SECOND QUARTERLY REPORT

INVESTIGATION OF ELECTRODE MATERIALS FOR ALKALINE BATTERIES

JPL 952265

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.

G. Myron Arcand

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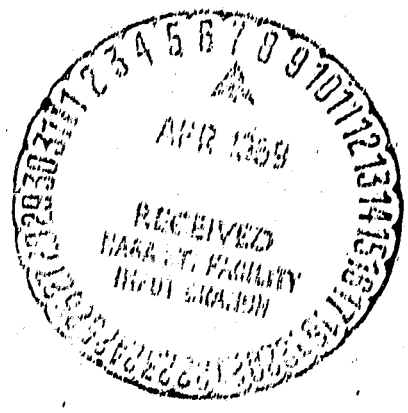

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ABSTRACT

The solubility of Ag_2O in 10 VF KOH was rechecked and found to be 3.5×10^{-4} VF in terms of the Ag(I) concentration. Silver(I) is fairly rapidly deposited on sheet zinc from KOH solutions with 90% of the dissolved silver plating out within the first 6 hours. Chronopotentiometric measurements indicate a 14% decrease in effective surface area of zinc sheet electrodes when silver is allowed to plate on them.

Potassium-amalgam electrodes have been discharged at 1200 mA/cm^2 without serious deterioration of discharge behavior. There is evidence that discharge capacity (defined as the percentage of recovery of charge during the discharge mode) is lower at low amalgam concentrations than at high values. Discharge capacity seems unaffected by charge or discharge rate where the total charge was constant. These capacities were generally in excess of 90%.

No loss in capacity was observed in Zn(Hg) electrodes in 10 VF KOH over a period of 28 days. At all KOH concentrations, K(Hg) electrodes lost at least 20% capacity within 32 days. The stand life of the Na(Hg) electrode was poor except in saturated NaOH where no significant loss was observed after a stand of 1710 hours (71 days).

Potassium-amalgam - AgO cells lost 28% in discharge capacity on being discharged immediately after charge at a very low rate. The loss is probably caused by an internal reaction between Ag(I) and potassium.

The extrapolated exchange-current density, i_o, for the hydrogen overpotential on zinc is greater than $100 \mu A/cm^2$ in 10 VF KOH while it is less at 1 VF KOH. This indicates a lower hydrogen overpotential in higher alkali concentrations. The i_o for this system on cadmium is about 12 mA/cm^2, suggesting a lower overpotential on cadmium than on platinum.

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.

A. DEPOSITION OF SILVER ON ZINC FROM KOH SOLUTIONS.

The experimental methods used in this part of the work have been described previously[1]. Solubility measurements were repeated with the tracer method in order to check those previously obtained polarographically[2].

Results and Discussion

The results of the solubility measurements are shown in Table 1. The average of all the values obtained is 3.5×10^{-4} VF, which compares favorably with that obtained previously. There seems to be very little, if any, trend in concentration up to 13 days, although there was some indication of decreasing concentration after stands of greater than 20 days. The slight peak around 140 hours is probably spurious.

Table 2 shows the decrease in silver(I) concentration in the presence of sheet zinc. These results are somewhat different in magnitude from those reported previously[1] because the concentrations are more nearly saturation values. Also, deposition times were generally shorter. It is apparent that the silver was reduced fairly rapidly in the first few hours and that at least 90% of the dissolved silver was plated out within five or six hours. The results are not sufficiently reproducible to allow calculations of reaction rates.

Table 3 shows the effect of the deposition of silver on the anodic chronopotentiometric behavior of zinc. The results are compared with

the behavior of pure zinc under identical conditions. In all cases, zinc plates were immersed in 10 VF KOH saturated with Ag(I) but not containing excess solid Ag_2O. The chronopotentiograms were run in 10 VF KOH at 100, 125, and 150 mA/cm^2. The values of $i\tau^{1/2}$ are remarkably constant considering the relatively poor control of deposition conditions. The average $i\tau^{1/2}$, 1.04×10^3 $mA\text{-}sec^{1/2}/cm^2$, is significantly lower than the 1.21×10^3 $mA\text{-}sec^{1/2}/cm^2$ for the untreated zinc. It would seem that the deposition of silver lowers the effective surface area of zinc by about 14% and that this decrease is essentially permanent. As many as 23 consecutive runs have been made on the same plate without significant change in the results. As reported previously[1], the initial runs on a treated plate show much smaller transition times but these level out to the values reported after several runs at a particular current density. It seems that there is a relatively large, temporary decrease in effective area which rapidly disappears to leave the permanent and relatively reproducible surface effect.

The data in Table 2 show that most of the dissolved silver is deposited on the zinc within a few hours. Therefore, under the conditions of these experiments, the amount of silver deposited is probably fairly constant. As yet, no attempt has been made to deposit silver in the presence of excess oxide. Such a procedure might produce significant differences in the anodic behavior of the zinc electrodes.

Proposed Work

The effect of more extensive silver deposition on the anodic behavior of zinc will be investigated. An attempt will be made to determine the amount of silver initially deposited and the amount remaining when the maximum transition time is attained. Since the rate of deposition in an unstirred solution will depend on the diffusion coefficient of the Ag(I) in the KOH solution, it is important to determine this value. The

diffusion coefficient will be studied by measuring transition times for the constant-current deposition of silver on a platinum electrode. Studies will be made at various Ag(I) concentrations in different KOH solutions.

B. THERMAL DECOMPOSITION OF AgO AND Ag_2O.

This quarter has been used in modifying the equipment in order to permit operation in controlled atmospheres and to allow more accurate direct measurements of rates of weight loss.

C. THE STUDY OF AMALGAM ELECTRODES.

Experimental

Most of the procedures have been described previously[1]. Several amalgam-AgO cells were constructed by placing a pool of mercury in the bottom of a polyethylene container and mounting a AgO cathode above the pool. The cathode was wrapped in several layers of polypropylene separator to prevent direct contact of the electrodes. Where the Na(Hg) anode was used, the cathode was 1 cm above the pool. The K(Hg)-AgO cells were charged at 5 mA but not to full capacity. Discharges were accomplished at a constant 0.5 mA controlled by an Electronics Measurements power supply.

Results and Discussion

A K(Hg) electrode was discharged at a rate of 1200 mA/cm^2 with the results shown by the solid line in Figure 1. This is compared with a similar electrode discharged at 80 mA/cm^2, shown as a dashed line in the figure. The comparative behavior is remarkable in that the curves are almost identical except for the sudden voltage drop at the high discharge rate after about 20% discharge. Otherwise, the curves coincide or are parallel. The results suggest that the amalgam electrode could be

discharged at even greater rates without seriously impairing its voltage and capacity characteristics.

The discharge capacity* shown by this electrode is remarkable, particularly in view of the discharge rate effects indicated in Table 4. Here, there seems to be a definite trend toward lower discharge capacity as the discharge rate is increased. There are two major differences in the electrodes which might account for the differences in behavior. The high-discharge electrodes had a much smaller surface area and had higher potassium concentrations (0.0069 A-hr/g as compared with 0.002 A-hr/g). Why either of these factors should cause the observed behavior is not known at present. The salient fact here is that, with proper design, this electrode can be made to deliver power at remarkably high rates.

Table 5 shows the apparent effect of charge rate on the discharge capacity of a Na(Hg) electrode. Here, the discharge capacity is seen to deteriorate significantly as the charge rate is increased. It can also be seen that the discharge capacity decreases with decreasing total charge. One would not expect the total charge to have such an effect on the discharge capacity, yet these observations tend to confirm the data shown in Table 4 and Figure 1. More work is necessary to investigate this specific point.

In the K(Hg) electrodes, charge rates ranging from 30 to 450 mA/cm^2 had no significant effect on discharge capacity provided the discharge rates were moderate (around 100 mA/cm^2). At a discharge rate of 300 mA/cm^2, the discharge capacity dropped to 84.3±0.9% for charge rates from 50 to 450 mA/cm^2. However, here again the total charge was lower than in the other cases, being 0.002 A-hr/g as compared with 0.0035 A-hr/g.

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*Discharge capacity is defined as the percentage of recovery of charge during the discharge mode.

Sodium-amalgam electrodes showed no effect of discharge rate over 50 to 450 mA/cm^2; however, the total charge was identical in all experiments.

Table 6 shows the stand-life behavior for the Zn(Hg) electrodes. In all cases, the electrolyte solutions were saturated with zinc oxide. The results were quite erratic except in 10 VF KOH where the electrodes lost essentially no charge over the period of the experiment.

Table 7 shows that the stand life for the K(Hg) electrode is not too satisfactory with a 20% loss occurring in about one month for a saturated KOH solution. Electrodes with lower KOH concentrations had shorter stand lives as would be expected.

Table 8 shows the behavior of Na(Hg) electrodes. The behavior of this system is generally better than that of the K(Hg) system. The maximum stand period observed thus far is 1710 hours or about 2½ months. The loss was only 1%. However, although the saturated NaOH system produced a stable electrode, the operating behavior was poor in that considerable noise was produced. This is probably caused by the transient formation of insoluble material on the amalgam surface during discharge. The result is increased resistance and decreased voltage. Since the film is transient, the voltage decreases are only momentary and cause spikes in the discharge curve. It is possible that this phenomenon could be eliminated by using solutions which are close enough to saturation to allow good stand-life characteristics but sufficiently dilute to prevent noise.

A K(Hg)-AgO cell was set up and discharged at 0.5 mA; the discharge curve is shown in Figure 2. More work should be done on this system although the AgO electrode tends to prevent realization of the optimum performance of the amalgam electrode. It is curious that the capacity of the amalgam electrode appears to be only about 62% although one would expect recovery of at least 90% at the low currents used. Since this experiment has been repeated with essentially the same results, it seems

unlikely the observations are spurious. The low-voltage plateau occurs during the oxidation of mercury and ultimately disappears when a high-resistance film of HgO is formed on the mercury surface.

In these experiments, the amalgam electrode was uncharged when the cell was constructed while the silver electrode was pre-charged. The cell was then charged for 5 minutes at 5 mA for a total charge of 4 16 x 10^{-5} A-hr. Thus, the total concentration of potassium in the amalgam was very small and there is already evidence to suggest a decreased discharge capacity under such circumstances. Possibly more important is the opportunity for Ag(I) dissolved in the electrolyte solution to be reduced directly at the amalgam surface both during charge and discharge. Polypropylene separators serve to prevent physical contact between the electrodes but do not stop the diffusion of Ag(I). The discharge had been in progress 30 minutes when the voltage dropped to the mercury plateau. This would be ample time for considerable reduction of Ag(I) by the potassium in the amalgam. Formation of silver at the surface would not hinder the behavior of the electrode other than to decrease its charge retention.

The Na(Hg)-AgO cell was set up as described and charged at 50 mA for 115 minutes for a total of 0 095 A-hr. The open-circuit voltage of the cell was 2.30 V at end of charge. The system was not charged to full capacity. The cell was then discharged at 300 mA (corresponding to 31.6 mA/cm^2) for 18.1 minutes, which corresponds to 95% discharge capacity. The cell was recharged at 100 mA for a total of 0.083 A-hr and discharged at 50 mA with a discharge capacity of 99%. The cell resistance in this case was quite high so that the immediate voltage drop was excessive. However, the discharge capacity was much higher than found in the previous cases with the K(Hg) anodes. These results seem to refute the argument that silver is reduced directly at the anode since combined operating times with the Na(Hg) electrodes ranged from 133 to 149 minutes

as compared with 35 minutes of operation for the K(Hg) electrode. On the other hand, the amount of sodium in the amalgam was much greater than potassium in the corresponding electrodes. This might be sufficient to swamp out the self-discharge effect. There is the further fact that there seems to be a higher discharge capacity when the total charge is large.

Proposed Work

Investigation of the stand life of the Na(Hg) electrode will continue Discharge measurements will be made at higher rates with both the Na(Hg) and K(Hg) electrodes using a hanging-drop configuration to obtain smaller surface areas. The behavior of Na(Hg) electrodes in electrolytes which are not quite saturated will be studied. The effect of metal concentration in the amalgam on discharge capacity will be considered further. The cycle life of the amalgam electrode will be determined. Separators which will decrease the diffusion of Ag(I) between electrodes will be used in amalgam-AgO cells to see if the expected high discharge capacity can be obtained. Different solvent systems will be tried in an attempt to improve stand life without impairing charge and discharge characteristics. The Li(Hg) and Al(Hg) electrodes will be investigated as well as the Ca(Hg)-$CaCl_2$ system.

D. HYDROGEN OVERVOLTAGE ON ZINC

Experimental

The general experimental arrangement has been reported[1]. Various cell configurations were used in which wire electrodes and wire-end electrodes were tried. These electrodes were mounted in various orientations from horizontal through vertical. No construction gave very satisfactory results Electrodes were pre-treated by cathodic electrolysis at various voltages and currents.

Results and Discussion

Results were not generally reproducible. Some of the variation can be attributed to the difficulty in accurately measuring the areas of the electrodes. However, this inaccuracy cannot account for the drift and fluctuation during any particular run. It seems likely that much greater care must be exercised in purifying the reagents used for the experiments. Greater consideration should be given to the orientation of cell components also.

In spite of the questionable nature of the results obtained, a trend seems to appear in the extrapolated exchange-current density, i_o, with KOH concentration, as is shown in Table 9. While scatter is severe, all indications are that i_o is greater than 100 $\mu A/cm^2$ in 10 VF KOH and less at 1 VF and 0.5 VF KOH. This suggests a greater problem with hydrogen evolution during overcharge conditions at concentrations normally used in alkaline cells than would be found at lower concentrations. Whether a reversal in trend might occur at even higher concentrations has not been determined yet.

A single run was made with a cadmium-wire electrode in 10 VF KOH which produced a fair Tafel region. Extrapolation of the plot yielded i_o = 12 mA/cm^2, indicating a much lower hydrogen overpotential than for zinc and even lower than that for platinum.

Proposed Work

Work will be continued to attempt to obtain reproducible overpotential measurements. A program will be initiated to determine the bubble-point overpotential on zinc and cadmium.

Table 1

Solubility of Ag(I) in 10 VF KOH at 25°

Equilibration Time (hours)	Ag(I) Concentration (VF x 10^4)
2	3.52
24	3.55
142	3.70
166	3.70
190	3.51
214	3.50
238	3.51
310	3.52
333	3.60
357	3.47
2	3.31
24	3.58
118	3.48
144	3.64
168	3.47
192	3.50
226	3.37
288	3.38
312	3.50
Average	3.50

Table 2

Removal of Silver from KOH Solution by Deposition on Zinc

Weight of Zn (g)	Deposition Time (hours)	Silver Concentration ($\underline{VF} \times 10^6$)
0.4049	0	340
	4	15
	6	5
	9	5
	29	1
0.3678	0	346
	2	104
	5	33
	7	11
0.4059	0	343
	4	27
	6	12
	28	7
0.3719	0	360
	2	70
	4	32
	6	32

Table 3

Chronopotentiometric Behavior of Zinc Anodes Plated with Silver

Current Density (mA/cm^2)	Transition Time (sec)	$i\tau^{1/2}$ ($mA-sec^{1/2}/cm^2$)
150	47.7	1059
125	68.3	1032
100	119	1091
	Average	1044
Untreated Zn		
150	65.7	1214

Table 4

Effect of Discharge Rate on Discharge Capacity of K(Hg) Electrodes

Charge Rate = 100 mA/cm^2

Charge = 0.002 A-hr/g Hg

Discharge Rate (mA/cm^2)	Discharge Capacity* (%)
50	95.8 ± 1.2
150	92.2 ± 1.2
250	91.7 ± 0.6
350	85.3 ± 1.4
450	83.2 ± 0.5

Table 5

Effect of Charge Rate on Discharge Capacity of Na(Hg) Electrodes

Discharge Rate = 300 mA/cm^2

NaOH Concentration = 10 VF

Charge Rate (mA/cm^2)	Charge (A-hr)	Discharge Capacity* (%)
50	0.034	96.5
100	0.019	91.1 ± 2.9
150	0.013	86.2 ± 4.7
200	0.012	83.0 ± 4.9
250	0.0075	79.5 ± 1.0

*Precision of averages estimated within 95% confidence limits.

Table 6

Stand Life of Zn(Hg) Electrodes

Discharge Rate = 16.7 mA/cm^2

KOH Concentration (VF)	Total Charge (A-hr)	Charge Rate (mA/cm^2)	Stand Time (hours)	Discharge Capacity (%)
1	0.125	2.0	169	79
			363	59
			510	37
			752	60
2	0.0725	1.7	100	84
			317	80
			653	85
10	0.1015	2.3	27	99
			265	100
			672	100

Table 7

Stand Life of K(Hg) Electrodes

Charge Rate = 2.3 mA/cm^2

Discharge Rate = 16.7 mA/cm^2

KOH Concentration (VF)	Total Charge (A-hr)	Stand Time (hours)	Discharge Capacity (%)
8	0.105	48	75
		149	67
10	0.1015	30	97
		149	88.5
		312	82
		576	35
10	0.0893	79	31
10	0.1062	121	76
		312	52
		391	36
		628	16
Saturated	0.105	30	96
		198	93
		531	91
		770	78

Table 8

Stand Life of Na(Hg) Electrodes

NaOH Concentration (VF)	Total Charge (A-hr)	Charge Rate (mA/cm^2)	Discharge Rate (mA/cm^2)	Stand Time (hours)	Discharge Capacity (%)
5	0.19	3.3	33	30	88
				220	96
10	0.0915	2.0	16.7	2.5	84
				195	94
				534	78
10	0.15	3.3	33	169	85
Saturated	0.080	2.0	16.7	52	100
				246	100
				1710	99

Table 9

Effect of KOH Concentration on i_o for Hydrogen on Zinc

KOH Concentration (VF)	i_o ($\mu A/cm^2$)
0.5	15.0
1.0	60.0
10	210
10	350

REFERENCES

[1]G. M. Arcand, "Investigation of Electrode Materials for Alkaline Batteries," August 25, 1968, First Quarterly Report on Contract JPL 952265

[2]G. M. Arcand, "The Reactions Pertaining to Zinc-Silver and Cadmium-Silver Batteries," August 1, 1968, Final Report on Contract JPL 951887

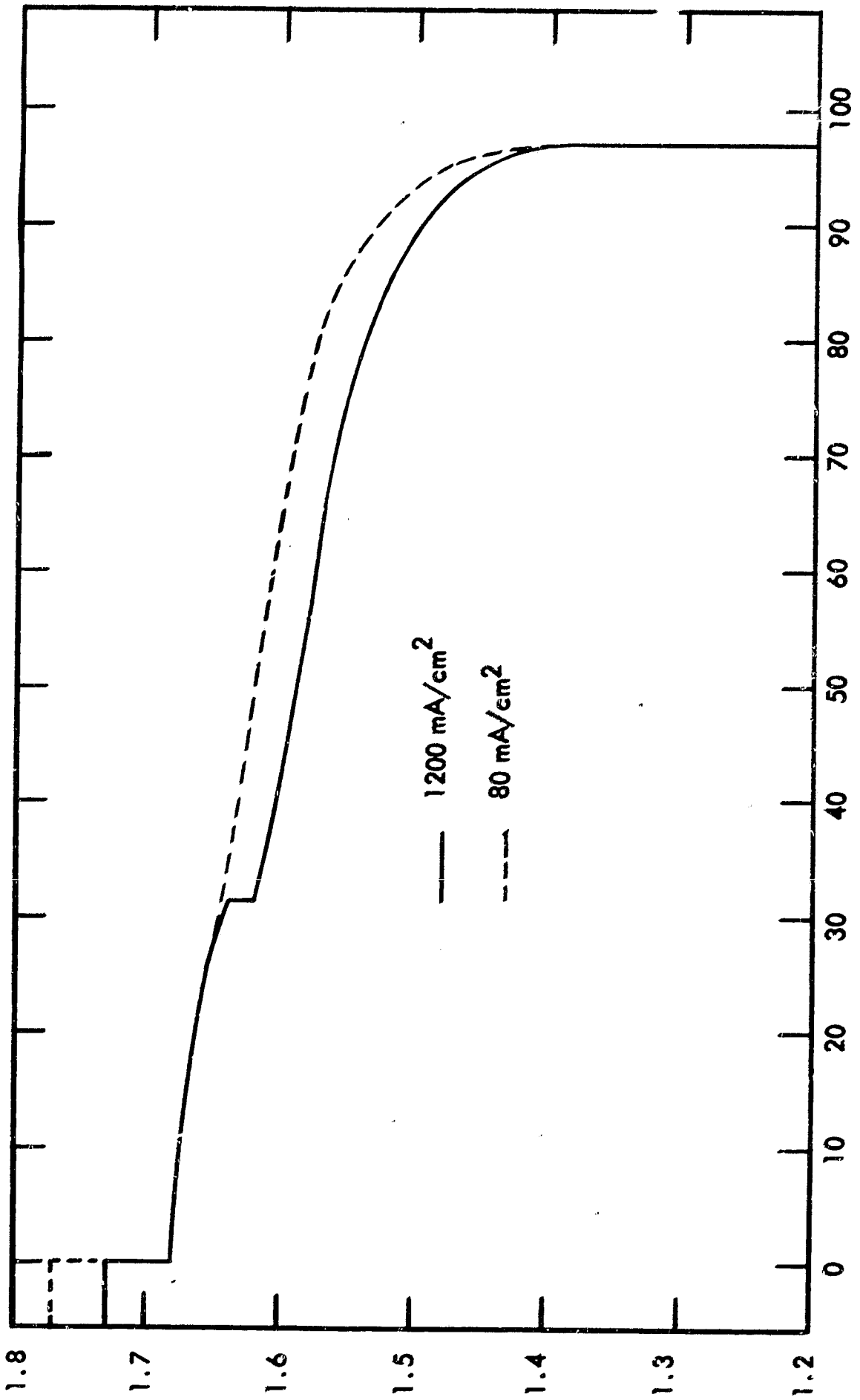
1200 mA/cm²
80 mA/cm²
Electrode Potential vs HgO/Hg (V)
1.8
1.7
1.6
1.5
1.4
1.3
1.2
0
10
20
30
40
50
60
70
80
90
100
Discharge of K(Hg) Electrode
Discharge Capacity (%)

Figure 1.

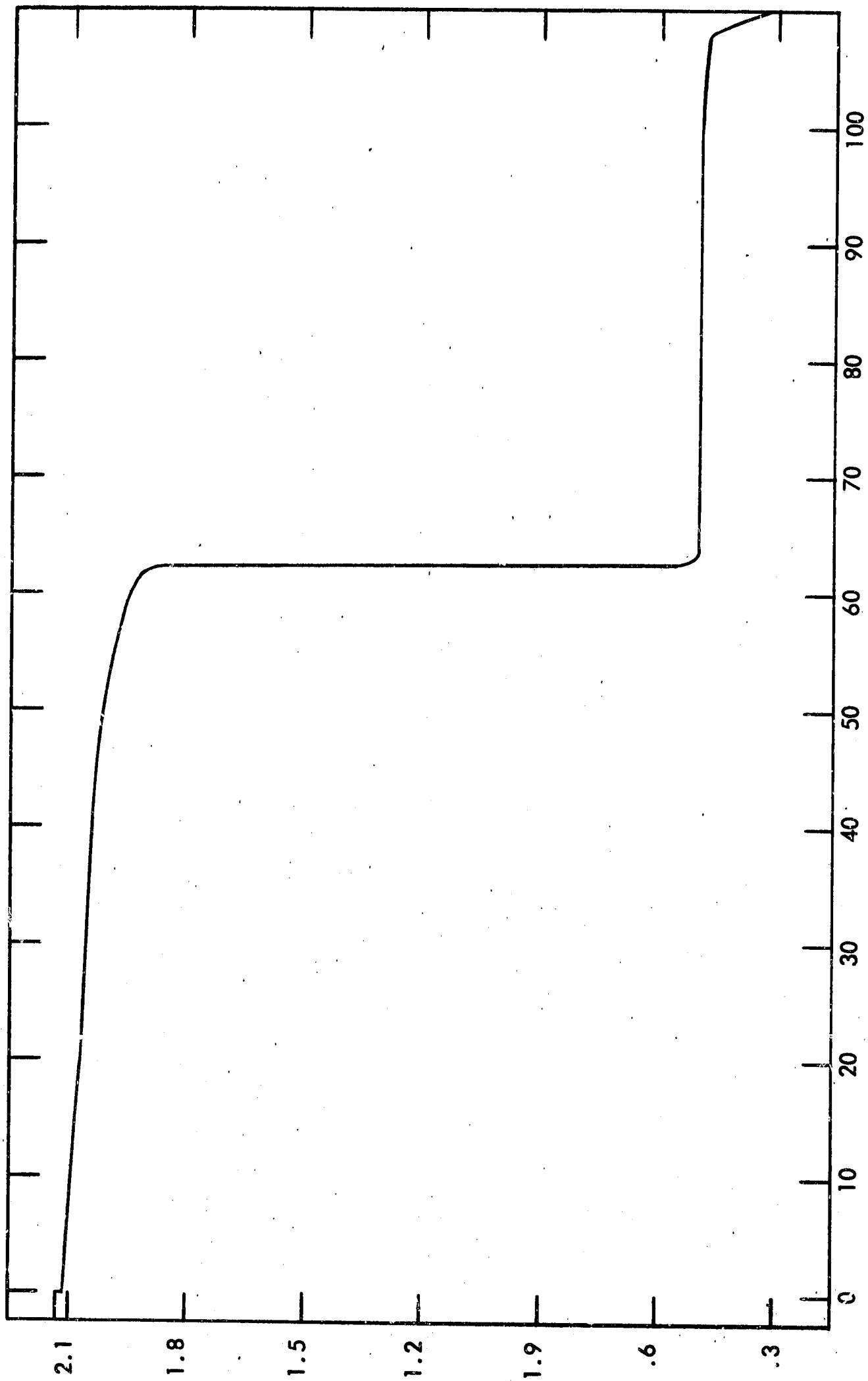

Figure 2. Discharge Behavior of K(Hg) - AgO Cell