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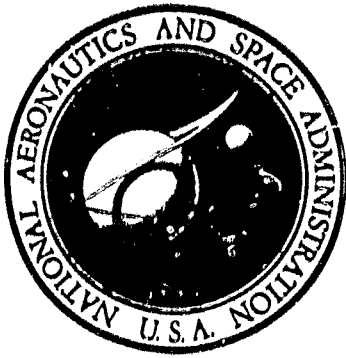
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Final Report

LOW-TEMPERATURE BALLOON BATTERY

By

W. N. Carson, Jr.
J. F. Wilfore

September 30, 1968

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

CONTRACT NAS 5-11556

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LOW-TEMPERATURE BALLOON BATTERY

FINAL REPORT

September 30, 1968

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Research and Development Center
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Contract NAS 5-11556

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

FOREWORD

This final report covers work performed be-
tween May 29, 1968 and September 29, 1968 under
Contract NAS5-11556, "Low-temperature Balloon
Battery." It has been prepared by the Research
and Development Center of the General Electric
Company in Schenectady, New York, for the Na-
tional Aeronautics and Space Administration
Goddard Space Flight Center, Greenbelt, Mary-
land.

Dr. R. C. Osthoff, Manager of the Electro-
chemistry Branch, in the Physical Chemistry
Laboratory of the Research and Development Cen-
ter, was Program Manager. The Program was
under the technical direction of Dr. W. N. Carson,
with the assistance of Mr. J. F. Wilfore, who was
responsible for computer equations and programs.

Detailed studies on the indicated systems were
carried out by the following members of the Re-
search and Development Center:

Dr. H. A. Catherino -- solid-state cells

Mr. C. R. Seaward -- silver chloride cells

Mr. R. N. King -- mercuric oxide-cadmium
cells

Mr. F. C. Laczko -- cell structure and
sealing

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Section 1

SUMMARY AND CONCLUSIONS

SUMMARY

This program was directed towards determining the suitability of four galvanic cell systems (mercuric oxide-cadmium, silver chloride-cadmium, silver chloride-zinc, and silver-iodine with solid state electrolyte) as the basis for the design of a low-temperature, rechargeable balloon battery. The general requirements to be met by the design are given in Table 1.

Table 1

BALLOON BATTERY REQUIREMENTS

Operation:	Discharge:	12 hours at -60° C
		20 milliamperes continuous plus 16 one-ampere pulses of 625 milliseconds, 40 seconds apart, every 90 minutes
		Capacity at -60° C at 20 milliamperes plus pulse load 2.0 ampere-hours
	Charge:	12 hours at -30°C
		67 milliamperes maximum available current
	Duration:	6 months, 12 desired
Battery Voltage:		12.0 volts ±20 percent charge and discharge
Aspect Ratio:		Less than 5.0 grams per square centimeter
Total Weight:		700 grams
Case Requirements:		Frangible, sealed operation, low-pressure operating capability

Experimental studies on the four cell systems showed that all four systems gave fair to good discharge performance at -60°C; all can be recharged at -60° C and -30°C with high efficiency. However, none of the systems can meet the weight specification of 700 grams if the remaining specifications are to be met as well. The best system, in terms of minimum total weight needed and performance at low temperatures, is the mercuric oxide-cadmium system with 60 percent cesium hydroxide electrolyte. This cell system was the one selected for further study.

The design of the cell to deliver one-ampere pulses at -60°C requires the use of a large electrode area; fortunately, this requirement is compatible with the design requirement of a low specific weight (grams per square centimeter) for the battery which is imposed by the limit for the aspect ratio of five grams per square centimeter. It should be noted that the specific weight for the battery is not the same as the aspect ratio, since the mechanical requirements lead to a configuration that allows more than one square centimeter of battery to be "exposed" to one square centimeter aspect.

A light weight, readily-fabricated cell case and collector design was obtained by using a design concept in which the case is a thin plastic material and the electrodes are painted or "printed" on the case by brush, spraying, or silk screening. The tentative design employs as the case a polyethylene film 0.0018 inch thick; this is treated with chromic acid to prime the surface. A pattern of rectangular patches which form the cell collectors and the intercell connectors is laid on the film by placing on the appropriate areas a thin layer of epoxy adhesive onto which a thin layer of conductive silver paint is deposited. The active cell materials and separator are deposited on the silver substrate in such a manner that when the film is folded and the appropriate edge seals made, the cells for the battery are formed, and the intercell connectors are in place. The result is a thin, flexible strip which can be folded or rolled into the final battery configuration.

The specific weight of the case and collector is 0.05 grams per square centimeter; the cell area is dependent upon the operating current density used to deliver the pulse. The specific weight of the active materials, separator, and electrolyte also vary with cell area, since these are fixed by the requirement for two ampere-hours total capacity. At the -60° operating point, the specific weight for these materials will be about 0.03 to 0.05 grams per square centimeter. In addition to the cell case, etc., the battery assembly will require additional material for support and vapor barrier; this has a specific weight of 0.1 grams per square centimeter; however, the area needed is not necessarily the same as the cell area, as it depends upon the configuration chosen to meet the aspect ratio requirement of five grams per square centimeter.

The basic design is versatile and will be readily manufacturable. A key feature is the ease with which the cell dimensions and inner connections can be changed without major change in manufacturing tooling or handling.

Tests on the fabrication method, on the performance of cells made to the design concept, and on the stability of the deposited silver conductor and active material were made on small scale units of about one-twentieth the size of the projected final design. These units were cycled ten to twelve times at the current densities and temperatures for the final cell. The results of the limited cycling were favorable; hence the basic design appears

to be feasible, and the design can serve as the basis for future development. Long term tests were precluded by the short contract period.

In related work on rechargeable mercuric oxide-cadmium cells employing a more conventional design, cycle tests have shown that over 1000 cycles can be obtained using a $C/10$ charge to a voltage cutoff, a $C/5$ discharge to 50 to 75 percent depth of discharge at room temperature. This number of cycles, if it can be obtained with the new design operating at the required temperatures, is about six times the number needed for the six months operating time, assuming only one substantial charge-discharge cycle per day. Pulse drains during charge are not considered to be a discharge cycle.

The customary electrolyte for the mercuric oxide-cadmium cell system is 31 weight percent potassium hydroxide, which can be used at high and low temperatures. However, this electrolyte has a freezing point of -65°C, which is too close to the operating point of -60°C for reliability. In addition, the performance of the cells is affected adversely by the closeness of the freezing point to the operating temperature. A shift was therefore made to 60 weight percent cesium hydroxide (freezing point -75°C) in order to increase the reliability and performance at -60°C.

In the investigation, the use of solar heat storage and thermal shielding was examined, with Melpar data and design concepts (Contract NAS5-11557). In using thermal shielding and heat storage, the hope is that the increase in cell performance (current density at a selected cell voltage) with the increase in temperature will allow a reduction in cell case, collector, and support weight by making possible the use of a smaller sized cell. This weight reduction, in turn, is used to offset the added weight needed for the heat storage material and thermal shielding. With the use of the Melpar design, the heat shield weight was found to be so large that only the use of a large heat differential of 40° to 50°C could reduce the overall weight of the battery to a minimum.

The design study on the battery configuration showed that a cylindrical design was both feasible and desirable, in that the option for adding heat storage and thermal shielding could be readily made at minimum weight increase. The tentative design calls for a cylinder with an arbitrarily chosen length of 75 centimeters, and a radius selected to give the aspect ratio of five grams per square centimeter. Calculations on the expected weight and size were set up with the additional constraint that the cylinder area should not exceed the cell area; this is unduly restrictive and leads to "no solution" for the design with heat storage. In any future design analyses, this constraint should be replaced by one that calls for the cell area to be equal to the cylinder area, with the proviso that the area is at least the value needed to give the maximum current density called out by the pulse output requirements; i.e. the radius must be some minimum value.

A parametric equation for the total battery weight was derived and is presented in Section 3, "Technical Studies." In the equation, the independent variable is the radius of the cylinder; provision is made for heat storage and thermal shielding. The assumption was made in the derivation of the equation that all of the mass of the battery is located on the circumference of the cylinder; this is valid for the battery proper, the support and heat storage material, but not for the thermal shielding. A corrected equation should be used in future studies.

Since the cylinder radius must be arbitrarily selected to give a design solution, it is possible to set a condition on the value of the radius. In this case, the condition is that the aspect ratio shall not exceed five grams per square centimeter. The result of applying this condition is an equation by which one can solve for the value of the radius when all of the cell and system parameters are assigned. However, the equation has both algebraic and transcendental type terms, and an analytic solution for r is not possible . A computer program was therefore set up in which the value of the radius is determined by an iterative process; the program is presented in this report, and the program tape, etc., will be stored in the senior author's project file for possible later use.

The value determined by the procedure gives the radius for which the total battery weight is the minimum necessary to meet the aspect ratio of five grams per square centimeter. This is not the minimum weight for a battery meeting the electrical load requirements. A revamping of the parametric equation is needed in future work to remove the restrictions placed ' on the design by the present equation.

A large fraction of the total battery weight is required as expected, for the cell cases, collectors, and support. If heat storage and thermal shielding are used, the ratio of structure weight to active cell material weight increases several-fold. For operation at any temperature, the active cell material weight is 410 grams (2 ampere-hours; 14 cells). For operation at -60° C with no heat storage or thermal shielding, the total weight ranges from 1150 grams to 1590 grams, depending on the current density assumed (0. 7 to 1. 1 milliamperes per square centimeter).

The assumptions and restrictions built into the computer program and the parametric equation do not allow a solution for the cylinder radius to be obtained when heat storage and thermal shielding are included; thus there was no solution, within the limits set, for the cylinder. A larger cylinder radius than the one giving a cylinder area equal to cell area, or a longer cylinder than seventy-five centimeters, is needed to amortize the shield and heat source weight.

An alternative design was examined in which the battery is built into a strip that is limited in width by the aspect ratio of five grams per square centimeter (i. e. , if a one-centimeter length of the strip is intercepted

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edgewise, the weight is five grams), and whose length is determined by the cell area required. This gives the following results:

- At -60° C (no heat storage or thermal shielding) total weight is 2,400 to 1700 grams, length 480 to 340 centimeters.

- At -50° C (with heat storage and thermal shielding) total weight is 7000 to 4200 grams, length 1400 to 820 centimeters.

- At -40° C, total weight is 2800 to 1900 grams, length 560 to 400 centimeters.

- At -30° C, total weight is 1800 to 1300 grams, length 360 to 250 centimeters.

These results show that if the heat storage-thermal shielding approach is used, consideration must be given to decreasing the cell area by increasing the operating temperature so that the savings in cell casing, etc., can offset the increase in weight due to the thermal shield and heat storage material needed. The results also show that a reduction in specific weight of the thermal shielding material is desirable. In the calculations described here, the parameters for the thermal shielding and heat storage material are taken from the final report by Melpar, Inc., on Contract NAS5-11557, August 1968.

CONCLUSIONS

The general conclusions that can be drawn for this study are:

1. A battery based on the use of mercuric oxide-cadmium cells can be cycled at -60°C, in accordance with the performance requirements set forth in the Request for Proposal.

2. The battery design with two-ampere-hours capacity for operation at -60°C will meet all requirements set forth in the Request for Proposal except the weight of 700 grams. A weight of 1200 to 1600 grams is needed.

3. Other cell systems can be operated at -60° C, but the mercuric oxide-cadmium system is the best with respect to total weight required and performance.

4. A 60 weight-percent cesium hydroxide electrolyte must be used in place of the customary 31 weight-percent potassium hydroxide electrolyte if operation at -60°C is planned.

5. Cell heating can be used, but a severe weight penalty is incurred unless the design allows a temperature difference of 30° C or more.

6. Additional work on the system is needed with respect to cell fabrication, cycle testing, and refinement of the design.

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Section 2

SPECIFIC RECOMMENDATIONS

The results of this preliminary study show the complete feasibility of obtaining a low-temperature battery based on the mercuric oxide-cadmium cell system. The following program is recommended for a follow-on to the study:

1. Complete the development of the "printed" battery design. This would include work on reducing the structural weight (cell cases, collectors, support, heat shielding, etc.) on proving the fabrication procedures, on maximizing the performance of the cell active materials, and on completing the evaluation of the cesium hydroxide electrolyte.

2. Complete the design study on battery configuration and heated versus unheated system. This would include completion of the computer calculations for the evaluation of a variety of configurations. Emphasis would be placed on obtaining the minimum weight design consistent with manufacturability, life, and meeting system requirements. Unless a sizable saving in weight is obtained by use of a heated system, it is felt an unheated system is the one of choice since it will be unaffected by the expected prolonged eclipse during operation, and will be simpler to fabricate.

3. Fabricate cells and test. This will vindicate the material and design studies, and furnish operational data for use of the batteries.

4. Examine charge control methods.

5. Fabricate batteries for customer evaluation and tests.

Section 3

TECHNICAL STUDIES

GENERAL

The purpose of this program was determination of the suitability of several cell systems* for use in low-temperature balloon batteries. The general system and functional requirements were given in Table 1. From these requirements, plus the constraints imposed by battery designs in general, a parametric equation for the weight of the battery can be derived. A set of parameters is derived from the battery characteristics and system requirements; part of such a set is shown in Table 2. Equation 1 is the parametric equation using these parameters:

$$W_T = n \cdot W_1 + \frac{n \cdot 1000}{J} \cdot W_2 + A \cdot W_3 = \text{Total Battery Weight (1)}$$

The actual assignment of the values for most of the parameters depends upon the experimental data obtained for a given battery system; the program was directed in large part towards determining data to allow assignment of values to the parameters for calculation of the total battery weight.

The values for the maximum and minimum voltages follow directly from the requirement of 12 volts ± 20 percent. The number of cells must be an integer, with an upper limit imposed by the requirement that the maximum voltage not be exceeded. In the design of the balloon battery, the charging voltage is the maximum cell voltage; hence its use in calculating n. The high drain voltage V_D is the voltage of the cell when the maximum load current is flowing, and is chosen to give the minimum design battery voltage.

The selection of the current density to be used in the design is made by entering the value of the discharge voltage, V_D, into the polarization curve for the cell. This gives the maximum current density that can be used within the design limits on cell voltage. The calculations and selection for current density are as follows:

1. Determine the number of cells, n, by dividing the maximum battery voltage by the charging voltage of the cell.

2. Determine the minimum cell voltage, V_D, by dividing the minimum battery voltage by the number of cells, n.

3. Determine the maximum allowable current density, J, by entering the minimum cell voltage, V_D, into the polarization curve and reading off J.

*Mercuric oxide-cadmium, silver chloride-cadmium, silver chloride-zinc, and silver-iodine solid state.

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Table 2

DESIGN PARAMETERS

Parameter	Symbol	Specification	Design
Maximum Volts	--	14.4 volts	14.4 volts
Minimum Volts	--	9.6 volts	10.0 volts
Number of Cells	n	Integer	$\frac{14.4}{V_C} \cong n$
Cell Open Circuit	E	-- volts	Value determined by cell system used
Charging Voltage	V_C	-- volts	Voltage of cell charging at $i=67$ milliamperes $n\,V_C \le 14.4$
High Drain Voltage	V_D	-- volts	Cell operating voltage for $i=1000$ milliamperes (pulse load) $n\,V_2 = 10$
Current Density	J	-- milliamperes per square centimeter	Determined at V_D
Active Material Weight	W_1	-- grams per two ampere-hours	Value set by system
Cell Case and Collector Weight	W_2	-- grams per square centimeter	Set by cell design
Support Weight	W_3	-- grams per square centimeter	Set by battery configuration
Support Area	A_s	-- square centimeters	Set by battery configuration

The active material weight, W_1, is the weight of cell material consumed in proportion to ampere-hours; i.e., anode and cathode active materials, consumed electrolyte, binder and electron carrier materials used in fabricating the electrode, etc. The cell case and collector, plus unconsumed electrolyte weight, are proportional to maximum current, and are thus dependent upon the operating current density, J. The support weight is a function of the battery configuration, which gives the total support area A_s, and the specific weight of this area. For cylindrical designs A_s is obviously equal to $2\pi rl$, where r is the cylinder radius and l is the length.

It must be emphasized that the total weight given by Equation 1 is useful only for comparisons, with W_3 or $A_s = 0$. A more complete equation is given later.

INITIAL SYSTEM STUDIES

Silver Chloride Cells

Silver Chloride cells with zinc and cadmium electrodes have been constructed and discharged at $-60°$ C. Figure 1 shows the polarization curves. The cause of the very steep drop in cell voltage at low current densities is not known; the drop-off appears to be associated with the silver chloride electrode because of the similarity of the curves for each cell.

The performance of the cells at $-60°C$ is surprisingly good, but not adequate for the balloon battery. A calculation of the value of the current density, J, needed to give a total weight of 700 grams to the basic silver chloride-cadmium battery (Equation 1, with W_3 or $A_s = 0$) is J = 2.5 milliamperes per square centimeter. The actual weight for the observed current density at the required discharge voltage, V_D, of J = 0.05 milliamperes per square centimeter is 18,350 grams. The values for the zinc cell are 1.5 milliamperes per centimeter and 1650 grams.

The electrolyte is the eutectic lithium chloride-water solution, 24.85 percent lithium chloride by weight, whose freezing point is approximately $-72°C$. This is the best electrolyte found for the systems; the relatively low conductivity at $-60°C$ (35×10^{-4} ohm^{-1} centimeter^{-1}) is discouraging for obtaining high current densities.

Since the electrode designs are close to optimum in design and the electrolyte is the only suitable one found, an improvement over the present J values is unlikely. For this reason, no further work was carried out on either system.

The test Cells were made up as follows:

Cathodes - Cut from a 0.014-inch rolled silver chloride sheet which was superficially reduced to form a thin metallic silver layer to serve as collector. This silver chloride sheet electrode was originally designed to serve as the cathode in torpedo propulsion batteries. Electrode size was 5.6 by 4.4 centimeters (25 square centimeters); theoretical capacity, 1.3 ampere-hours.

Anodes - Zinc anode cut from a pure zinc sheet, 25 square centimeters; theoretical capacity, 7 to 8 ampere-hours. Cadmium anode was a VO-4 negative, one ampere-hour capacity, precharged in alkali, washed and dried before use. Similar electrodes in nickel-cadmium cells give more than 95 percent capacity.
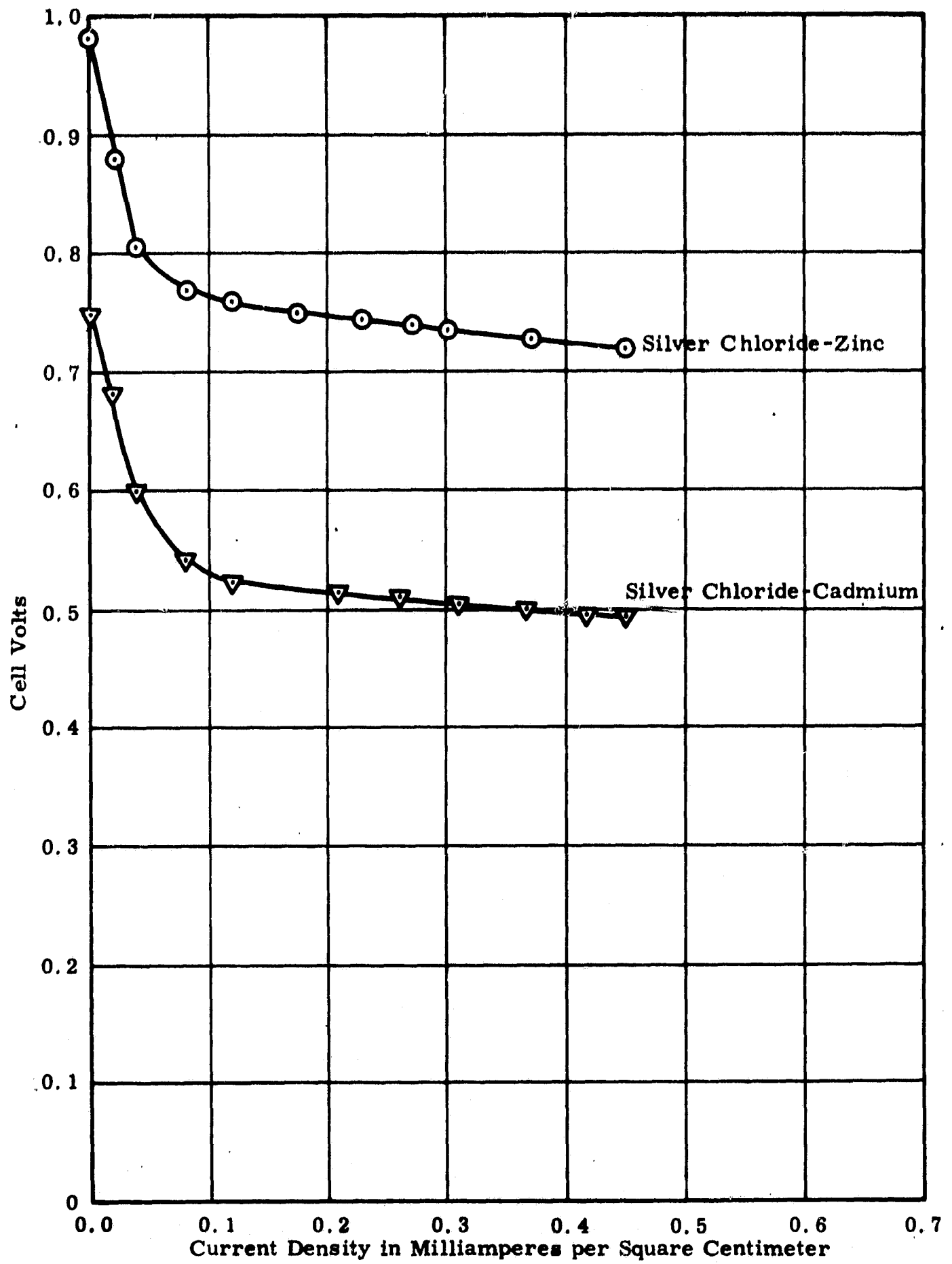
Figure 1. Polarization Curves for Silver Chloride Cells (25 Percent Lithium Chloride Electrolyte; -76° F)

<u>Electrolyte</u> - 25 mole percent lithium chloride; this is the eutectic composition, freezing point -72°C. Five cubic centimeters used per cell.

<u>Cell Cases</u> - Lucite plastic, electrode spacing about 0.015 inch.

Capacity on discharge at -60°C at 4 milliamperes per cell was only a fraction of the anode or cathode capacity. Cells accepted one recharge at -30°C. No other tests were run.

<u>Solid-state Cells</u>

Cells of the type:

$$Ag/RbAg_4I_5/RbI_3(C)$$
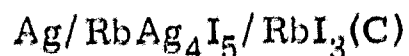
have been constructed and operated at -60°C. Figure 2 is the polarization curve for the cell. This cell can be discharged and charged at least 50 cycles at relatively high rate. However, the cell system calculations indicate that this system is unsuitable for the balloon battery application, since the necessary weight of the active cell materials (silver, rubidium tri-iodide) is greater than 700 grams. Using the present value of J of 0.24 milliamperes per square centimeter, a total battery weight of over 55,000 grams is obtained. The assigned parameters and calculation are shown in Table 3.

Table 3

SOLID ELECTROLYTE CELL CALCULATIONS

$E = 0.64$ volts

$n \cong \dfrac{14.4}{0.64} = 22.6; n = 22$

$V_D = \dfrac{10}{22} = 0.46$ volts per cell

$J = 0.24$ milliamperes per square centimeter

$W_1 = 470$ grams per equivalent; 17.6 grams per ampere-hour

$W_2 = 0.42$ grams per square centimeter

$W_3 = 0.20$ grams per square centimeter

$W_T = 22 \times 2.0 \times 17.6 + \dfrac{22,000}{J_2} (0.42 + 0.20)$

$\qquad = 785 + \dfrac{13,600}{J_2}$

$\therefore$ no J_2 for $W_T = 700$

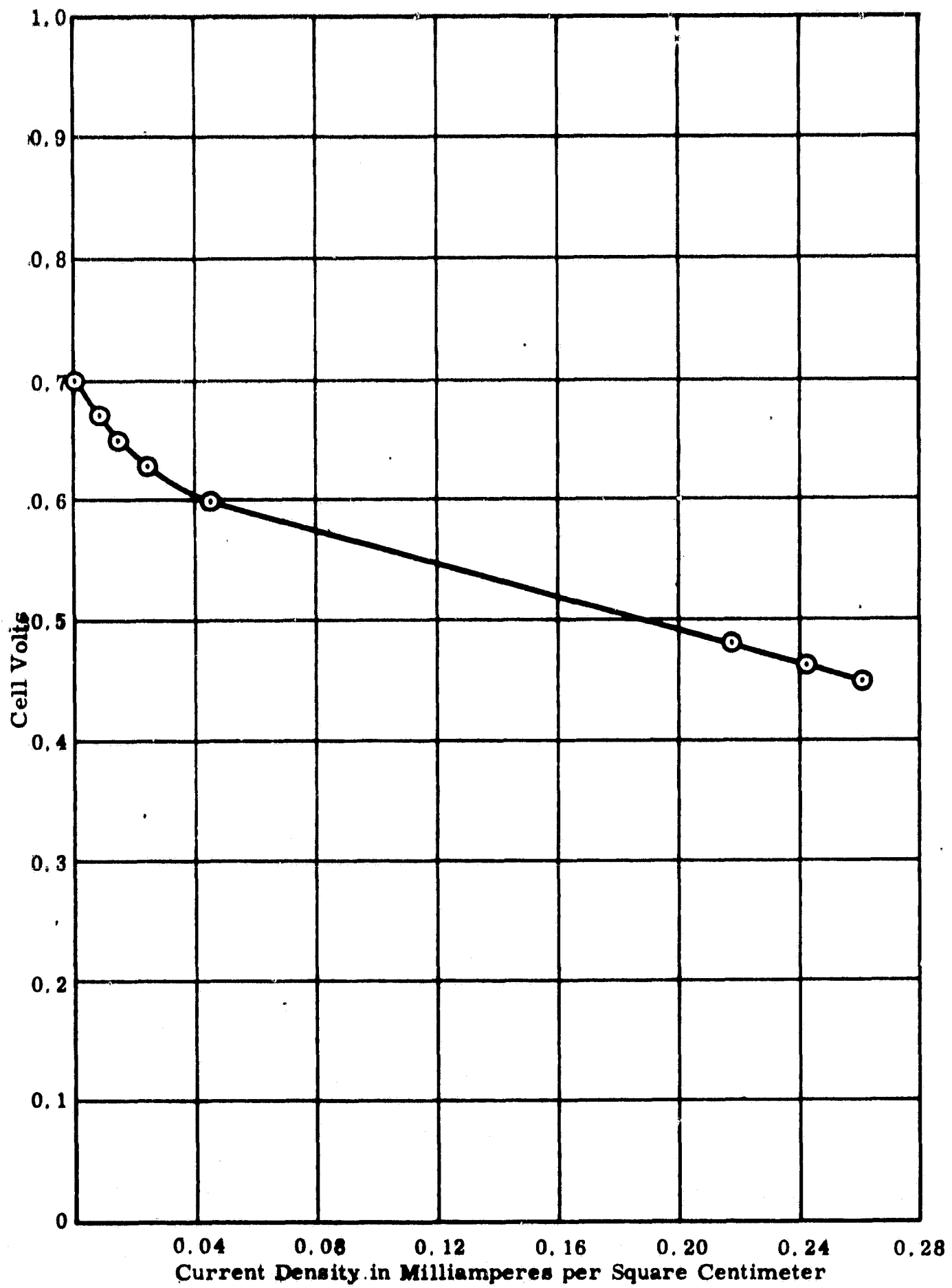$W_T = 785 + \dfrac{13,600}{0.24} > 55,000$ (present values)

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Figure 2.   Polarization Curve for a Silver-Iodine Cell
(RbAg$_4$I$_5$ Electrolyte; -76°F)

Because of the high weight of the active materials, no further work on this cell system is planned for this program. The original, optimistic calculations on this cell neglected to include the rubidium iodide necessary to carry the iodine; the inclusion of that material nearly doubles the previous equivalent weight, which was already quite large.

The experimental cells were disks 1-1/8 inches in diameter (6.5 square centimeters), and about two millimeters thick. Five layers were used; fabrication was accomplished by pressing at room temperature, at 35,000 psi. The wafer was used without further packaging; the performance is quite stable at -60°C.

Layer I was an expanded silver metal grid with a silver wire spot-welded to the screen to serve as a lead.

Layer II was the solid electrolyte, $RbAg_4I_5$. This material was prepared by mixing rubidium iodide with silver iodide in a 1-to-4 mole ratio and fusing in a pyrex beaker on a hot plate. Upon cooling, the resulting solid mass was pulverized in a mortar and used without further processing.

Layer III was a mixture of rubidium iodide, iodine and a powder 75 percent by weight carbon, 25 percent polyethylene. First, the rubidium iodide and iodine were made up in a 50-50 mole percent mixture. Then, the carbon-polyethylene powder was added so as to constitute ten percent of the resulting mixture by weight.

Layer IV contained the carbon-polyethylene powder mixed with graphite (Pettinos 6427) in a weight ratio of 20 to 80. This layer served as a collector electrode and separated the reactive species in layer III from the material composing layer V.

Layer V was a silver screen identical to that of layer I. Actually, its form and composition is unimportant, provided that a good electrical contact is made with layer IV.

These layers were placed in the die in the order given above and pressed. Interestingly, the $RbAg_4I_5$ electrolyte appears to have flowed under the pressure and made good contact with layers I and III.

Mercuric Oxide-Cadmium Cells

Mercuric oxide-cadmium (Mercad) cells were successfully cycled under balloon battery conditions. The cells were 600 milliampere-hour button-type cells with 0.67 square inch electrodes (4 square centimeters) and mesh collectors. These were cycled by discharge at -60°C at 50 milliamperes to 0.6 volt cutoff, and charged at 10 to 20 milliamperes to a 1.05 volt cutoff at -30°C. Over 20 cycles were obtained, with no indication of difficulty. Similar cells have been cycled at room temperature for over 100 cycles.

Figure 3 shows the discharge polarization curve at -60°C (-76°F). The steep slope is attributed to the electrolyte resistance. The capacity on discharge is about 50 percent of the room temperature capacity; this low value is also attributed to the electrolyte. The performance of the design is not adequate to meet the goal of 700 grams total. Table 4 gives the calculation of weight for the design, a total of 1160 grams.

Table 4

MERCURIC OXIDE-CADMIUM CELL CALCULATIONS

$$E = 0.925 \text{ volts}$$

$$n = \frac{14.4}{E} = 15.6; \quad n = 15$$

$$V_D = \frac{10}{15} = 0.67 \text{ volts per cell}$$

$$J = \text{Adjustable variable}$$

$$W_1 = 14.5 \text{ grams per ampere-hour}$$

$$W_2 = 0.030 \text{ grams per square centimeter}$$

$$W_3 = 0.020 \text{ grams per square centimeter}$$

$$W_T = 2 \times 15 \times 14.5 + \frac{15,000 \times 0.05}{J}$$

$$= 435 + \frac{750}{J}$$

$$J = \frac{750}{700 - 435} = \frac{750}{265} = 2.83 \text{ millamperes per square centimeter}$$

If $J = 1.2$ milliamperes per square centimeter (present value)

$$W_T = 435 + \frac{750}{J} = \underline{1160} \text{ grams}$$

The use of 31 weight-percent potassium hydroxide solutions as the electrolyte in alkaline cells is based in part on the fact that this is the composition of the eutectic in the potassium hydroxide-water system. Part of the phase diagram is shown in Figure 4. Data for this figure were taken from the Solvay Technical and Service Bulletin* The freezing point of the

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*Caustic Potash, Solvay Technical and Service Bulletin 15, Solvay Process Division, Allied Chemical Corporation, 40 Rector Street, New York, N.Y. 10006.
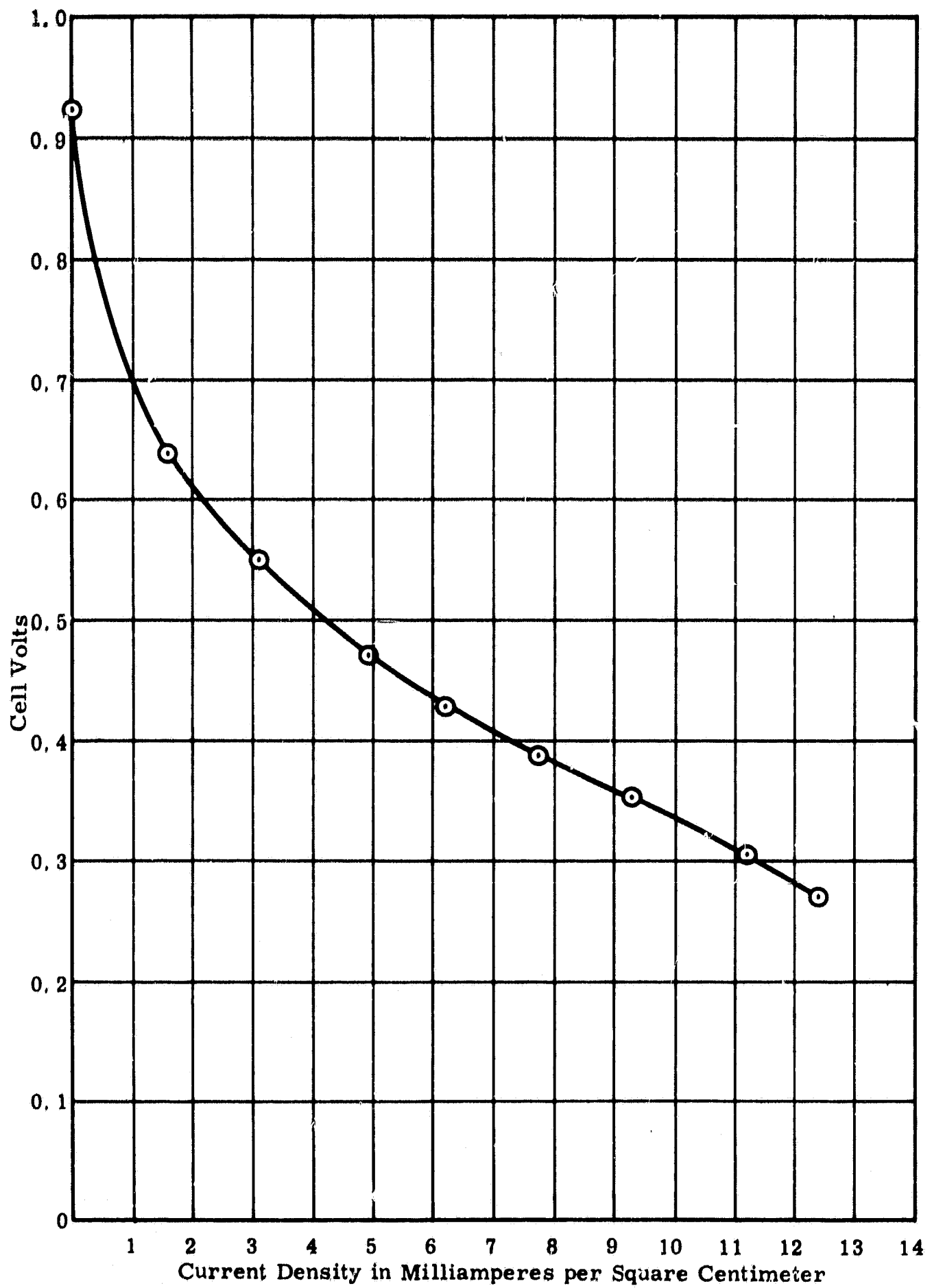
Figure 3.   Polarization Curve for a Mercuric Oxide-Cadmium Cell
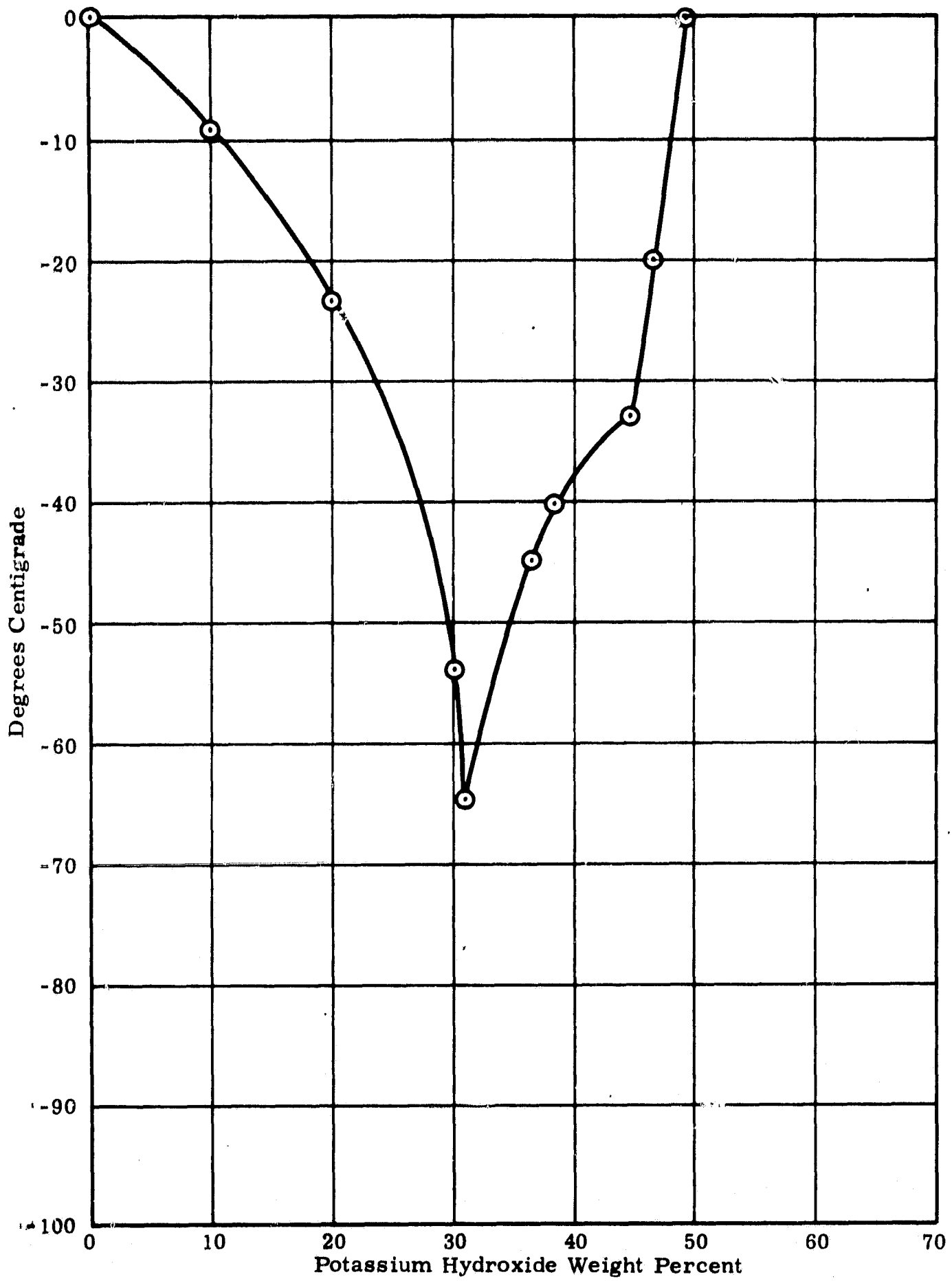(31 Percent Potassium Hydroxide; -76° F)

Figure 4.   Freezing Point Curve for a Potassium Hydroxide-
Water System

eutectic (-65°C) is uncomfortably close to the operating point of the balloon battery (-60°C), and this situation leads to a number of design problems.

The relatively steep slopes of the branches of the curve around the eutectic point indicate that small changes in composition of the solution from 31 weight-percent will give solutions that will freeze at -60°C. Since the viscosity of solutions near their freezing point is high, a severe drop in electrolyte conductivity will also occur as the solutions approach their freezing point. This freezing and the drop in conductivity degrade the performance of a cell at low temperature by decreasing the current densities for a given cell voltage and decrease in available capacity.

Changes in the composition of the electrolyte in the electrode pores and near the electrode faces do, in fact, occur during operation of a cell. In the mercuric oxide-cadmium cell, a large part of the change will result from the water involved in the cell reaction:

$$HgO + H_2O + Cd \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Hg + Cd(OH)_2$$
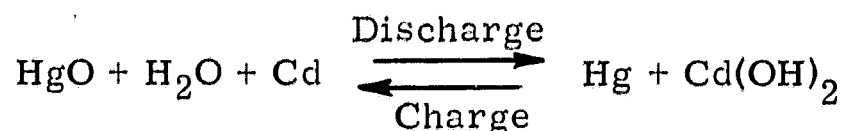
In highly viscous systems, the diffusion of water will be slow and the local change in electrolyte composition will tend to be relatively large, with subsequent freezing and marked fall-off in cell capacity. Figure 5 shows the discharge characteristics of a cell with thick electrodes and too little electrolyte to prevent a large change in electrolyte composition on discharge. The cell was discharged through 42.5 ohms. Even at 25°C, the local electrolyte changes seriously affected the cell discharge behavior. A normal cell with excess electrolyte gives the discharge characteristic shown by the dotted line.

The rationale for using cesium hydroxide for the electrolyte appears in Figure 6, which shows a portion of the phase diagram for the cesium hydroxide-water system. Data were taken from the bulletin on cesium compounds* The 60 weight-percent solution, which freezes at -75°C, was selected for the tests. Figure 7 shows the charge-discharge curve for a thick-electrode cell at -60°C and -30°C respectively. The discharge at 25°C on a 45 ohm load is shown in Figure 8. The results are encouraging, since there is a substantial gain in utilization above 0.6 volt. Thin cell design should give a notable improvement on utilization and high drain rate capability. Limited thin cell tests made in the last part of the program effort showed good behavior; however, an improvement in positive mix formulation and application will be necessary before completely satisfactory cells are obtained.

Figure 9 gives the latest polarization data for mercuric oxide-cadmium cells, using thick electrodes and a 60 percent cesium hydroxide electro-

*Technical Data--Cesium Compounds, Rare Earth Division, American Potash and Chemical Corporation, West Chicago, Illinois 60185.
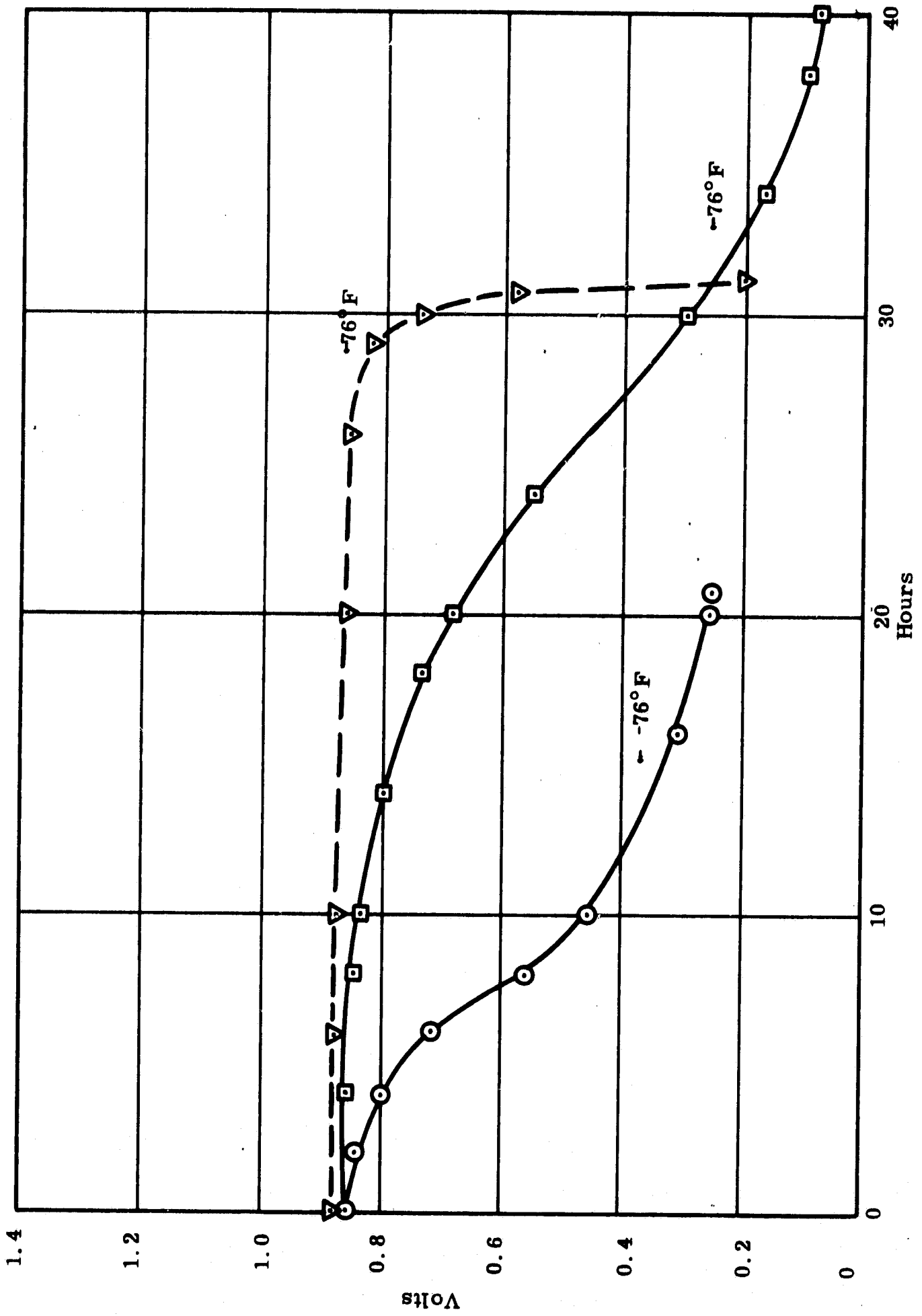
Figure 5. Mercuric Oxide-Cadmium Cell Discharge (31 Percent Potassium Hydroxide Electrolyte)
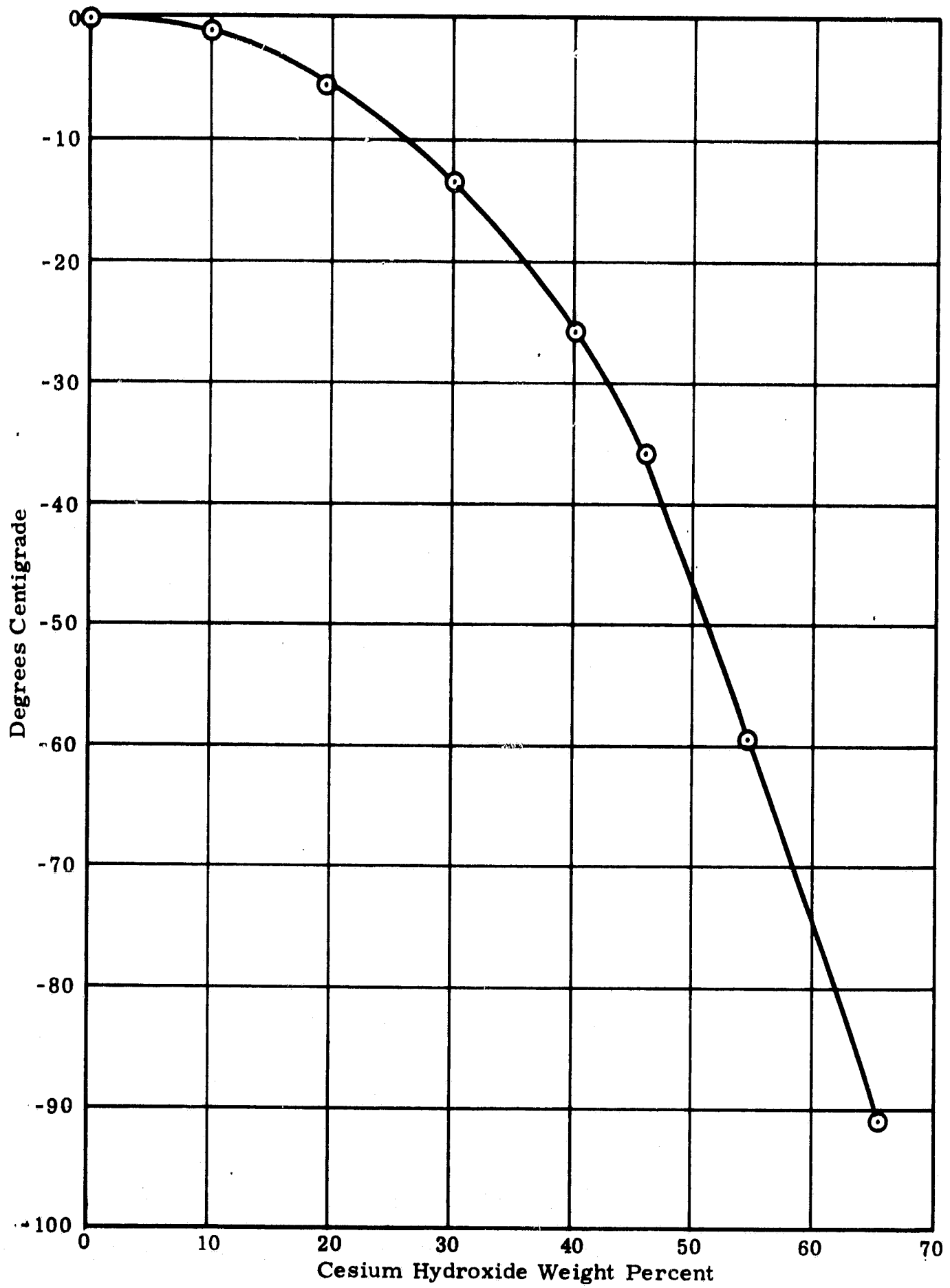
20

Figure 6.   Freezing Point Curve for a Cesium Hydroxide-Water System
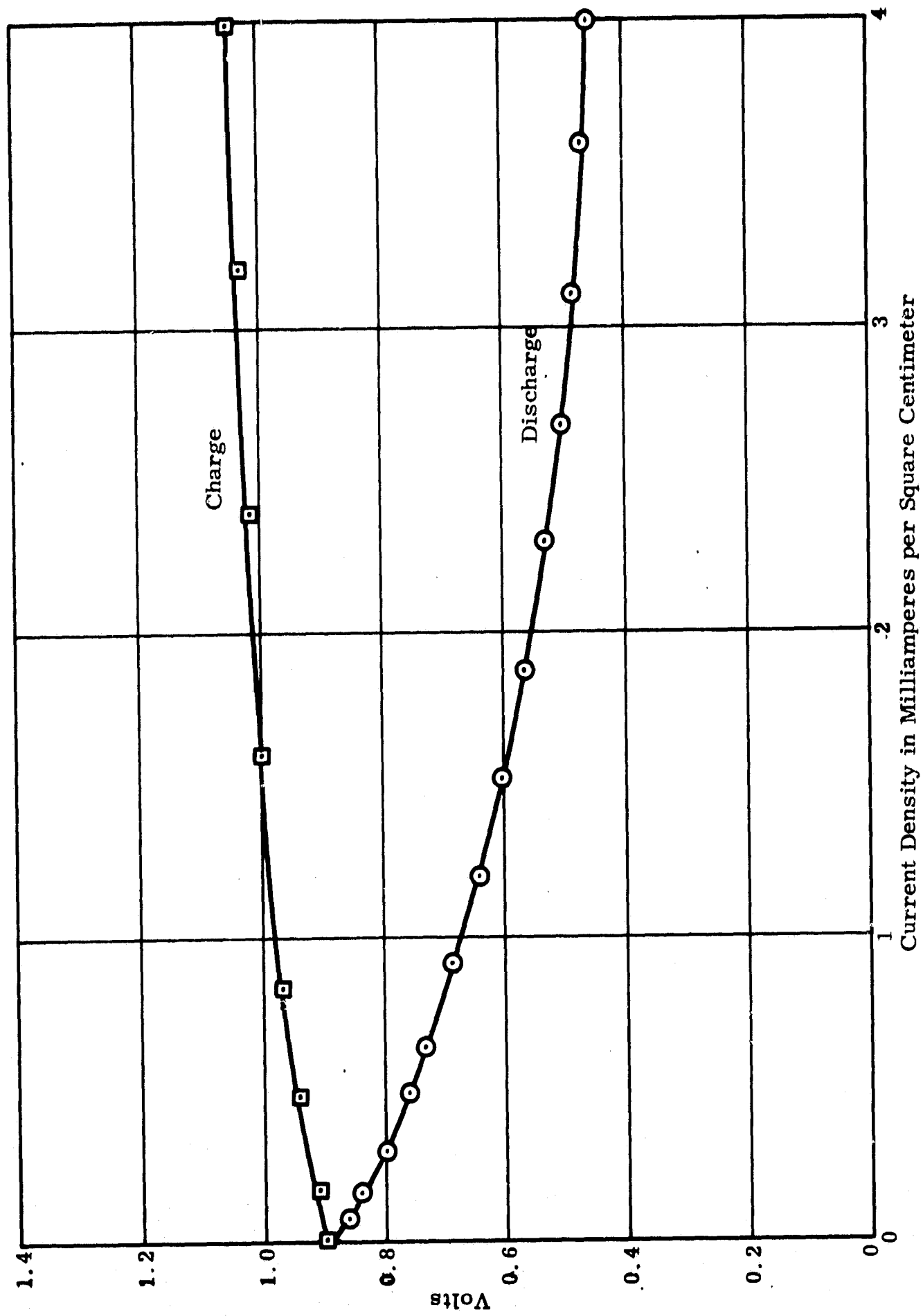
Figure 7. Polarization Curves for a Mercuric Oxide-Cadmium Cell with Thick Electrodes (60 Percent Cesium Hydroxide; Charge -30° C; Discharge -60° C)
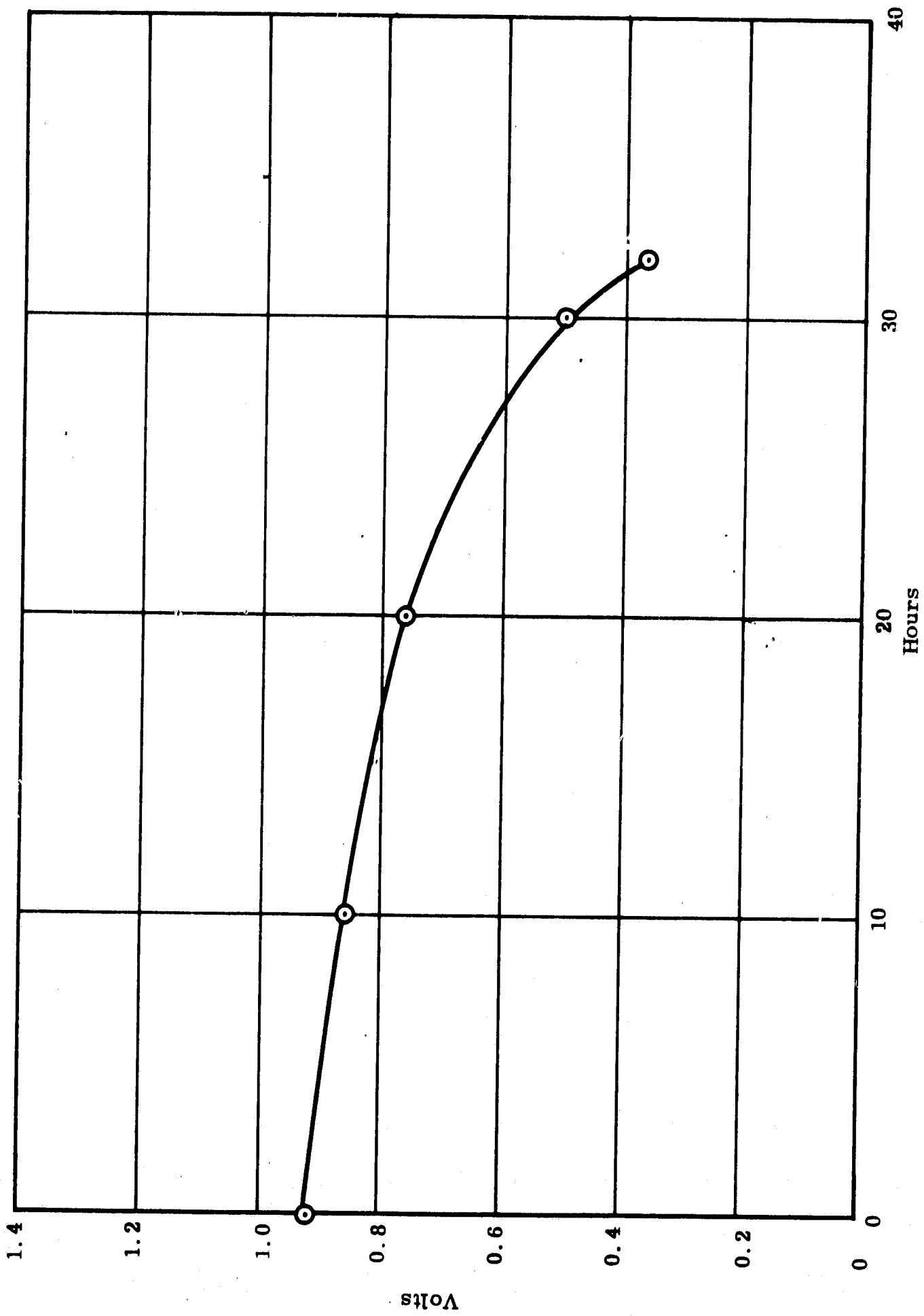
22

Figure 8.   Discharge Curve for a Mercuric Oxide-Cadmium Cell -- Thick Electrode
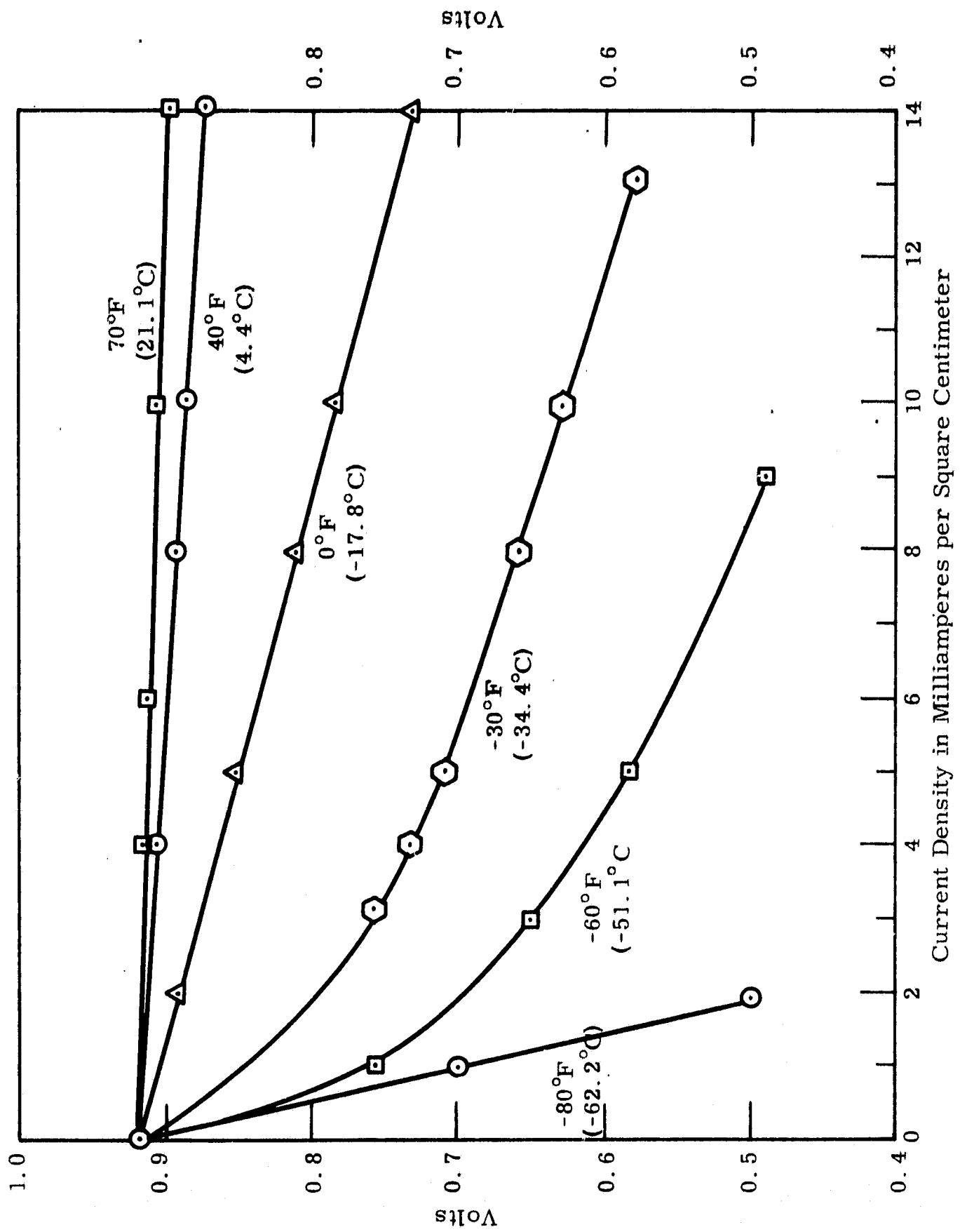(60 Percent Cesium Hydroxide; 76° F)

Figure 9. Polarization Curves for Mercuric Oxide–Cadmium Cells at Various Temperatures (60 Percent Cesium Hydroxide)

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lyte. The improvement in current density with increase in temperature is due largely to the decrease in electrolyte resistance.

Charging should offer no problems at the low current density to be used. Essentialy 100 percent current efficiency is obtained; the overcharge generates silver (I) oxide. The rapid, relatively large rise in cell voltage at the end of charge should allow the use of a simple charge control system. No evidence of hydrogen generation has been found; more tests are indicated.

The test cells were nominal 200 milliampere-hour cells, with a cell area of 0.5 square inch. The cadmium electrodes were made by pressing a mix of 15 parts by weight of cadmium oxide, one part silver flake, and one part polyethylene coated graphite onto a nickel grid. The electrodes were charged at the C/10 rate for 16 hours in alkali, rinsed free of alkali in water, rinsed free of water in alcohol, and dried in nitrogen to form the "charged" anode. The mercuric oxide electrode is similarly made, using six parts mercuric oxide, one part polythylene graphite, and two parts silver flake. Cell cases are Lucite plastic; the separators, Nylon polymer (0.008 inch) saturated with electrolyte.

CELL STRUCTURE STUDIES

The current design approach is to use a thin film of plastic for the cell case. This permits a simple approach to battery construction. Figure 10 shows the construction schematically. In the proposed fabrication, a thin film of polyethylene is used as the cell case. The film is primed with chromic acid, and a thin layer of a flexible epoxy (Emerson and Cumming Eccobond 286) is "printed" on the areas for the cell collector and intercell connectors. These are arranged on the sheet as shown in the figure.

The cell collectors and intercell connectors are painted on, using a silver conductive paint (duPont 4817). The active materials are then put on in a thin layer in the appropriate locations, the separators are put in place, and the sheet is folded lengthwise to form the cells. The cells are heat-sealed on the edges and across the intercell leads, with a small fill hole left on the edge. Electrolyte is added to each cell, and the fill hole sealed. The cell portion of the battery is now complete; it can be folded or rolled into the final configuration.

The active materials are mixed with a relatively large amount of electron carrier material--silver flake or graphite, or both, and a binder, in this case a solvent diluted epoxy. Additional work is needed on the positive electrode. The negative electrode uses cadmium oxide, silver flake, graphite, and the silver epoxy paint diluted with butyl acetate as the binder. Silver in the positive tends to migrate, and use of nickel and graphite is indicated, with a more wettable binder.
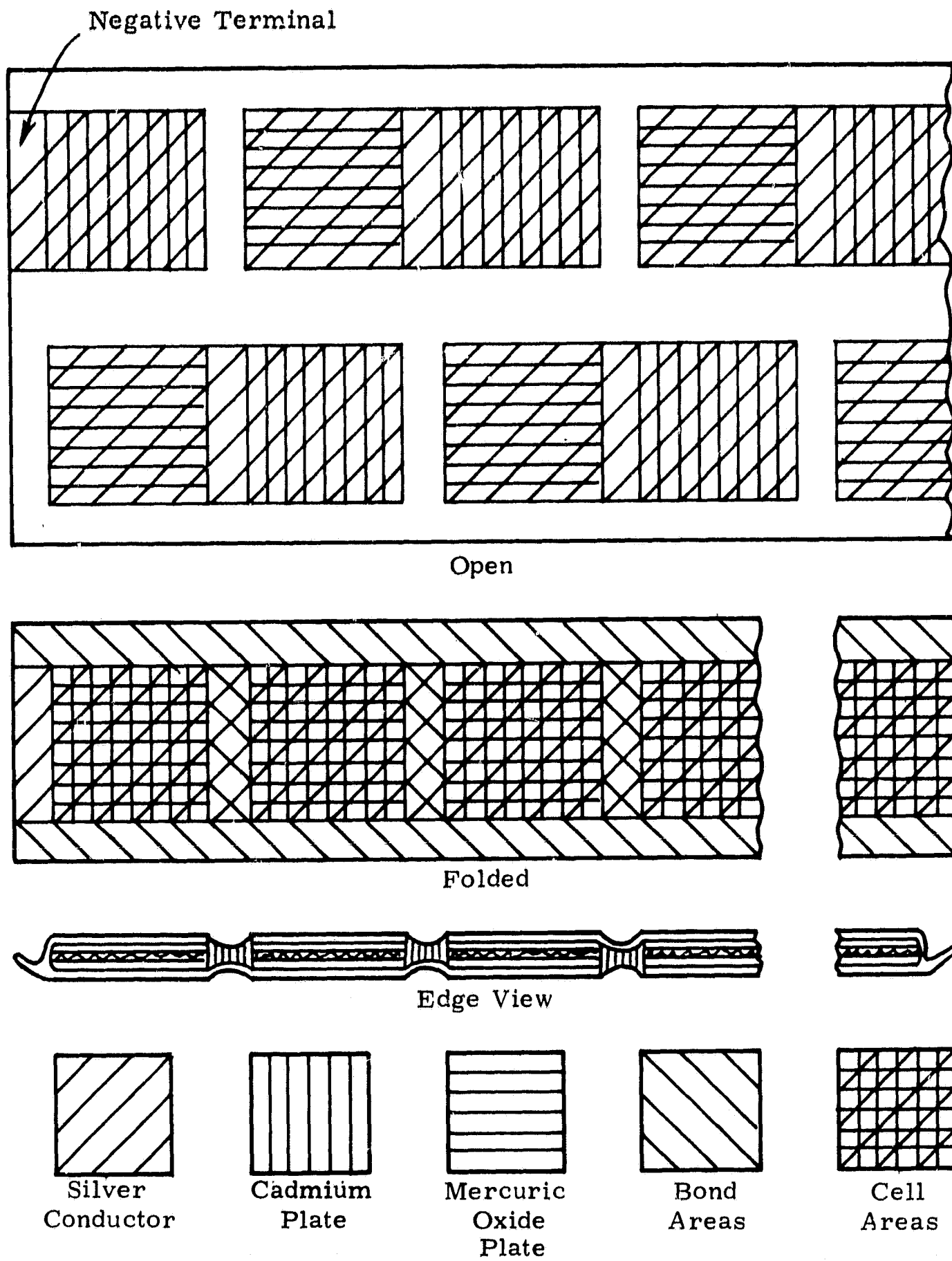
25

Negative Terminal

Open

Folded

Edge View

| Silver Conductor | Cadmium Plate | Mercuric Oxide Plate | Bond Areas | Cell Areas |

Figure 10. Schematic Diagrams of Battery Construction

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The present design for the battery calls for a cylindrical support of stiff plastic or thin metal (aluminum), 30 inches (75 centimeters) long. The radius of this cylinder is selected so that the aspect ratio of five grams per square centimeter is met. The plastic battery is wrapped in one to four layers, depending on cell area, around this support; and outer layer of laminated aluminum foil-paper-polyethylene is used to act as a water and gas vapor barrier. If heat storage and thermal shielding are used, these will be applied to the cylinder as appropriate; the heat-storage material container could act as the support.

A successful attempt to place a thin layer of silver directly on the polyethylene substrate has been made, but the stability of the film under exposure to alkali etc. is not yet known. The method is an electroless plating method consisting of priming the film, sensitizing with tin and palladium solutions, followed by immersion in the plating bath. A highly adherent, smooth deposit is built up in a few minutes; this film tarnishes quickly. A major disadvantage is the high scrap-silver loss due to limited plating bath stability.

A similar nickel plate can be made and would be preferable for the positive electrode substrate. Tests on the alternate plates are recommended in future work. The use of vapor deposition in vacuum for silver is not feasible, since the necessary heat injures the plastic film. Vapor deposition from nickel carbonyl vapor is a possibility, since only a low temperature (120°C) is needed; however, this process uses the highly poisonous, readily vaporized nickel carbonyl and requires considerable equipment to do the depositions safely.

Sealing the thin polyethylene sheet to itself by heat is difficult. However, an excellent heat seal is readily obtained if an additional polyethylene strip, approximately 0.005 inch thick, is placed in the seal zone. No effective heat seal to the epoxy or silver plated areas can be made; however, the Eccobond 286 gives a suitable seal. No difficulties in sealing the cells into the final battery configuration are anticipated.

Section 4

DESIGN ANALYSIS

The analysis for this investigation has been concerned with development of a valid parametric equation for the battery system weight, by means of the cylindrical configuration. The equation derived and presented in this report is satisfactory for comparisons and determining the effect of changes in parameter values; however, some of the restrictions and design assumptions are unnecessary and an improved equation should be derived in future work. The restriction of cylinder area to the minimum cell area set by the operating current density should be changed to the condition that the cylinder area and cell area be matched to each other, and that the cell area is at least the minimum area needed to give the allowable current density. The assumption that all of the battery mass is concentrated on the cylinder shell at the calculated cell radius should be changed so that the thermal shielding weight is included only as the thermal shield is involved in the aspect ratio calculation.

In the calculation results, the parameters and design considerations for the heat storage and thermal shield were taken from the final report by Melpar, Incorporated, (August 1968) for National Aeronautics and Space Administration Contract NAS5-11557. The reduction of the specific thermal shield weight is highly desirable, and should be investigated in future work.

Table 5 shows the set of equations used to set up the weight calculation, and the formula for calculation of the radius of the cylinder around which the battery proper is wrapped. This formula is implicit in r, and a reiteration method is used in the computer program. The angle θ_r enters the computation as a consequence of imposing the aspect ratio requirement.

Figure 11 shows the rationale. The arc length of the circle intercepted by a one-centimeter length parallel to the diameter is a maximum at the end of the diameter. Since the circle is a cross-section of the cylinder, an intercept of one square centimeter will intercept a strip $2r\theta_r$ by one square centimeter in area. This times the specific weight of the cylinder, i.e., $W_T/2\pi rl$, gives the mass of the material intercepted, e.g. the aspect ratio density. This cannot be greater than five grams per square centimeter; hence, the limit is derived by setting the expression equal to the aspect ratio. The reiteration equation is then obtained by solving for r implicitly. The computer program thus has algebraic, trignometric, and logarithmic terms. The arc tan function was used to match the subrouting available in the computer for calculation of arc functions.

Table 6 gives the results of the calculations. With the area limit, no solution for r is found when heat storage and thermal shielding are included. The results for the ambient (-60°C) operation are shown (no thermal shield or heat storage).
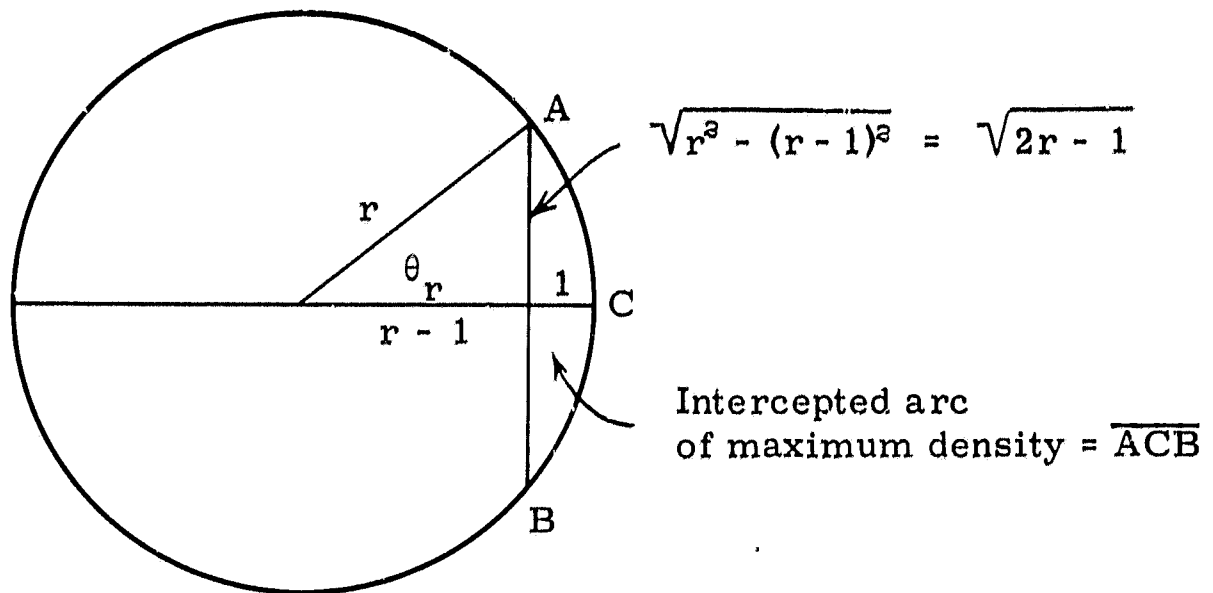
Table 5

ANALYSIS EQUATIONS

W_T = Total weight = $W_A + W_C + W_S + W_H$

W_A = Weight of active materials = $n \cdot W_1$

W_C = Weight of cell case = $\dfrac{n \cdot 1000}{J} \cdot W_2$

W_S = Weight of support and thermal shield = $2\pi r l (W_3 + W_4)$

W_H = Weight of heat-storage material = $2\pi l \ A_{log} \left(\dfrac{\mu \times \Delta T \times t}{W_5} \right)$

Aspect ratio condition $D = \dfrac{W_T \times r \times \theta_r}{\pi r l} \leq 5$

Cell area condition $\dfrac{n \cdot 1000}{J} \geq 2\pi r l$

θ_r = Angle of maximum arc intercept = $\arctan\left(\sqrt{\dfrac{2r - 1}{r}} \right)$,

r' = $\dfrac{W_T \times r \times \theta_r}{\pi \times 1 \times D}$ reiteration formula used in computer; vary r until $r' = r$.

PARAMETERS

D = Aspect ratio density = 5.0 grams per square centimeter

l = Length of cylinder = 75 centimeters

r = Cell radius = centimeters (variable in calculation)

r_s = Shield radius = (r + 4) centimeters

A_{log} = Log mean radius = $\dfrac{r_s - r}{\ln \dfrac{r_s}{r}}$ = $\dfrac{4}{\ln\left(\dfrac{r+4}{4}\right)}$,   centimeters

μ = Thermal loss coefficient = 0.0732 cal/cm² x hr x °C

= 0.15 Btu/ft² x hr x °F

ΔT = Temperature difference on discharge = $T_o -(-60°C)$ = $T_o + 60$

T_o = Operating temperature, $T_o > -60°C$

t = Discharge time = 12 hours

n = Number of cells ≈ $\dfrac{14.4}{V_C}$ ≈ 14 cells

V_C = Cell voltage on charging ≈ 1.0 volt

V_D = Cell voltage on discharge = $\dfrac{9.6}{n}$ = 0.685 volts

J = Current density on pulse discharge (1 ampere) at 0.685 volts, millampere per square centimeter

W_1 = Specific weight, cell active materials for 2 ampere-hour capacity = 29.0 grams

W_2 = Specific weight, cell case materials, including collector and separator = 0.05 gram per square centimeter (cell)

W_3 = Specific weight, cylinder case and battery cover, 0.10 gram per square centimeter (core)

W_4 = Specific weight, shield material plus heat storage container = $(0.28 + \dfrac{0.56}{r})$ grams per square centimeter (core)

W_5 = ΔH of heat storage material = 176 - 0.4 (To + 25) calories per gram[*]

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[*]This is for Melpar material S.H.S. - 25, melting point -25°C

$$\sqrt{r^2 - (r-1)^2} = \sqrt{2r-1}$$

Intercepted arc
of maximum density $= \overline{ACB}$

Length of Arc $\overline{ACB} = 2r\,\theta_r$

$$= 2r\ \text{arc tan}\ \left(\frac{\sqrt{2r-1}}{r-1}\right)$$

W_T = Weight of cylinder

$2\pi rl$ = Area of cylinder

W_x = Specific weight of cylinder (surface) $= \dfrac{W_T}{2\pi rl}$ g/cm^2

Weight of $\overline{ACB} = \dfrac{W_T \cdot 2r\ \text{arc tan}\,\theta_r}{2\pi rl}$

$$= \frac{W_T\ r\ \text{arc tan}\ \left(\dfrac{\sqrt{2r-1}}{r-1}\right)}{\pi rl}$$

$$\leq D\left(\begin{array}{c}\text{assigned aspect}\\ \text{ratio, } 5\text{g/cm}^2\end{array}\right)$$

Figure 11. Arc Length Calculation

Table 6

CYLINDRICAL CONFIGURATION*

$$W_T = nW_1 + \frac{n \cdot 1000}{J} \quad W_2 + 2\pi r W_3$$

$$= 400 + \frac{700}{J} + 47.1 r$$

$$r' = \frac{W_T \times r \times \theta_r}{\pi 1 \theta} = \frac{W_T \times r \times \arctan\left(\frac{\sqrt{2r-1}}{r-1}\right)}{1180}$$

J (ma/cm^2)	r Calculation (cm)	W_T (grams)
0.7	3.78	1584
0.8	3.10	1427
0.9	2.63	1307
1.0	2.29	1214
1.1	2.04	1138

*To = -60°C; no heat storage or thermal shield.

Table 7 gives the results of a set of calculations made on a strip model, where the limit of five grams per square centimeter is now set so that the edgewise contact of one centimeter length does not intercept more than five grams. In this calculation, the strip length 1 is the variable.

Table 8 gives the computer program print-out for the cylinder calculations. This is in Fortran; the program tape will be retained in the senior author's project record for future use if needed.

Table 7

STRIP CONFIGURATION[1]

J (ma/cm²)	W_T [3] (grams)	l (cm)	A [4] (cm²)	Aspect [5] (g/cm²)
To = -60°C [2]				
0.7	2,406	482	10,000	0.24
0.8	2,156	431	8,750	0.25
0.9	1,960	392	7,760	0.25
1.0	1,806	362	7,000	0.26
1.1	1,676	335	6,370	0.26
To = -50°C [6]				
1.0	7,000	1400	7,000	1.00
1.2	5,924	1182	5,850	1.02
1.4	5,129	1020	5,000	1.03
1.6	4,532	908	4,360	1.04
1.8	4,222	820	3,880	1.08
To = -40°C [6]				
3.0	2,782	556	2,330	1.20
3.5	2,530	509	2,000	1.25
4.0	2,264	454	1,750	1.29
4.5	2,204	414	1,560	1.33
5.0	1,910	392	1,400	1.37
To = 30°C [6]				
6.0	1,803	362	1,170	1.55
7.0	1,611	324	1,000	1.61
8.0	1,468	294	825	1.68
9.0	1,354	271	780	1.74
10.0	1,262	252	700	1.81

1) For double sided strip, i.e., cells on each side of support

2) No heat storage or thermal shield

3)

$$W_T = n \cdot W_1 + \frac{n \times 1000}{2 \times 5} \times \left(2 W_2 + W_3 + W_4' + A_{\log} \frac{\mu \times \Delta T \times t}{W_5} \right) + W_6 \, l$$

$A_{\log}$ = one square centimeter
W_4' = 0.55 (for 16 shields) grams per square centimeter
W_6 = specific weight of end shield = 0.48 grams per centimeter length

4) Area of cells/2, e.g., $\dfrac{N \times 1000}{2 \times J}$

5) Weight per square centimeter of strip normal to plane of strip.

6) With heat storage and thermal shield.