120
	4	11.6
	77	3.7
0.3114	0.25	312
	4	254
	22	38.9
0.5059	0.25	190
	2	160
	24	6.5
0.4792	0.25	296
	1.5	268
	23	22.2
0.4467	0.25	298
	24	55.8
0.4190	0.25	276
	23	6.6

Table 1 (contd.)

Weight of Zn (g)	Deposition Time (hours)	Silver Concentration (VF x 10^6)
0.5116	0.25	213
	25	14
0.3978	0.25	165
	25	4.9
	144	4.7
0.3599	0.25	215
	22	15
	70	4.8
	166	2.9
	336	2.6
*	---	187
0.3896**		175
	48	4.3
	360	3.1
	528	3.2

* No zinc present

** Zinc added after two hours

Table 2

Chronopotentiometric Transition Times for Zinc Anodes Plated with Silver

Expt.	Deposition Time (hours)	Transition Time (sec)
1*	23	24.8
		48.7
		50.6
2**	4	24.2
		41.1
		43.8

* Deposition made in electrolysis cell.

** Anode transferred to electrolysis cell after silver deposition.

Transition time without prior deposition = 69 sec.

Table 3

Stand Life

"Cadmium-Amalgam" in K0H Solutions

K0H Concentration (VF)	Stand Time (hours)	Charge Recovery (%)
10	1	87
	2	96
	19	94
	30	94
	68	94
	119	93
	336	75
8	162	78

Table 4

Stand Life

"Cadmium-Amalgam" in 10 VF KOH Saturated with CdO

Stand Time (hours)	Charge Recovery (%)
6.5	80
29	77
122	64
290	71
38	84
87	87
232	52

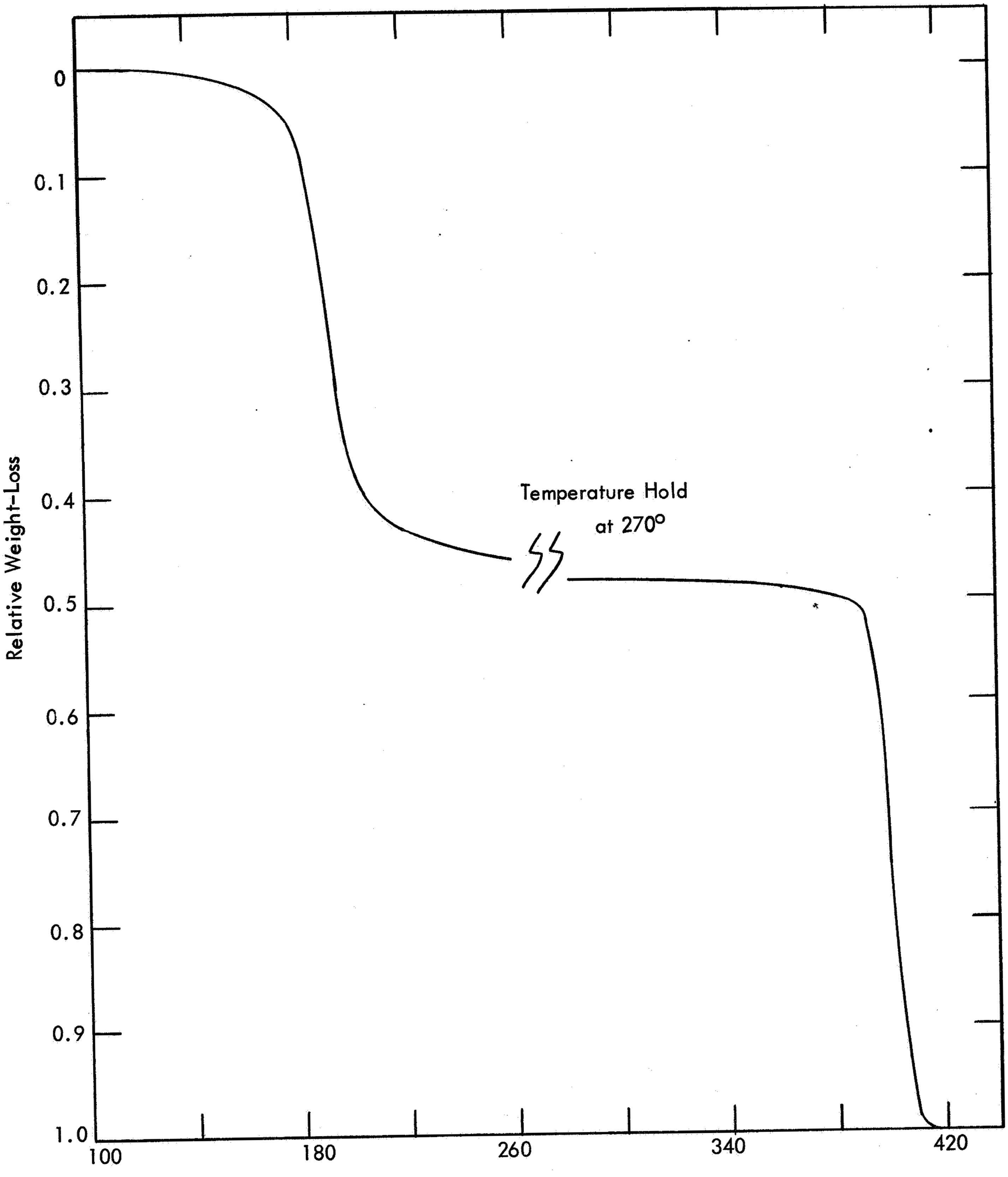

Figure 1. Thermogram of Ames AgO at $\Delta T = 5°/\text{min}$.

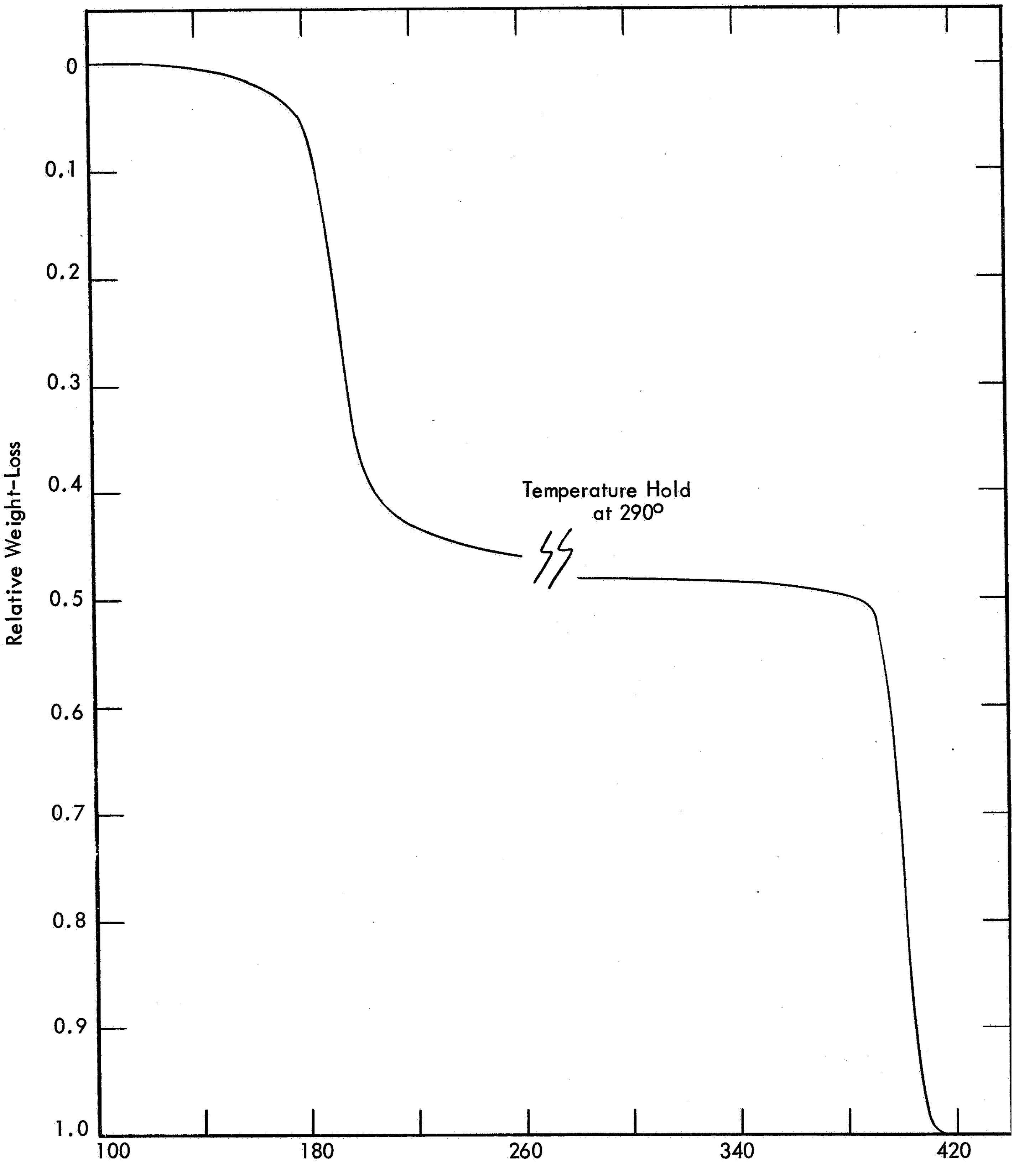

Figure 2. Thermogram of Ames AgO at $\Delta T = 5°/\text{min}$.

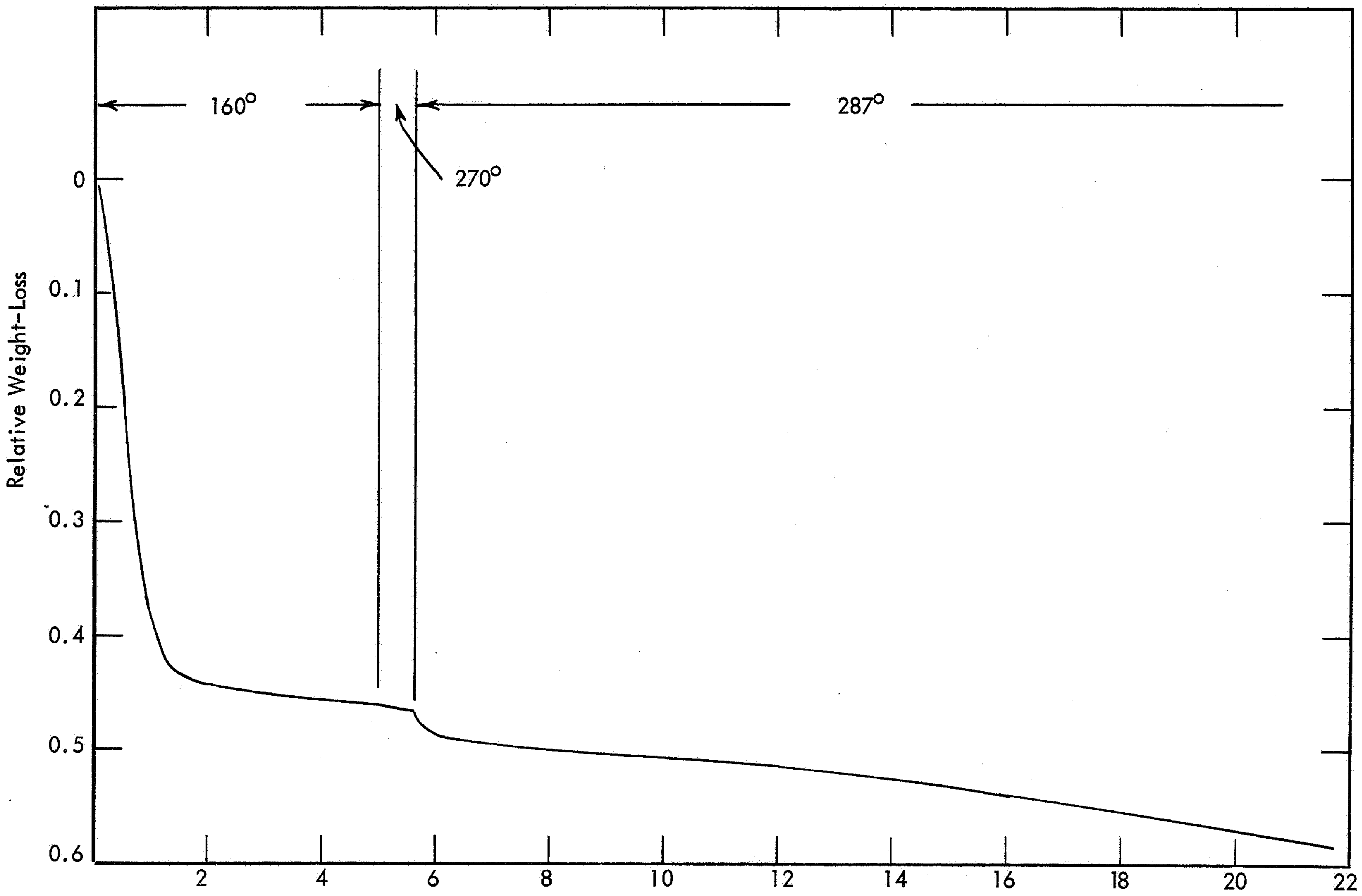

Figure 3. "Constant-Temperature" Thermogram of Ames AgO

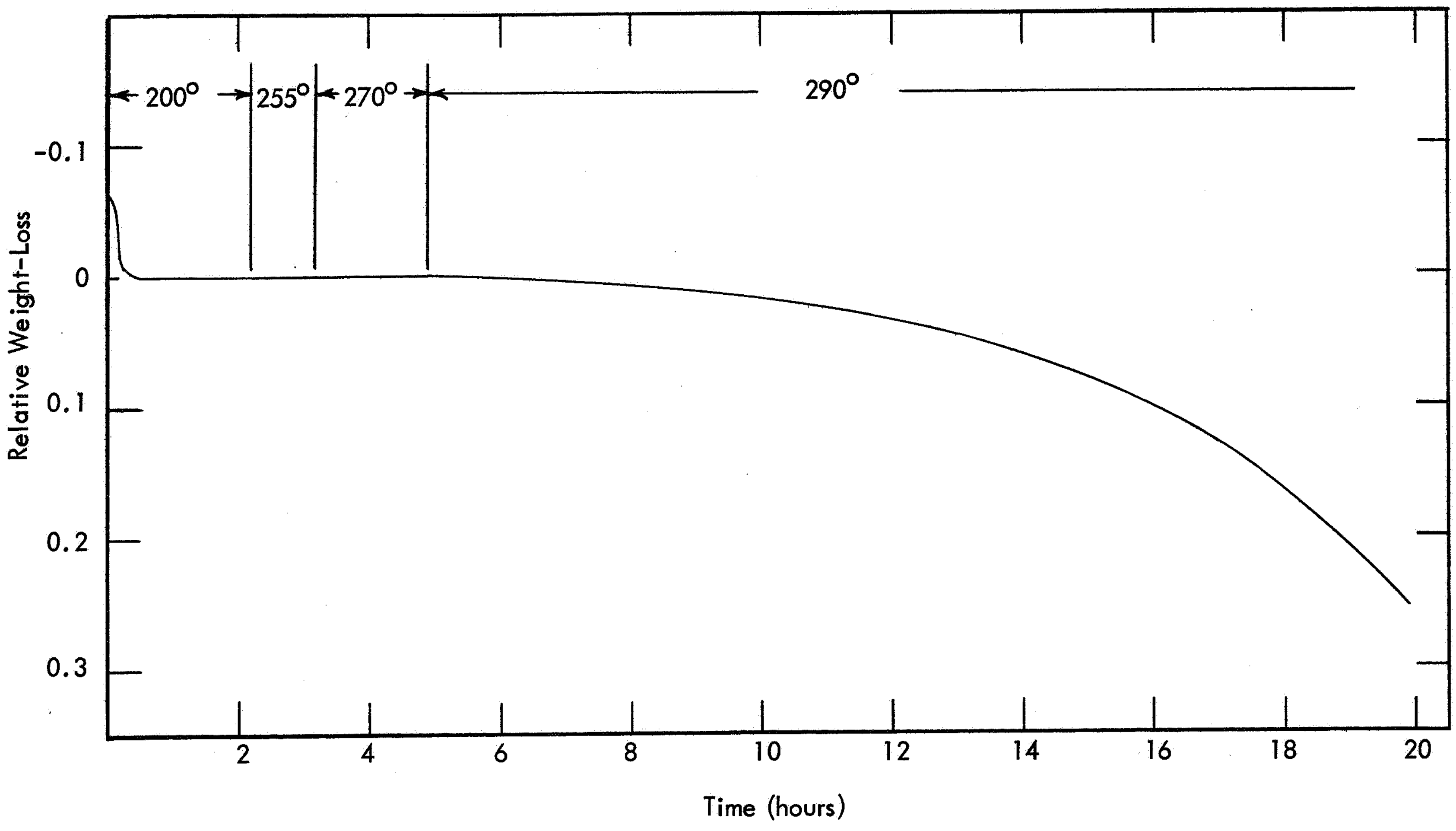

Figure 4. "Constant-Temperature" Thermogram of K & K Ag_2O

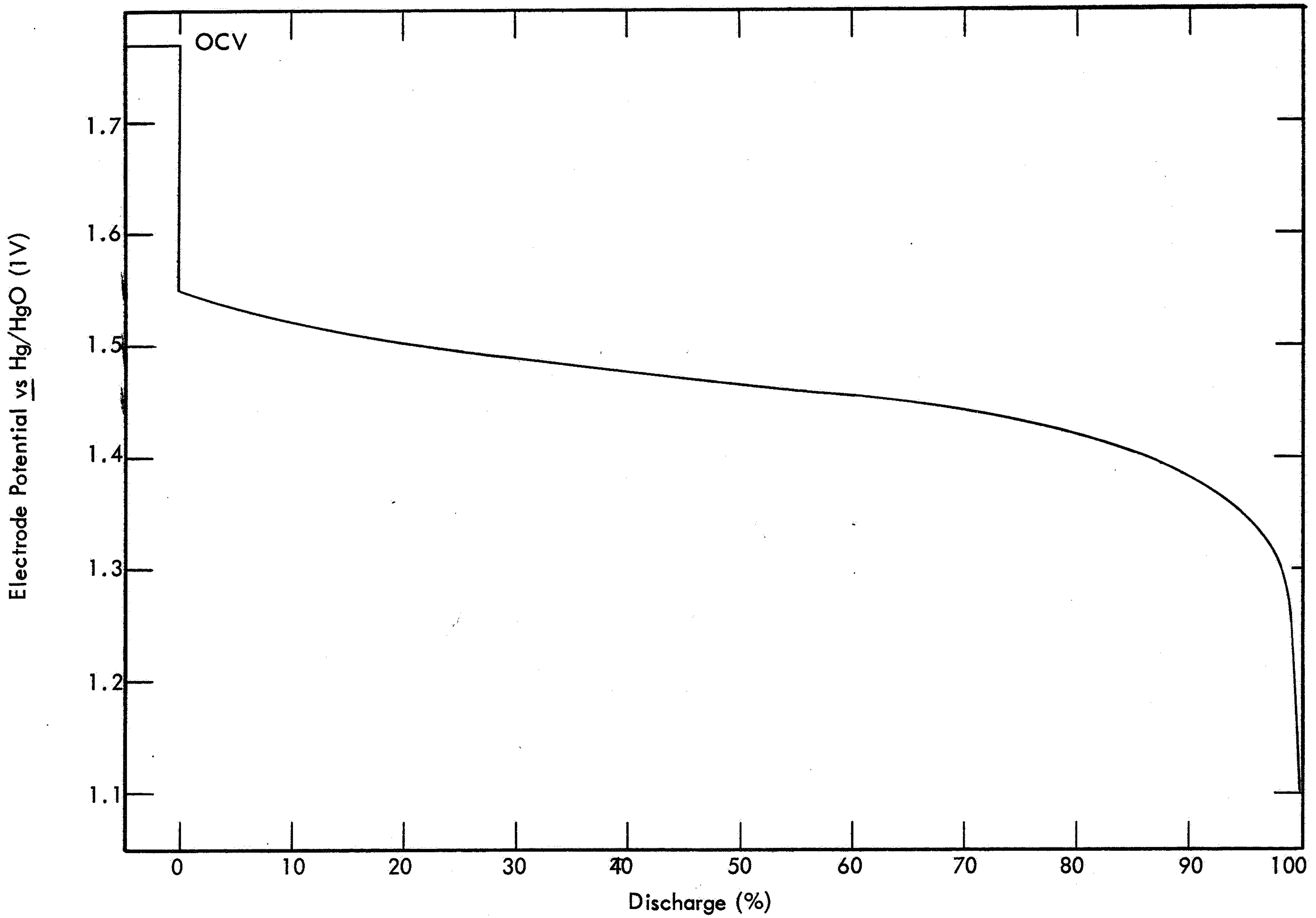

Figure 5. Discharge of K(Hg) Electrode in 10 VF KOH at 215 mA/cm^2

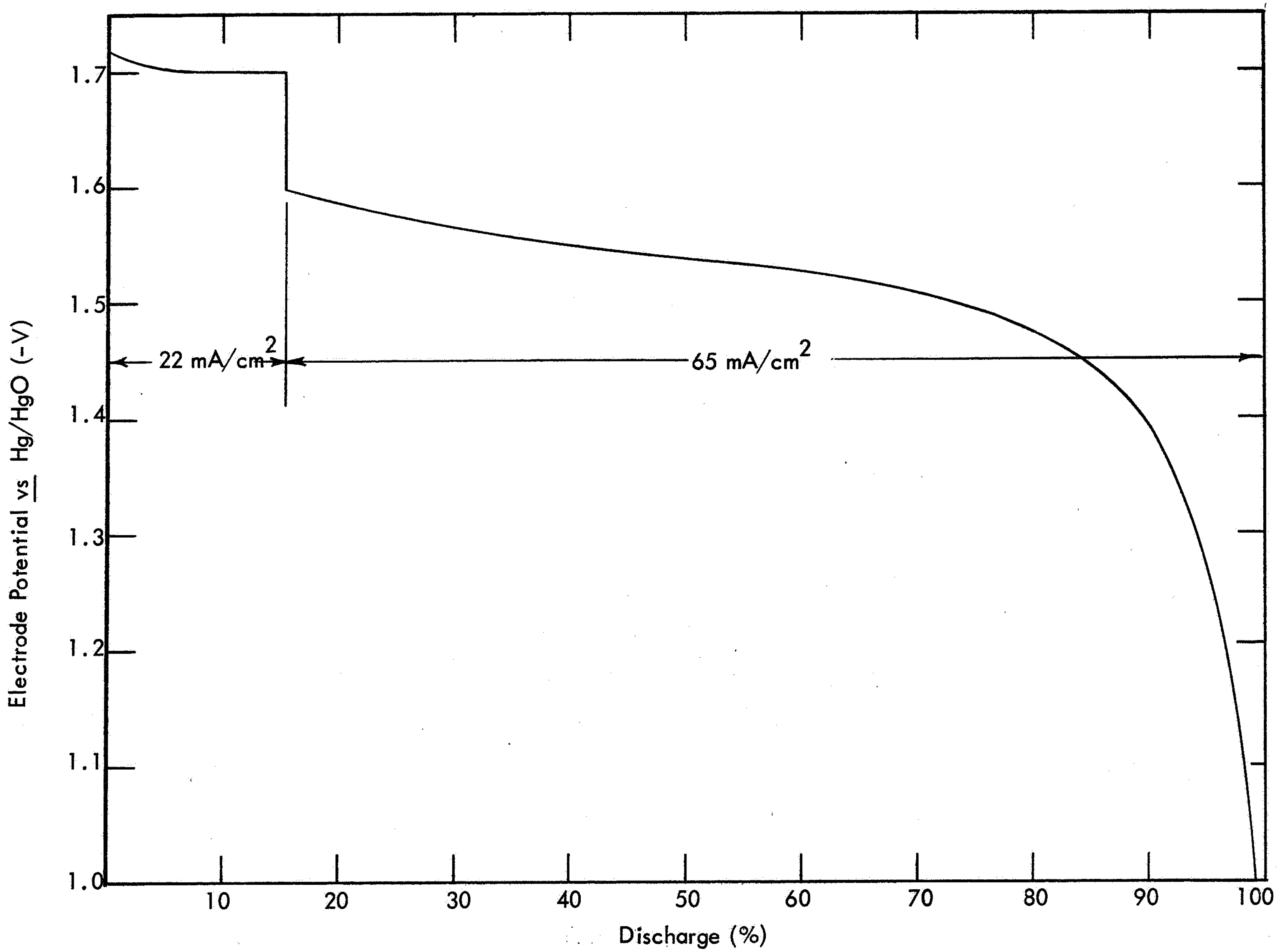

Figure 6. Discharge of Mg(Hg) Electrode in 10 VF KOH

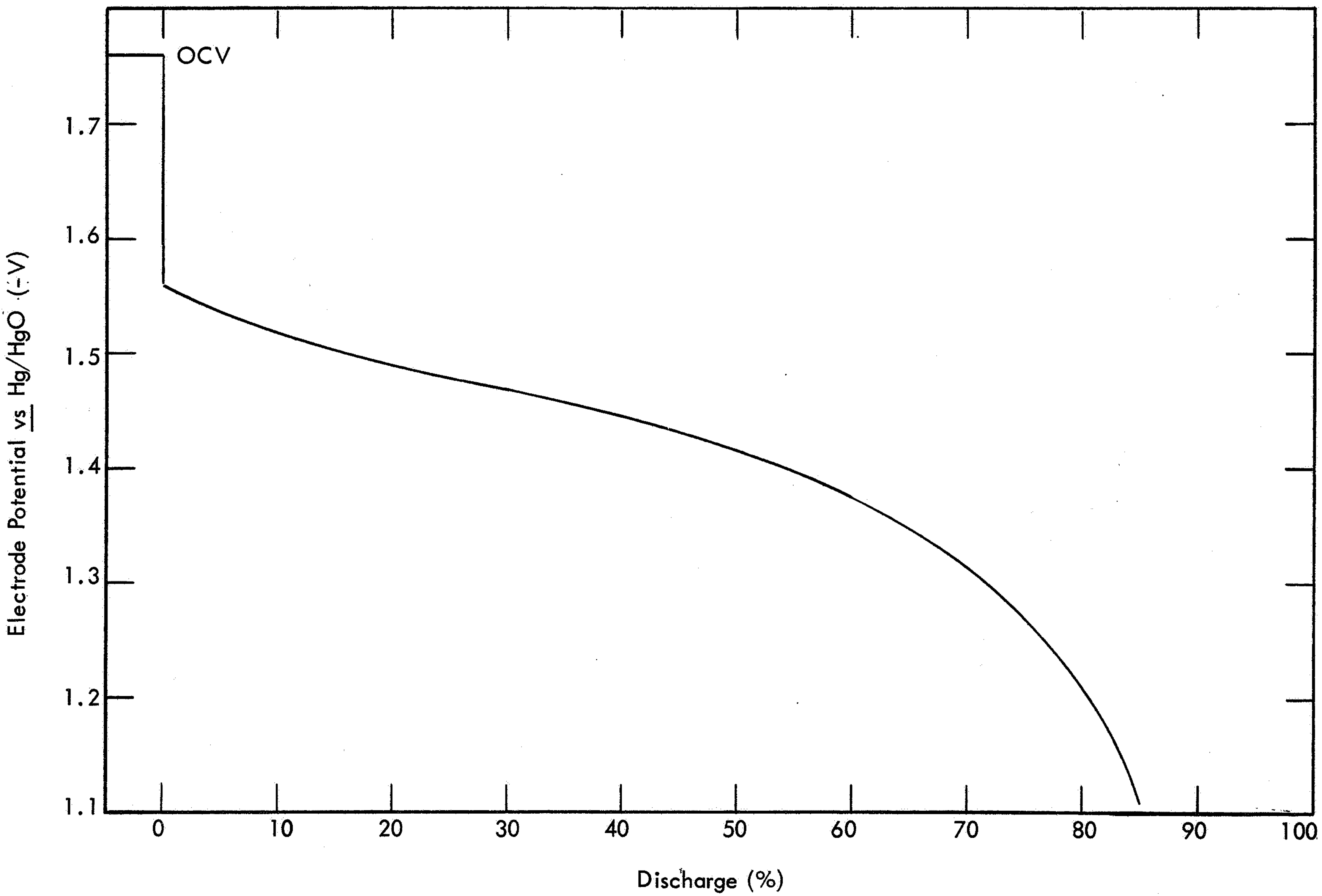

Figure 7. Discharge of Ca(Hg) Electrode in 10 VF KOH at 65 mA/cm^2

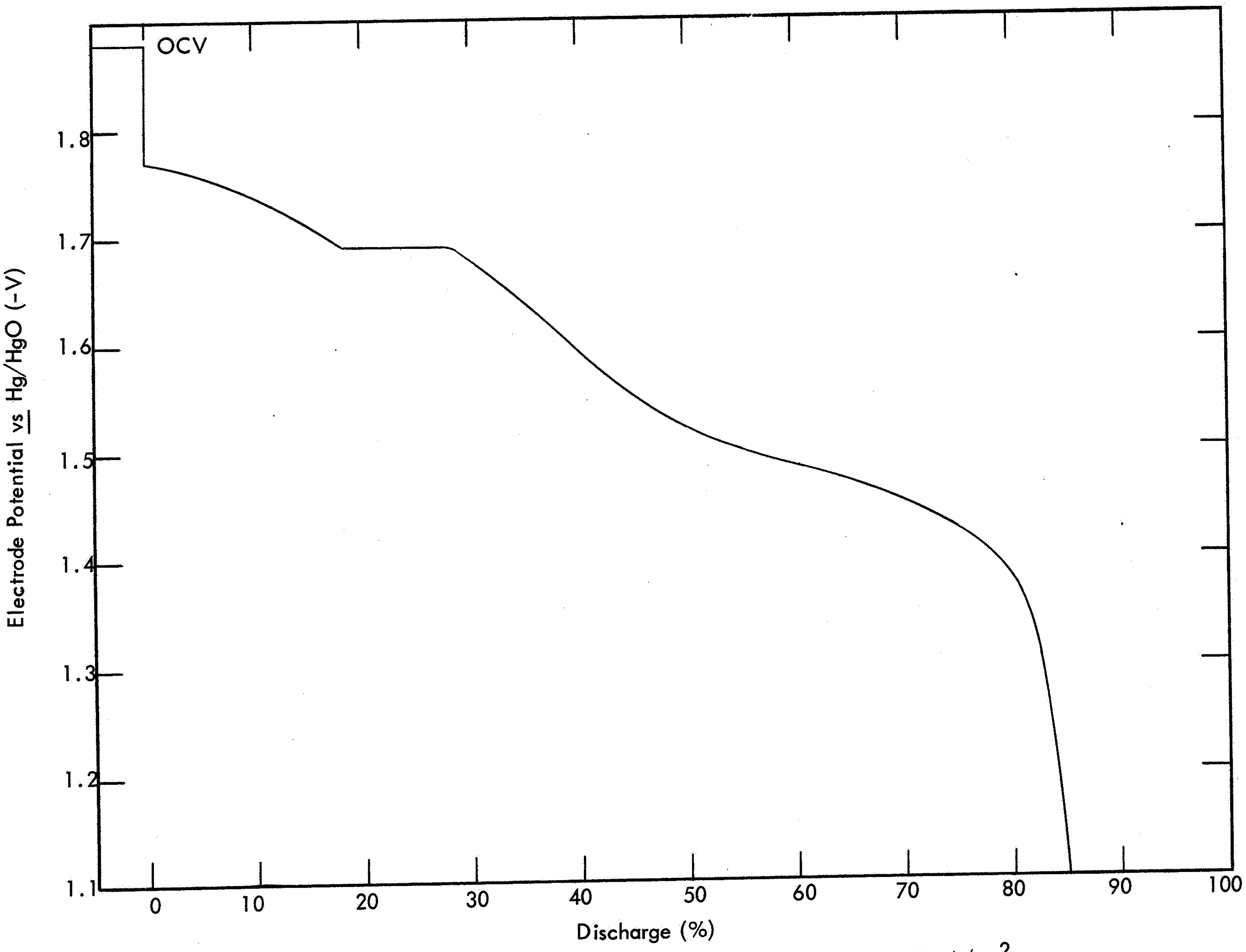

Figure 8. Discharge of Ba(Hg) Electrode in 10 VF KOH at 64 mA/cm^2

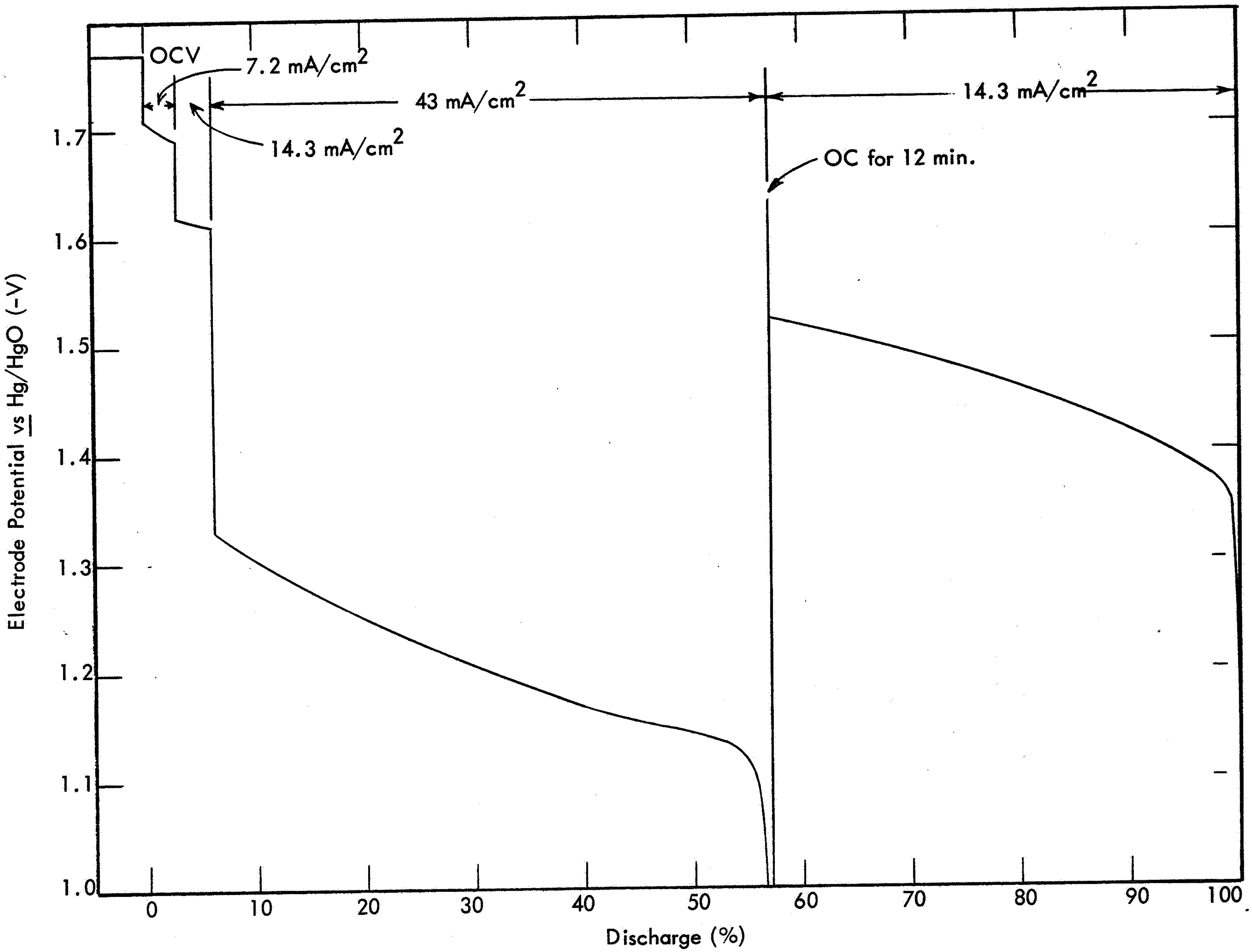

Figure 9. Discharge of Al(Hg) Electrode in 10 VF KOH

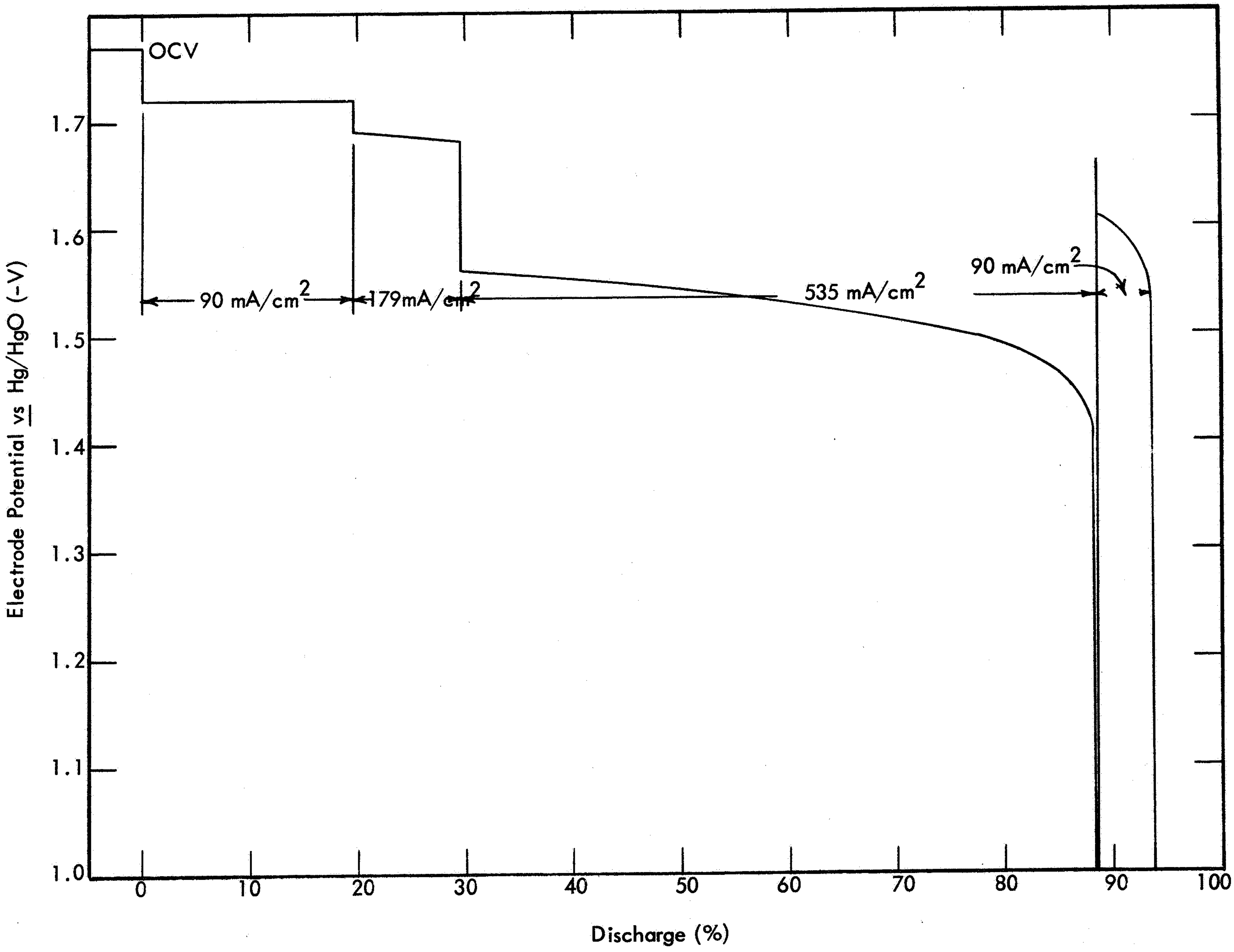

Figure 10. Discharge of Cd(Hg) Electrode in 10 VF KOH

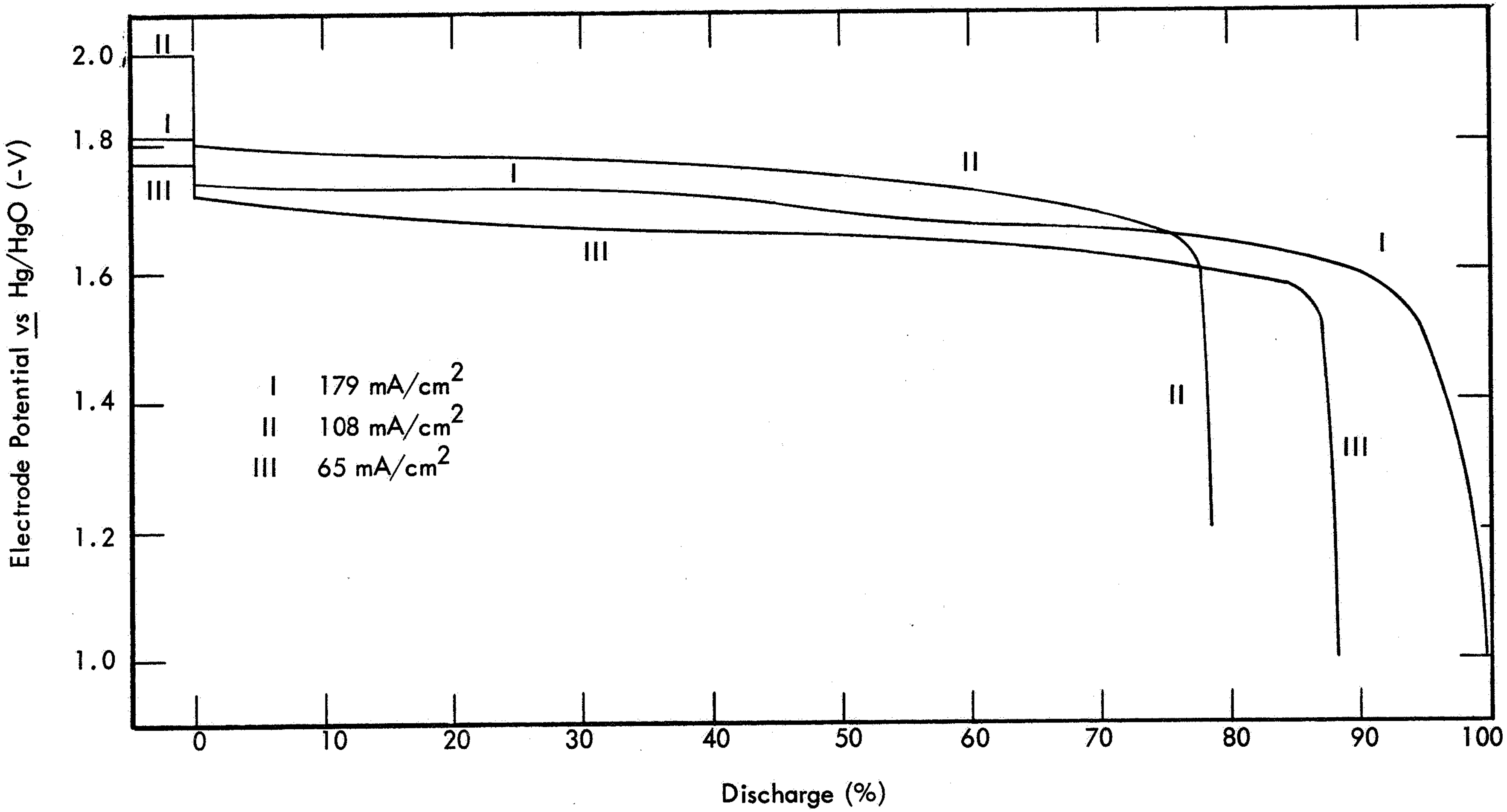

Figure 11. Discharge of "Cd(Hg)" Electrodes in 10 VF KOH at Different Rates

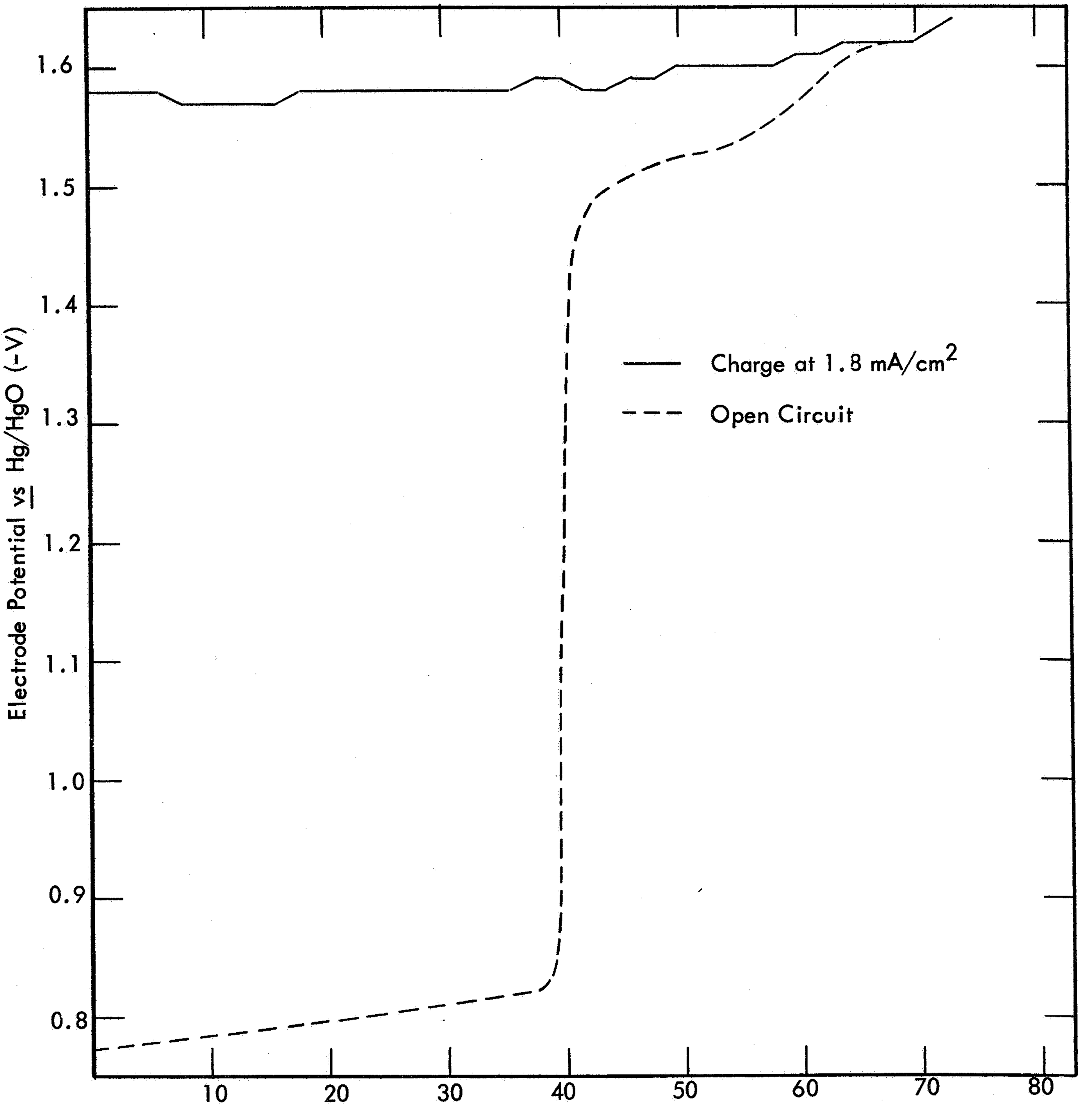

Figure 12. Alternate Open-Current-Charge Behavior of the "Cd(Hg)" Electrode

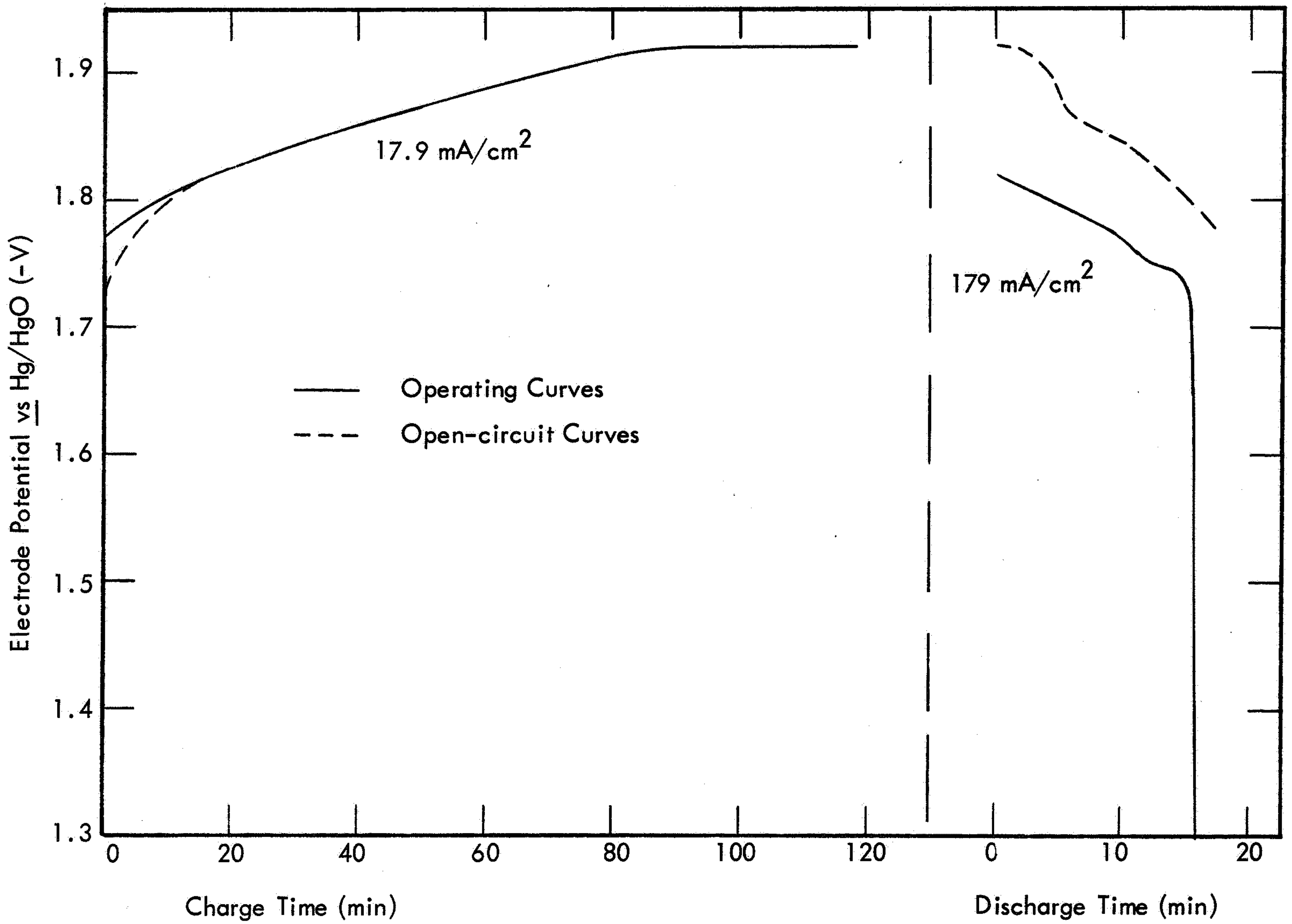

Figure 13. Alternate Open-Circuit-Operate Behavior of "Cd(Hg)" Electrode

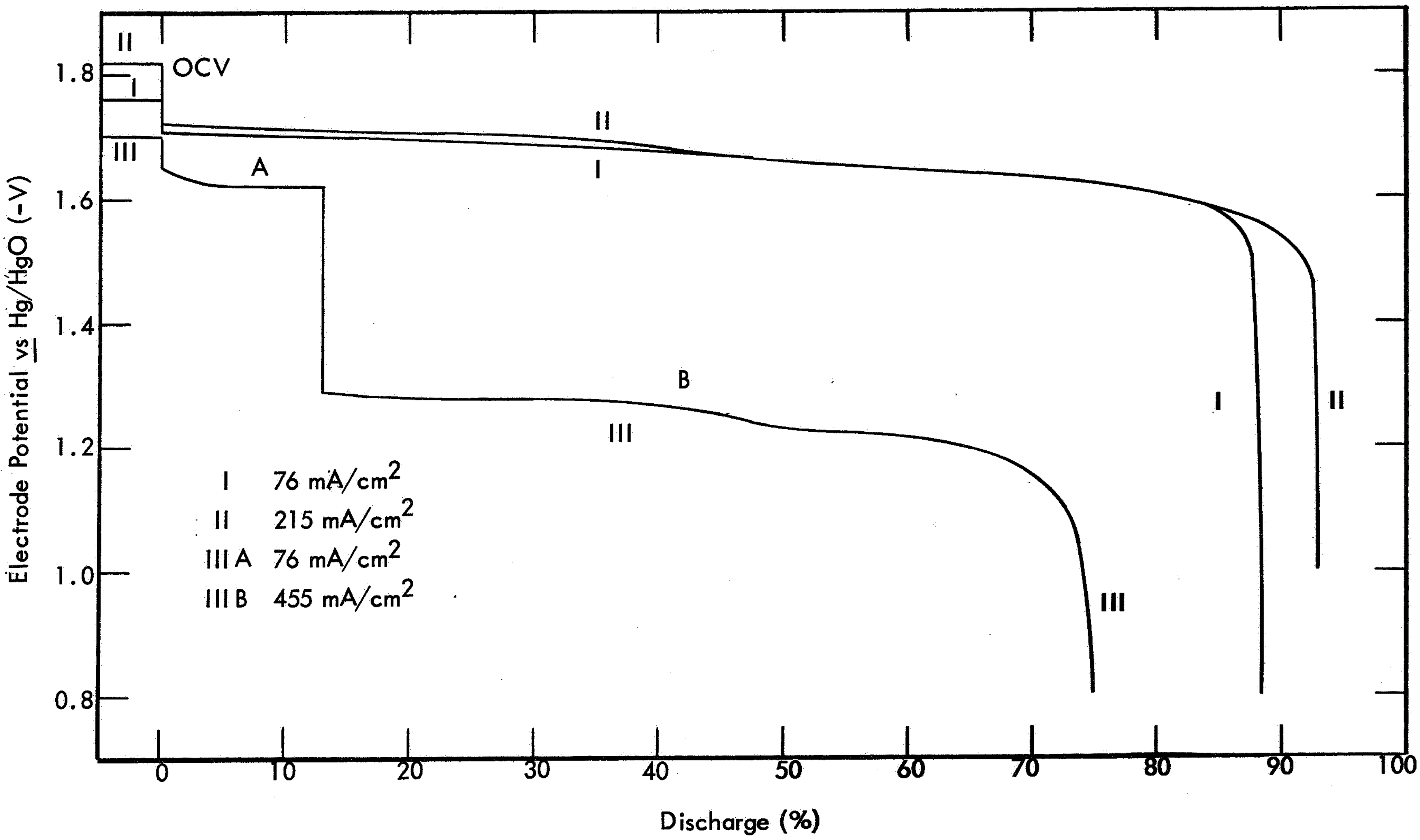

Figure 14. Discharge of K(Hg) Electrodes in 10 VF KOH

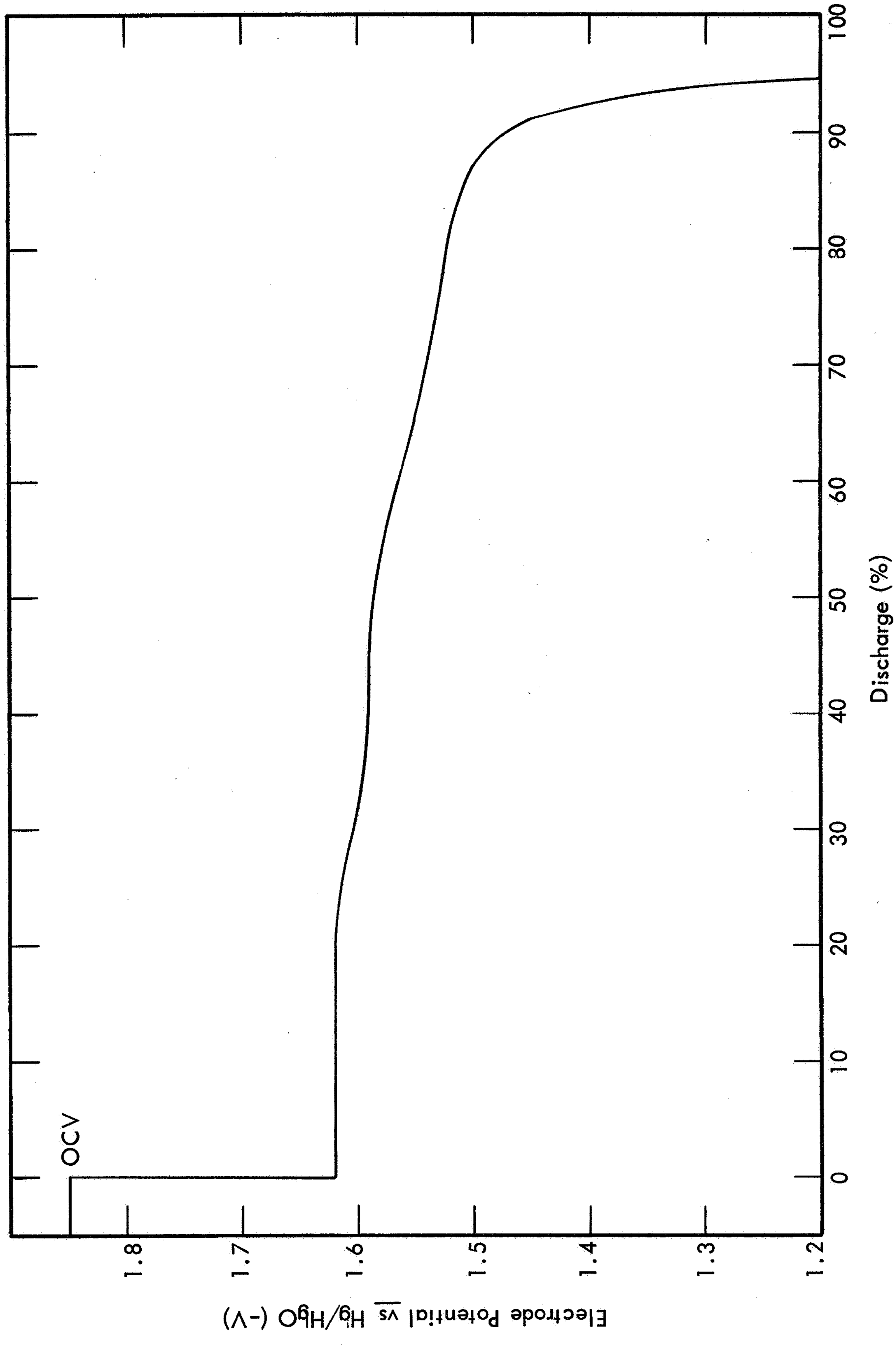

Figure 15. Discharge of K(Hg) Electrode in 5 VF KOH at 216 mA/cm^2

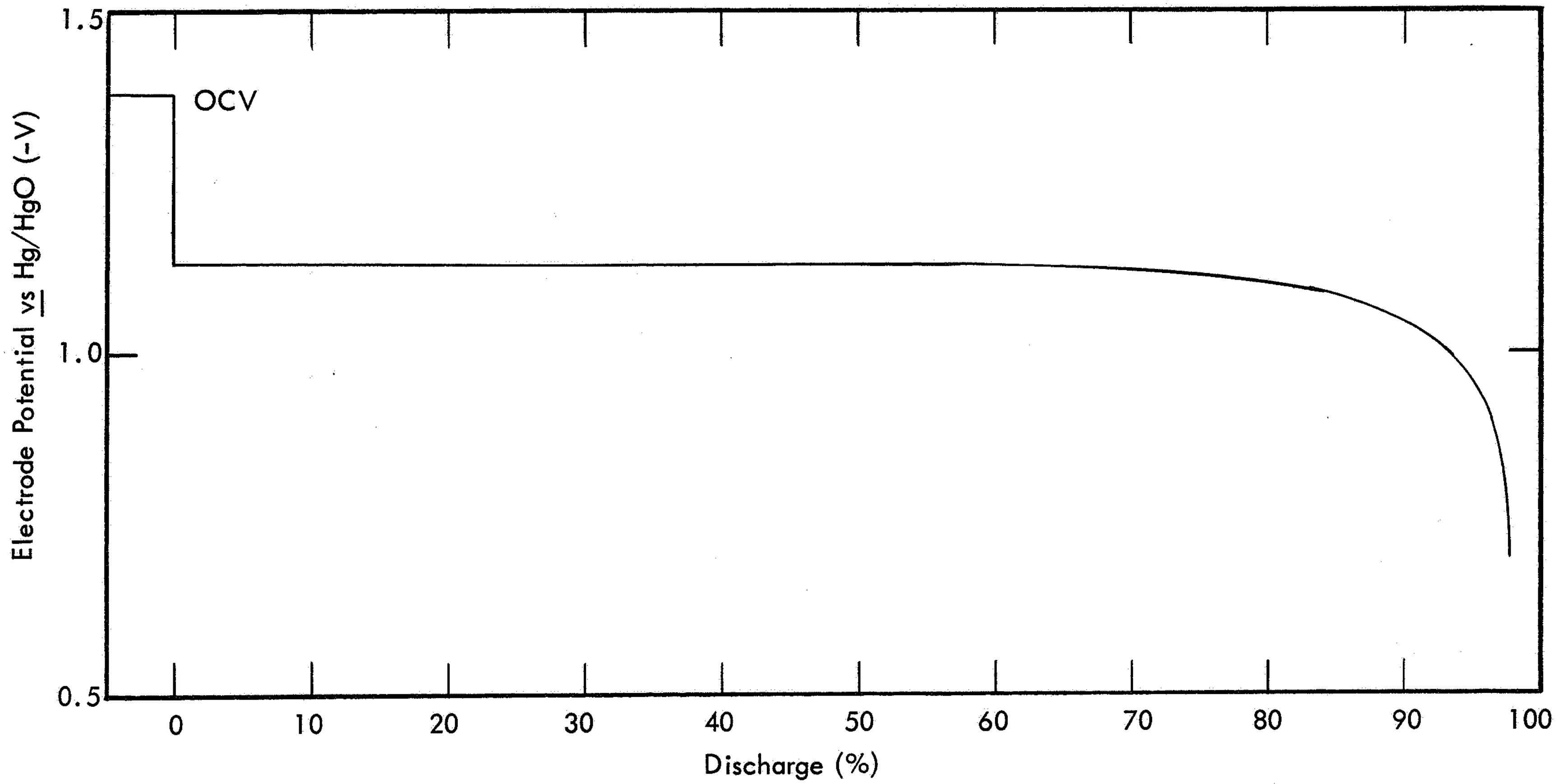

Figure 16. Discharge of Zn(Hg) Electrode in 10 VF KOH at 219 mA/cm^2

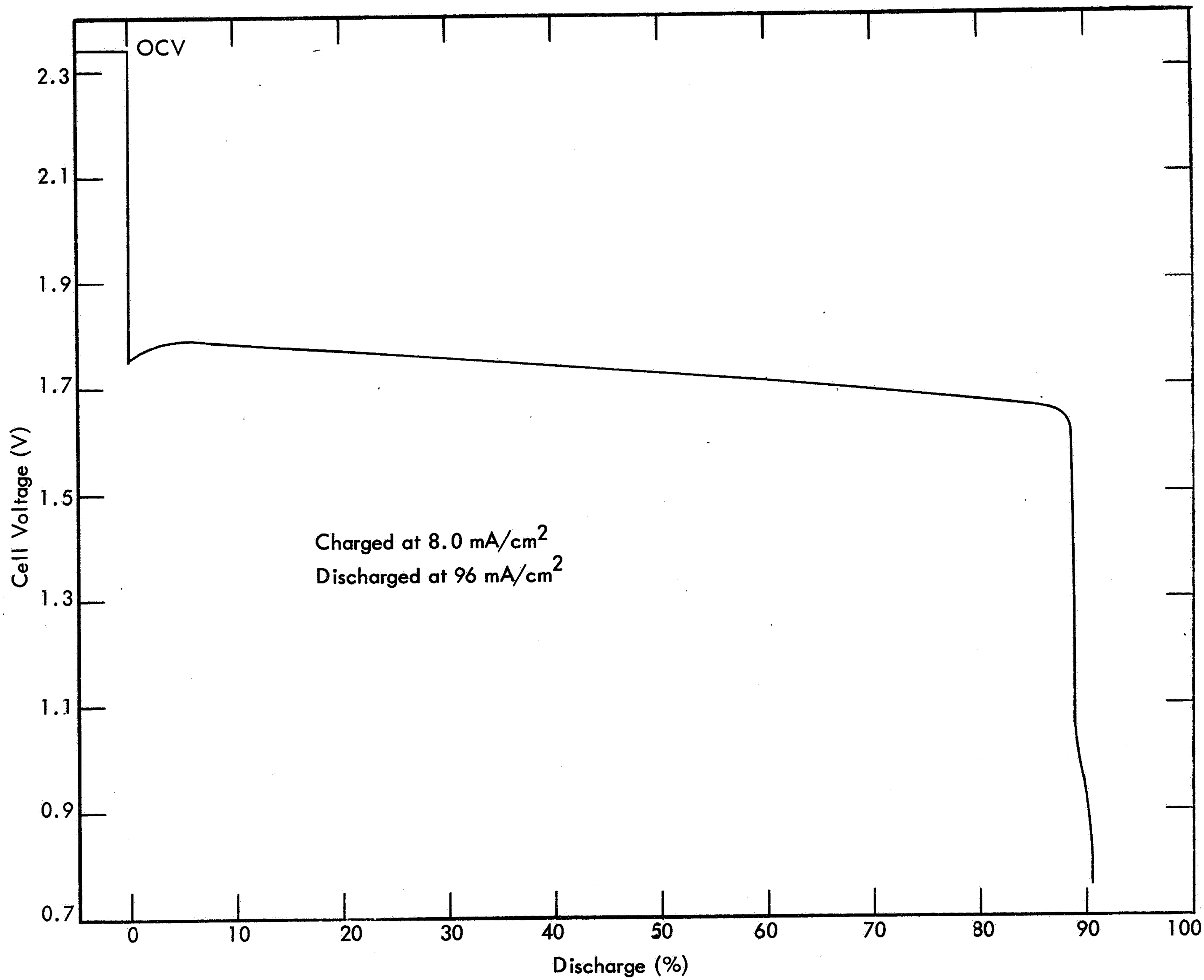

Figure 17. Discharge of AgO - "Cd(Hg)" Cell

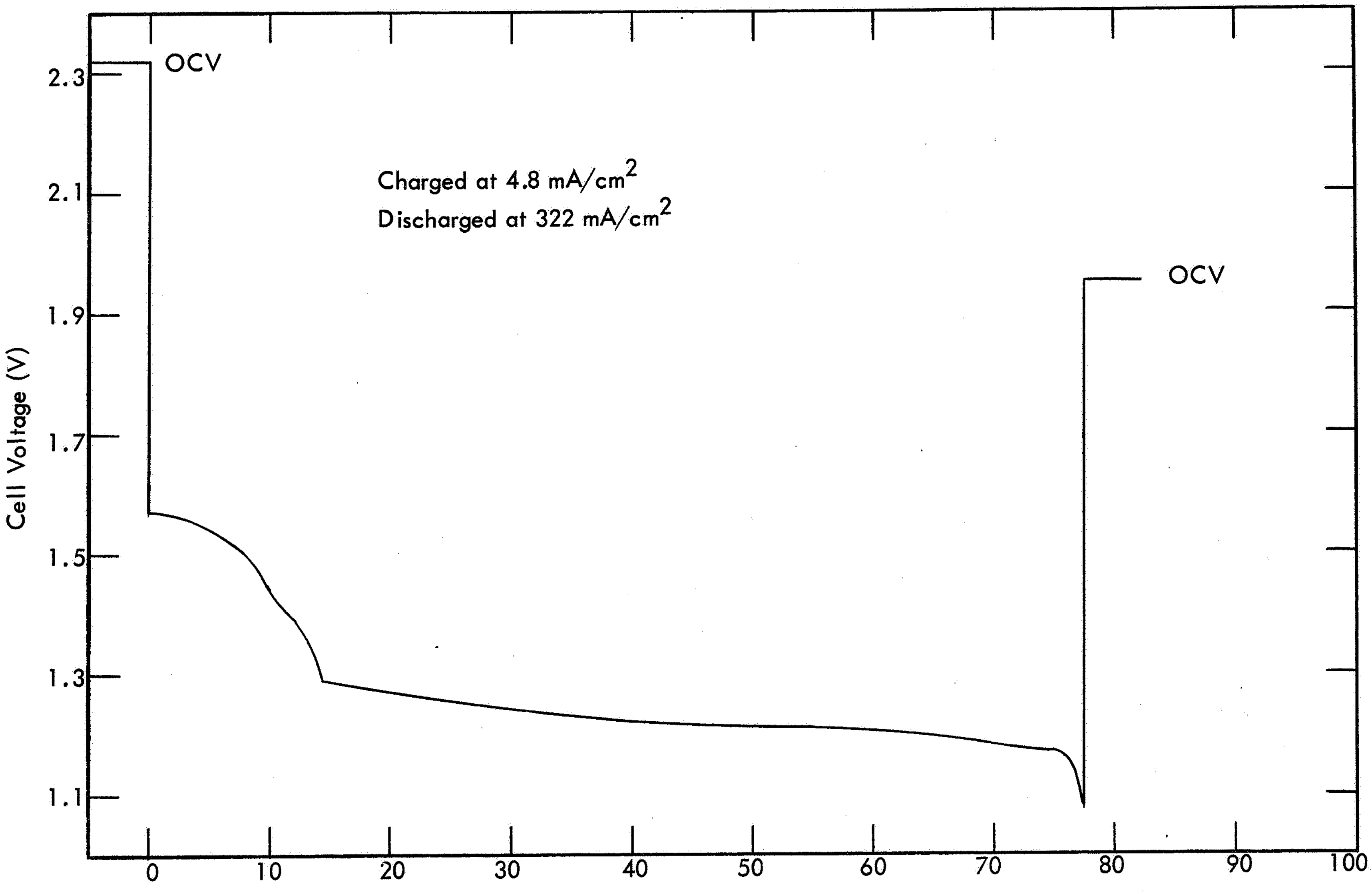

Figure 18. Discharge of Re-charged AgO - "Cd(Hg)" Cell

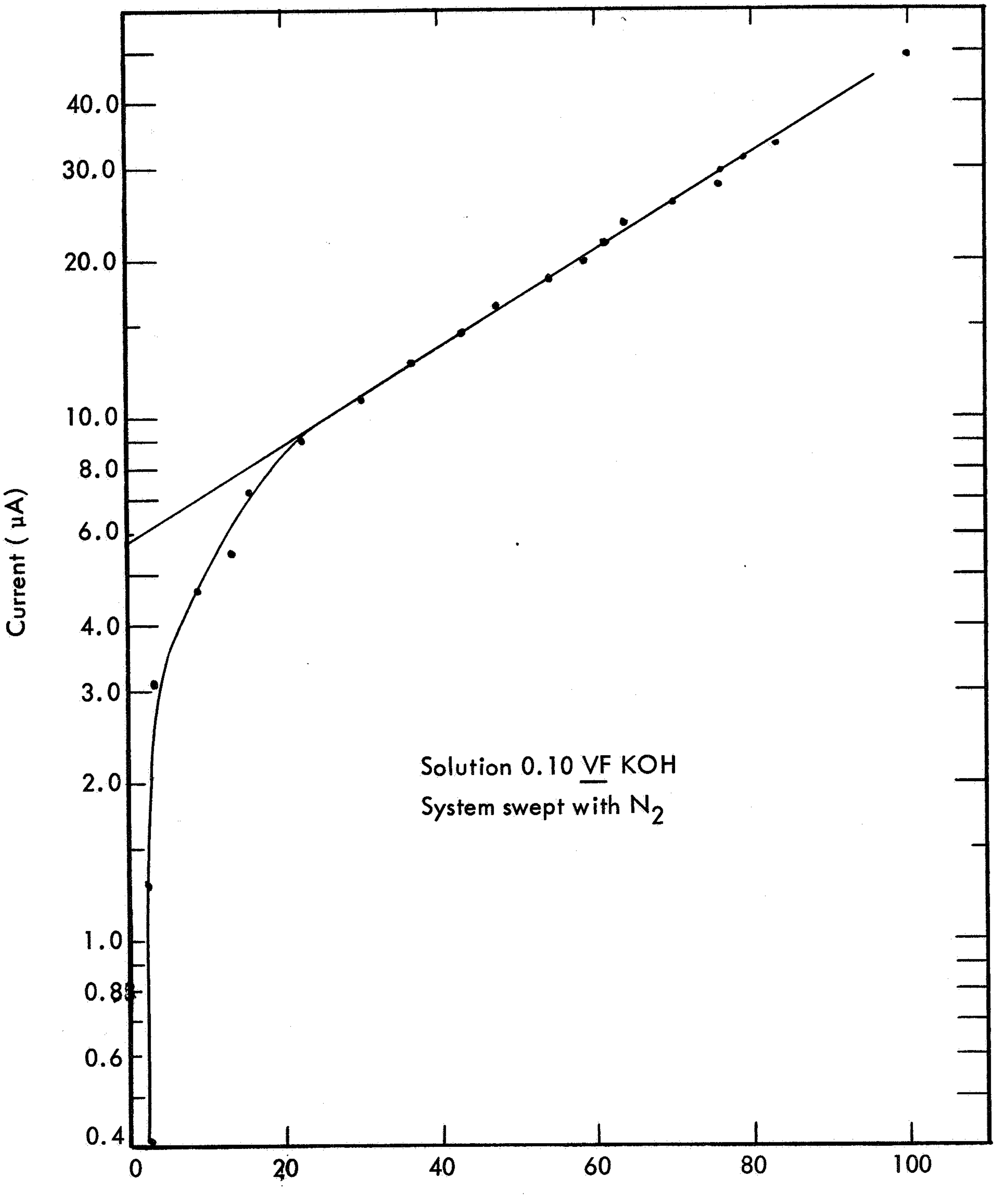

Figure 19. Hydrogen Polarization on Sheet Zinc Electrode

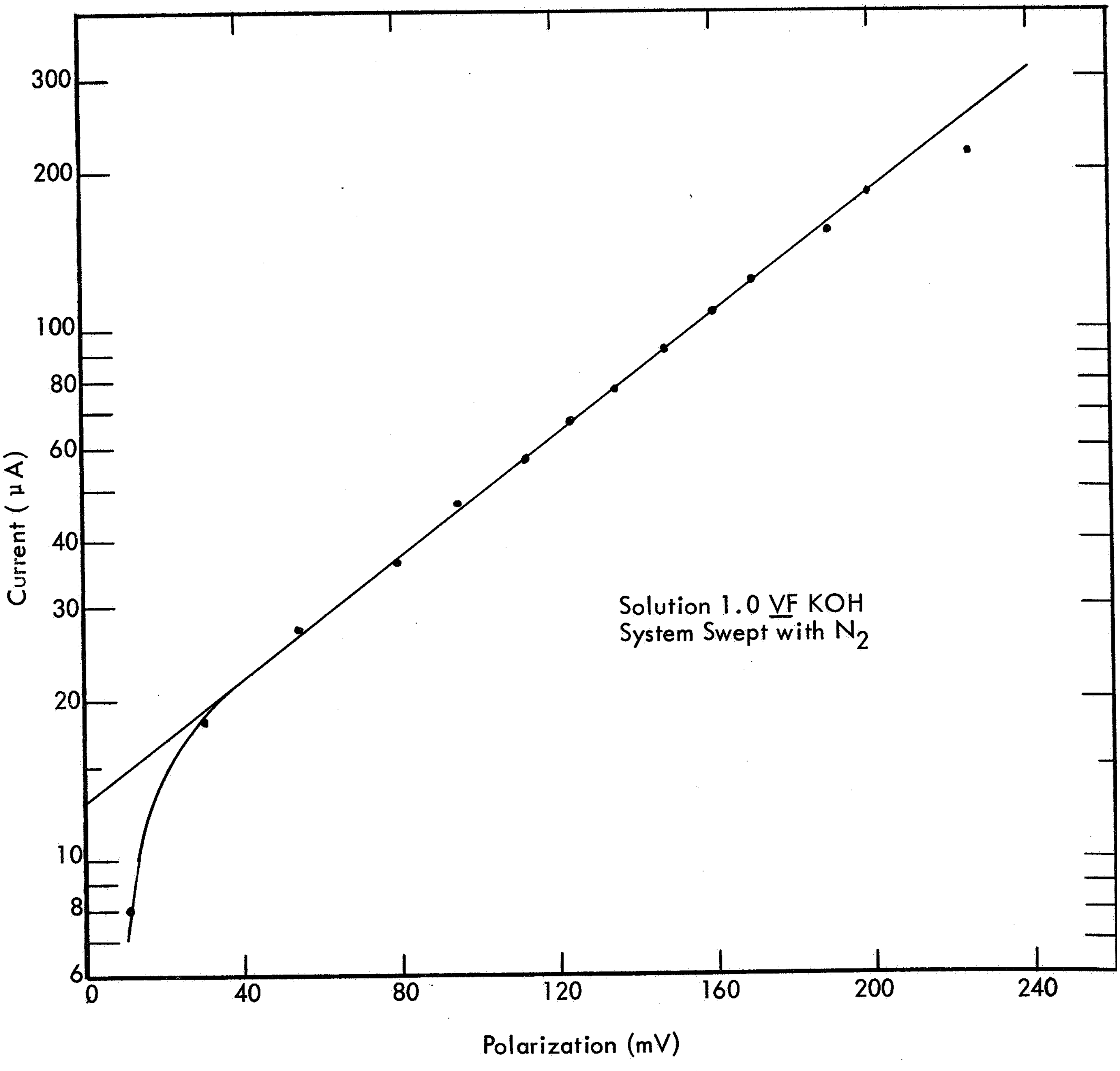

Figure 20. Hydrogen Polarization on Zinc Wire Electrode

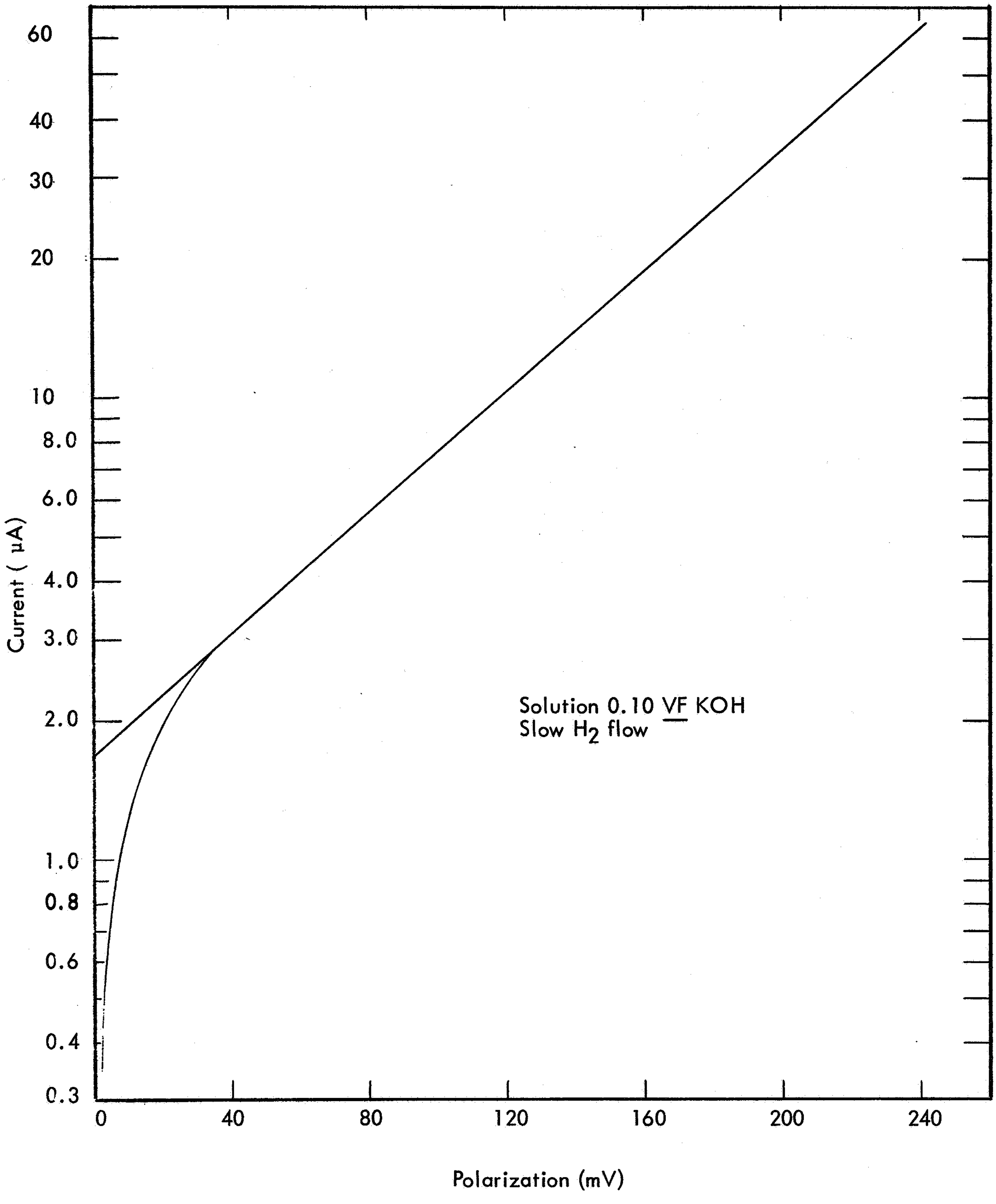

Figure 21. Hydrogen Polarization of Zinc Wire Electrode

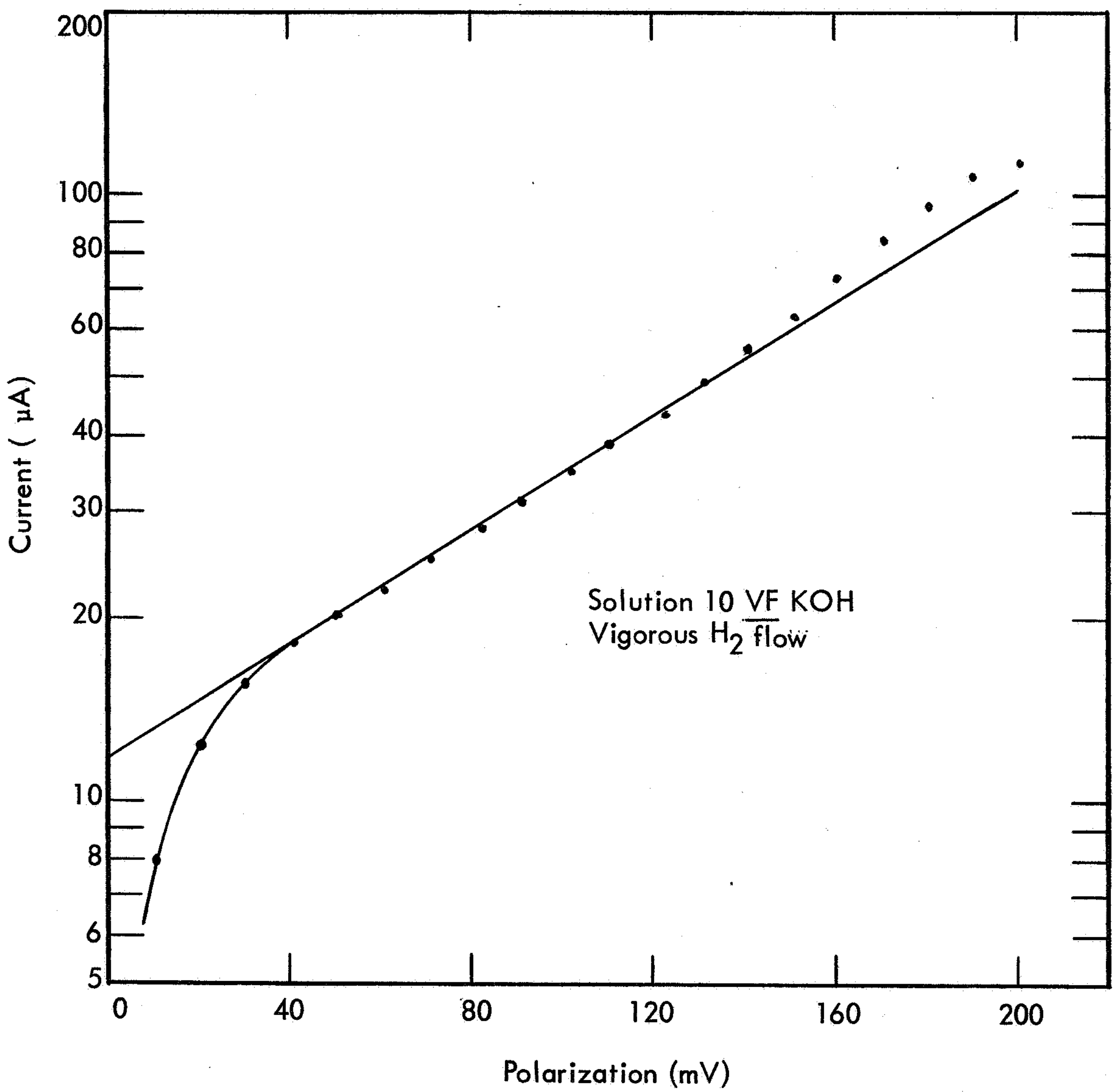

Figure 22. Hydrogen Polarization of Zinc Wire Electrode

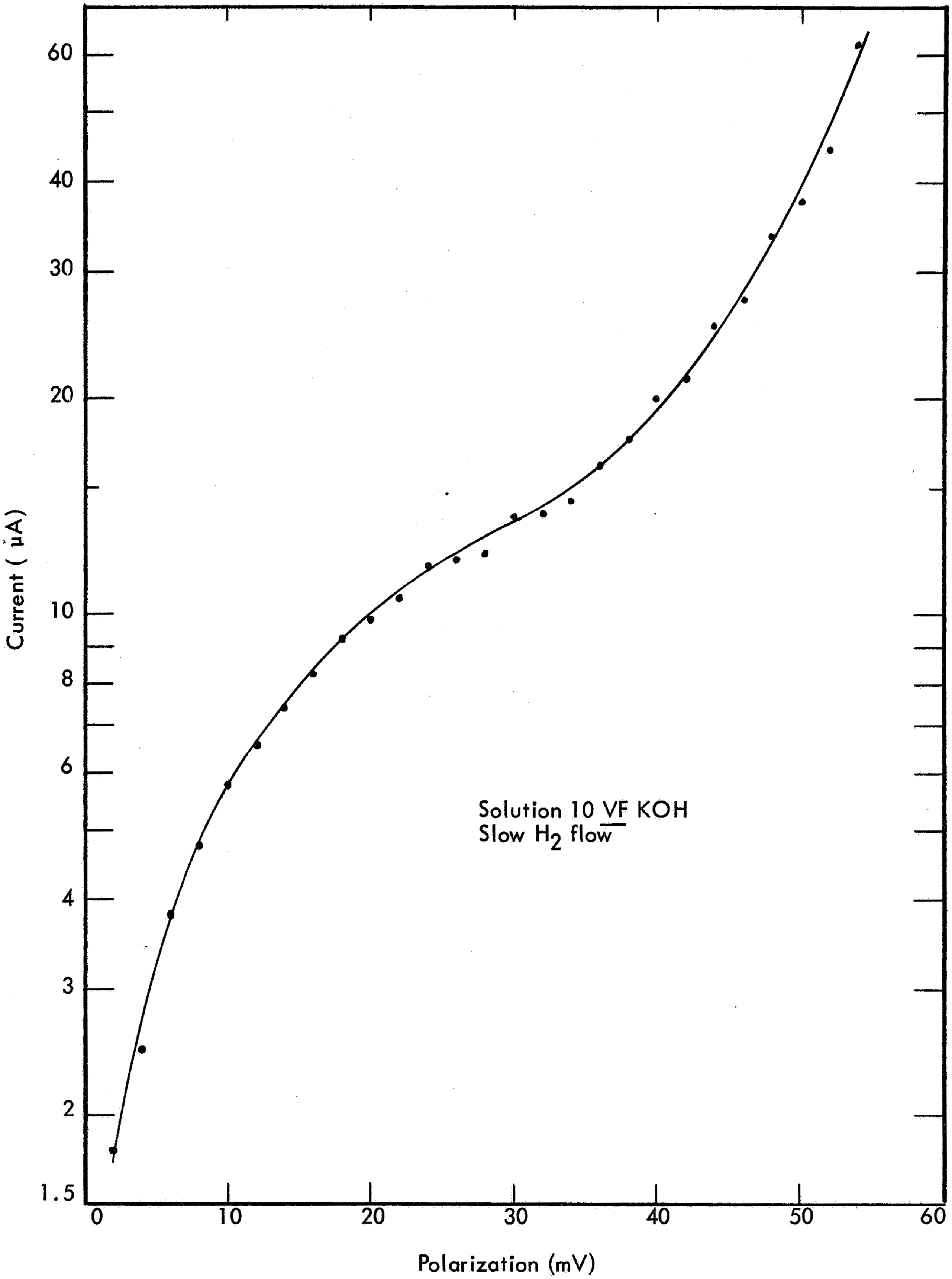

Figure 23. Hydrogen Polarization of Zinc Wire Electrode

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