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STUDY PAPERS ON THE AUXILIARY ELECTRODE

FACILITY FORM 602

N66 11765	
(ACCESSION NUMBER)	(THRU)
88	1
(PAGES)	(CODE)
CR 67987	03
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE $ ________

CFSTI PRICE(S) $ ________

Hard copy (HC) 3.00

Microfiche (MF) .75

ff 653 July 65

PUBLISHED BY THE
ELECTROCHEMICAL WORKING GROUP
OF THE
INTERAGENCY ADVANCED POWER GROUP

OCTOBER 1965

PIC-BAT 209/9

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This Publication was Prepared for the Interagency Advanced Power Group by the Power Information Center under Contract NASr-191. Questions concerning this publication should be directed to the following address:

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FOREWORD

These papers were collected at the request of Joseph M. Sherfey of NASA-Goddard Space Flight Center and are published for distribution to the members of the Electrochemical Working Group of the Interagency Advanced Power Group (IAPG) and to a limited distribution list. To assure wider distribution, this publication will be available from the Defense Documentation Center (DDC) to all qualified requesters.

The Interagency Advanced Power Group wishes to express its thanks to the authors for these papers. The interest demonstrated by their cooperation in the information exchange activities of the IAPG is gratifying.

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PLATINIZED CARBON CLOTH AUXILIARY ELECTRODES

by

Philip F. Grieger

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Bloomfield, New Jersey

9 August 1965

ABSTRACT

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The advantages of platinized carbon cloth auxiliary electrodes are enumerated and discussed briefly.

To illustrate how these electrodes perform in hermetically sealed nickel/cadmium cells, results are given for a series of tests in which a cell made with a Gulton V07 electrode pack, a VCB Black auxiliary in the side position, and 20 ml of 30% KOH electrolyte was charged at room temperature at five rates in the range C/10 to 5C. The shape of the signaling voltage vs. % charge curve is good: there is wide freedom of choice in selecting the automatic cut-off input in the critical range of 100% to 150% charge. Adequate overcharging is thus realized.

Signaling voltage as a function of pressure is nearly independent of charging rate. In consequence, for a selected cut-off voltage, say, 0.6 or 0.7, input depends mainly upon the electrode pack's characteristic O_2 pressure build-up as a function of % charge, and input achieved is roughly independent of charging rate except at very low rates, such as C/10, where the increase in O_2 pressure is delayed.

Even at the 5C rate little or no H_2 was evolved on the auxiliary electrode, and in any event there was no permanent increase in background pressure.

Auxiliary electrode performance depends upon the state of charge of the cell: the auxiliary delivers less power as charging proceeds. It is hypothesized that this effect is due to water liberated by the active materials during charging, the auxiliary in the side position being sensitive to quantity of electrolyte. As a result, somewhat paradoxically at first consideration, the shape of the signaling voltage vs. % input curve is much better than it would be if auxiliary performance remained constant from the start of charge.

PLATINIZED CARBON CLOTH AUXILIARY ELECTRODES

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Introduction

The use of carbonized cloths electroplated with platinum as auxiliary electrodes for use in nickel/cadmium cells -- now being investigated under contract with the United States Army Electronics Command (Ref. 0) -- was expounded at the 19th Power Sources Conference in Atlantic City, New Jersey, May 19, 1965 (Ref. 5). That paper (appearing as section 2 in this publication) concerned: (1) the Jaffe invention (Ref. 6), which formed the initial basis for the present project work, (2) preliminary experiments designed to compare a variety of platinized substrates, and (3) the plan of the Main Experiment (designed to test one kind of platinized cloth, in two position, in two kinds of nickel/cadmium cells, under a wide range of charging conditions with respect to rate and temperature). Results of the Main Experiment are presently being obtained but because a complete analysis of the findings has not yet been made, it would be premature to discuss this experiment at present. Instead, results obtained with just one cell at room temperature, when charged at a wide range of rates, will be discussed. The observations are recent, and some of the questions raised by them remain to be settled by future experimentation, but it is hoped that this subject matter will be helpful to the members of the IAPG. Before considering the results in question, however, it may be of interest -- in view of the many proprietary materials now available as a result of fuel cell research -- to itemize the reasons for investigating platinized carbon cloth auxiliary electrodes.

Advantages

First, they are unbreakable. Certain fuel cell electrodes are more or less crumbly, and pieces might dislodge from their edges as a result of the treatment the cells receive in use -- thereby giving rise to the danger of shorts.

Second, they can be cut into any shape, tightly folded (Ref. 4, page 41), and rolled. These properties make such auxiliary electrodes, (1) easy to incorporate in cells of any shape, (2) suitable for installation in waste space of the cell.

Third, they are light weight, approximately 0.2 gram per square inch, and thin (Ref. 1, page 46). For example, one layer of VCB* plated with black

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* Carbon as opposed to graphite cloth. National Carbon Co., fourth reference in Ref. (5).

platinum plus two layers of suitable separator material were found to have a thickness of only 0.031 inch when compressed dry between two sheets of Lucite (Ref. 4, page 13). When installed in hermetically sealed cells these auxiliary electrodes add only a negligible amount to the weight, and nothing or a negligible amount to the volume.

Fourth, they require no waterproofing treatment: on the contrary they absorb and immobilize electrolyte. In consequence, they suffer no change in electrochemical performance as a result of deterioration of waterproofing agent due to attack by the cell electrolyte. Moreover, because they absorb electrolyte they can be used in multilayer assemblies without interposition of electrolyte absorbent separators* (Ref. 4, page 14).

Fifth, being prepared by electrodeposition instead of impregnation, compaction, or some other means, replicability in making them can be controlled within narrow limits (Ref. 4, page 9, with data summarized on page 35). Moreover, with respect to replicability of intrinsic O_2 reduction characteristics**, it was found that performance was independent of plating order (Ref. 2, pages 68 and 69; Ref. 3, pages 9, 29 and 38).

Sixth, these auxiliary electrodes exhibit good reproducibility of performance when a given piece is tested successively, and this repeatability at room temperature is not significantly affected by continuous operation or exposure to -40°F (Ref. 5, pages 8 and 9; Ref. 1, pages 76 and 77).

Seventh, the polarization curves (which govern the signaling power in the presence of O_2, c.f. Ref. 5, page 3) are strongly dependent upon O_2 pressure (Ref. 5, page 8 including Table II; also Ref. 1, pages 59 through 64, pages 69, 70 and 71). With the proper choice of signaling circuit resistance, and the proper choice of auxiliary electrode size -- for the present electrodes this size is convenient (on the order of 1 square inch), being neither impracticably small nor large -- signaling power increases strongly with increase in O_2 pressure (Ref. 1, pages 68 and 77), and hence, charging can be reliably terminated after the cell has received an adequate overcharge. This ability is considered to be extremely important from the standpoint of good battery management. If the auxiliary electrode automatically cuts off charging when O_2 begins to be evolved from the nickel electrode, the cell may function fairly satisfactorily at first, but eventually capacity (of the nickel electrode) will suffer.

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* Compare the wick-electrode structure taught by Jaffe (Ref. 6, his Fig. 4) who used a nonabsorbent auxiliary electrode material, i. e., perforated palladium foil.

** As revealed when a group of electrodes is compared in a given way, for example, as in the Preliminary Experiments of this project (Ref. 5, page 7, also Ref. 1, page 19).

Eighth, the present auxiliary electrodes when soaked with 30% KOH electrolyte, catalyze the H_2 plus O_2 reaction (Ref. 3, page 16) at a safe and convenient rate. Therefore any small amount of H_2 that might be evolved during the early stages of charging (Ref. 2, page 14) will be consumed once O_2 has been evolved from the nickel electrode. It is believed as the result of considerable experience* that the dangers of an explosive H_2 plus O_2 reaction are not increased by putting a platinized carbon cloth auxiliary electrode into a hermetically sealed cell.

Ninth, these auxiliary electrodes are relatively inexpensive: 1 square inch of VCB cloth (preferred substrate) costs only about 2 cents, even when purchased in small quantities; on this much cloth the preferred platinizing procedure deposits about 40 milligrams of platinum (Ref. 4, page 35), which has a value of about 12 cents at current prices.

Tenth, electronic connection to these electrodes is readily made by lightly pressing them in contact with a metallic current tap (e.g., nickel, nickel plated steel, or steel).

Make-Up of Test Cell

Cell No. 10, made using a Gulton V07 electrode pack and can, a VCB Black auxiliary (Ref. 5, page 7), cut to 1-3/8 x 1-7/8 inches, in the side position, and electrolyte corresponding to the semi-dry condition (Ref. 4, Sections IV, B, 1 through 8), was originally made for use in the Main Experiment (Ref. 4, page 60), but because of a change in plans it became available for the testing described here.

After washing and drying the electrode pack** the auxiliary electrode was positioned as shown in Figure 1 -- the auxiliary being electronically insulated from the pack by two layers of separator material.

With the aid of soft nickel L-shaped shims the electrode pack and auxiliary were inserted into the can (to which had been welded a 1/4 inch steel flange to accommodate the cover) as shown in Figure 2. After installing the cover, pressure gage, filler tube, and the retainer plates (Fig. 3), the cell was leak tested. The cell having been found tight, 20.0 ml of 30% KOH were added through the filler tube: this is about 4.0 ml less electrolyte than that required to saturate the pack and auxiliary electrode (Ref. 4, page 18; for the technique used to add electrolyte see Ref. 4, page 20).

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* A wide range of H_2 and O_2 mixtures was left for protracted periods in contact with various platinized carbon or graphite cloths moistened with 30% KOH, and no explosion, or even violent reaction, occurred.

** Both outermost plates are nickel positives.

With the hose and clamp still on the cell, the auxiliary electrode was pretested by determining its polarization curve at room temperature, in the presence of 1 atmosphere O_2, while the cell was charged at 0.35 amperes for about 1 hour at most (Ref. 4, pages 21 and 22). The auxiliary electrode external leads were attached to the cell using one of the top screws that held the retaining plates together. This screw only was tightened with a screwdriver and wrench, the others having been adjusted with finger pressure so that the plates fit snugly to the can when its internal pressure was that of the room. Thus the electronic path to the auxiliary was through: retaining plate, can, nickel L-shim.

Following pretesting, the cell was evacuated, discharged to virtually zero volt through a 1 ohm resistor, and then overdischarged until both electrodes had failed (about -1.44 volts). The cell was then evacuated again, filled with O_2 to 1 atmosphere, and finally sealed with a binding head screw in place of the filler tube (for the exact procedures see Ref. 4, page 25).

Before making any full-scale charging tests the cell was given several conditioning cycles at room temperature, for example, 12.5 hour charge at 0.7 ampere followed by discharge at 1.4 amperes to 1.0 volt. Output at the C/5 rate was close to 7 ampere hours.

Auxiliary Electrode and Cell Performance at Different Charging Rates

Taking the nominal capacity of the cell as 7 ampere hours, it was charged at 1C (7 amperes), 2C, C/10, 3C, and 5C, in that order, charging being terminated by hand when the pressure gage reading reached 60 psi, or when pressure appeared to be substantially steady. Because the cell was initially filled with O_2 at 1 atmosphere, absolute pressure at the start of each test was close to zero (about 2.5 psi), and because the gas at the end of charging contained little if any H_2, it follows that at this point (60 psi) the pressure of O_2 in the cell was about 5 atmospheres. After charging was terminated, observations were made while the cell stood on open circuit for several hours*, and then its output to 1.0 volt was determined at the 3C rate; subsequently the cell was discharged under its own remaining power to virtually zero volt. Performance of the nickel/cadmium electrode pack, as concerns pressure at the start of charging, input accepted at 60 psi (or lower if the pressure was steady), and output at 21 amperes is summarized in Figure 4.

Ambient temperature during charging and discharging was between 75°F and 79°F.

In performing the charging tests the auxiliary and cadmium electrodes were externally joined (to emulate the signaling circuit between points y and z in Figure 2 of Ref. 5) through a milliammeter and resistor whose combined

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* There was very little overshoot: at most pressure rose to 61 psi.

resistance, R_S, was 6.5 ohms. The following observations were made during charging: cell voltage, pressure gage reading, signaling voltage, i.e., between the auxiliary and the cadmium electrodes, and signaling current (called I_s in Figure 2 of Ref. 5).

Figures 5 and 6 show signaling voltage and cell pressure as a function of input for the 1C and 5C charging runs respectively. Performance of the auxiliary electrode is almost perfectly adapted to charging control of the cell in question.

At the 1C rate (Figure 5), signaling voltage remains below 0.1 volt until input reaches about 100% of rated cell capacity, thereafter it rises as O_2 pressure in the cell increases: almost linearly between 110% and 130% input, somewhat more gradually thereafter, and only shows a tendency not to increase markedly with pressure after about 160% input. Sufficiently wide latitude is thus afforded in choosing the cut-off point. For example, if it was decided to terminate charging when the cell had received an input of 120% of rated capacity, a terminating device with a voltage reliability of ± 10% would behave as follows:

Description	Signaling Voltage	% Input at Automatic Termination of Charging
Low (-10%)	0.41	118
Intended cut-off	0.46	120
High (+10%)	0.51	122

Again, if it was decided to terminate charging when the cell had received an input of 130% of rated capacity a 10% device would behave as follows:

Description	Signaling Voltage	% Input
Low	0.58	127
Intended cut-off	0.64	130
High	0.70	136

Finally if it was decided to terminate charging when input reached 140%, the situation would be as follows:

Description	Signaling Voltage	% Input
Low	0.67	133
Intended cut-off	0.75	140
High	0.83	150

From the 5C charging results (Fig. 6), it can be seen that the situation at this rate, which is probably about as high as would ever be used in practice, is nearly as good at 1C. With a cut-off pressure of 60 psi less overcharging is possible at 5C than at 1C, so using 110%, 120% and 130% as intended overcharges, a terminating device with ± 10% reliability would perform as follows:

Desired Input, %	Range, %
110	102-114
120	116-124
130	126-138

The shape of these signaling voltage vs. input curves is thus seen to be good because voltage remains at a low value until the cell is approximately fully charged and then rises with increase in O_2 pressure -- just about keeping pace with it. The voltage rise is neither too rapid nor too gradual. Too steep a rise would result in excellent cut-off at a given input but would allow no freedom in choosing the cut-off. Too gradual a rise would result in wide variations in input for a control device with ± 10% reliability, or, put another way, would require a control device with a very close tolerance on operating point. Thus the curves shown in Figures 5 and 6 afford good balance between freedom in selecting input cut-off and latitude in designing the control circuit.

If it is acceptable to have the charger operate at a single rate, such as 1C, then the discussion given above provides sufficient basis for judging the merits of a given auxiliary electrode. However, if it is desired to have an adjustable charger which can be set to operate at any given rate within wide limits, such as C/10 up to 5C, then it is worth-while to consider the problem somewhat more generally, as follows.

Automatic charge control by means of an O_2-reduction auxiliary electrode depends mainly upon two factors: first, the O_2 evolution characteristics of the cell itself and second, the response of signaling voltage to pressure.

As to the first factor, the build-up of O_2 pressure during charging at the 1C and 5C rates can be seen in Figures 5 and 6, and to give some idea of the point at which O_2 evolution becomes important over the entire range of charging rates, inputs corresponding to zero pressure are summarized below:

Charging Rate	Input, Ampere Hours, for Zero Pressure Gage Reading
C/10	9.6
1C	7.9
2C	8.1
3C	8.1
5C	7.2

If the rate of reaction of O_2 with the cadmium electrode at 1 atmosphere absolute is on the order of C/20, say, then these results are understandable.

As to the second factor, signaling voltage is plotted as a function of pressure in Figure 7 for all five charging rates studied. The curves are remarkably close together, all the points falling within a satisfactorily narrow band.

Taking both factors into account, it is anticipated from these results that for a given cut-off voltage, input will be roughly the same for 1C, 2C, 3C and 5C, but will be substantially higher for C/10 because O_2 pressure build-up is noticeably slower at this low charging rate. When the values are read off the five plots showing signaling voltage vs. input, this turns out to be true:

Charging Rate	Input, % of Seven Ampere Hours, at Cut-off Voltage of	
	0.6	0.7
C/10	171	230
1C	129	135
2C	134	141
3C	139	147
5C	130	137

It is believed that from the users' standpoint the rates of most interest will fall in the range 1C to 5C: less than 1C takes too long, more than 5C saves no appreciable time in comparison with the time required to put the battery into, and take it out of, the charger. Over this range, with the present cell type and auxiliary electrode, about the same input is attained for a fixed value of cut-off voltage. At much lower rates the input is considerably greater because of the slower O_2 pressure build-up; this, of course, depends upon the characteristics of the nickel/cadmium electrode pack, and does not reasonably reflect upon the behavior of the auxiliary electrode -- on the contrary, the auxiliary electrode exhibits excellent behavior in that signaling voltage as a function of pressure is nearly independent of charging rate over the wide range from C/10 up to 5C.

Besides having excellent characteristics as regards charge termination -- which is, of course, the main thing -- this system is gratifying in another respect: little or no H_2 was evolved during the early stages of charging*.

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* Carson states in the published version of his paper presented at the 18th Power Sources Conference (Ref. 7) that "at high charging rates, hydrogen is always evolved in charging".

This possibility, its implications, and ways of overcoming it have been discussed at some length (Ref. 2, pages 4 through 15), and in view of these considerations, R_s was intentionally chosen as 6.5 ohm in the hope of preventing rapid evolution of H_2. It should be pointed out, however, that from the standpoint of making signaling voltage as responsive to O_2 pressure as possible, a somewhat lower value of R_s would have been chosen (Ref. 1, page 30). For a first try, 6.5 ohms turned out to be a good compromise. From Eq(2) of Ref. 5 it is predicted that H_2 evolution rate, even at the 5C rate, should not exceed

$$200/6.5 = 31 \text{ milliamperes.}$$

For the 5C charging experiment, I_s was between 15 and 22 milliamperes before O_2 evolution became clear (4.67 ampere hours input), and for 1C charging was between 6 and 16 milliamperes up to 7.00 ampere hours input. Whether or not these small currents are due to H_2 cannot be established from the present observations, but if H_2 was evolved, it ultimately reacted with O_2 -- as it could on the auxiliary electrode itself (Ref. 3, page 16) -- or was otherwise consumed. This can be seen from the cell pressures at the start of charge as itemized in Figure 4.

Auxiliary Electrode Performance as Related to State of Charge of the Cell

Having found out that the shape of the signaling voltage vs. input curve is good and that signaling voltage as a function of pressure is nearly independent of charging rate, the user can, in a sense, consider the subject closed. It is submitted, however, that something is going on in the cell that might not be suspected from the results given so far, and for those who wish to explore the matter further, the following supplemental discussion is presented.

As a point of departure compare the performance of the auxiliary electrode in the pretest and full-scale charging experiments. In the pretest the polarization curve at 1 atmosphere absolute of O_2 was determined (Ref. 4, page 48), and from these results signaling voltage and current can be estimated for R_s = 6.5 ohms as shown in Ref. 5, Figure 3. On the other hand, if no appreciable H_2 was evolved during the early stages of charging in the full-scale tests, then at a pressure gage reading of +2.5 psi (to make approximate allowance for the background pressure), the cell gas should correspond closely to 1 atmosphere O_2 also. For these experiments signaling voltage at this pressure can be read from Figure 7. The results are collected below:

Determination	Signaling Voltage	I_s, Milliamperes
Pretest	0.81	123
C/10	0.34	46
1C	0.30	48
2C	0.29	48
3C	0.30	49
5C	0.37	58

Clearly there is a marked difference in auxiliary electrode performance as determined in the two kinds of tests.

It could be argued that in the pretest the cell was connected to a large reservoir of O_2 at 1 atmosphere, but that in the runs at C/10, 1C, etc., the cell gas was roughly half H_2 by the time pressure gage reading reached 2.5 psi. If so, most of the H_2 would have had to evolve from the cadmium electrode rather than the auxiliary, because on the assumption that I_s is due only to H_2 evolution during the early stages of charging, no more than 0.1 atmosphere of H_2 can be accounted for by the time pressure reaches 2.5 psi. Cell No. 10 could be charged to 2.5 psi and the gas analyzed at this point. Until this is done the H_2 explanation remains a possibility, although an unlikely one, because H_2 content at 2.5 psi would be expected to increase strongly with increase in charging rate, but the observed signaling voltages at C/10 and 5C are nearly the same -- what difference there is being in the wrong direction.

Another possibility is that auxiliary electrode behavior depends upon the state of charge of the cell. This possibility is worth looking into because in the pretest the cell was virtually in the discharged condition (being charged to no more than 0.35 ampere hours), whereas in the tests at C/10, 1C, etc., the cell had received an input of greater than 100% by the time pressure reached 2.5 psi. Thinking that there might be such a relationship, signaling voltage and current were measured during discharge following the first charging at 1C, and then, because the results seemed interesting, more systematically and completely during the next experiment in which the cell was charged at 2C. Results for this latter run are summarized and condensed in Figure 8.

Following this tabulation it is seen that signaling voltage and current dropped suddenly by a measurable amount when charging current was turned off. This is explained as due to the drop in cadmium electrode polarization (cell potential fell by 0.11 volt) in view of Eq(1) in Ref. 5 which shows that signaling current and voltage decrease with decrease in cadmium electrode polarization. While the cell stood on open circuit for about two hours, signaling voltage dropped as O_2 was consumed.

When pressure reached 26 psi the cell was discharged at 21 amperes. The analogue of Eq(1) in Ref. 5 that applies during discharge in the presence of O_2, shows that signaling voltage decreases with increase in cadmium electrode polarization, but in spite of this and the further decrease in O_2 pressure from 26 psi to 21 psi, signaling voltage (and current) rose during the first 12 minutes of discharge from initial values of 0.51 volt (and 79 milliamperes) to 0.76 volt (and 114 milliamperes). This strongly suggests, if it does not prove, that auxiliary electrode behavior depends upon the state of charge of cell. This implies that for each state of charge there is a family of polarization curves (one for each pressure) of the sort shown in Figure 3 of Ref. 5. From the standpoint of producing power the best set is for the cell in the discharged condition, the whole family contracting inward toward the axis of ordinates as charging proceeds.

To continue reading the results listed in Figure 8, signaling voltage finally fell during the last stages of discharge at 21 amperes to 1.0 volt, doubtless because cadmium electrode polarization increased markedly. For the same reason there was a big drop in signaling voltage when the cell was discharged to 0.1 volt under its own power, but note that after 20 minutes stand on open circuit following the end of discharge, signaling voltage became nearly as high as it was at the end of the 21 ampere discharge -- even though absolute O_2 pressure was only 2/3 as great. This indicates a further improvement in O_2 polarization characteristics of the auxiliary as a result of completely discharging the cell, and corroborates the idea that auxiliary electrode performance depends upon state of charge.

Finally the cell was charged for a few minutes at 0.35 amperes, i.e., the same current used in the pretest, while pressure fell to 2 psi so that the cell gas should have been nearly the same as in the pretest. Signaling voltage was 0.76 and signaling current was 116 milliamperes. Considering that during pretest the cell had not yet been given any conditioning cycles, it is reasonable to think that cadmium electrode polarization was higher then than after conditioning, and the higher cell voltage during the pretest, viz., 1.38 as opposed to 1.29 in Figure 8 is consistent with this thought. In fact if it is assumed that of the 0.09 volt difference in cell potential, 0.05 volts are due to cadmium electrode polarization, then agreement is seen between the results of the pretest and the experiment given in Figure 8.

It is concluded that the auxiliary electrode underwent no permanent change during the testing reported here but rather that some transitory and repeatable change occurred within the cell, the change being related to state of charge.

It is generally recognized that water is liberated in a nickel/cadmium cell during charging. If 0.5 equivalent of water were formed for each equivalent of nickel active material that is charged, then roughly 1 ml of water would be produced in charging the present cell. In the pretesting of other side position cells for the Main Experiment it was found that the addition of 3.5 ml of supplemental electrolyte to a cell that had first been tested with 20.0 ml of electrolyte resulted in a marked decrease in auxiliary electrode performance (Ref. 4, pages 49 and 50), and in view of the findings that 41 ml of supplemental electrolyte caused little if any more decrease than 3.5 ml, (Ref. 4, pages 51 and 52) it is surmised that an increase in electrolyte volume from 20 ml to 21 ml, or even less, during charging could easily account for the difference in performance observed in the pretest and charging at C/10, 1C, 2C, etc.*

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* Of course during charging average electrolyte concentration is decreased slightly because the water produced dilutes the electrolyte and because a small amount of KOH may be taken up by the nickel active material, but these effects are minor in comparison with the major effect due to increase in volume of electrolyte.

It follows from this that a cell made with a side position auxiliary but 23.5 ml or 34.0 ml of electrolyte should show no difference in auxiliary performance between the pretest and full-scale charging test results. For cells made with the auxiliary in the top position the pretest results with cells made for use in the Main Experiment show that addition of 3.5 or 14.0 ml of supplemental electrolyte has only a relatively small effect on auxiliary performance (Ref. 4, pages 54 through 57). Therefore it also follows that for top position cells there should be little difference between the pretest and full-scale results for any of the quantities of electrolyte used. Detailed comparisons will be given in the fifth Quarterly Progress Report of this project, but it can be stated generally that these expectations are confirmed experimentally in every instance. Thus, for a cell made with the auxiliary in the side position and 20 ml of electrolyte, there is strong reason to believe that the big difference in auxiliary performance observed in the pretest and at the end of discharge (Figure 8) on the one hand, and in the full-scale tests at C/10, 1C, 2C, etc., on the other, is due to an increase in volume of electrolyte caused by water produced during charging.

From the users point of view the indicated decrease in auxiliary electrode performance with increase in state of charge has a beneficial result: it is largely responsible for the good shape of the signaling voltage vs. input curve in Figures 5 and 6. If signaling voltage were 0.81 at 1 atmosphere absolute of O_2 for a roughly full charged cell, as it is for a discharged cell, then in Figure 5 signaling voltage at 100% input would be about 0.8 and little further increase could be expected as O_2 pressure built up during the critical overcharge range (100% to 150% input). Freedom to select the preferred cut-off input would thus be lost.

In Figure 7, the cells are substantially fully charged throughout most of the pressure build-up depicted there and, hence, the effect of increasing electrolyte volume with state of charge should be relatively small. The closeness of the curves is regarded as due to fortuitous cancellation of secondary effects. Thus cadmium electrode polarization increases with increase in charging rate and this tends to make the curve higher in Figure 7, the higher the charging rate (c.f. Eq(1), Ref. 5). In opposition to this, there is doubtless a concentration polarization component of auxiliary electrode polarization due to the fact that KOH concentration is lower in the vicinity of the nickel electrode (in the present instance the auxiliary also) than in the vicinity of the cadmium electrode during charging, and in view of Eq(1), Ref. 5, this increase in auxiliary electrode polarization with increase in charging rate tends to make the curve lower in Figure 7, the higher the charging rate. As a result, it turns out that signaling voltage is highest at the 1C rate over most of the pressure range.

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3. Report No. 3, Ref. 0.

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7. W. N. Carson, Jr., "Auxiliary Electrode for Charge Control", Proceedings, 18th Annual Power Sources Conference, 19-21 May 1964.

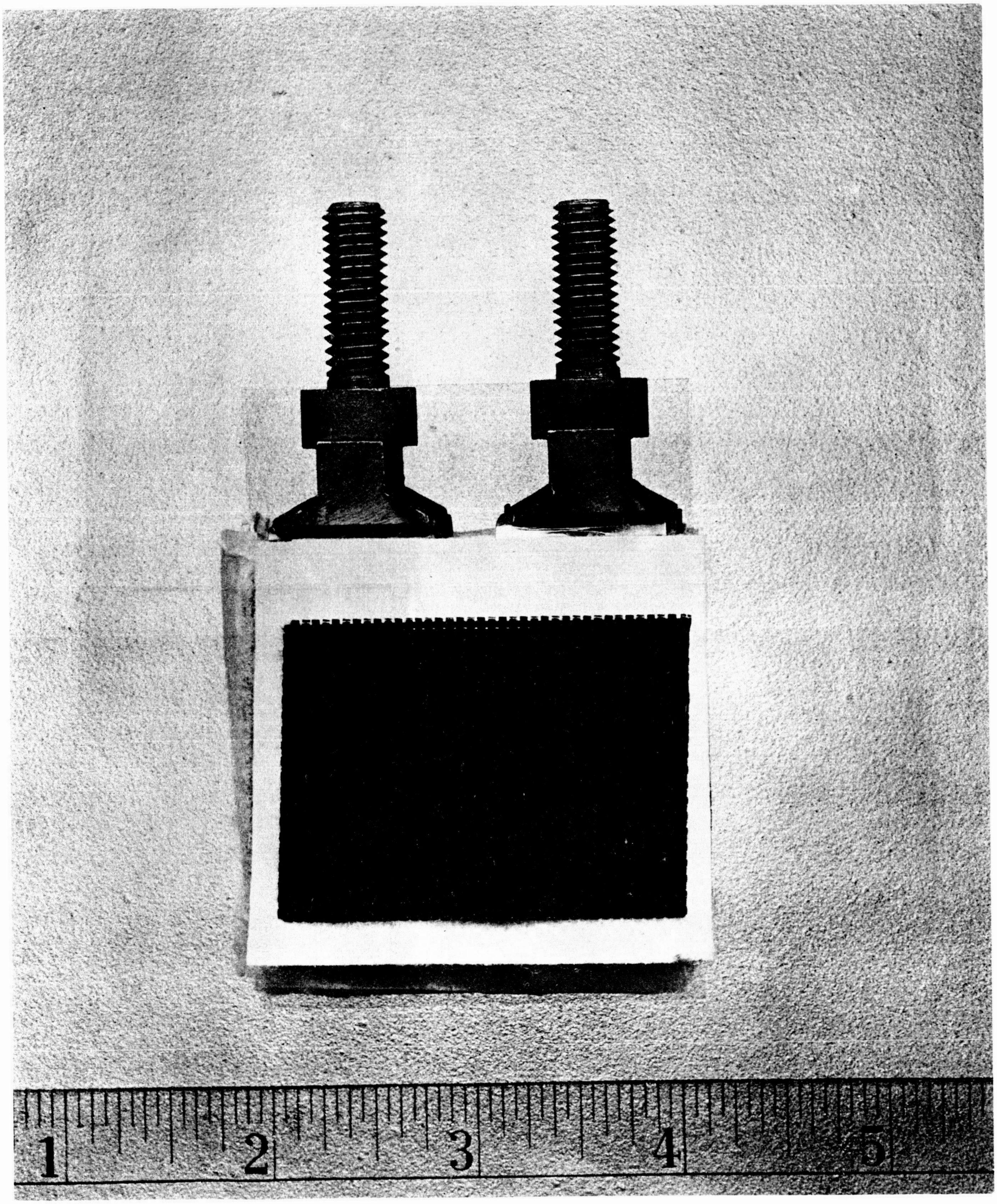

Figure 1. Photograph of VO7 Electrode Pack with Auxiliary in Side Position.

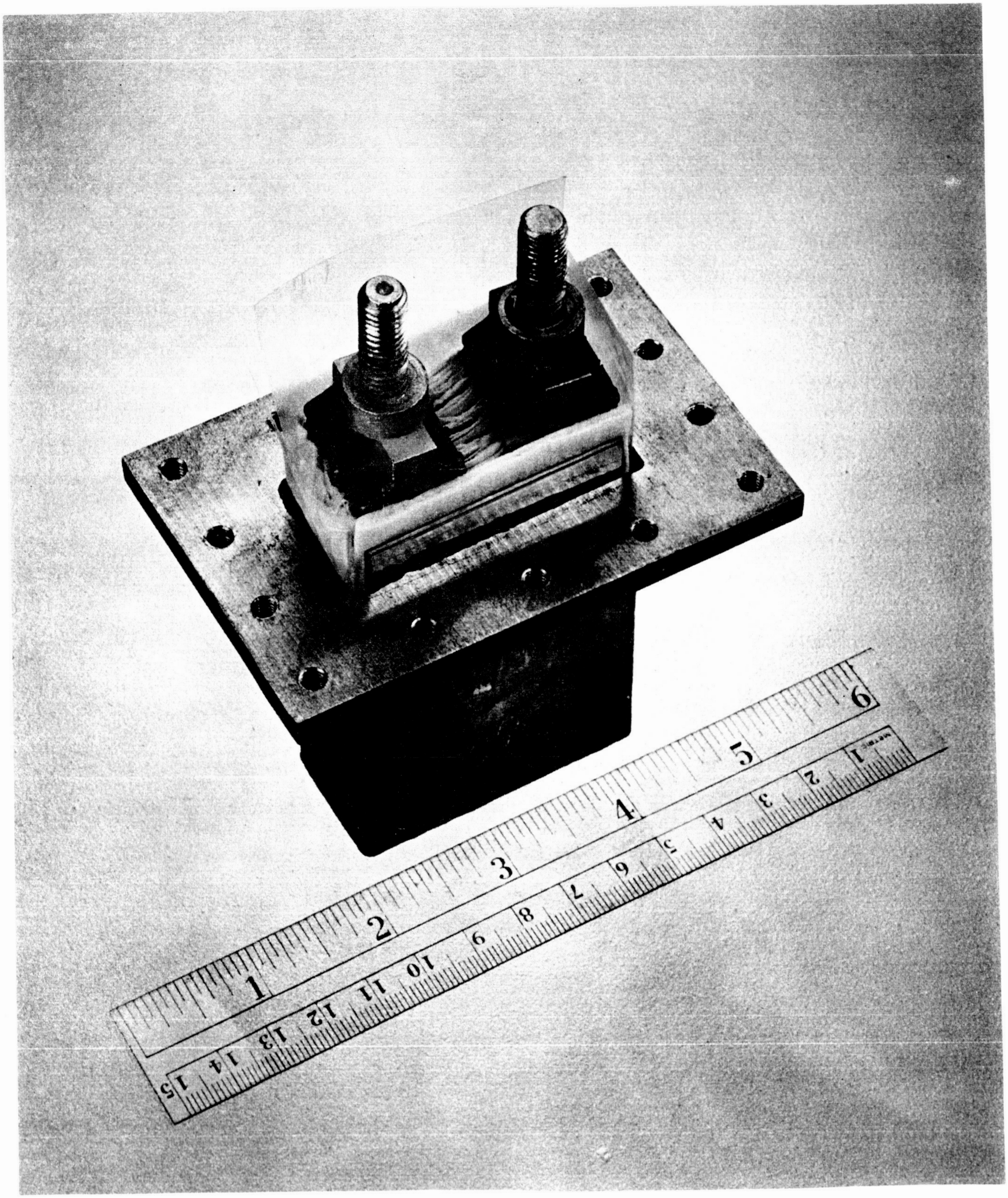

Figure 2. Inserting the Pack with Side Position Auxiliary.

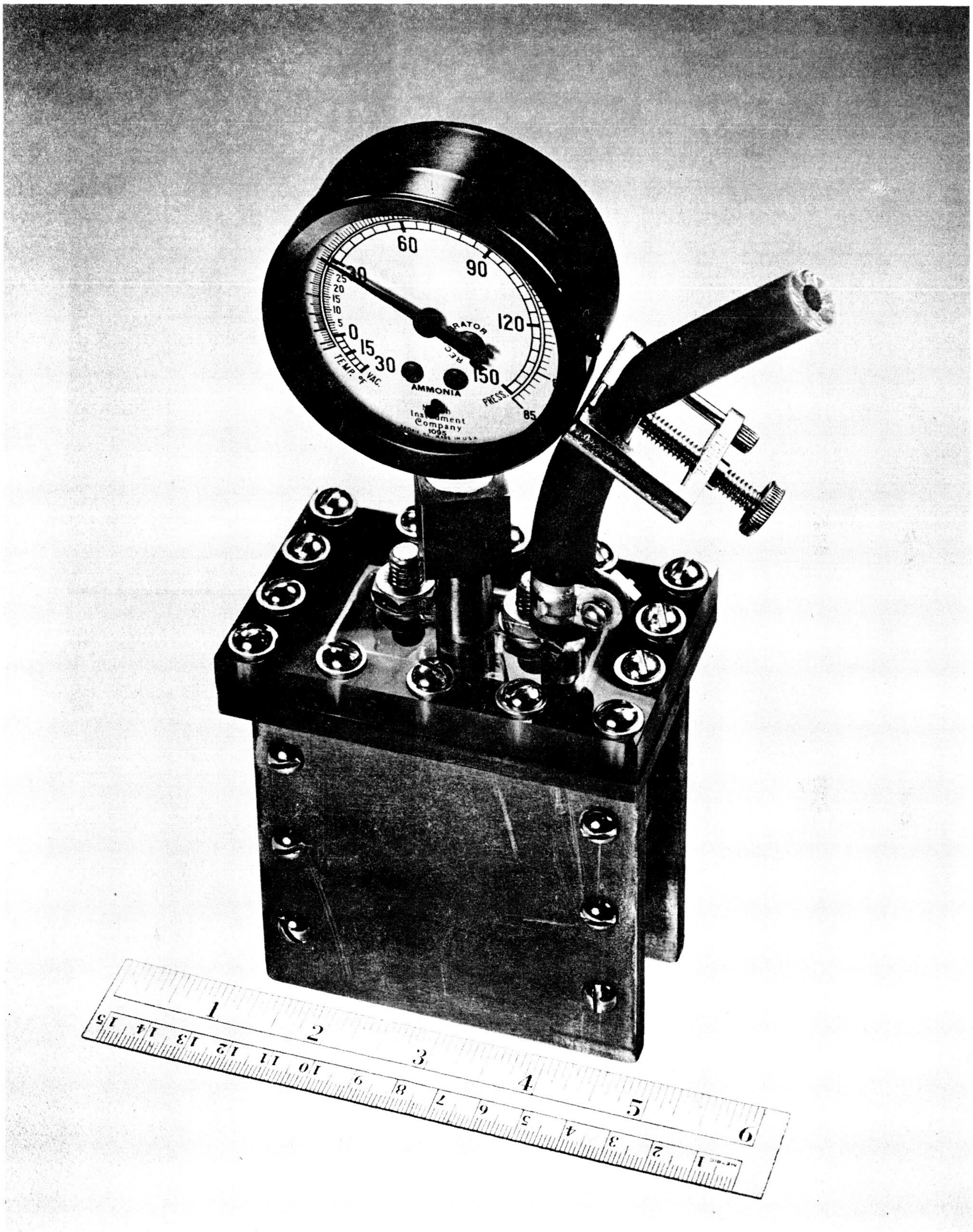

Figure 3. Assembled Cell Ready for Leak Testing.

Charging Rate	Initial Pressure, in. of Hg	Input		Output at 3C to 1.0 Volt	
		Hr:Min:Sec	Ampere Hours	Min:Sec	Ampere Hours
C/10	-25	40:36*	28.42*	18:11	6.36
1C	-23	1:39	11.55	18:35	6.50
2C	-24	:47:18	11.04	18:39	6.53
3C	-25	:31:05	10.88	19:20	6.77
5C	-25	:17:20	10.11	17:34	6.15

* To steady pressure gage reading of 55 P.S.I.

Performance of Cell No. 10 when Charged to a Pressure Gage Reading of 60 P.S.I. at Various Rates

Figure 4

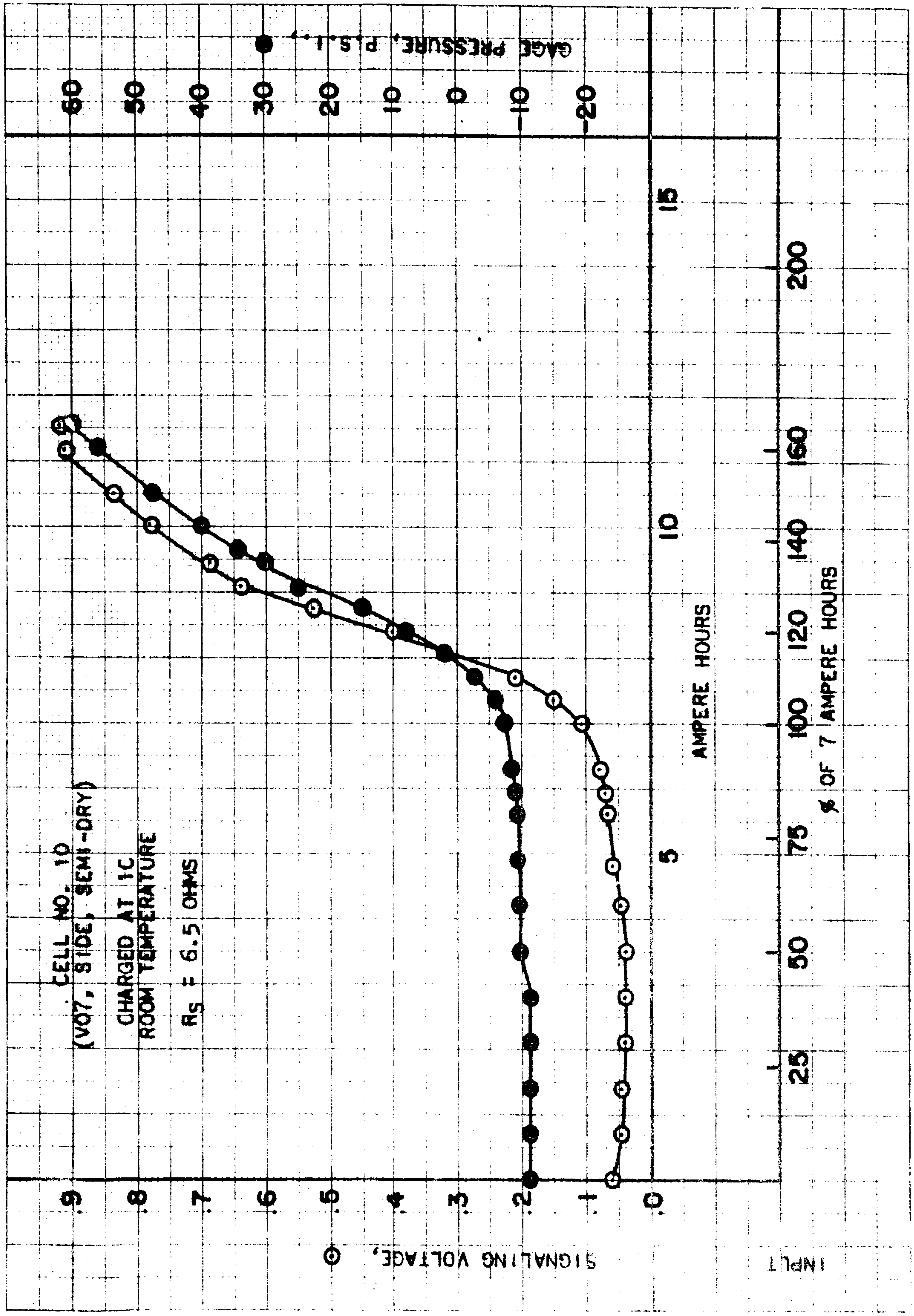

Figure 5. Signaling Voltage and Cell Pressure during Charging at the 1C Rate (7 Amperes).

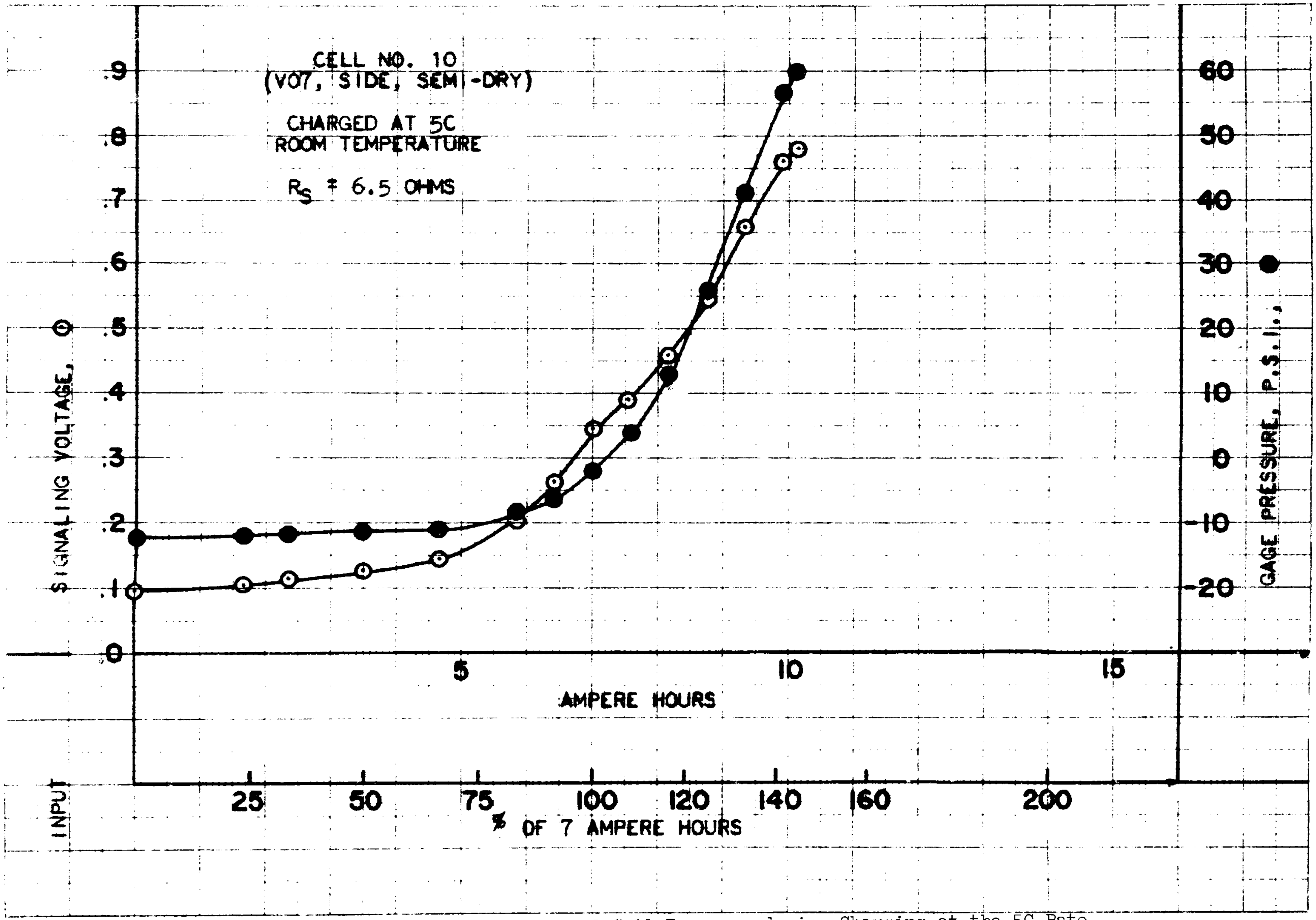

Figure 6. Signaling Voltage and Cell Pressure during Charging at the 5C Rate (35 Amperes).

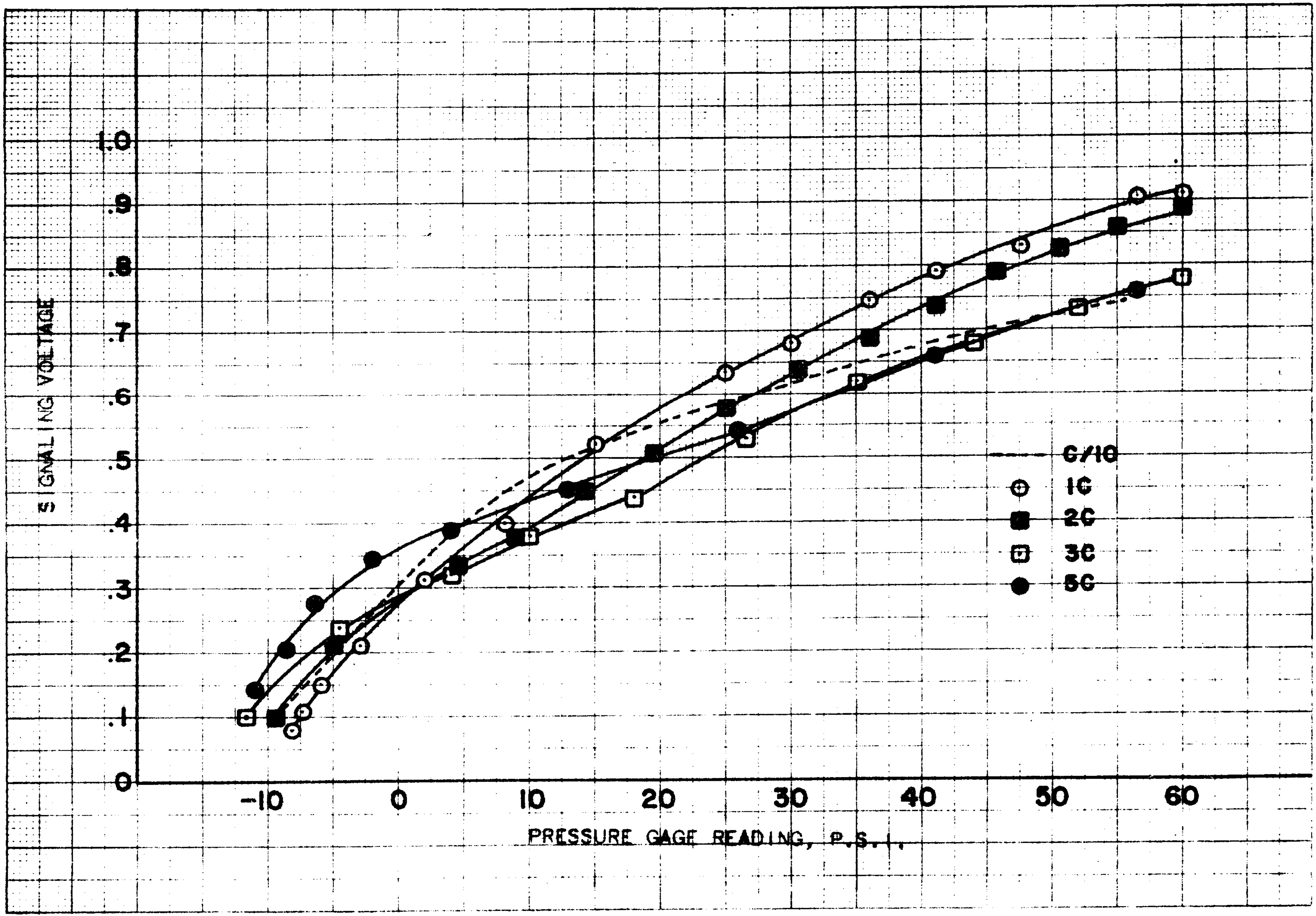

Figure 7. Signaling Voltage as a Function of Pressure for Cell No. 10 when Charged at Various Rates.

Operation	Cell Current, Amperes	Elapsed Time, Minutes	Volts		I_s, Milliamperes	Pressure Gage Reading, P.S.I.
			Cell	Signaling		
Charge	14	0+	1.45	0.06	9	-11.8
	14	47.3	1.57	0.89	135	+60
O.C.	0	0+	1.46	0.81	123	+60
	0	38	1.39	0.77	117	50
	0	128	1.38	0.55	83	26
Discharge	21	0+	1.26	0.51	79	26
	21	3	1.22	0.58	87	25
	21	6	1.22	0.65	99	25
	21	9	1.21	0.73	110	23
	21	12	1.20-	0.76-	114+	21
	21	15	1.18-	0.75+	114+	20
	21	16	1.16+	0.74+	112	19+
	21	17	1.15	0.73	110	19
	21	18.65	1.00	0.68	105	18+
Discharge*	5	4	0.80	0.43	62	15
	2.3	10	0.38	0.25	38	12
	0.7	34	0.10	0.24	35	8
O.C.	0	0+	0.88	0.55	85	8
	0	20	1.03	0.62	94	7
	0	30	1.06	0.63	94	5
Charge	0.35	0+	1.22	0.75	114	5
	0.35	6	1.29	0.76+	116	2

Auxiliary Electrode Behavior for Cell No. 10

During Discharge Following Charging at 2C.

Figure 8

PIC-BAT 209/9
Section 2

EVALUATION OF AUXILIARY ELECTRODE MATERIALS*

by

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Primary Battery Division

McGraw Edison Company

Bloomfield, New Jersey

19 May 1965

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* Presented at the 19th Annual Power Sources Conference, 19 May 1965

EVALUATION OF AUXILIARY ELECTRODE MATERIALS

Philip F. Grieger
Primary Battery Division
McGraw Edison Company
Bloomfield, New Jersey

Principles of the Jaffe Invention

The idea of using auxiliary electrodes to consume the gases in hermetically sealed cells dates back to the 1930s (Ref. 1), but S. S. Jaffe (Ref. 2), about ten years ago, while working in the Thomas A. Edison Research Laboratory, was the first to propose making the current (that flows through the external connection between the main cadmium and an auxiliary O_2 reduction electrode) do useful work by powering a relay arranged to terminate charging of the cell (Figure 1).

The interrelationship of the three electrodes during charging is shown in Figure 2. The current, I, enters the nickel electrode and divides; in the electrolyte the signaling current, I_s, enters the auxiliary electrode and the remainder, $I-I_s$, enters the cadmium electrode. At the auxiliary O_2 is reduced, or in the absence of O_2, H_2O may be reduced to H_2. In either instance I_s flows in the external signaling circuit -- considered to have a resistance R_s (e.g. the resistance of a relay coil) -- in the direction shown in Figure 2. Charging is automatically terminated when power generated in the signaling circuit is sufficient to operate the terminating device, such as a relay as shown in Figure 2.

Setting the sum of the potential changes in going around the loop x, y, z, x equal to zero, it turns out that

$$I_s = \left[(I-I_s)\ R_e + P_{Cd}\ (I-I_s) + E^o(\text{aux, Cd}) - P_{aux}\ (I_s) - I_sR_e'\right]/R_s \qquad \text{Eq. (1)}$$

where $P_{Cd}(I-I_s)$ = polarization of the cadmium electrode

E^o(aux, Cd) = open circuit potential of the auxiliary/cadmium sub-cell, that is, about + 1.1 volt if O_2 is being reduced, or - 0.02 if H_2 is being evolved.

$P_{aux}(I_s)$ = polarization of the auxiliary electrode.

The first two and the last three terms within brackets are grouped naturally to give

$$I_s = (W + V')/R_s \qquad \text{Eq. (2)}$$

where W is the total polarization of the main cell less the polarization of the nickel electrode, V' is the potential difference between the working auxiliary and an idle cadmium reference located at x.

Imagine that at the start of charging there is no O_2 present in the gas space. At first almost all the current, I, goes into reduction of cadmium hydroxide but some H_2 may be evolved on the auxiliary*. The open circuit potential of the H_2/Cd cell is substantially zero, so V' is approximately $-P_{aux}(I_s)$; W is considerably less than the total nickel/cadmium cell polarization, probably being less than 0.2 volt at the 5C rate. Even if the auxiliary exhibited no H_2 overvoltage, the H_2 evolution rate, with a resistance of 5 ohms in the signaling circuit, would be, from Eq. (2), no more than

$$I_s = 200/5 = 40 \text{ milliamperes.**}$$

Hydrogen evolution rate*** will decrease with decrease in charging rate, but the total volume evolved per charging to a fixed O_2 cut-off pressure will be roughly the same for rates in the range 1 to 5C.

After O_2 has been evolved from the nickel electrode as charging proceeds****, the O_2 reduction polarization characteristics of the auxiliary govern the signaling current. As a first approximation W can be neglected in comparison with V' and Eq. (2) becomes

$$I_s = V'/R_s.$$

As a specific example, let the O_2 reduction behavior of the auxiliary, as a function of O_2 pressure, be characterized by the family of V' vs. I_s curves shown in Figure 3, where straight lines radiating from the origin with slopes corresponding to resistances of 5, 3, and 1.5 ohms are included. The intersections of these lines with the polarization curves indicate the current that would flow in the signaling circuit if its load were equal to any one of these three values. These currents and the corresponding power generated by the signaling sub-cell are summarized in Table I. By using a relay whose coil had a resistance of 3 ohms and which operated at 200 milliwatts, charging would be terminated when O_2 pressure had built up to about 2 atmospheres. With polar-

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* The presence of sorbed oxygen or other effective positive active material on the auxiliary will delay (and even completely prevent) H_2 evolution.

** At this rate only about 8 ml of H_2 (room temperature and 1 atm.) would be evolved in 10 minutes of charging.

*** It depends, of course, upon cell construction: the lower the electrolyte resistance and cadmium electrode polarization, the better. Also the higher the H_2 overpotential of the auxiliary, the better.

**** H_2 evolved during the early stages of charging can now react with O_2, either on the auxiliary electrode or a specially provided catalyst body.

ization curves such as those shown in Figure 3, it is possible, by properly selecting the signaling circuit resistance, to arrange matters so that charging is terminated when the cell has received a satisfactory overcharge.

For the charging of cells in series, Jaffe teaches three schemes: where charging of the battery as a whole is terminated when (1) any one of the cells, or (2) a pilot cell reaches cut-off pressure, or (3) where charging of the cells is terminated one-by-one as each reaches its cut-off pressure (his Figs. 6, 7, and 8, respectively in Figure 1).

As can be seen from Figure 1, Jaffe used flooded cells, but recently interest has been shown in using this method to control the charging of semi-dry hermetically sealed cells at very high rates, such as up to 5C, which cannot otherwise be accommodated for protracted periods. For example, at last year's Power Sources Conference papers on this subject by W. N. Carson, Jr. of General Electric Co., and H. M. Seiger, R. C. Shair, and P. F. Ritterman of Gulton Industries were presented (Ref. 3).

TABLE I

SIGNALING CURRENT AND POWER CALCULATED FOR THE POLARIZATION CURVES OF FIGURE 3

O_2 pressure, atmospheres	Signaling current, milliamperes	Signaling power, milliwatts
	5 ohms	
0.5	150	113
1	155	120
2	165	136
	3 ohms	
0.5	185	103
1	235	166
2	270	219
	1.5 ohms	
0.5	225	76
1	315	149
2	480	346

Platinized Cloths

It was contemplated in the present investigation to use a carbonized cloth substrate electroplated with platinum as the auxiliary electrode. Besides having good O_2 reduction characteristics, such a material is flexible and in principle lends itself to use in rectangular or cylindrical cells where it would add very little to the volume or weight. For example, it was visualized that a sheet of such material could be placed at the end of the electrode pack, where, on one side it would be separated from an end nickel electrode plate by means of the cell pack separator, and on the other side would be in electronic contact with the metal can wall which would act as external terminal of the auxiliary electrode -- the nickel and cadmium electrodes being insulated from the can. In another respect such electrodes gave promise, because, being prepared by electrodeposition, the chances of making them replicably seemed good. Reproducibility of the polarization curves of a given electrode with use, and replicability from electrode to electrode are clearly important in insuring reliable charge control.

Evaluation Tests

Previous work in the Thomas A. Edison Research Laboratory, begun by A. Fleischer and continued by R. M. Taylor and T. L. Treitler with the assistance of L. A. Middlecamp, had been done with WCB graphite cloth (Ref. 4), plated with either grey or black platinum, for use in fuel cells. There are now on the market about a dozen carbon or graphite cloths. Some of these, it was thought, might be better substrates than WCB cloth, and it was uncertain whether black or grey platinum would be better for a particular cloth. With a variety of cloths that spanned the range of physical characteristics (type of weave, thickness, etc.) preliminary experiments were done in the hope of limiting, to one or two, the number of auxiliary electrode materials to be tried in hermetically sealed nickel/cadmium cells.

Four kinds of graphite or carbon cloth, and two kinds of platinum for comparison, were chosen as substrates for preliminary testing, as follows:

Graphite cloth, WCB (National Carbon, Ref. 4)
Carbon cloth, VCB (National Carbon, Ref. 4)
Graphite cloth, WCJ (National Carbon, Ref. 4)
Carbon cloth, CCA-1 (Hitco, Ref. 5)
Platinum screen (48 mesh, 6 mil wire)
Platinum foil (1 mil, perforated)

Each of the six substrates was plated in the same way with grey or black platinum. Pieces 1-3/4 by 2-1/4 inches* were tested using a horizontal

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* Depending upon the substrate and the kind of platinum the weight of platinum was between 50 and 300 milligrams.

configuration as shown schematically in Figure 4; the jig being housed in a gas-tight container (Figure 5). Potential difference between the test electrode and the nickel reference, V, was measured as a function of current; V' was estimated as V' = 1.30 -V.

In Preliminary Experiment No. 1 (P.E. No. 1), which lasted one week, polarization curves for the twelve different auxiliary electrodes were determined at room temperature in pure O_2 at various pressures, on Monday, Wednesday and Friday and at -40°F on Thursday; on Tuesday the cells were operated at constant current for four hours*. P.E. No. 3 was a replicate of P.E. No. 1.

Typical polarization curves for Black and Grey at 2 atmospheres and room temperature are shown in Figures 6 and 7. (Figure 3 actually is data obtained in P.E. No. 1 on Friday with VCB Black at the three pressures.)

Current at V' = 0.6 volt, in milliamperes (called $I_s(0.6)$ for short) was used as a convenient index of performance because, as the family of curves in Figure 3 suggests, the greater $I_s(0.6)$ is at 2 atmospheres, say, the greater is the variation of signaling power with O_2 pressure for a given signaling circuit resistance in the range of interest. The 12 substrates measured at 3 pressures on 3 days in 2 experiments yield 12 x 3 x 3 x 2 = 216 values which can be considered most succinctly in terms of the analysis of variance as given in Table II. Here, as a first approximation, it is assumed that error is represented by the interactions. From inspection of all the polarization curves it probably would be taken for granted that O_2 pressure, as between 0.5, 1.0, and 2.0 atmospheres, is a determining factor of performance, and the analysis of variance does show that pressure is extremely significant. Kind of substrate and platinum (Black is better than Grey) are highly significant. Day of testing is not significant, which indicates that reproducibility is good and that room temperature performance is not appreciably affected by continuous operation for four hours or by testing at -40°F. Comparing the substrates, VCB is better than WCB which in turn is much better than any of the others. The best combination is VCB Black. At -40°F, $I_s(0.6)$ is roughly only 1/10 what it is at room temperature, but the same order of merit is found.

In spite of the rather large indicated error of 30%, it is believed that by means of this analysis important factors have been found out. In P.E. Nos. 1 and 3 the quantity of electrolyte was not supposed to be a factor but, because this was controlled by subjective means that depended upon the technique of the person assembling the cells, it was probably a major contributor to error in P.E. Nos. 1 and 3. Replication error, although not significant in Table II, is sizable and shows that the assembly technique when practiced on two different occasions (by the same person but two weeks apart) gave rise to considerably different results.

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* Current was selected so that at the start of the run V' lay in the range 0.88 to 0.77 volt.

TABLE II

ANALYSIS OF VARIANCE FOR P.E. NOS. 1 AND 3 USING $I_s(0.6)$, IN MILLIAMPERES, AS PERFORMANCE INDEX

		$X10^{-2}$			F (d.f., 120)	
Source	d.f.	S.S.	M.S.	F	95%	99%
Pressure	2	18,633	9,317	252	3.07	4.79
Substrate	5	13,867	2,773	75	2.29	3.17
Platinum	1	1,768	1,768	48	3.92	6.85
Replication	1	107	107	2.9	3.92	6.85
Day	2	203	102	2.8	3.07	4.79
	11	34,578				
Total S.S.	215	42,207				
Interactions, by diff.	204	7,629	37			

Mean of 216 $I_s(0.6)$ values = 202

Assuming $S^2 = 3,700$

$S = 60.8$

error = (100%) 60.8/202 = 30%

References

1. A. Dassler, German Patent 602,702, September 14, 1934, and U.S. Patent 2,104,973, January 11, 1938. A recent innovation is by P. Ruetschi and B. D. Cahan, U.S. Patent 3,080,440, March 5, 1963.

2. S. S. Jaffe, U.S. Patent 3,005,943, October 24, 1961.

3. W. N. Carson, Jr., "Auxiliary Electrode for Charge Control"; H. N. Seiger, R. C. Shair, and P. F. Ritterman, "The Adhydrode in Charge Control", Proceedings, 18th Annual Power Sources Conference, 19-21 May 1964.

4. New Product Market Development, National Carbon Company, Division of Union Carbide Corporation, 270 Park Avenue, New York 17, New York.

5. Hitco is a trade name of the H. I. Thompson Fiber Glass Company, 1600 West 135th Street, Gardena, California.

6. Similar to the construction used by Gulton Industries in one of their projects: H. N. Seiger, "Investigations Leading to the Development of Improved Sealed Nickel-Cadmium Batteries", Report No. 4, 1 April to 30 June 1961, DA 36-039 SC-85390.

7. Signal Corps Technical Requirement, "Batteries, Storage, Sealed Nickel-Cadmium", SCL-6868A, 18 September 1963.

Additional preliminary experiments were done with the best materials, viz., VCB Black and Grey and WCB Black under more controlled conditions: four different states being achieved by blotting each of the components with the aid of a specified weight for a fixed time. The analysis of variance, again applied to $I_s(0.6)$, shows that random error is markedly decreased, in comparison with P.E. Nos. 1 and 3, and that quantity of electrolyte is highly significant. There is an optimum quantity of electrolyte, with too little being much worse than too much. Once again VCB Black was found to be best, and it was decided that this was the only platinized cloth that need be tested in actual hermetically sealed nickel/cadmium cells.

In the Main Experiment, which is now underway, VCB Black is being used as the auxiliary electrode in two kinds of commercial cells (Gulton V07 and Union Carbide N78), which are modified by welding a flange onto the can so as to accommodate a Lucite cover bearing a pressure gage (Ref. 6). The plan of the experiment calls for 32 cells. Two positions of the auxiliary are being used: side and top. In the side position the auxiliary is next to a nickel electrode plate (both outside plates are nickel electrode plates in the V07 and N78). Of the three quantities of electrolyte under examination, two provide excess free-flowing electrolyte in an attempt to obtain increased capacity from the cells.

In order to evaluate the ability of the auxiliary to control charging under a wide range of conditions, three rates (C/10, C, and 5C), three temperatures (0^oF, room temperature, and 120^oF), and two initial states of charge (none and 50%) will be used. During charging and discharging, pressure and signaling current will be monitored; charging will be stopped when pressure reaches the same specified value in all cells. Adequacy of the charging will be judged in terms of the USAEL's normal, high rate, and low temperature discharge tests (Ref. 7).

This report is based on work being done for the Power Sources Division, United States Army Electronics Laboratory, Fort Monmouth, N. J. under Contract Number DA 28-043 AMC-00152(E). During the first quarter the work was done largely by S. S. Jaffe, L. A. Middlecamp, and J. D. Moulton; since then principally with the assistance of J. Orshich and G. A. Mueller.

Oct. 24, 1961 **S. S. JAFFE** **3,005,943**

SEALED STORAGE CELL USING LIQUID ELECTROLYTE

Filed April 10, 1957

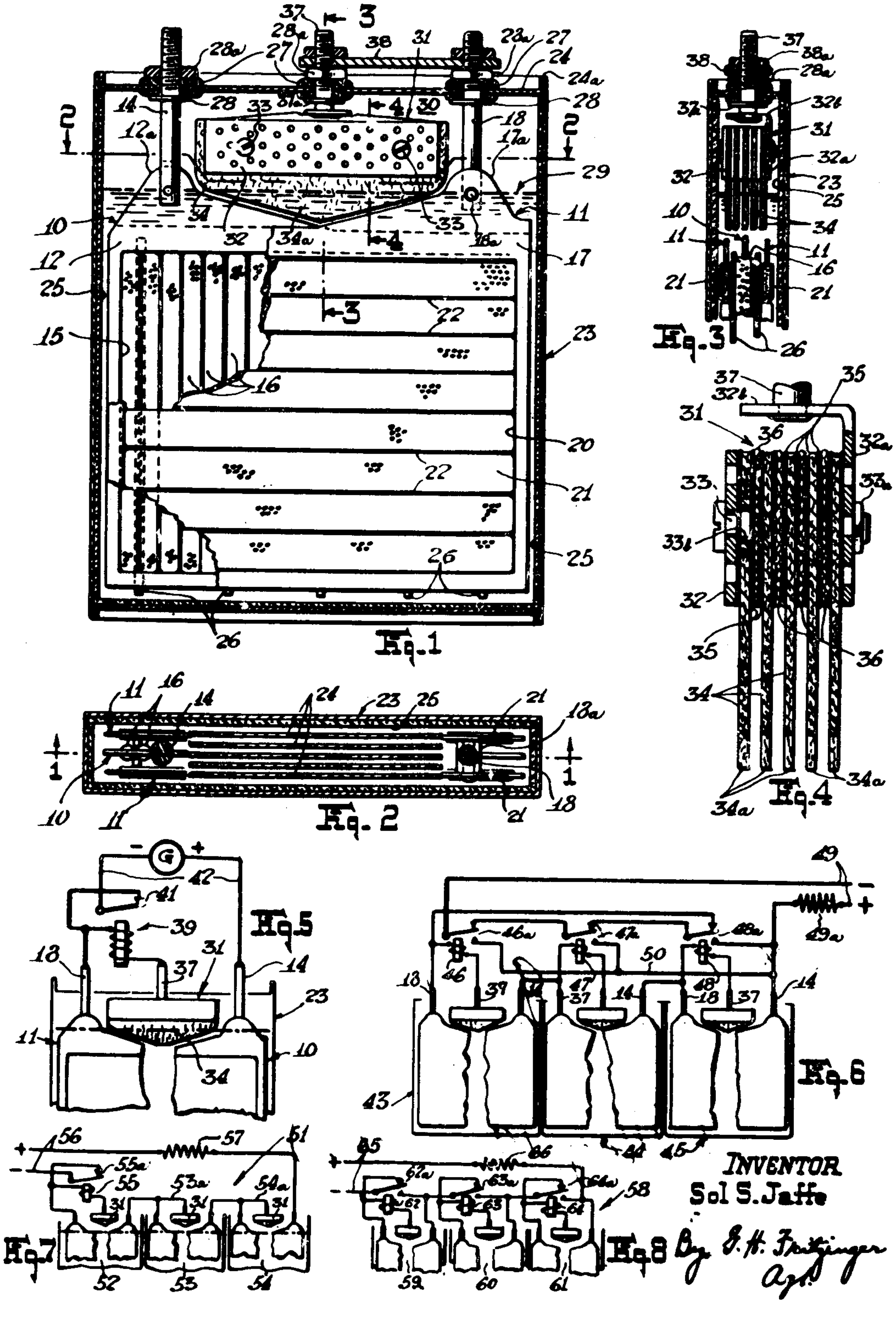


Figure 1. Reproduction of the cover sheet of the Jaffe auxiliary electrode patent.

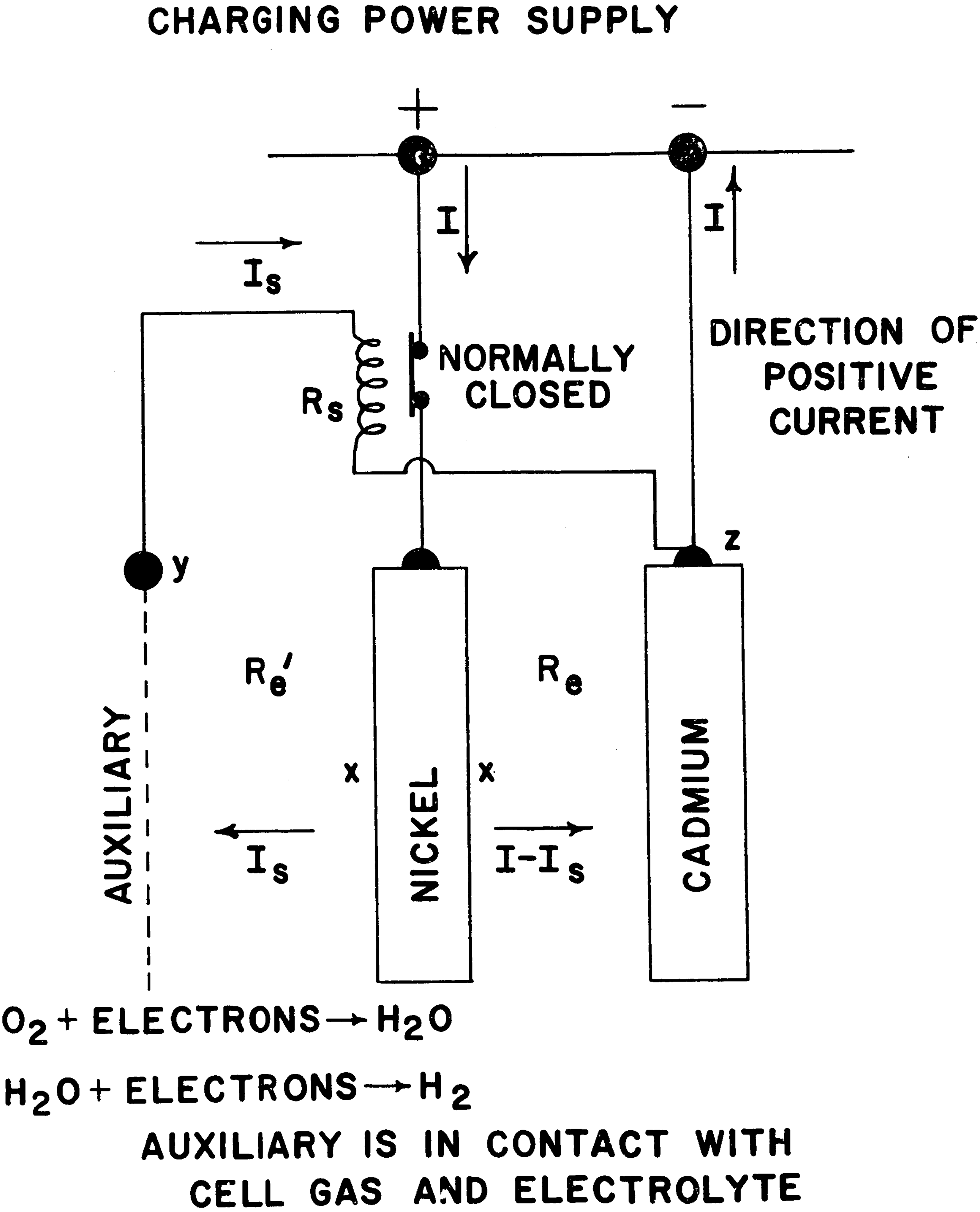


Figure 2. Interrelationship of the auxiliary and main electrodes during charging showing distribution of the total current, I. Signaling current is represented as I_s.

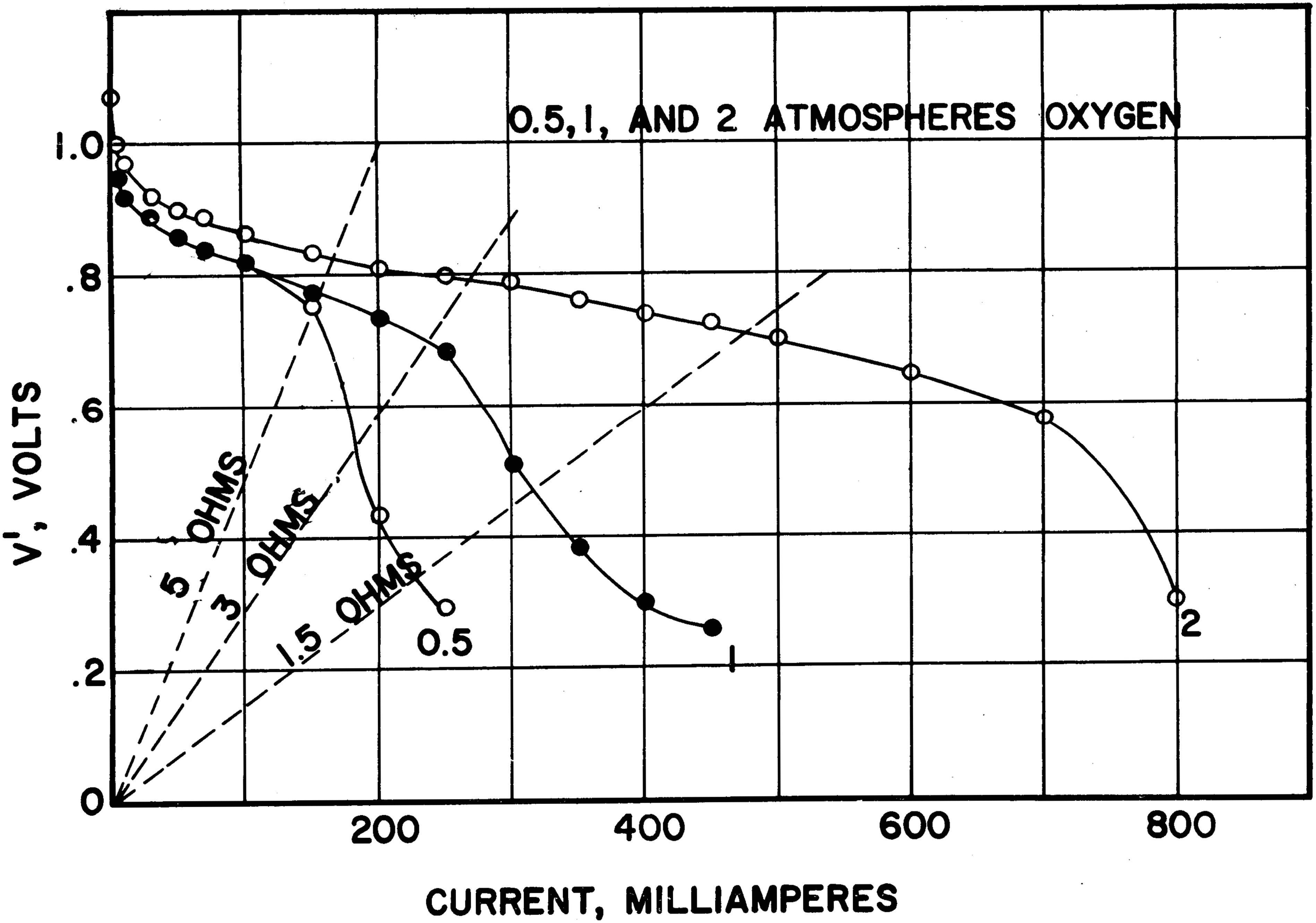


Figure 3. Polarization Curves at different O_2 pressures showing graphical estimation of signaling current as a function of pressure for three signaling circuit resistances.

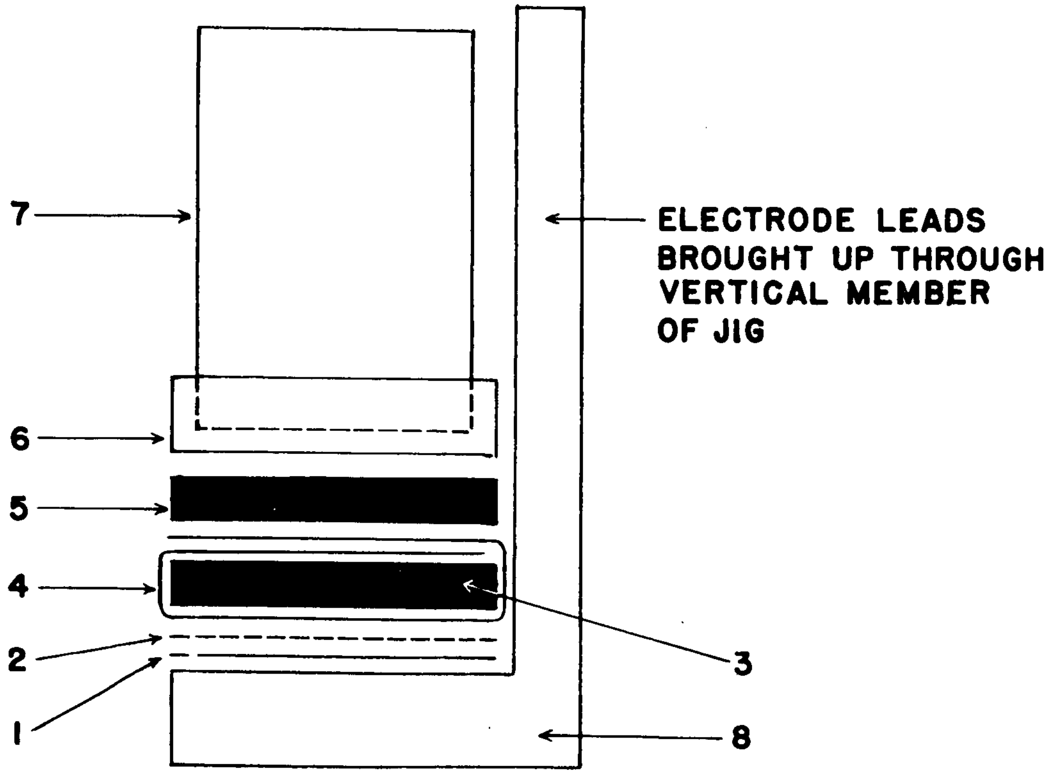
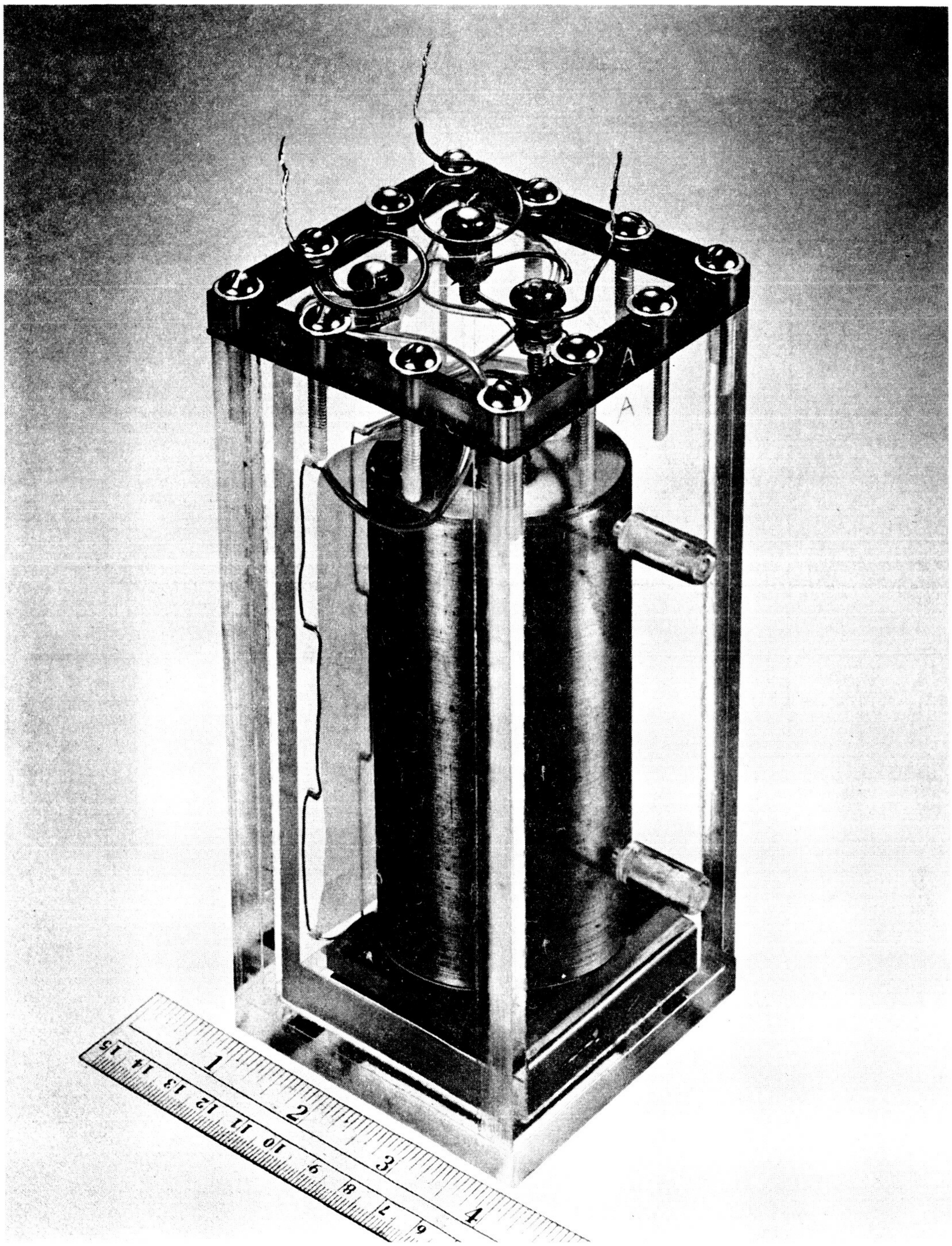


Figure 4. Diagrammatic side view (expanded) of means for evaluating auxiliary electrode materials. 1. Current tap (nickel sheet) for auxiliary electrode, 2. Auxiliary electrode material, 3. Opposing electrode (Nickel positive), 4. Separator, 5. Reference electrode (partially discharged Nickel positive), 6. Hold-down plate (Lucite) with circular seat, 7. Weight (steel, 4.2 pounds), 8. Jig (Lucite).



Photograph of Jig and Electrode Stack inside Cell Container

Figure 5

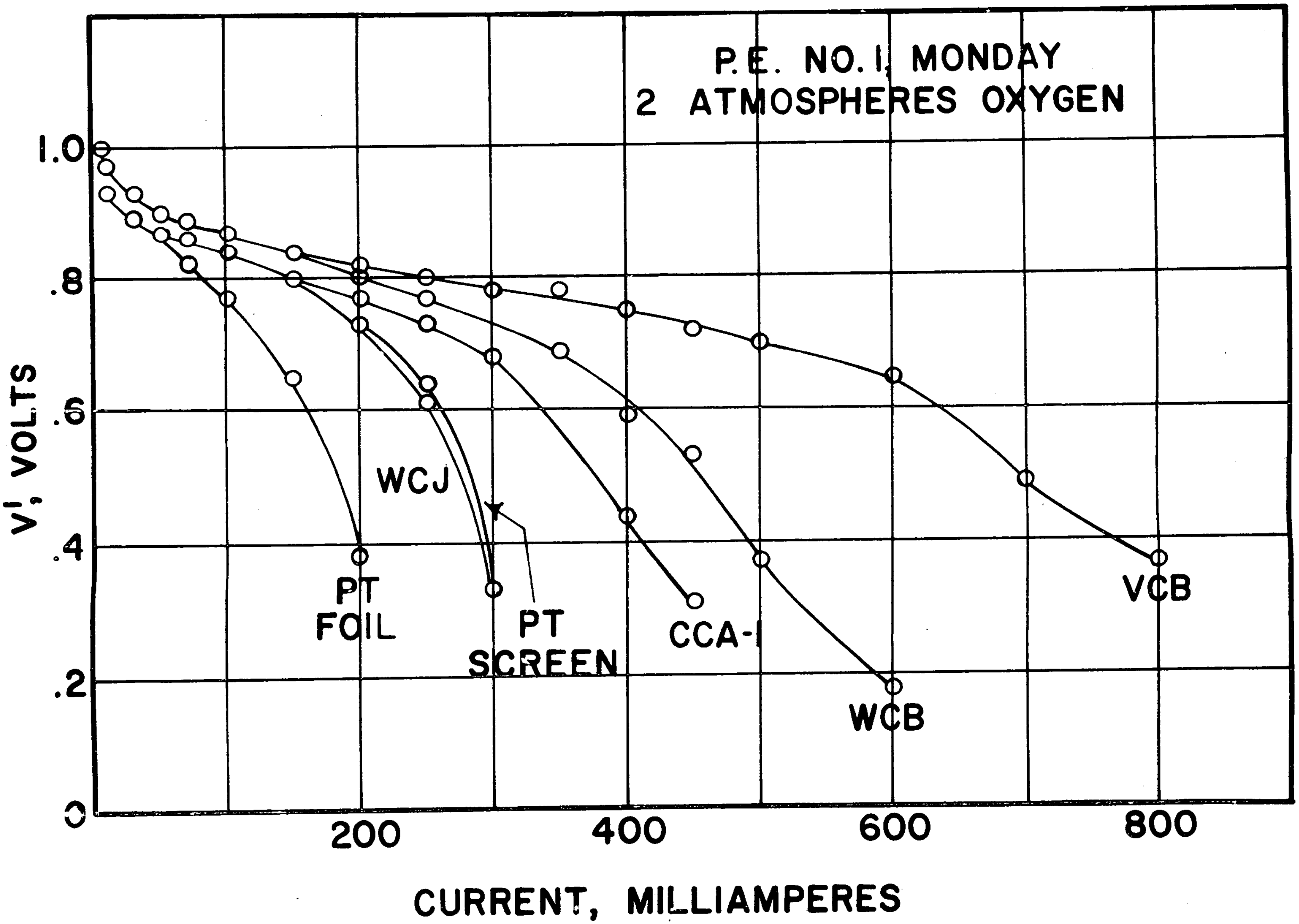


Figure 6. Polarization curves for Black at room temperature.

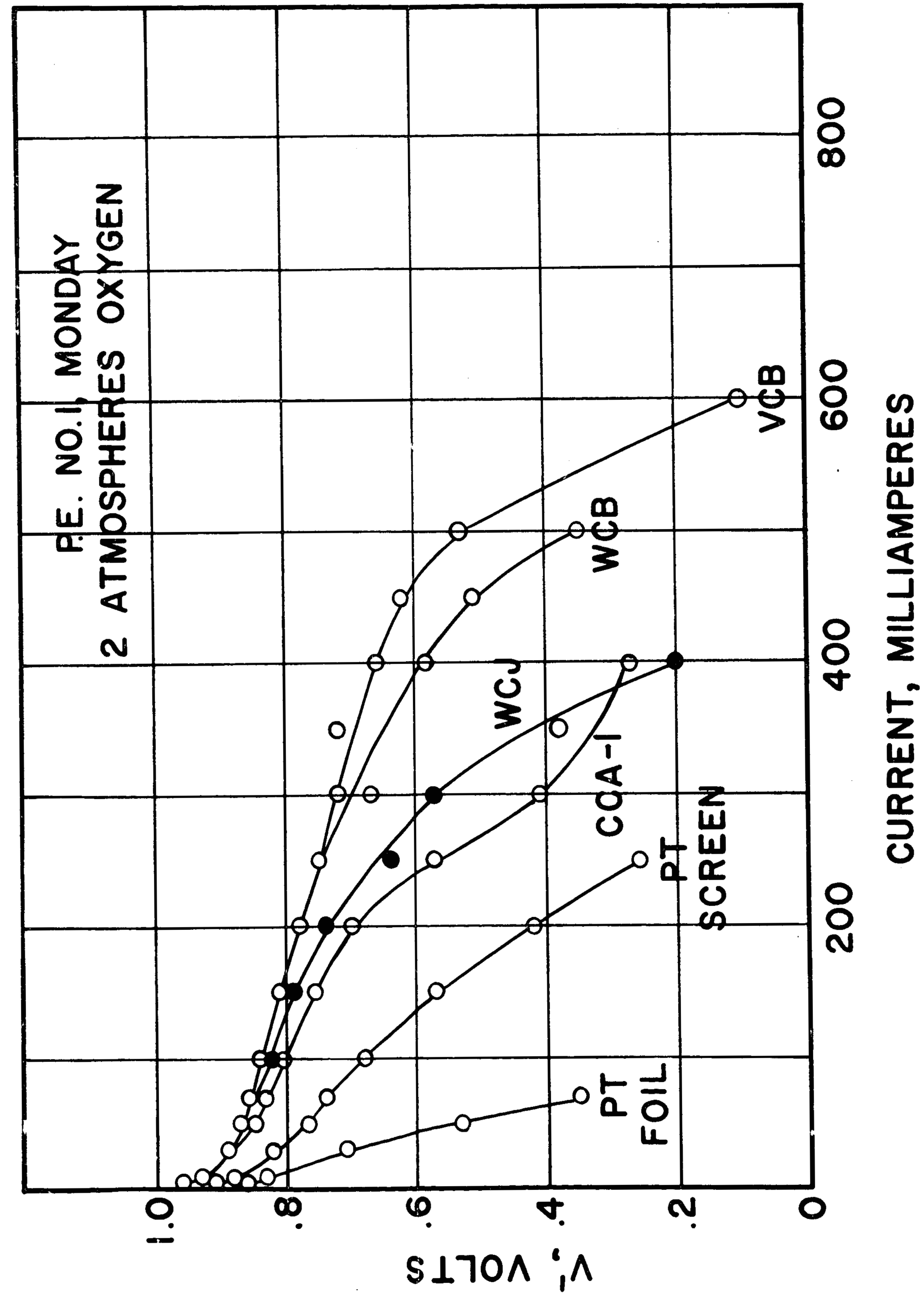


Figure 7. Polarization curves for Grey at room temperature.

PIC-BAT 209/9
Section 3

AUXILIARY ELECTRODES FOR USE IN SILVER AND NICKEL-CADMIUM CELLS

by

W. N. Carson
A. J. Catotti
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General Electric Company

1965

PIC-BAT 209/9

AUXILIARY ELECTRODES FOR USE IN SILVER AND NICKEL-CADMIUM CELLS

W. N. Carson
A. J. Catotti
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General Electric Company

Introduction

We have investigated the use of auxiliary electrodes in nickel-cadmium, silver-cadmium and silver zinc cells for NASA over the past two years under Contracts NAS 5-3707, NAS 5-2817 and NAS 5-3669. Final reports for these projects have been issued. This paper is intended mainly to present a summary of the results of interest to designers of power supplies using these cells.

Nickel-Cadmium Applications

Auxiliary electrodes may be used for both overcharge and over-discharge control of nickel-cadmium sealed cells.

Charge Control

Sealed nickel-cadmium cells are designed so that they are positive limiting on charge. Oxygen is then liberated at the positive nickel hydroxide electrode as the positive electrode approaches full charge and is reduced at the negative cadmium electrode.

As a result of balanced evolution and recombination of oxygen, a conventional sealed cell is capable of continuous overcharge at rates up to about C/6.

By incorporating a high performance gas electrode into the cell and attaching it to the negative terminal through a definite resistance the recombination of oxygen within the cell can be improved. In addition, a definite signal (voltage) change can be detected between the negative terminal and the gas electrode (herein referred to as the 3rd electrode) when oxygen is evolved from the positive plate at the onset of overcharge.

Protection Against Overdischarge

When a battery of cells is completely discharged, the lowest capacity cells will be overdischarged and one or both electrodes may reverse, generate gas by electrolyte electrolysis.

To insure against cell capacity losses due to negative plate fading and minimize problems with oxygen evolution generating a premature charge control signal, a cell was designed which was positive-limiting on discharge. In this manner hydrogen is evolved from the positive plate when it is reversed. If we attach this overdischarge control electrode (herein called the 4th electrode) to the negative cell terminal through a low resistance, we have a completed circuit for recombination of the hydrogen. When sufficient hydrogen is present, the 4th electrode will become more negative than the cadmium electrode and hydrogen will be oxidized in preference to the cadmium. When the cadmium electrode is still in the charged state, the rate of recombination is very slow since the difference in E^o's is only about 20 mv. However, if cell reversal is taking place at a high rate, the cadmium electrode soon becomes discharged, forcing the E^o of cadmium to be much more positive. As this occurs, the gas (or 4th) electrode has a greater driving force available and can react with the hydrogen at significantly higher rates. Fuel cell work has shown that these gas electrodes work well at current densities of over 100 ma/cm^2 continuously.

In order to prevent excessive pressure build up during reversal, cells were designed so that the cadmium plates would reverse soon after the positive nickel and thereby quickly develop the large ΔE required for rapid oxidation of hydrogen.

Gas Electrode Selection

In order to insure efficient operation and rapid combination of evolved gas it was decided to use proven Teflon-wetproofed fuel cell electrodes as the 3rd and 4th electrode materials. A more detailed discussion of electrode testing and selection for nickel-cadmium cells can be found in the final report of NASA Contract NAS 5-3707.

Design Considerations

The above contract required that a cell of nominal 6 AH capacity be developed which would be immune to damage from both overcharge and overdischarge. In order to test the cell's capability to withstand such operation the following test cycle was proposed:

a. Charge at 1.615 amps for 65 minutes (105 amp min).
b. Discharge at 3.0 amps for 35 minutes (105 amp min).
c. Charge at 1.615 amps for 65 minutes (105 amp min).
d. Discharge at 3.0 amps for 50 minutes (150 amp min).

The cell had to be able to withstand 200 of the above cycles at temperatures of 45°C, 25°C and 5°C.

In addition, the cell had to be capable of being fully and safely charged at rates ranging from C/10 to 2C and at temperatures from 50°C to 0°C.

In order to accommodate the additional electrodes, it was decided to build the cell with two "covers" containing two insulated terminals on the top cover for positive and negative electrodes, one bottom terminal for the 3rd electrode (charge control) and the other insulated bottom terminal for a reference electrode. The can was used as the 4th electrode terminal.

The internal construction of the cell is shown schematically in Figure 1. A third (charge control) electrode was located on one edge of the pack with a piece of separator between the pack and the electrode. A section of corrugated PVC was placed between the electrode and the cell case for insulation and to provide a gas space. The reference electrode, consisting of a small piece of partially charged positive plate, was placed on the bottom of the pack assembly completely enclosed with a wrap of separator. Fourth electrodes were assembled on both broad faces of the plate pack, with a layer of separator between the electrode and the adjacent negative plate. Gas space was provided between the can and the electrode by a piece of corrugated PVC.

Cell Testing

The cells were assembled and tested with pressure gages and reference electrodes (consisting of a partially charged positive plate).

On the first overcharge cycle the cells were charged at the C/2 rate to the signal voltage of 0.5 V DC (control electrode to negative) and then discharged at the 2 hour rate. The data is summarized in Table 1. All cells gave greater than 6.3 AH capacity on the first cycle.

The data have been plotted in Figure 2 for cell #2. During charge a hydrogen pressure develops due to evolution of hydrogen on the auxiliary electrode. It it were considered desirable to minimize this effect, a somewhat larger resistor could be used to replace the 10 milliohm connection. The charge current being used to generate hydrogen during the early stages of charging at this rate is estimated to be about 60 mA or about 2% of the total. At these charge rates the generation of hydrogen is not serious since the potential of the auxiliary will become more negative as the hydrogen pressure increases until the auxiliary potential becomes equal to the negative at which time the hydrogen current will be insignificant.

The hydrogen pressure disappears completely as soon as oxygen starts evolving at a significant rate from the positive plate, i.e., near the end of the full charge. (The hydrogen combines chemically on the catalyst surface with the oxygen.) At this time the voltage between the control and negative electrode rises sharply. The data in Table 1 show that the auxiliary to negative current also increases sharply at this point indicating that the oxygen generated on overcharge is recombining on the auxiliary electrode. The recombination is so efficient that the pressure remains at a very low value during the overcharge period.

In order to measure the cell's capability to sustain overdischarge, the cells were cycled as noted before:

a. Charge 1.615 amps for 65 minutes
b. Discharge at 3.0 amps for 35 minutes
c. Charge at 1.615 amps for 65 minutes
d. Discharge at 3.0 amps for 50 minutes.

After 200 such cycles, the first cells exhibited pressures of 15 to 71 psig.

In addition to providing reversal protection, the 4th electrode cell also allows us to completely discharge the cells periodically. This destroys the often damaging memory effect which has been known to cause apparent loss of battery capacity in cycling.

In Figure 3 is shown a schematic for the cell and circuit used to accomplish the reversal cycle. It should be noted that a 10 ohm resistor is used between the 3rd electrode and the negative. The 4th electrode is connected to the negative by a zero-center ammeter having a resistance of 17 milliohms.

A typical cycle after several weeks of operation at room temperature is shown in Figure 4.

Positive and negative voltages are shown with respect to the nickel hydroxide/nickel reference electrode along with total cell voltage. The pressure and gas recombination current through the 4th electrode are also shown. The free gas volume in the cell is about 50 cm^3.

It can be seen that the cell delivers 83% of the capacity charged on the first discharge and 89% on the second discharge.

During the early part of the cycle, hydrogen is combining on the 4th electrode, decreasing the pressure and resulting in a slight current flow observed on the lower curve. During the first short reversal, hydrogen evolution from the reversed positive plate slows down the rate of pressure decay. The pressure continues to decay until the second deep reversal and then rises rapidly until the cadmium electrode is discharged. At this point recombination occurs quite rapidly.

Cells operate similarly at temperatures of 0°C to 40°C, the only difference being that recombination occurs more rapidly at the higher temperatures and consequently lower pressures are observed.

Detailed data from some of the production cells at 25°C is given in Table 2.

Additional Test Data

Although the 4th electrode cell was developed to provide reversal protection, it has shown the value of additional electrode area for overcharge control. To further investigate the phenomenon of high rate charge control several cells of 6 AH nominal capacity were constructed with large gas electrodes assembled to the sides of the pack and connected externally to the negative cell terminal.

One of the cells was operated on a 90 minute duty cycle, charging for 60 minutes at 5.0 amp and discharging at 6.0 amps for 30 minutes.

This corresponds to 166% recharge. It was hoped that by this method we might eliminate the problem of insufficient overcharge, from which other 3rd electrode cells seem to suffer, on deep discharge cycles. The cell was maintained at room temperature throughout the test, and operated for 900 cycles before it failed because of an internal short. The performance was remarkably stable throughout cell life as can be seen from the discharge curves of Figure 5. Maximum charging voltage reached was 1.51 volts, and cell pressure never exceeded +5 psig.

A second cell was tested to determine stabilization of cell pressure and voltages during high rate overcharges. It was also desired to determine the capacity of the cell when charged in this manner. The cell was charged at 3.0 amps and 6.0 amps until pressure and voltage stabilized. The tests were carried out in a water bath maintained at 25°C, 0°C and 40°C.

The mode of operation was that the cell would develop maximum pressure up until full charge was obtained, due to hydrogen evolution from the gas electrodes. When full charge was obtained oxygen was liberated from the positive plate and this combined catalytically with the hydrogen in the cell to reduce the pressure. At no time did cell pressure exceed +30 psig and after the evolution of oxygen had begun pressure would remain at no more than a few pounds above atmospheric. Summary data of operation are shown in Table 3.

An additional test was started to determine if continuous high rate overcharge would have an effect on the life or capacity of the cell, providing temperature was kept under control. After 7 days of continuous charge at the C rate at room temperature, the cell still maintained better than nominal capacity. After 30 days capacity was about 95% of nominal. Charging voltage stabilized at about 1.51 volts, and pressure stabilized at about +2 psig. This test is continuing.

Future Applications

Possible applications for 3rd and 4th electrode cells for commercial as well as military uses are many.

The four electrode cell may find use in the aerospace field where high rate charge cut off would be desirable. Should the charge cut off fail, the larger electrodes would provide protection by consuming gas evolved on overcharge. In these cases large amounts of heat would be generated, however, and this would have to be dissipated through the vehicle's radiator. The fourth electrode would provide protection against unintentional cell reversal, or could be utilized if it is desired to completely discharge a battery to destroy memory effects.

It might also be possible to employ sealed cells in many cases where flooded cells are now used, such as for aircraft starting, where it is necessary to recharge rapidly. In many cases, it is necessary to use a flooded cell to accommodate the required high rate charging. Use of sealed cells in these applications would greatly reduce maintenance problems.

Silver Cell Application

The use of auxiliary electrodes in silver cells is primarily, if not solely, for recombination of hydrogen or oxygen generated in the cell during use. The electrodes promote the recombination of these gases and thus allow sealed cell operation without excessive pressure rise. The benefits are:

a. A sealed cell design for both silver-cadmium and for silver-zinc cells is feasible.

b. Battery packaging can be minimal, since constraint of pressure during operation is not needed.

c. Cells retain charge balance, since no material is vented on cycling.

The principal disadvantage is an increase in cell size; however, this increase may not be necessary in some designs.

The auxiliary electrode materials used in our silver cell investigations are summarized in Table 4. Unless otherwise noted, the electrodes are made by mixing the catalyst, electron carrier and Teflon binder into a smooth paste and spreading it on a wire mesh or screen in a thin layer. This layer is pressed at pressures up to 5000 psi and the Teflon binder sintered at 350° - 375°C. A second thin layer of Teflon is sintered on one side of the electrode to give increased waterproofing. This "dry" side is placed in the cell so that it faces the gas space. The "wet" side is placed in contact with cell electrolyte held in separator material.

The current densities shown are for continuous use, and can be exceeded for short periods of time without damage to the electrode. In use, oxygen should never be evolved from any of the electrode materials shown by electrolysis as this is generally destructive of the electrode structure. Evolution of hydrogen is permissible at rates not exceeding the combining rates shown.

The current densities shown in the table are for operation at 25°C. Operation at higher temperatures up to 110°C is possible although some shortening of life will be observed at temperatures much above 65°C. The electrode performance (allowable current density at any fixed electrode voltage) increases markedly with increase in temperature. The performance falls with decrease in temperature; for oxygen electrodes with platinum catalyst the fall off is to 80% at 0°C; for hydrogen electrodes with platinum catalyst, the fall off is to about 60% at 0°C. The performance of the non-platinum-catalyzed electrodes for oxygen has not been measured below room temperature in detail.

The early auxiliary electrodes were actually pieces of experimental fuel cell electrodes and did not have optimum properties for auxiliary use. In particular, mixtures of palladium and platinum black were used as the catalyst for the standard type electrode; the presence of palladium has been found to be undesirable for cell use since it tends to dissolve on stand. The latest materials for auxiliary electrodes do not use any palladium in their construction.

The migration of silver, nickel or platinum from the auxiliary electrode in silver-cadmium cells is of little concern since the effect on either the silver electrode or cadmium electrode is nil. However, migration of any of these metals to zinc electrodes in silver-zinc cells will be undesirable. Hence, non-leaching electrodes are desirable. Fortunately, in silver-zinc cells, the electrode is used to recombine hydrogen, which keeps the metals reduced and prevents the loss of small amounts in solution.

The construction or modification of silver cells to incorporate auxiliary electrodes can be varied from placing a small electrode on top of the electrode pack, placing larger electrodes along the sides of the electrode pack, or placing electrodes whose cross-sectional area is about the same as the cell electrode on the sides of the pack. In any design, protection of the auxiliary electrode from "drowning" or being covered with electrolyte is needed. Auxiliary electrode cells are described in the final reports in more detail. Connection to cell electrodes can be external or internal.

Auxiliary electrodes have been tested for silver-cadmium cells for over a year to date. The results show that cells capable of being overcharged at rates up to C/10 can be made using a single auxiliary electrode whose cross-sectional area is equal to the area of a single plate. Better performance is obtained if an electrolyte reservoir is supplied to keep the separators wet during operation.

In one test carried out in our laboratories, a battery of six 5 ampere-hour silver-cadmium cells with auxiliary electrodes were placed on continuous overcharge at constant voltage of 9.12 ± 0.06 volts (average 1.52 ± 0.01 volts/cell) for over eight months. The auxiliary electrodes were left unconnected to determine the gas recombination behavior. The results can be summarized as follows: The pressure in the cell rose slowly to 25-30 psia during the first few weeks, then suddenly fell to less than 5 psia during the first few weeks, then for the remainder of the charge. All individual cell voltages remained in the range of 1.52 ± 0.11 volts over the period, and all cells gave discharge capacities at end of charging of over 7 ampere-hours.

In this battery, attempts to charge the cells later in the test program with the auxiliary electrodes attached to the cadmium electrode failed, since silver dendrites had formed connecting the auxiliary electrode to the positive. These dendrites were very fragile as they were broken by mere handling of the cell. The results are given in detail in the final report for NAS 5-3669.

In silver-zinc cells, auxiliary electrodes containing platinum catalysts cannot be connected to the zinc electrode, as the self-discharge of zinc is greatly enhanced. Silver and spinel electrodes can be used if they are attached through a diode. However, if platinum-catalyzed hydrogen electrodes are used, these can be attached directly to the silver electrode without inducing self-discharge; these electrodes will remove any oxygen generated in the cell by catalyzing the direct combination of hydrogen and oxygen. In the presence of excess hydrogen, the combination rate is sufficient to prevent build-up of oxygen pressure at any reasonable rates of oxygen generation on overcharge, thus preventing formation of explosive mixtures. In our tests, no sign of explosion, etc. have ever been observed in silver cell work. At high rates (1C or larger) rapid combination of oxygen and hydrogen may result in overheating the electrode catalyst.

The use of platinum-catalyzed auxiliary electrodes in silver-zinc cells to recombine the hydrogen formed during charge and stand allows sealing of the cell. Any oxygen formed during charging will be removed by direct combination, and hence no oxygen auxiliary electrode is needed if the hydrogen auxiliary is provided.

In summary, the use of auxiliary electrodes in silver cells permits use of sealed cell designs that can operate at low pressures with proper design. Non-magnetic type electrodes are available. Both hydrogen and oxygen can be recombined. Since silver cells should not be overcharged at high rates, relatively small auxiliaries suffice, and the major cost is a small increase in cell size to allow for gas passages, and a proportionately much smaller increase in weight.

FIGURE 1

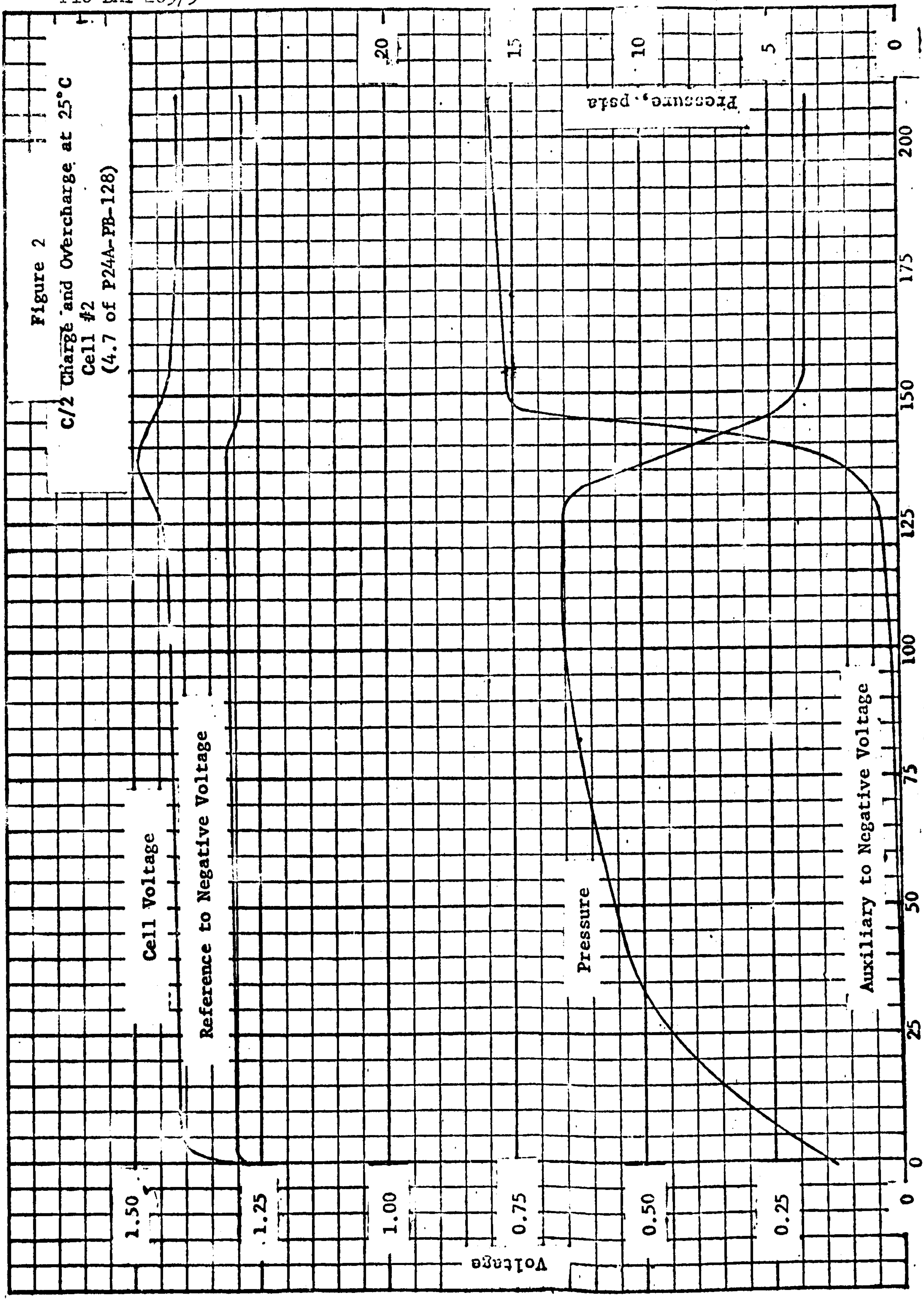
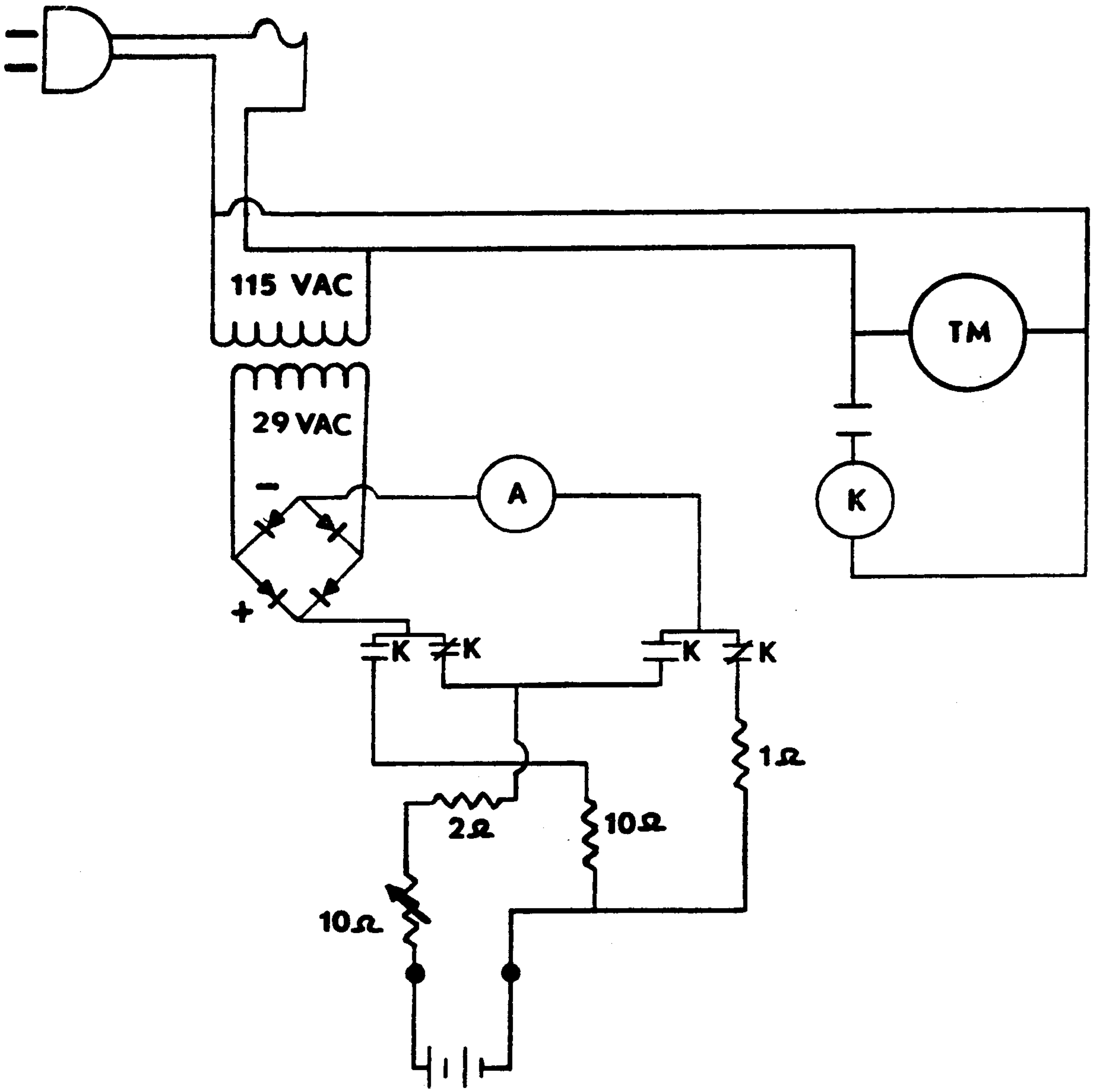


Figure 2
C/2 Charge and Overcharge at 25°C
Cell #2
(4.7 of P24A-PB-128)

FIGURE 2



CYCLE: 215 MIN.

TM Contact (min.)

Open – 0 65
Closed – 65 100
Open – 100 165
Closed – 165 215

Figure 3

Automatic Cycle Circuit

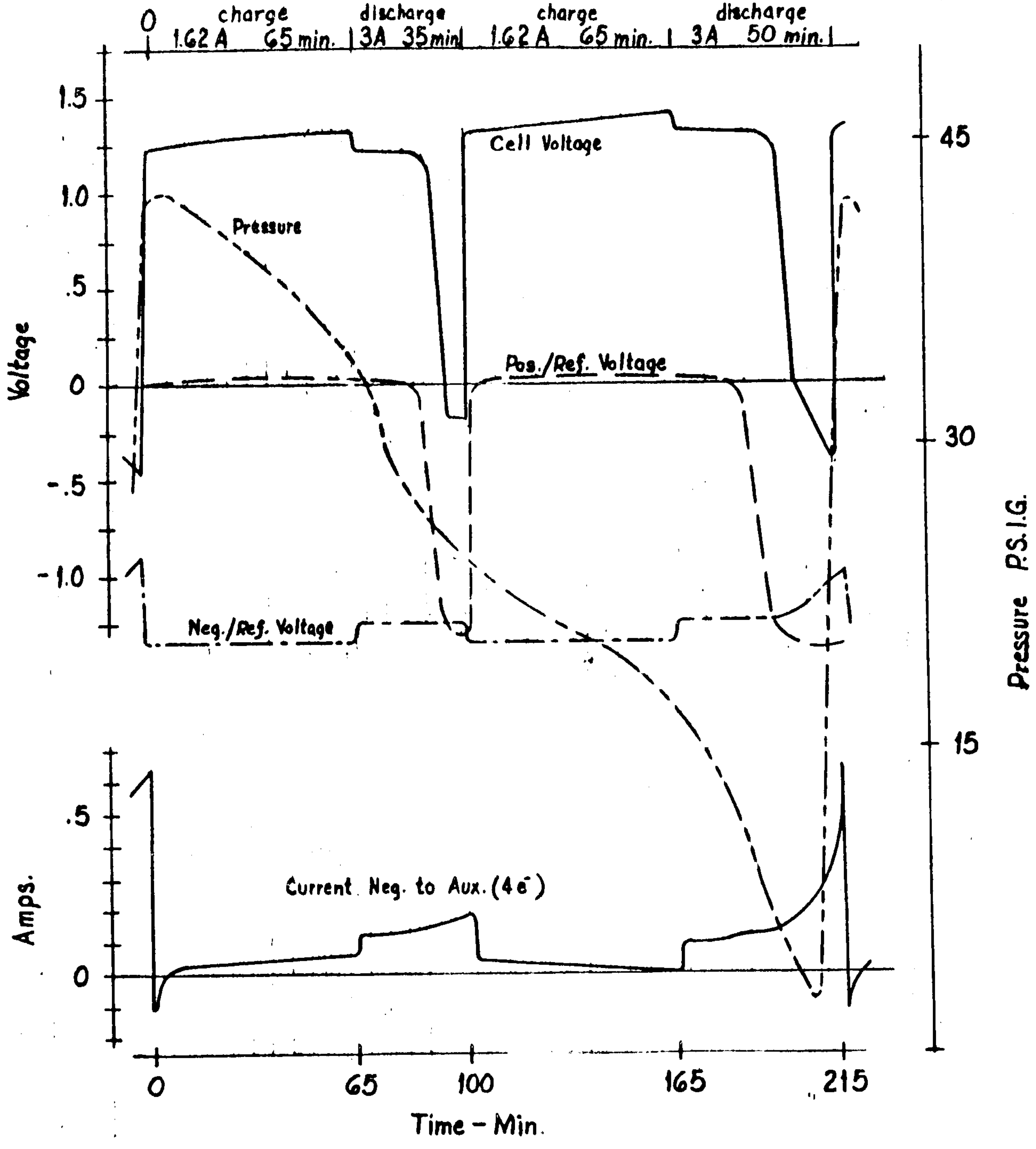


FIGURE 4 - TYPICAL CHARGE & OVER-DISCHARGE CYCLES

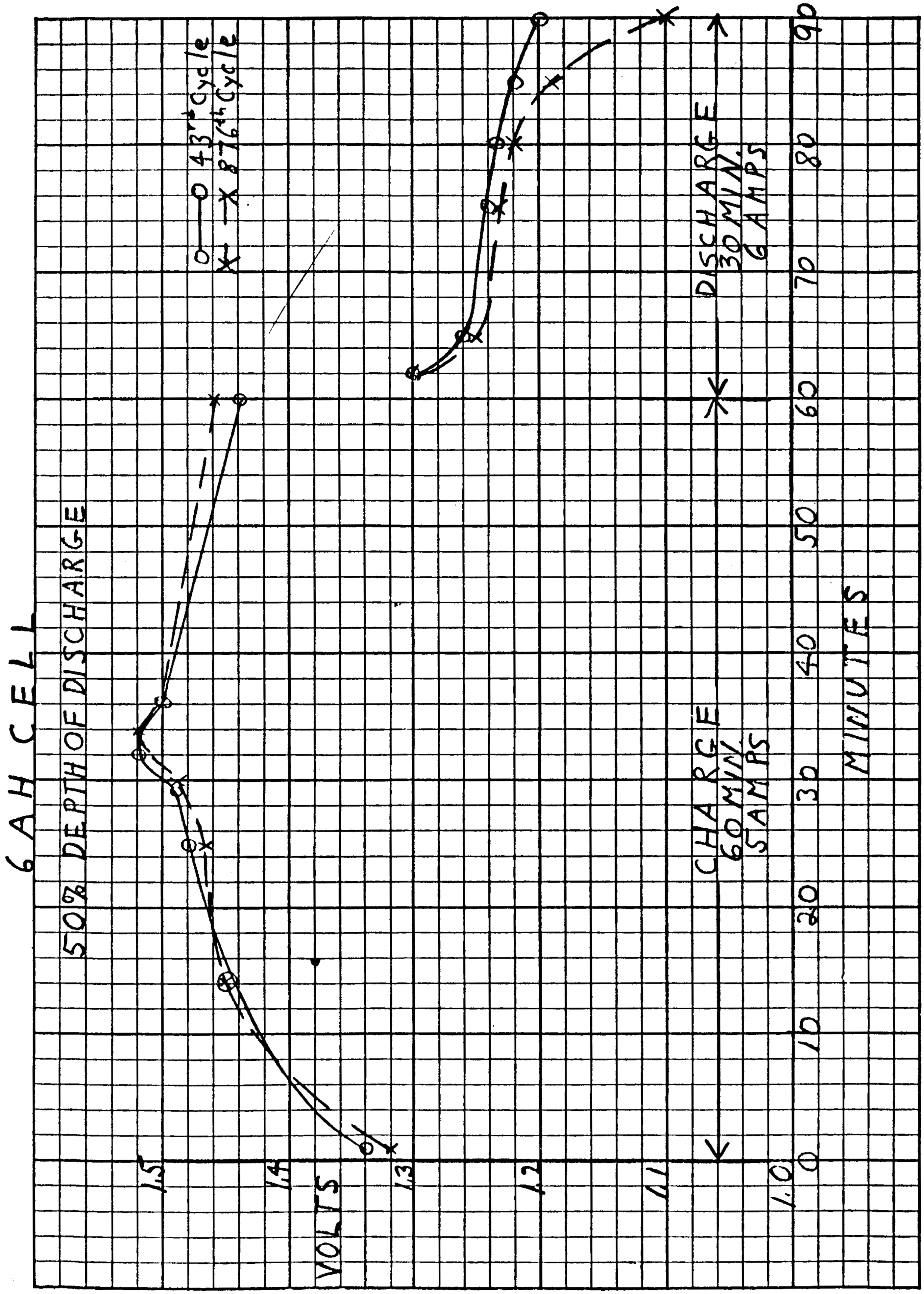

6AH CELL
50% DEPTH OF DISCHARGE
o—o 43rd Cycle
x – x 876th Cycle
VOLTS
1.5
1.4
1.3
1.2
1.1
1.0
CHARGE
60 MIN.
5 AMPS
DISCHARGE
30 MIN.
6 AMPS
0
10
20
30
40
50
60
70
80
90
MINUTES

FIGURE 5

DETAILED DATA OF CHARGE CONTROL AT ROOM TEMPERATURE
(4.6 and 4.7 of P24A-PB-128)

Ref. Para.	Test Number Test Description	1-1					1-2					1-3					1-4					1-5				
		Cell V	Pressure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pressure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pressure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pressure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pressure	Ref. Neg.	4th e I	3rd Neg.
	Charge 3.0 amps to signal																									
	60 min	1.42	+ 3#	1.30	0	.03	1.42	+ 4#	1.31	0	.03	1.42	0	1.31	0	.03	1.42	0	1.31	0	.03	1.42	0	1.31	0	.03
	93 min	1.43	+ 6#	1.30	0	.02	1.43	+ 9#	1.32	0	.02	1.43	+ 4#	1.31	0	.02	1.43	+ 4#	1.31	0	.02	1.43	+ 4#	1.31	0	.02
	110 min	1.44	+ 8#	1.31	0	.02	1.44	+12#	1.32	0	.02	1.44	+ 6#	1.31	0	.02	1.44	+ 6#	1.31	0	.02	1.44	+ 6#	1.31	0	.02
	120 min	1.45	+ 9#	1.31	0	.03	1.45	+13#	1.32	0	.03	1.45	+ 6#	1.31	0	.03	1.45	+ 7#	1.31	0	.03	1.45	+ 7#	1.32	0	.03
	128 min	1.46	+ 9#	1.31	0	.04	1.46	+14#	1.33	0	.04	1.47	+ 7#	1.31	0	.04	1.46	+ 7#	1.31	0	.03	1.46	+ 7#	1.32	0	.04
	135 min	1.48	+ 9#	1.31	0	.04	1.49	+14#	1.33	0	.04	1.49	+ 6#	1.31	.20	.04	1.48	+ 6#	1.32	0	.03	1.48	+ 7#	1.32	0	.04
	140 min	1.50	+ 6#	1.31	0	.05	1.50	+10#	1.33	.20	.05	1.50	+ 4#	1.31	.40	.05	1.50	+ 3#	1.32	.20	.05	1.50	+ 4#	1.32	.20	.05
	143 min		-10"			.12		- 8"			.10		-26"			.23		-22"			.19		-26"			.16
	145 min		-24"			.19		-22"			.45		-26"			.80		-19"			.20		-26"			.22
	149 min	1.49	-25"	1.30	1.9	.28	1.49	-23"	1.31	2.2	.78	1.49	-26"	1.28	2.0	.80	1.49	-21"	1.30	2.1	.55	1.49	-26"	1.31	2.2	.40
	155 min	1.48		1.29	2.1	.80	1.47		1.30	2.4	.86	1.48		1.27	2.1	.85	1.47		1.29	2.3	.78	1.49		1.30	2.3	.70
	Discharge 3.0 amps to 1.0 volt																									
	Capacity			6.6 AH					6.4 AH					6.4 AH					6.4 AH					6.5 AH		
	Charge 3.0 amps																									
	33 min		-14"					-10"					-15"					-12"					-14"			
	82 min		- 9"					- 5"					-11"					- 9"					-12"			
	105 min	1.43	- 7"			.02	1.43	- 4"			.02	1.43	-10"			.02	1.43	- 9"			.02	1.42	-11"			.02
	115 min	1.43	- 6"	1.30			1.43	- 4"	1.31			1.43	- 9"	1.31			1.43	- 8"	1.30			1.43	-10"	1.31		
	127 min					.02					.03					.03					.03					.03
	138 min	1.49		1.30		.12	1.49		1.32		.14	1.49		1.30		.49	1.49		1.31		.11	1.49		1.32		.14
	142 min					.31					.39					.86					.20					.39
	147 min		-25"			.83		-23"			.73		-26"			.81		-21"			.76		-26"			.75
	160 min	1.44	-24"				1.43	-22"				1.44	-26"				1.43	-21"				1.44	-26"			
	175 min	1.42					1.42					1.43					1.42					1.43				
	190 min	1.42		1.26			1.41		1.28			1.42		1.27			1.42		1.28			1.41		1.27		
	200 min	1.42					1.41					1.42					1.42					1.42				
	208 min	1.42	-25"	1.25			1.41	-22"	1.28			1.41	-26"	1.27			1.41	-22"	1.28			1.41	-26"	1.27		
	210 min																									
	Discharge 6.0 amps to 1.0 volt																									
	Capacity			6.5 AH					6.1 AH					6.3 AH					6.5 AH					6.4 AH		

TABLE 1

			1-7					1-8					1-9					1-10					1-11				
Ref. Para.	Test Number	Test Description	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.
	Charge 3.0 amps to signal		1.42	+ 2#	1.30	0	.03	1.42	+ 2#	1.30	0	.02	1.42	+ 2#	1.31	0	.03	1.42	- 7"	1.30	0	.03	1.42	- 7"	1.31	0	.03
	60 min		1.43	+ 5#	1.30	0	.02	1.43	+ 5#	1.30	0	.01	1.43	+13#	1.31	0	.03	1.43	+ 8#	1.30	0	.03	1.43	+ 6#	1.31	0	.02
	93 min		1.44	+ 7#	1.31	0	.02	1.44	+ 7#	1.30	0	.02	1.44	+16#	1.32	0	.03	1.44	+10#	1.30	0	.02	1.44	+ 8#	1.31	0	.02
	110 min		1.45	+ 8#	1.31	0	.03	1.45	+ 8#	1.31	0	.02	1.45	+17#	1.32	0	.02	1.45	+12#	1.30	0	.02	1.45	+ 9#	1.31	0	.03
	120 min		1.46	+ 8#	1.31	0	.03	1.47	+ 8#	1.31	0	.02	1.46	+17#	1.32	0	.02	1.47	+12#	1.30	0	.03	1.46	+ 9#	1.31	0	.04
	128 min		1.48	+ 9#	1.31	0	.03	1.50	0	1.30	.20	.03	1.49	+16#	1.32	0	.03	1.49	+ 8#	1.30	.20	.04	1.49	+ 9#	1.31	0	.04
	135 min		1.50	+ 7#	1.31	0	.05	1.50	- 20"	1.28	1.1	.09	1.50	+10#	1.32	.10	.05	1.50	- 5"	1.30	.40	.05	1.50	+ 4#	1.31	.20	.05
	140 min			- 5"			.14		- 22"			.82		- 4"			.09		- 25"			.08		- 26"			.23
	143 min			- 26"			.15		- 20"			.84		- 5"			.15		- 24"			.09		- 26"			.30
	145 min		1.49	- 26"	1.30	2.0	.45	1.48	- 24"	1.25	2.1	.85	1.48	- 5"	1.30	2.1	.45	1.48	- 24"	1.29	2.4	.20	1.49	- 26"		2.0	.80
	149 min		1.48		1.29	2.3	.72	1.47		1.24	2.5	.85	1.46		1.29	2.6	.80	1.46		1.28	2.5	.36	1.48			2.1	.83
	155 min																										
	Discharge 3.0 amps to 1.0 volt																										
	Capacity			6.5 AH					6.4 AH					6.4 AH					6.4 AH					6.4 AH			
	Charge 3.0 amps																										
	33 min			- 14"					- 11"					0					- 14"					- 14"			
	82 min			- 11"					- 9"					- 12"					- 9"					- 10"			
	105 min		1.42	- 9"			.02	1.42	- 6"			.02	1.42	+ 2#			.02	1.42	- 8"			.02	1.42	- 8"			.02
	115 min		1.43	- 9"	1.30			1.43	- 6"	1.30			1.43	+ 3#	1.31			1.43	- 6"	1.30			1.43	- 8"	1.31		
	127 min						.03					.02					.03					.03					.03
	138 min		1.49		1.30		.11	1.49		1.29		.36	1.49		1.31		.11	1.49		1.29		.09	1.49		1.30		.23
	142 min						.17					.87					.22					.09					.70
	147 min			- 26"			.70		- 24"			.88		- 5"			.81		- 25"			.49		- 26"			.84
	160 min		1.45	- 25"				1.44	- 24"				1.43	- 5"				1.43	- 25"				1.45	- 26"			
	175 min		1.43					1.41					1.41					1.41					1.43				
	190 min		1.42		1.27			1.42		1.22			1.41		1.28			1.41		1.27			1.42		1.25		
	200 min		1.42					1.42					1.41					1.40					1.41				
	208 min		1.42	- 26"	1.27			1.42	- 23"	1.22			1.41	- 4"	1.28			1.40	- 25"	1.27			1.41	- 25"	1.25		
	210 min																										
	Discharge 6.0 amps to 1.0 volt																										
	Capacity			6.6 AH					6.0 AH					5.9 AH					6.6 AH					6.1 AH			

TABLE 1 (Continued)

Ref. Para.	Test Number Test Description	1-12					1-13					1-14					1-15				
		Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.	Cell V	Pres-sure	Ref. Neg.	4th e I	3rd Neg.
	Charge 3.0 amps to signal																				
	60 min	1.42	- 6"	1.31	0	.03	1.42	-10"	1.30	0	.03	1.42	-14"	1.27	0	.03	1.42	-10"	1.31	.50	.03
	93 min	1.43	+ 6#	1.31	0	.02	1.43	+ 5#	1.30	0	.02	1.43	0	1.28	0	.02	1.43	+ 3#	1.31	0	.02
	110 min	1.44	+ 8#	1.31	0	.02	1.44	+ 7#	1.30	0	.02	1.44	+ 1#	1.28	0	.02	1.44	+ 4#	1.31	0	.02
	120 min	1.45	+ 8#	1.31	0	.03	1.45	+ 8#	1.30	0	.03	1.45	+ 3#	1.28	0	.03	1.45	+ 5#	1.31	0	.03
	128 min	1.47	+ 8#	1.31	0	.04	1.46	+ 8#	1.30	0	.04	1.46	+ 3#	1.28	0	.04	1.46	+ 5#	1.31	0	.04
	135 min	1.49	+ 7#	1.31	.20	.04	1.50	+ 7#	1.30	.20	.04	1.47	+ 4#	1.28	0	.05	1.49	+ 3#	1.31	0	.05
	140 min	1.50	0	1.31	.20	.06	1.50	+ 2#	1.30	.40	.05	1.49	+ 3#	1.28	0	.05	1.50	- 4"	1.31	.10	.06
	143 min		-22"			.19		-22"			.18		- 5"			.08		-26"			.22
	145 min		-21"			.83		-24"			.19		-26"			.08		-26"			.82
	149 min	1.49	-22"	1.29	2.0	.85	1.49	-25"	1.28	2.2	.43	1.48	-26"	1.10	1.6	.78	1.49	-26"		2.1	.85
	155 min	1.48		1.28	2.1	.85	1.47		1.26	2.4	.60	1.29		.94	2.0	.70	1.48			2.1	
	155 min - off																				
	Discharge 3.0 amps to 1.0 volt Capacity		6.3 AH					6.4 AH					6.5 AH					6.4 AH			
	Charge 3.0 amps																				
	33 min		-12"					-18"					-18"					-16"			
	82 min		- 8"					-11"					-12"					-12"			
	105 min	1.42	- 6"			.02	1.42	-10"			.02	1.42	-11"			.02	1.42	-11"			.02
	115 min	1.43	- 6"	1.30			1.43	-10"	1.30			1.43	-10"	1.27			1.43	-11"			
	127 min					.03					.03					.03					.03
	138 min	1.49		1.29		.57	1.49		1.29		.13	1.43		1.09		.10	1.49		1.30		.77
	142 min					.83					.18					.13					.86
	147 min		-22"			.84		-23"			.69		-27"			.77		-26"			.89
	160 min	1.44	-22"				1.43	-20"				1.30	-26"				1.42	-26"			
	175 min	1.42					1.42					1.38					1.41				
	190 min	1.42		1.25			1.41		1.22			1.37		.98			1.40		1.24		
	200 min	1.42					1.41					1.36					1.40				
	208 min	1.41	-21"	1.25			1.40	-19"	1.22			1.36	-26"	.98			1.40	-24"	1.24		
	210 min - All cells off except cell #14																				
	Discharge 6.0 amps to 1.0 volt Capacity		6.1 AH					5.9 AH										6.3 AH			
	#14 after approximately 24 hours overcharge at 3.0 amps											1.41	-25	1.09	3.0	.81					

TABLE 1 (Continued)

DETAILED DATA - 3rd AND 4th OVERDISCHARGE CYCLES
(4.5 of P24A-PB-128)

Ref. Page	Test Number / Test Description	1-1				1-2				1-3				1-4				1-5				1-7				1-8			
		Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure	Cell V	Ref.to Neg.	4th e I	Pressure
	<u>3rd Cycle</u>																												
	Charge 1.615 amps for 65 minutes																												
	40 min	1.39	1.30	0		1.39	1.30	.10		1.38	1.30	0		1.38	1.30	.20		1.38	1.30	.20		1.48	1.29	.20		1.38	1.29	.30	
	60 min	1.40	1.30	0		1.40	1.30	.1		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0		1.39	1.29	0	
	64 min	1.40	1.30	0	+ 4#	1.40	1.30	0	-12"	1.39	1.30	0	-15"	1.39	1.30	0	-9"	1.39	1.30	0	-13"	1.39	1.30	0	-18"	1.39	1.29	0	-11"
	Discharge 3.0 amps for 35 minutes																												
	5 min	1.28	1.23	.10	- 8"	1.28	1.25	.20	-16"	1.29	1.26	.20	-15"	1.29	1.25	.30	-14"	1.29	1.25	.30	-17"	1.29	1.25	.10	-20"	1.29	1.25	.10	-15"
	26 min	-.17	1.23	.30	-10"	-.17	1.25	.10	-10"	-.17	1.26	.10	-10"	-.17	1.25	.10	- 6"	-.16	1.25	.30	-10"	-.16	1.25	.10	-10"	-.17	1.25	.30	-10"
	30 min	-.19	1.23	.30	+ 5#	-.19	1.25	.40	+ 5#	-.18	1.26	.10	+ 7#	-.18	1.24	.30	+10#	-.18	1.25	.40	+ 8#	-.18	1.25	.40	+ 7#	-.18	1.25	.40	+ 6#
	32 min	-.19	1.22	.50	+19#	-.19	1.25	.50	+18#	-.18	1.26	.40	+20#	-.18	1.24	.40	+25#	-.18	1.24	.40	+20#	-.18	1.25	.50	+19#	-.18	1.25	.50	+19#
	35 min	-.20	1.22	.60	+26#	-.20	1.25	.60	+26#	-.19	1.25	.40	+30#	-.18	1.24	.40	+35#	-.18	1.24	.50	+30#	-.18	1.25	.50	+28#	-.18	1.25	.60	+29#
	Charge 1.615 amps for 65 minutes																												
	32 min	1.39	1.30	0	+25#	1.38	1.30	0	+16#	1.37	1.30	0	+20#	1.37	1.30	0	+23#	1.37	1.30	.20	+18#	1.37	1.30	.20	+16#	1.37	1.30	.20	+16#
	38 min	1.40	1.31	0	+24#	1.40	1.31	0	+12#	1.39	1.30	0	+15#	1.39	1.30	0	+16#	1.39	1.30	0	+13#	1.39	1.30	0	+ 8#	1.39	1.30	0	+11#
	64 min	1.40	1.31	0		1.40	1.31	0		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0	
	Discharge 3.0 amps for 50 minutes																												
	1 min	1.31	1.24	.50		1.31	1.27	.40		1.33	1.27	.30		1.33	1.26	.10		1.33	1.26	.30		1.33	1.27	.40		1.33	1.26	.40	
	19 min	1.21	1.22	.10	- 2"	1.22	1.25	.10	-12"	1.23	1.26	.40	- 6"	1.23	1.25	0	- 8"	1.23	1.25	.10	-12"	1.23	1.25	0	-20"	1.23	1.25	0	-15"
	28 min	-.13	1.25	0	- 8"	-.05	1.25	0	-21"	-.07	1.25	.20	-18"	-.07	1.25	.20	-17"	-.07	1.25	0	-23"	-.12	1.25	0	-24"	-.06	1.25	0	-20"
	32 min	-.16	1.25	.10	0	-.17	1.26	.20	-10"	-.17	1.26	.10	- 6"	-.17	1.25	.10	- 5"	-.17	1.26	.10	-13"	-.17	1.26	.30	-11"	-.17	1.25	.10	-14"
	35 min	-.18	1.24	.10	+11#	-.18	1.25	.40	+ 5#	-.18	1.26	.10	+ 8#	-.18	1.24	.30	+ 9#	-.18	1.24	.30	+ 5#	-.18	1.26	.40	+ 3#	-.18	1.25	.40	+ 4#
	38 min	-.19	1.24	.50	+27#	-.20	1.25	.60	+22#	-.21	1.26	.50	+25#	-.21	1.24	.50	+29#	-.19	1.24	.50	+23#	-.19	1.26	.50	+19#	-.19	1.26	.60	+21#
	41 min	-.29	1.13	.60	+40#	-.29	1.15	.80	+34#	-.31	1.14	.90	+38#	-.32	1.08	1.0	+44#	-.30	1.10	1.0	+36#	-.28	1.18	.80	+34#	-.28	1.18	1.0	+35#
	45 min	-.42	1.0	1.4	+51#	-.42	1.05	1.5	+43#	-.45	1.02	1.5	+50#	-.48	.92	1.6	+54#	-.42	.97	1.1	+47#	-.40	1.09	1.3	+42#	-.38	1.11	1.4	+45#
	50 min	-.75	.68	2.4	+52#	-.79	.71	2.5	+43#	-.80	.71	2.4	+50#	-.76	.65	2.4	+55#	-.70	.70	2.4	+50#	-.51	.98	2.2	+51#	-.46	1.05	2.0	+52#
	<u>4th Cycle</u>																												
	Charge 1.615 amps for 65 min																												
	44 min	1.39	1.30	0	+38#	1.39	1.31	0	+28#	1.39	1.31	0	+35#	1.39	1.30	0	+34#	1.39	1.30	0	+33#	1.39	1.31	0	+29#	1.38	1.30	0	+30#
	60 min	1.39	1.30	0		1.40	1.31	0		1.39	1.31	0		1.40	1.30	0		1.39	1.30	0		1.39	1.31	0		1.39	1.30	0	
	64 min	1.40	1.30	0	+34#	1.40	1.31	0	+24#	1.40	1.31	0	+30#	1.40	1.30	.20	+28#	1.40	1.30	.20	+23#	1.40	1.30	0	+22#	1.40	1.30	0	+23#

TABLE 2

Ref. Para.	Test Number Test Description	1-9				1-10				1-11				1-12			
		Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure
	3rd Cycle																
	A. Charge 1.615 amps for 65 minutes																
	40 min	1.39	1.30	.30		1.38	1.30	.30		1.39	1.30	0		1.39	1.30	0	
	60 min	1.39	1.30	0		1.39	1.30	0		1.39	1.30	.50		1.39	1.30	0	
	64 min	1.39	1.29	0	-10"	1.39	1.30	0	-14"	1.39	1.30	0	0	1.39	1.30	0	- 8"
	B. Discharge 3.0 amps for 35 minutes																
	5 min	1.29	1.25	.30	-17"	1.29	1.26	.30	- 6"	1.29	1.25	.30	-19"	1.29	1.25	.20	-15"
	26 min	-.17	1.25	.30	-15"	-.17	1.26	.10	- 2"	-.16	1.26	.30	- 8"	-.16	1.26	.10	- 5"
	30 min	-.18	1.25	.40	+ 5#	-.18	1.26	.40	+ 9#	-.18	1.25	.40	+ 9#	-.18	1.26	.40	+10#
	32 min	-.18	1.25	.50	+15#	-.18	1.26	.50	+23#	-.18	1.25	.40	+21#	-.18	1.26	.40	+25#
	35 min	-.18	1.25	.60	+26#	-.18	1.26	.60	+34#	-.18	1.25	.50	+34#	-.18	1.26	.40	+36#
	C. Charge 1.615 amps for 65 minutes																
	32 min	1.37	1.30	.20	+15#	1.37	1.30	.20	+19#	1.37	1.30	.20	+20#	1.37	1.30	.20	+25#
	38 min	1.39	1.30	0	+10#	1.39	1.30	0	+14#	1.39	1.30	0	+14#	1.39	1.30	0	+19#
	64 min	1.39	1.30	0		1.39	1.30	0		1.39	1.30	0		1.39	1.30	0	
	D. Discharge 3.0 amps for 50 minutes																
	1 min	1.33	1.26	.40		1.33	1.27	.40		1.32	1.26	.40		1.33	1.27	.10	
	19 min	1.23	1.25	.10	-16"	1.23	1.25	.10	- 4"	1.23	1.25	.20	-14"	1.23	1.26	.20	- 2"
	28 min	-.06	1.25	0	-21"	-.06	1.25	0	- 6"	-.11	1.25	0	-22"	-.09	1.25	.20	-15"
	32 min	-.17	1.25	.10	-14"	-.17	1.26	.10	0	-.17	1.26	.30	-10"	-.17	1.26	.30	- 2"
	35 min	-.18	1.25	.40	+ 4#	-.18	1.26	.40	+ 9#	-.18	1.25	.40	+ 6#	-.18	1.26	.10	+10#
	38 min	-.20	1.27	.60	+18#	-.20	1.25	.60	+28#	-.21	1.24	.60	+23#	-.21	1.25	.50	+29#
	41 min	-.28	1.16	.90	+30#	-.30	1.17	1.2	+42#	-.30	1.14	.80	+42#	-.30	1.14	.80	+45#
	45 min	-.40	1.08	1.5	+40#	-41	1.08	1.6	+52#	-.41	1.03	1.0	+55#	-.43	1.03	1.1	+56#
	46 min	-.45	1.02	1.9	+45#	-.53	.96	2.3	+55#	-.70	.75	2.1	+62#	-.74	.76	2.4	+58#
	50 min	-.60	.88	2.4	+46#	-.67	.84	2.5	+59#	-.81	.66	2.4	+58#	-.82	.70	2.4	+60#
	4th Cycle																
	A. Charge 1.615 amps for 65 minutes																
	44 min	1.39	1.30	0	+27#	1.38	1.31	0	+30#	1.39	1.31	.10	+35#	1.39	1.31	0	+36#
	60 min	1.39	1.30	0		1.39	1.31	0		1.39	1.31	0		1.39	1.31	0	
	64 min	1.39	1.30	0	+23#	1.39	1.31	0	+24#	1.39	1.31	0	+28#	1.40	1.31	0	+30#

Ref. Para.	Test Number Test Description	1-13				1-14				1-15			
		Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure
	3rd Cycle												
	A. Charge 1.615 amps for 65 minutes												
	40 min	1.38	1.29	0		1.39	1.25	.30		1.38	1.30	0	
	60 min	1.39	1.29	0		1.39	1.37	0		1.39	1.30	0	
	64 min	1.39	1.29	0	- 8"	1.39	1.35	0	-12"	1.39	1.30	0	-14"
	B. Discharge 3.0 amps for 35 minutes												
	5 min	1.29	1.24	.20	-16"	1.28	1.30	.30	-10"	1.29	1.25	.10	-18"
	26 min	-.16	1.24	.10	-14"	-.20	1.25	.30	-25"	-.16	1.26	.30	-14"
	30 min	-.18	1.24	.30	+ 5#	-.23	1.24	1.5	-15"	-.18	1.25	.40	+ 4#
	32 min	-.18	1.24	.40	+19#	-.32	1.21	1.5	- 5"	-.18	1.25	.40	+16#
	35 min	-.18	1.23	.40	+30#	-.35	1.18	2.2	+ 2#	-.18	1.25	.50	+28#
	C. Charge 1.615 amps for 65 minutes												
	32 min	1.37	1.29	0	+16#	1.39	1.33	0	+ 2#	1.37	1.30	.20	+19#
	38 min	1.39	1.29	0	+16#	1.41	1.32	0	+ 7#	1.39	1.30	0	+14#
	64 min	1.39	1.29	0		1.41	1.32	0		1.39	1.30	0	
	D. Discharge 3.0 amps for 50 minutes												
	1 min	1.33	1.25	.30		1.29	1.26	.80		1.32	1.26	.40	
	19 min	1.23	1.24	.20	0"	1.18	1.23	.40	-25"	1.23	1.25	0	-11"
	28 min	-.06	1.24	.20	-12"	-.17	1.22	.20	-26"	-.08	1.25	.20	-20"
	32 min	-.17	1.24	.10	- 3"	-.22	1.22	.40	-25"	-.17	1.26	.10	-11"
	35 min	-.18	1.24	.10	+ 9#	-.33	1.16	1.6	-25"	-.18	1.25	.40	+ 3#
	38 min	-.21	1.20	.50	+26#	-.38	1.14	1.6	-15"	-.20	1.24	.50	+20#
	41 min	-.36	1.03	.90	+41#	-.43	1.12	1.6	0	-.29	1.15	.70	+36#
	45 min	-64	.73	2.1	+49#	-.47	1.08	1.6	+ 6#	-.39	1.06	1.2	+50#
	46 min	-.88	.55	2.5	+50#	-.56	1.02	1.6	+10#	-.62	.82	2.6	+53#
	50 min	-.92	.51	2.4	+49#	-.59	1.0	1.5	+16#	-.75	.74	2.6	+52#
	4th Cycle												
	A. Charge 1.615 amps for 65 minutes												
	44 min	1.38	1.29	.20	+35#	1.50	1.39	.60	+26#	1.39	1.31	0	+35#
	60 min	1.39	1.29	0		1.39	1.30	0		1.39	1.31	0	
	64 min	1.39	1.29	0	+30#	1.39	1.30	.20	+28#	1.39	1.31	0	+30#

TABLE 2 (Continued)

Ref Para.	Test Number / Test Description	1-9				1-10				1-11				1-12				1-13				1-14				1-15			
		Cell V	Ref. to Neg.	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure	Cell V	Ref. to Neg.	4th e I	Pressure
	B. Discharge 3.0 amps for 35 minutes																												
	2 min	1.32	1.27	.40		1.32	1.27	.40		1.32	1.27	.40		1.32	1.27	.40		1.32	1.25	.10		1.32	1.27	.50		1.32	1.26	.40	
	20 min	1.23	1.26	.10	0	1.23	1.26	.20	+ 2#	1.23	1.26	.30	+ 5#	1.23	1.26	.10	+ 8#	1.23	1.24	.10	+14#	1.22	1.26	10	+ 6#	1.23	1.26	.30	+ 9#
	25 min	1.18	1.26	.20	- 4"	1.18	1.26	.20	0	1.18	1.26	.30	0	1.18	1.26	.30	+ 4#	1.18	1.24	.30	+ 9#	1.11	1.25	.40	- 5"	1.18	1.26	.10	+ 4#
	30 min	-.15	1.25	.20	-11"	-.15	1.26	.20	-12"	-.17	1.26	.20	- 2"	-.16	1.26	.30	+ 1#	-.15	1.24	.20	+ 7#	-.20	1.24	.40	-14"	-.17	1.26	.30	+ 2#
	34 min	-.19	1.25	.40	+ 3#	-.19	1.25	.40	+ 9#	-.19	1.26	.40	+ 9#	-.19	1.26	.40	+15#	-.19	1.24	.30	+16#	-.49	1.04	2.3	-21"	-.19	1.26	.40	0
	C. Charge 1.615 amps for 65 minutes																												
	7 min	1.34	1.29	0		1.34	1.30	0		1.34	1.31	0		1.34	1.31	0		1.34	1.29	0		1.34	1.29	.20		1.34	1.30	0	
	15 min	1.36	1.30	0		1.36	1.30	0		1.36	1.30	0		1.35	1.30	0		1.35	1.29	0		1.35	1.29	0		1.35	1.30	0	
	28 min	1.37	1.30	0		1.37	1.31	0		1.37	1.30	.20		1.37	1.30	0		1.37	1.29	0		1.37	1.29	0		1.37	1.30	0	
	51 min	1.39	1.30	0	+ 5#	1.39	1.31	0	+ 6#	1.39	1.30	0	+ 7#	1.39	1.31	0	+11#	1.39	1.29	0	+14#	1.39	1.29	0	-5 "	1.39	1.31	0	+ 9#
	65 min				+ 5#								+ 6#				+ 9#				+13#				-9 "				+ 7#
	D. Discharge 3.0 amps for 50 minutes																												
	23 min	1.20	1.25	0		1.19	1.25	0		1.20	1.25	0		1.20	1.26	0		1.20	1.24	0		1.19	1.24	0		1.20	1.25	0	
	25 min	1.16	1.25	0		1.14	1.25	0		1.15	1.25	.20		1.16	1.26	.20		1.15	1.24	0		1.04	1.24	0		1.15	1.25	0	
	31 min	-.17	1.25	.10	-22"	-.16	1.26	.20	- 9"	-.18	1.25	.20	-23"	-.17	1.25	.30	-15"	-.17	1.24	.30	-18"	-.18	1.23	0	-24"	-.18	1.25	0	-24"
	35 min	-.19	1.25	.20	+ 3#	-.20	1.25	.30	+ 9#	-.21	1.24	.30	+ 4#	-.20	1.25	.30	+ 5#	-.21	1.21	.30	+ 6#	-.47	1.05	2.0	-21"	-.20	1.25	.10	0
	37 min	-.27	1.20	.70	+13#	-.28	1.19	.80	+19#	-.28	1.16	.60	+15#	-.28	1.18	.60	+18#	-.30	1.11	.50	+17#	-.79	.82	2.5	-26"	-.27	1.18	.60	+10#
	38 min	-.29	1.16	.90	+18#	-.31	1.15	1.1	+25#	-.30	1.13	.80	+22#	-.31	1.13	.70	+27#	-.34	1.06	.60	+26#	-1.01	.60	2.4	-26"	-.29	1.15	.70	+19#
	40 min	-.34	1.10	1.4	+25#	-.38	1.10	1.1	+32#	-.36	1.07	.90	+32#	-.38	1.08	.80	+35#	-.41	.99	.80	+34#	-1.16	.40	2.1	-26"	-.31	1.13	.80	+29#
	43 min	-.41	1.06	1.4	+31#	-.42	1.06	1.4	+40#	-.41	1.03	.90	+44#	-.44	1.02	1.0	+46#	-.59	.76	2.1	+40#	-1.43	.11	2.0	-26"	-.39	1.06	.90	+38#
	49 min	-.54	.91	2.2	+37#	-.69	.81	2.1	+45#	-.79	.66	2.2	+51#	-.83	.68	2.3	+48#	-.94	.49	2.4	+40#	-1.47	.06	2.0	-26"	-.63	.81	2.4	+48#
	50 min	-.71	.78	2.4	+38#	-.79	.72	2.4	+44#	-.86	.61	2.1	+52#	-.86	.65	2.3	+47#	-.97	.47	2.4	+39#	-1.47	.06	2.0	-26"	-.78	.707	2.4	+48#

TABLE 2 (Continued)

Ref. Para.	Test Number	Test Description	1-1				1-2				1-3				1-4				1-5				1-7				1-6			
			Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure	Cell V	Ref. to Neg	4th e I	Pressure
	Discharge 3.0 amps for 30 minutes																													
	2 min		1.32	1.25	..30		1.32	1.27	.40		1.32	1.27	.40		1.32	1.26	.10		1.32	1.26	.40		1.33	1.27	.40		1.33	1.27	.40	
	20 min		1.24	1.25	.10	+12#	1.23	1.26	.30	+ 2#	1.23	1.27	.10	+10#	1.23	1.25	.10	+ 7#	1.23	1.25	.10	+ 6#	1.23	1.26	.30	+ 1#	1.23	1.26	.30	- 1"
	25 min		1.17	1.25	.10	+10#	1.18	1.26	.10	- 2"	1.18	1.27	.30	+ 5#	1.18	1.25	.10	+ 3#	1.18	1.25	.10	+ 8#	1.16	1.26	.10	- 8"	1.19	1.26	.20	-
	30 min		-.18	1.26	0	+ 9#	-.16	1.26	0	- 6"	-.17	1.27	.10	+ 4#	-.16	1.25	.20	+ 1#	-.16	1.24	.30	- 2"	-.18	1.26	.30	-10"	-.15	1.26	.20	-1
	34 min		-.18	1.24	.20	+ 5#	-.19	1.26	.40	+ 2#	-.19	1.26	.40	+15#	-.19	1.24	.10	+18#	-.19	1.23	.40	+ 9#	-.19	1.26	.40	+ 2#	-.19	1.25	.40	+ 5
	Charge 1.615 amps for 65 minutes																													
	8 min		1.35	1.29	0		1.34	1.30	0		1.34	1.31	0		1.34	1.30	0		1.34	1.30	0		1.34	1.30	0		1.34	1.30	0	
	15 min		1.36	1.29	0		1.35	1.30	0		1.36	1.31	0		1.36	1.30	0		1.35	1.30	0		1.36	1.30	0		1.35	1.30	0	
	28 min		1.37	1.30	0		1.37	1.30	0		1.37	1.31	0		1.37	1.30	0		1.37	1.30	0		1.37	1.30	0		1.37	1.30	0	
	51 min		1.39	1.30	0	+14#	1.39	1.30	0	+ 7#	1.39	1.31	0	+13#	1.39	1.30	0	+11#	1.39	1.30	0	+ 9#	1.39	1.30	0	+ 5#	1.39	1.30	0	+ 5
	65 min					+13#				+ 7#				+11#				+10#				+ 7#				+ 4#				+ 5#
	Discharge 3.0 amps for 50 minutes																													
	23 min		1.19	1.24	0		1.19	1.25	0		1.20	1.26	0		1.20	1.25	0		1.20	1.25	0		1.20	1.25	0		1.20	1.25	0	
	25 min		1.14	1.24	.20		1.16	1.25	.20		1.16	1.26	.20		1.16	1.24	.20		1.15	1.24	.20		1.13	1.25	.20		1.17	1.25	.20	
	31 min		-.18	1.24	0	-16"	-.16	1.25	0	-17'	-.17	1.26	0	-17"	-.17	1.24	0	-16"	-.18	1.24	.10	-22"	-.17	1.25	.10	-21"	-.17	1.25	.10	-2
	35 min		-.19	1.23	0	+ 5#	-.20	1.25	.10	+ 2#	-.20	1.25	.50	+ 5#	-.21	1.22	.10	+ 8#	-.19	1.23	.10	+ 3#	-.19	1.26	.10	+ 2#	-.19	1.25	.20	+ 5
	37 min		-.27	1.15	.50	+15#	-.27	1.17	.70	+13#	-.28	1.19	.50	+15#	-.29	1.12	.60	+20#	-.28	1.13	.60	+12#	-.27	1.21	.70	+13#	-.26	1.20	.80	+1
	40 min		-.32	1.09	.50	+33#	-.37	1.08	.80	+26#	-.36	1.10	.60	+32#	-.41	1.0	.90	+34#	-.34	1.04	1.0	+30#	-.38	1.10	1.2	+28#	-.34	1.10	1.1	+29
	43 min		-.41	1.01	1.0	+41#	-.43	1.03	1.2	+34#	-.43	1.03	1.2	+40#	-.50	.91	1.4	+42#	-.42	.97	1.1	+36#	-.41	1.07	1.2	+34#	-.40	1.10	1.4	+35
	49 min		-.59	.81	1.9	+48#	-.81	.67	2.1	+35#	-.76	.73	2.1	+45#	-.77	.65	2.1	+45#	-.62	.76	2.0	+44#	-.48	1.0	1.4	+44#	-.44	1.07	1.5	+45
	50 min		-.80	.62	0	+48#	-.87	.62	0	+35#	-.86	.64	0	+45#	-.84	.59	2.1	+44#	-.74	.66	2.1	+44#	-.62	.87	2.0	+45#	-.49	1.02	1.8	+47

TABLE 2 (Continued)

TABLE 3

HIGH RATE OVERCHARGE DATA

6 AH CELL

Charge Rate Amps	Temp. °C	Stabilized Volts	psig	Discharged AH C Rate
3.0	25	1.45	- 3	5.7
6.0	25	1.53	+11	5.2
3.0	0	1.59	+ 4	4.4
6.0	0	1.66	+17	3.3
3.0	40	1.39	0	5.5
6.0	40	1.44	+11	5.8
6.0	25	1.55	+12	6.0
6.0	0	1.66	+16	4.5

TABLE 4

AUXILIARY ELECTRODE MATERIAL CHARACTERISTICS

Type (1)	Catalyst	Electron Carrier (2)	Continuous Drain (3)	Remarks
Standard	Platinum Black	Nickel	50	4,5
Modified Std.	Platinum Black	Silver	50	4,5,6,7
Silver-Powder	Silver Flake	Silver	0.2-0.5	5,6,7
Silver-Mesh	--	--	0.1-0.2	5,6,8
Silver-Spinel	Spinel	Silver	3-5	5,6,9
Silver-Carbon	Silver Carbon	Silver or Nickel		5,6,10

1. Unless otherwise noted, electrode is a mixture of catalyst, electron carrier, and Teflon pasted on backing screen and pressed to sinter Teflon at 350°-375°C.
2. Screen and the flake metal added to mix are of the same metal in all cases.
3. Rating for gas pressure of 150 mm at room temperature in ma/cm^2.
4. Recombines hydrogen.
5. Recombines oxygen.
6. Non-magnetic structure.
7. Silflake 131 (Handy & Harmon) used as catalyst.
8. Designer's Metals expanded silver metal mask AG-079-2 used without waterproofing or other treatment.
9. Spinel was cobalt aluminate $CoAl_2O_4$, made by sintering stoichiometric mixture of the metal nitrates at 550°C in oxygen.
10. Silver Carbon Catalyst is a proprietary carbon impregnated with highly active dispersion of silver. This electrode has not been tested in working cells to date; test data, however, is commensurable with other electrode data.

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Section 4

THE ADSORBED HYDROGEN ELECTRODE*

Gulton Industries, Inc.

Metuchen, N. J.

September 1965

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* Paper prepared by the Research Laboratory Staff of Gulton Industries for the IAPG.

THE ADSORBED HYDROGEN ELECTRODE *

Gulton Industries, Inc.
Metuchen, N. J.

The Adsorbed Hydrogen Electrode reduces oxygen by a mechanism best explained employing hydrogen atoms. An acronym for this lengthy electrode description is Adhydrode ®.

The nature of electrode processes depends upon the electrode material, electrolyte concentration, pH, temperature, and electrode potential. Under battery conditions using the Adhydrode material, 8N aqueous potassium hydroxide near room temperature and maintaining a potential in the neighborhood of -0.8 volt (versus a standard hydrogen electrode), and a partial pressure of oxygen in excess of 10 PSIA, the oxygen reduction presumably occurs via the proposed mechanism. Under other conditions, or with different electrode materials, oxygen reduction may occur through a different mechanism.

The Adhydrode is being incorporated into cells in two different manners. In one mode of use, a small Adhydrode is employed. A resistor of 0.1 to 5 ohms maintains the potential of the Adhydrode at the potential of the cadmium electrode. When oxygen is released by the positive electrode, some of it is reduced at the Adhydrode. This upsets the equilibrium conditions and causes a flow of current through the resistor. The potential thus developed constitutes a signal which is then employed to interrupt the charge.

The second mode of use is to have enough Adhydrode material in the cell to significantly enhance the overcharge capability. This is termed the "passive Adhydrode", whereas the former mode of usage has been termed the "active Adhydrode".

The active Adhydrode is readily incorporated into space cells as shown in Figure 1. Such cells have been supplied to NASA/GSFC and are being tested by several groups including NAD, Crane. Other means of including the active Adhydrode have been used for a 100 AH sealed cell being made for NASA/Langley.

The passive Adhydrode is most readily incorporated into cells that have but a few electrodes, such as button cells. VO-.250 A button cells, now in production, are capable of being charged and continuously overcharged at the C/4 rate.

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* Paper prepared by the Research Laboratory Staff of Gulton Industries for the IAPG.

An interesting use of the passive Adhydrode has been in prismatic space cells ordered by Mr. E. Stroup of NASA/Goddard. These cells were specially designed to contain more Adhydrode area than active material area. The purpose of this design was to have a cell that could be charged and continuously overcharged at the C/1 rate for 10 days at -10°C. Thirty of these cells have already been delivered after satisfactory testing in our laboratory.

Theory

A model for cells containing the Adhydrode is given in Figure 2. The cell contains a positive electrode (+), a cadmium electrode (-), and the third electrode. The cell container is indicated by the dashed line. The third electrode is connected to the negative electrode through the resistor, R.

When there is very little or no oxygen in the cell, the third electrode is very close to the potential of the negative electrode and the flow of current is small. Now, consider the situation when oxygen is present in the system while the negative electrode is in a charged state, but on open circuit. The source of the oxygen may equally well, for our purpose, be injected into the cell or come from an overcharge of the positive electrode. For this condition, the following reactions were elucidated:

$$O_2 + 4H - (M) \xrightarrow{k} 2H_2O \qquad (1)$$

$$4H_2O + 4e^- (M) \xrightarrow{i} 4OH^- + 4H - (M) \qquad (2)$$

$$2Cd + 4OH^- \xrightarrow{i} 2Cd(OH)_2 + 4e^- \qquad (3)$$

$$\overline{2Cd + O_2 + 2H_2O \text{ ——— } 2Cd(OH)_2.} \qquad \text{overall}$$

The symbol k is the specific rate constant for a chemical step, while the i's indicate the electrochemical steps. In the overall reaction the negative electrode is discharged.

If the experimental conditions are changed to that of overcharge, then the source of oxygen is from the positive electrode. It can no longer be unequivocably stated that the sole source of electrons is the negative electrode. It can be shown experimentally that this reaction can indeed occur with electrons exclusively from the charge process, but this does not resolve the question on the source of electrons during overcharge, and, for practical purposes, more detailed knowledge is not required.

For the Adhydrode, when oxygen removes the hydrogen atoms (equa. 1), then reaction 2 must proceed to replace hydrogen on the vacant sites. This requires the electrons which are supplied by reaction 3, and in this way, a flow of electrons through the resistor R of Figure 2 occurs. The charge current is considered to cause the reverse of equa. 3 so that at a steady state, the state of charge of the negative electrode is unaltered.

If the value of resistor R is reduced to zero, the situation for the passive Adhydrode is obtained. The recombination rate will be a function of the partial pressure of oxygen and area of Adhydrode.

Adhydrode Control Circuits

From a complete power system point of view, the Adhydrode is a transducer which gives an electrical response proportional to the oxygen pressure present in a nickel-cadmium or silver-cadmium cell. This electrical signal is detected and used to control the battery charger.

For laboratory evaluation of the Adhydrode concept, the circuit shown in Figure 3 is one of the simplest to construct. The battery charger can be any power supply capable of a constant current output and able to meet the power requirements of the battery. When the circuit is first energized, the charger supplies current to the cell. This current surge causes the Adhydrode to give a false signal which will last a few seconds. To prevent this false signal from interfering with charging, a time delay relay is placed in the circuit, so that it is opened 45 seconds after charging begins. The fact that the contacts of the time delay relay short terminals 1 and 2 of the meter relay, causes the meter relay to ignore the false signal. Thus, charging current cannot be interrupted during the first 45 seconds of charging, which is more than enough time for the false signal to decay. When oxygen pressure in the cell increases to a value sufficient to cause the Adhydrode to generate a signal capable of tripping the meter relay, contacts MR1 and MR2 open. When MR1 opens, charging current is terminated. MR2 is opened to prevent a high Adhydrode signal from overloading the meter relay.

A block diagram of a circuit which can be used in a space power system is shown in Figure 4. This circuit is designed to terminate charging current when the Adhydrode to cadmium current of either of two cells reaches a pre-selected level. This system may be extended to operate on any number of Adhydrode cells. The direct current signals of both Adhydrode cells are converted to pulsating currents by the choppers which are static on-off switches driven by a multivibrator. The outputs of the choppers are connected to separate transformers which isolate each Adhydrode cell. Isolating the Adhydrode cells at this point allows the remainder of the circuit to be grounded without shorting either cell. Grounding is necessary because it reduces electrical interference, and allows equal detection of both Adhydrode signals.

The output of the isolation transformers are amplified by conventional A.C. amplifiers. The amplified, A.C., Adhydrode signals are rectified and filtered by the demodulators. At the output of the demodulators, there are two D.C. signals which are proportional to each of the Adhydrode signals. These signals are fed into a modified Schmitt trigger. When the amplified output signals of both Adhydrode cells are below a selected level, the output of the Schmitt trigger permits the electronic switch to conduct charging current from the charger to the cells. When one or both of the amplified Adhydrode signals are above the selected level, the output of the Schmitt trigger causes the electronic switch to terminate the charging current. The electronic switch is designed to always permit the flow of current in the discharge direction.

Figure 5 shows the actual network which will perform the same function as the block diagram in Figure 4. The choppers used should have a low input impedance and a low error voltage throughout the temperature range desired. Transistors Q_1, Q_2, and Q_3, Q_4 form both A.C. amplifiers. They are designed for a stabilized gain throughout a wide temperature range. Transformers T_2 and T_4 are required for full wave rectification of the A.C. Adhydrode signals. They should have a wide frequency pass band so that distortion of the signals is kept to a minimum. The filtered D.C. signals will cause transistors Q_5 or Q_6 to conduct when one of them exceeds the level of the voltage across resistor R_1. When this happens, the collector voltage of Q_7 will fall to almost ground potential. This prevents the zener diode Z_1 from conducting and turns off transistors Q_8 and Q_9, thus terminating the charging current which had been flowing through Q_9. Diode D_1 allows the cells to be discharged whenever external loads require it.

Adhydrode Characteristics

The Adhydrode acts as a self-generating transducer. Its presence in the cell is unobtrusive until oxygen is produced by the charge process. At this time, a wide range of usage becomes available based upon the load resistor between the Adhydrode and the negative electrode. This is exemplified in Figure 6, which depicts the power transfer characteristics and Figure 7, where the signal is shown as a function of pressure. These data were taken in six ampere hour cells (VO-6HSAD). When the load resistor is small, the signal is due to a large current. The limit of zero is, of course, the case of the passive Adhydrode. When the load resistor is greater, then the signal consists of a large voltage at low current. At intermediate values, a maximum power transfer to the load is obtained. This is similar to, but not identical with, the usual power transfer considerations. When treated as a source of EMF and an internal resistance, it is found that the value of EMF changes when considering a constant internal resistance. Conversely, considering a constant EMF, the internal resistance changes.

The signal in Figure 7 is the voltage across the resistor. The Adhydrode is considered to be a current source, and, as such, this sort of plot appears to favor the 100 ohm load. In a plot of Adhydrode current instead of voltage, the 0.5 ohm load would appear more favorable. An important significance of Figure 7 is that it shows that any mismatches in the Adhydrode signal may be compensated by adjusting the load resistor.

The value of Adhydrode load also influences the pressure decay characteristics of a cell. Figure 8 shows the pressure decay in a VO-6HSAD cell with a 0.5 ohm load resistor. When the load resistor is increased, the current is correspondingly smaller. At large enough values, the active Adhydrode provides no enhancement of the pressure decay characteristics.

The advantages of third electrodes are found when charging cells at rates exceeding those presently recommended, namely, greater than the C/10 rate. Data obtained at the Engineered Magnetics Division of Gulton Industries are shown in Figure 9. These are the Adhydrode signal across a 1 ohm resistor during charge at the C/3, C/2, and C/1 rates. Also, from the same laboratory, the effect of temperature on the Adhydrode signal is shown in Figure 10. The behavior of the curve corresponding to 110° F corresponds to the known pressure behavior of the nickel-cadmium system.

An example of a VO-6 HSAD cell in cycle is shown in Figure 11. The charge rate is 5.4 amperes and the discharge rate is 4.5 amperes for 62 minutes (50% depth of discharge). The cell pressure is low for approximately 30 minutes, and then starts a more rapid rise. The Adhydrode signal (across a 0.5 ohm resistor) follows the pressure. A meter relay circuit is employed to interrupt charge at a 50 mV signal. No readings above 50 mV are measured so that the flat portion between 38 and 64 minutes should be read:

$$\text{Adhydrode Signal} \geqq 50 \text{ mV}.$$

The cell is on open circuit from 38 minutes in "sunlight" until the "dark side" is reached at 59 minutes. The Adhydrode signal decays during the discharge along with pressure, and by the end of the discharge, the cycle is ready to repeat itself again. It is interesting to note that this cell remains in vacuum during the cycle.

Discussion

The data already indicate a value for the Adhydrode for high rate charging. The Adhydrode may be used in an active mode or in a passive mode. The passive mode, until recently, has been restricted to commercial cells of the button type. VO-.250 A button cells are in production. These cells are capable of being charged and continuously overcharged at the C/4 rate. Recently, a space type was specially designed to be subjected to a C/1 rate overcharge at -10°C for 10 days. The ability of the passive Adhydrode to reduce oxygen at even this temperature permitted such a cell to be fabricated.

The Adhydrode is restricted to systems that have a cadmium electrode. This requirement comes about because of the necessary potentials which lie between -0.6 and -1.0 volt (NHE) in a strongly basic solution. Thus, it is useful in the nickel-cadmium and silver-cadmium systems. Application in the silver-cadmium system is more complicated than in the nickel-cadmium cell because of the greater changes in electrolyte level. A direct incorporation of the Adhydrode in silver-cadmium cells already designed, is not practical. New silver-cadmium cells must be designed with the proper configuration for use with the Adhydrode.

If the Adhydrode load resistor is too great, then a cell might not be ready to accept charge when the "bird" goes into "sunlight". One way to enhance this is simply to reduce the value of the resistor. A second way to enhance recombination is to build a cell containing both the active and passive Adhydrodes. Such cells are under construction at this time.

Best results in this laboratory have been obtained using Adhydrode load resistors of 0.5 to 5 ohms. When the signal is obtained, charge is completely interrupted. Tests have not been satisfactory when the charge rate is merely reduced to the C/10 rate after the signal is obtained.

The Adhydrode concept is still relatively new. Testing has not yet been extensive. Because of the various modes of use, such as (1) selection of the load resistor, (2) determining the signal to use as cut-off, (3) use of trickle charge versus pulse charging, (4) temperature effects, (5) and hybrid electrodes, life cycling data has not yet been obtained. The future does hold prospects of increased cycle life and increased reliability of cells containing Adhydrodes.

There is evidence (see Figure 11) that cells can memorize even at high charge rates. Overdischargeability of cells is desirable to protect against possible cell reversal. A practical reversal protection system employing readily obtainable diodes and a judicious proportioning of electrodes has been developed. This overdischarge protection system is compatible with both active and passive Adhydrodes.

The Adhydrode is inexpensive enough to warrant commercial exploitation as well as for aerospace and aircraft. Since most consumers of cordless products will not have the sophisticated control equipment, it appears that passive Adhydrodes will become more important.

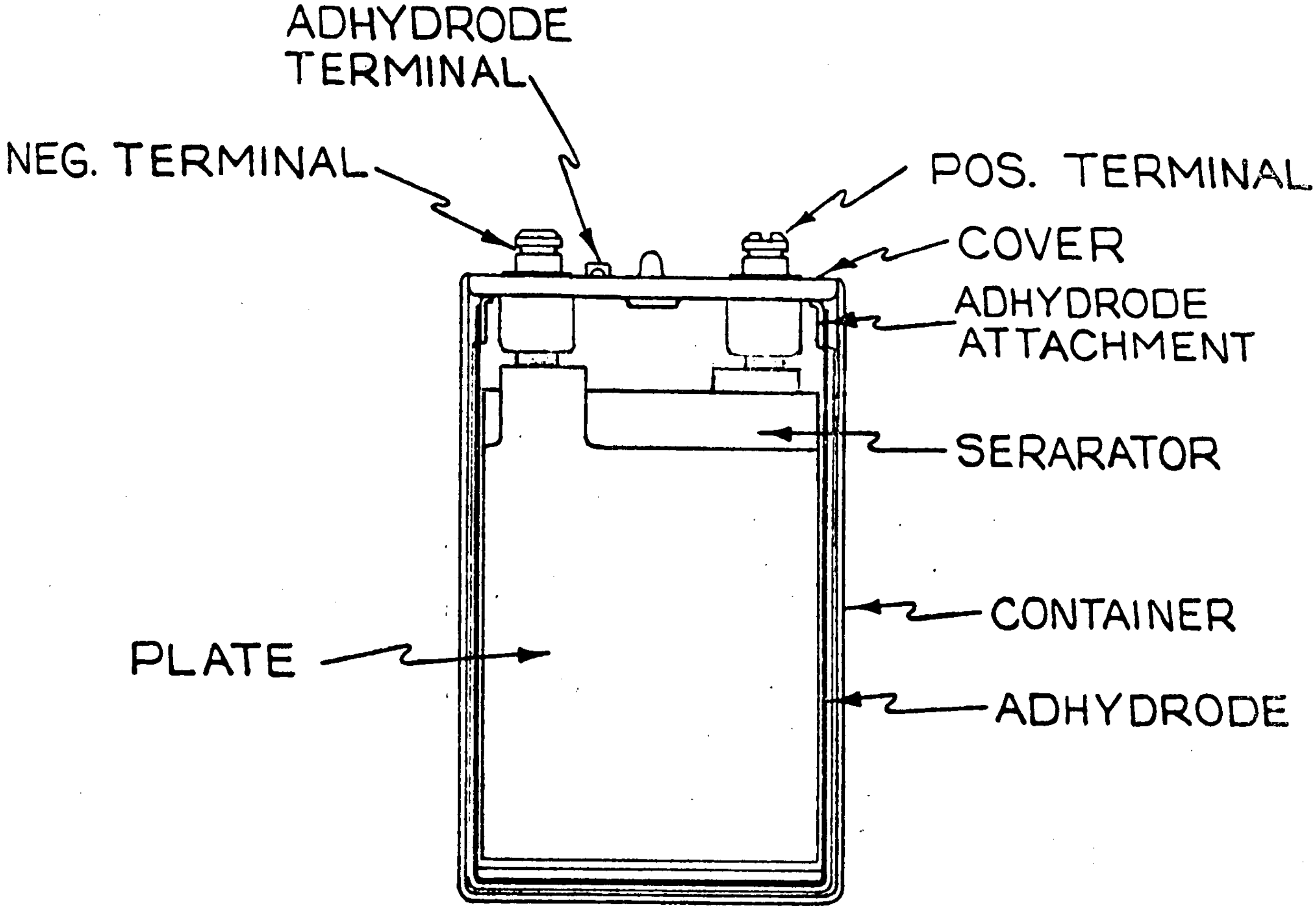


FIG. 1 VO-6HSAD HERMETICALLY SEALED NICKEL CADMIUM CELL *for* SPACE USE EMPLOYING THE ADHYDRODE MATERIAL AS A CONTROL ELECTRODE.

* AS SUPPLIED TO THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

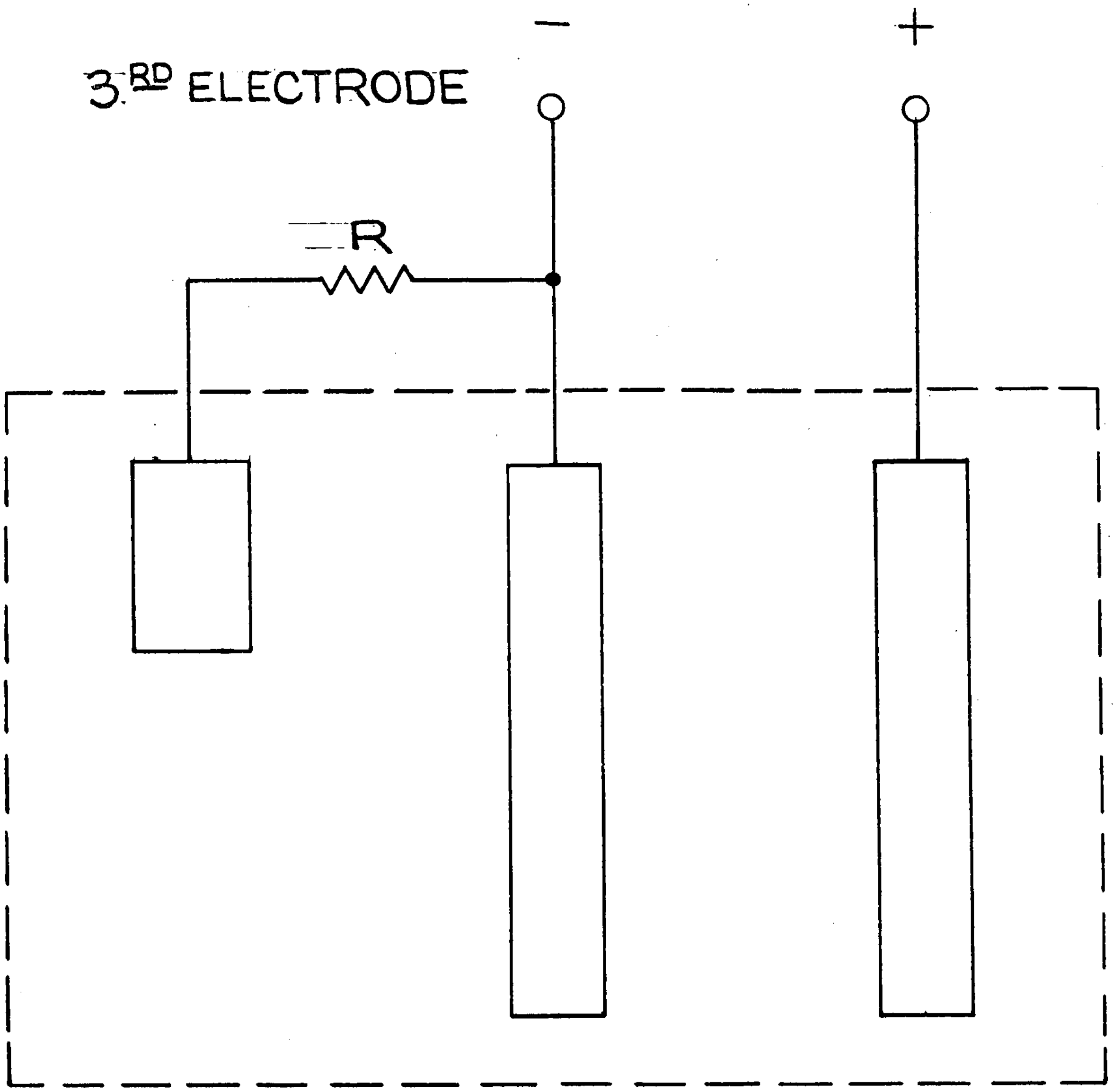
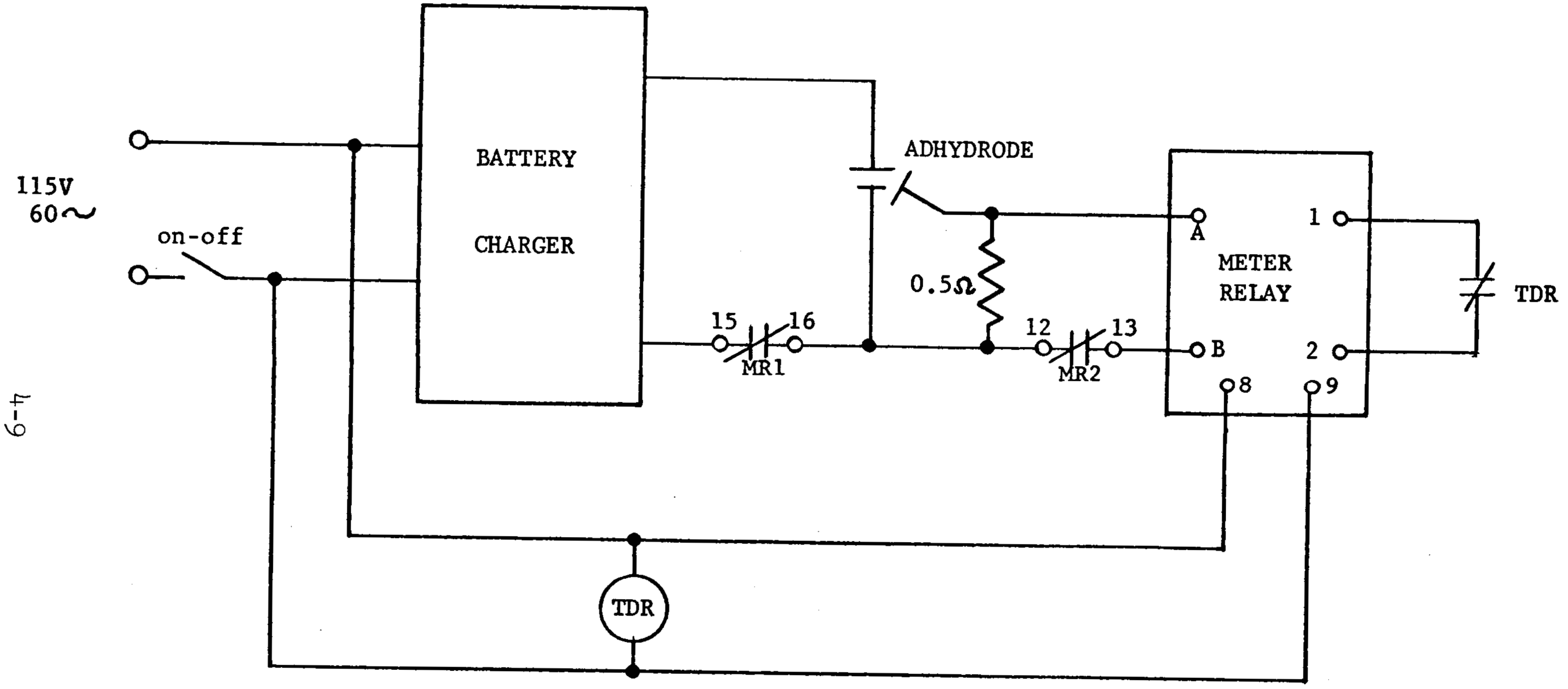


FIG. 2 MODEL *for* THIRD ELECTRODE



TDR - Amperite Delay Relay #115C45

Meter Relay - Simpson Electric #16460

FIG. 3 CONTACTLESS METER RELAY CHARGE CONTROL CIRCUIT

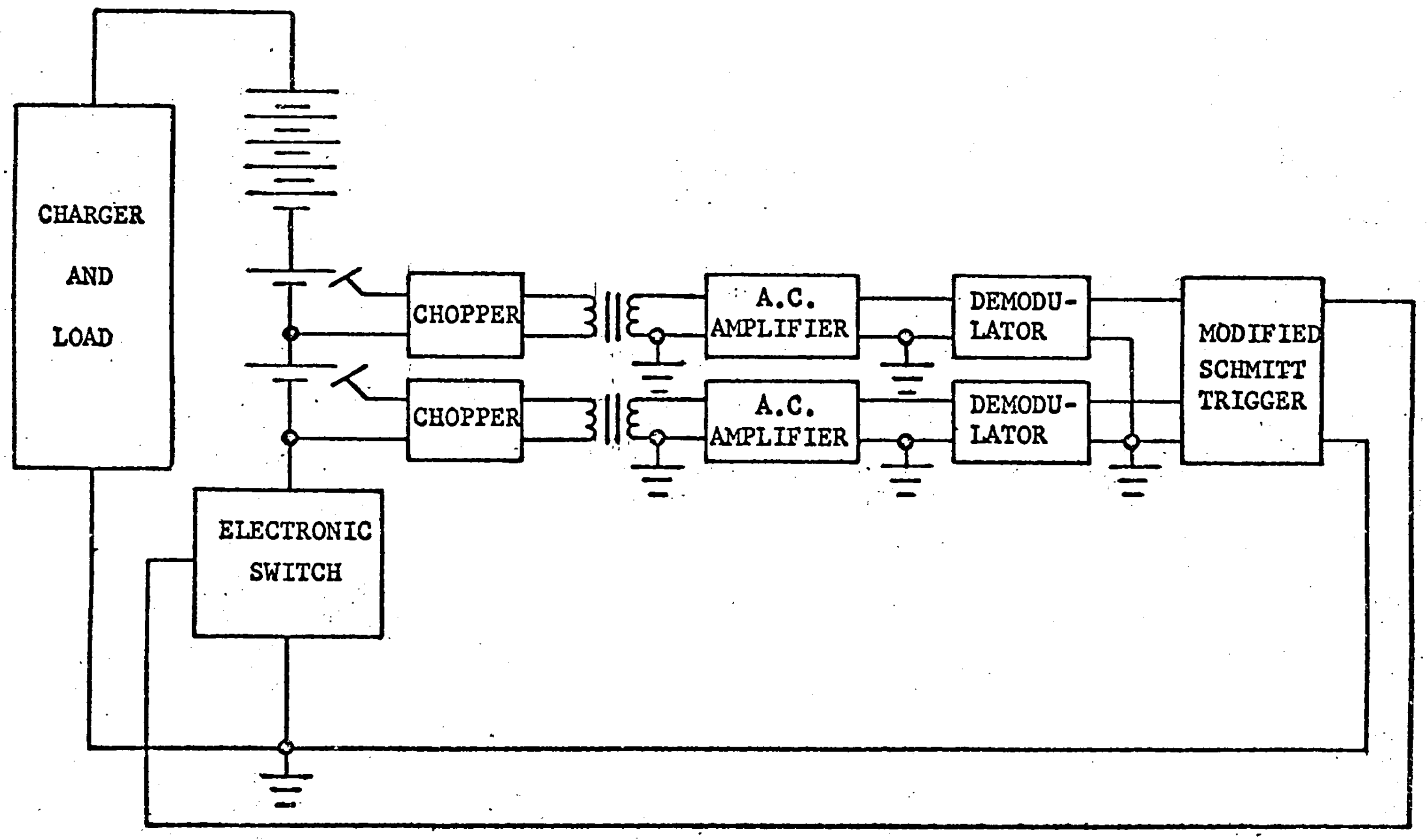


FIGURE 4. ADHYDRODE CHARGE CONTROL CIRCUIT

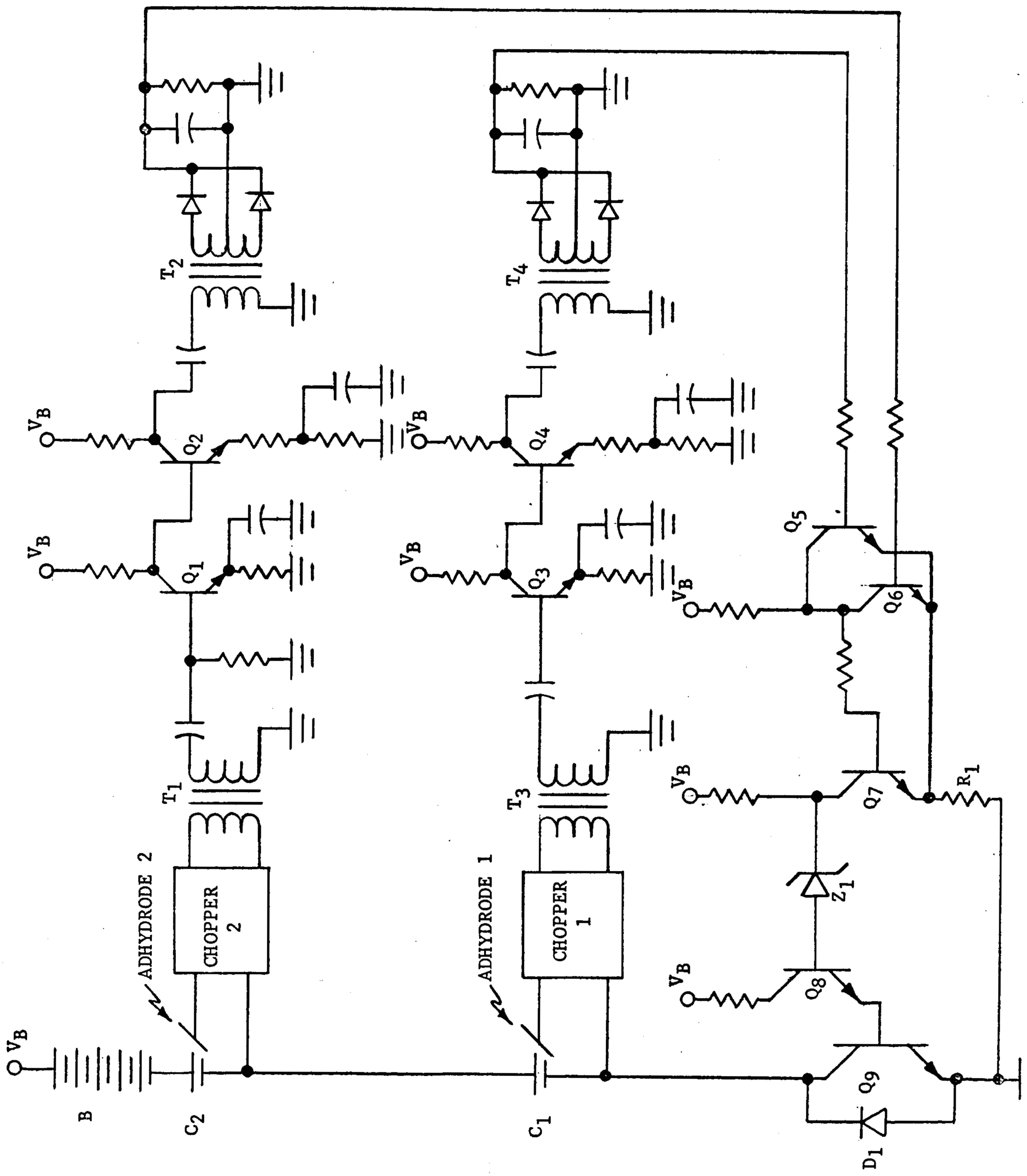


FIG. 5 ADHYDRODE CHARGE CONTROL CIRCUIT

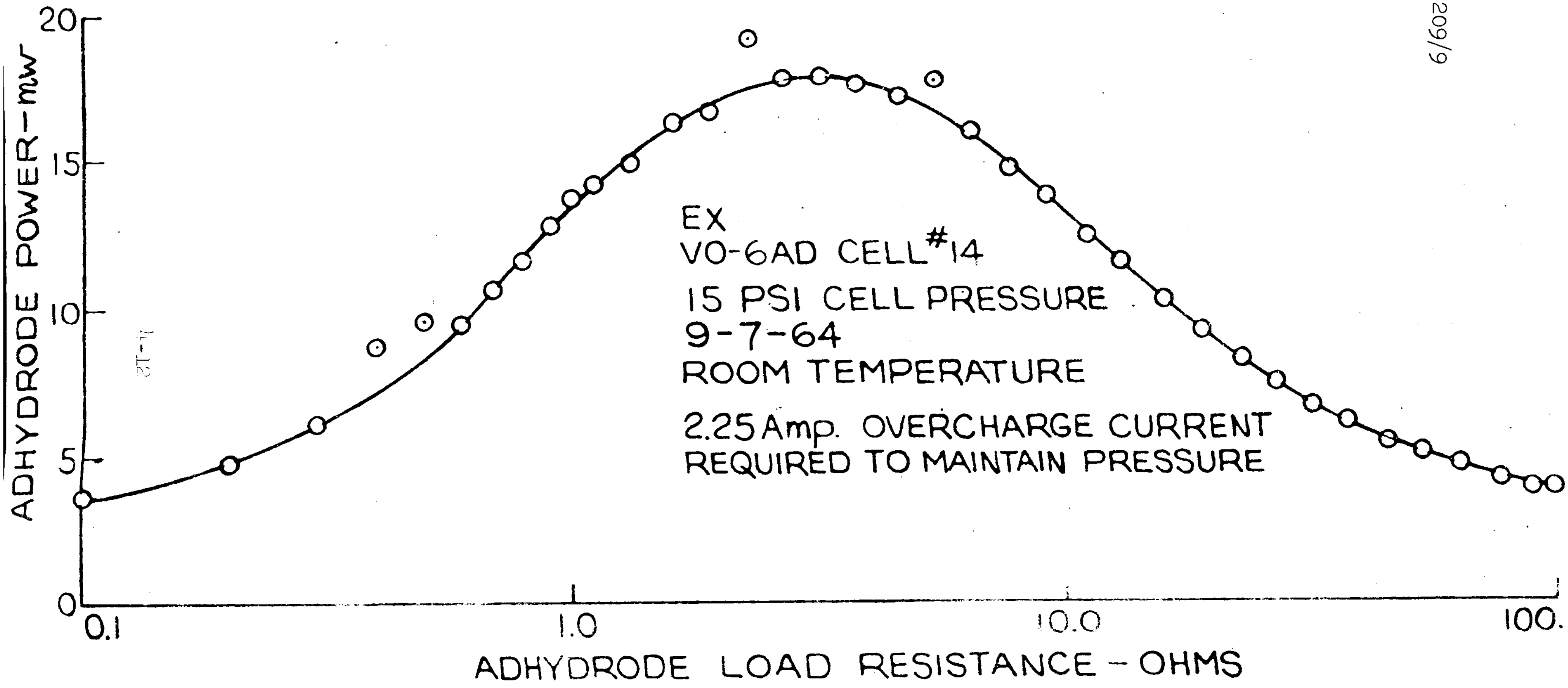


FIGURE 6. ADHYDRODE POWER OUTPUT VERSUS ADHYDRODE LOAD RESISTANCE FOR 15 PSIG CELL PRESSURE

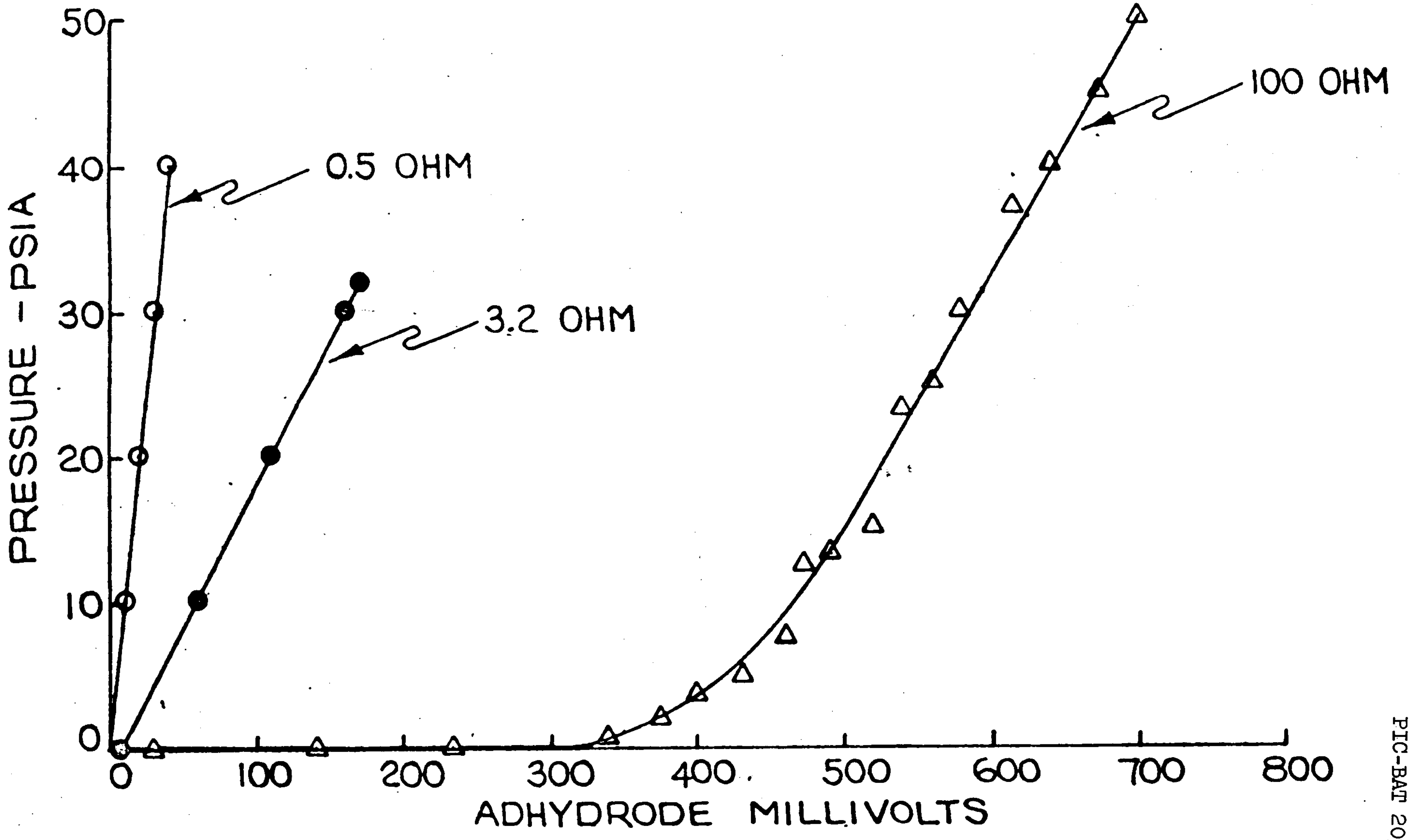


FIGURE 7. CELL PRESSURE VERSUS ADHYDRODE VOLTAGE FOR ADHYDRODE LOAD RESISTANCES OF 0.5, 3.2, AND 100 OHMS.

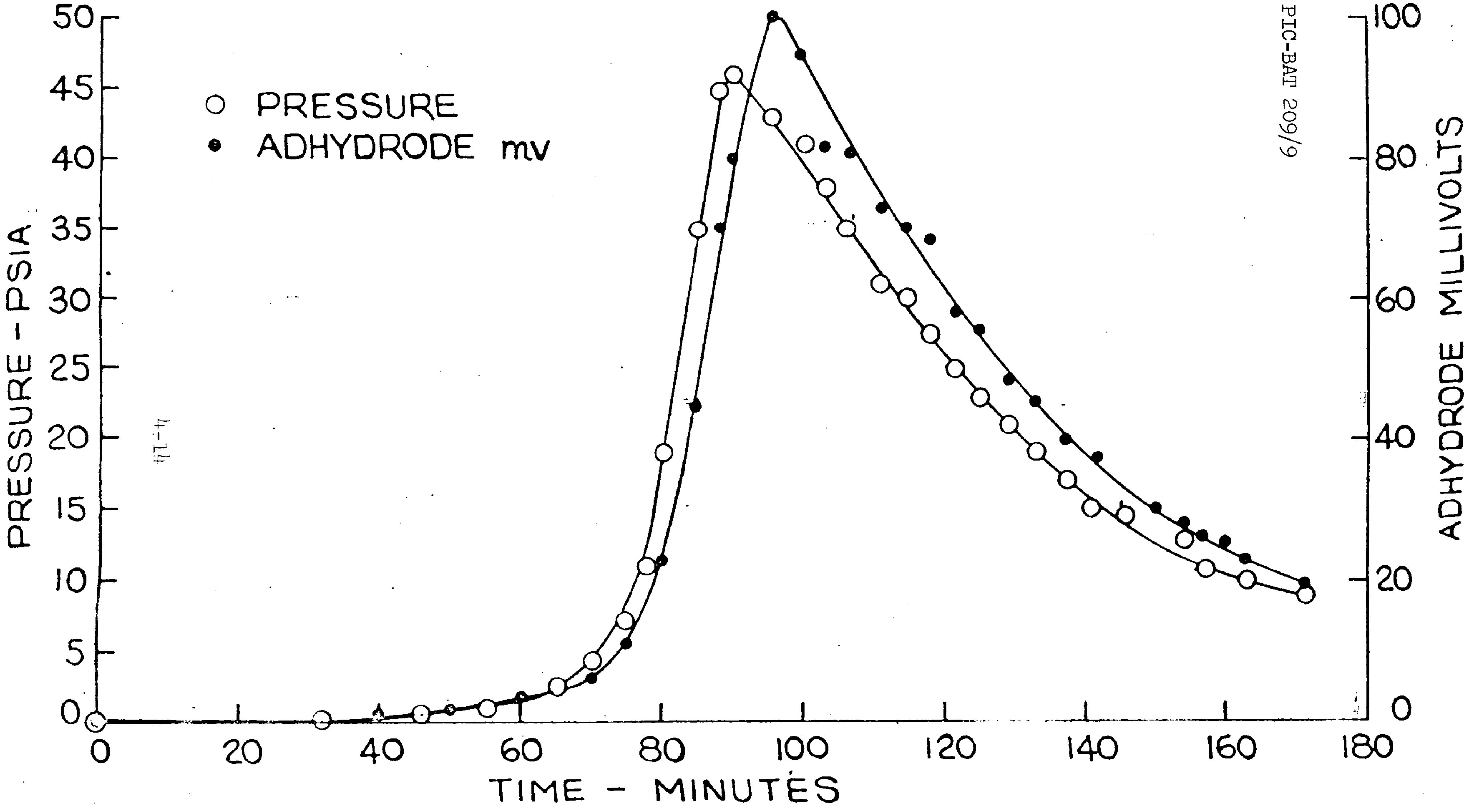


FIGURE 8. CELL PRESSURE AND ADHYDRODE VOLTAGE VERSUS TIME FOR 0.5 OHMS ADHYDRODE LOAD RESISTANCE

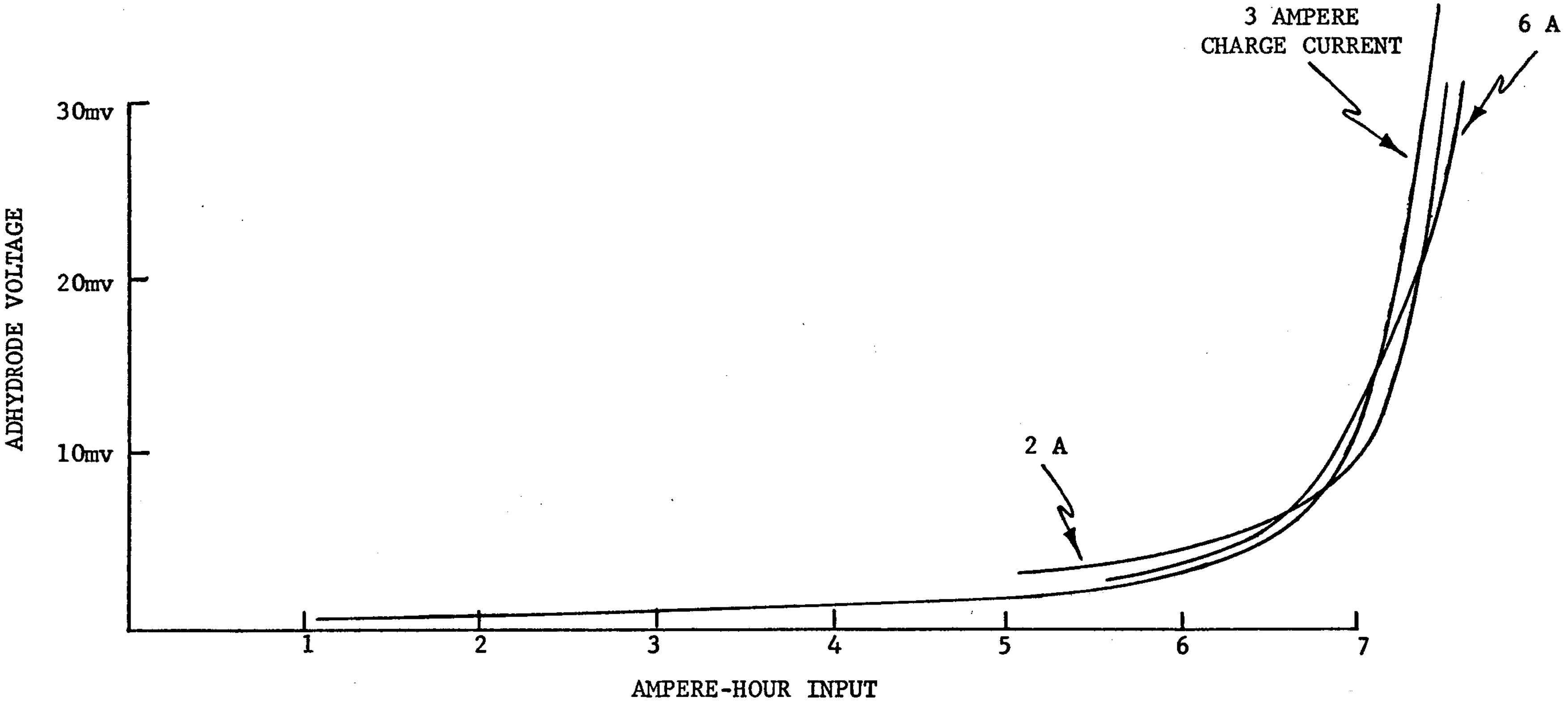


FIGURE 9. CHARGING CHARACTERISTICS OF GULTON 6 AMPERE-HOUR ADHYDRODE CELL

Engineered Magnetics-Gulton Industries, Inc.

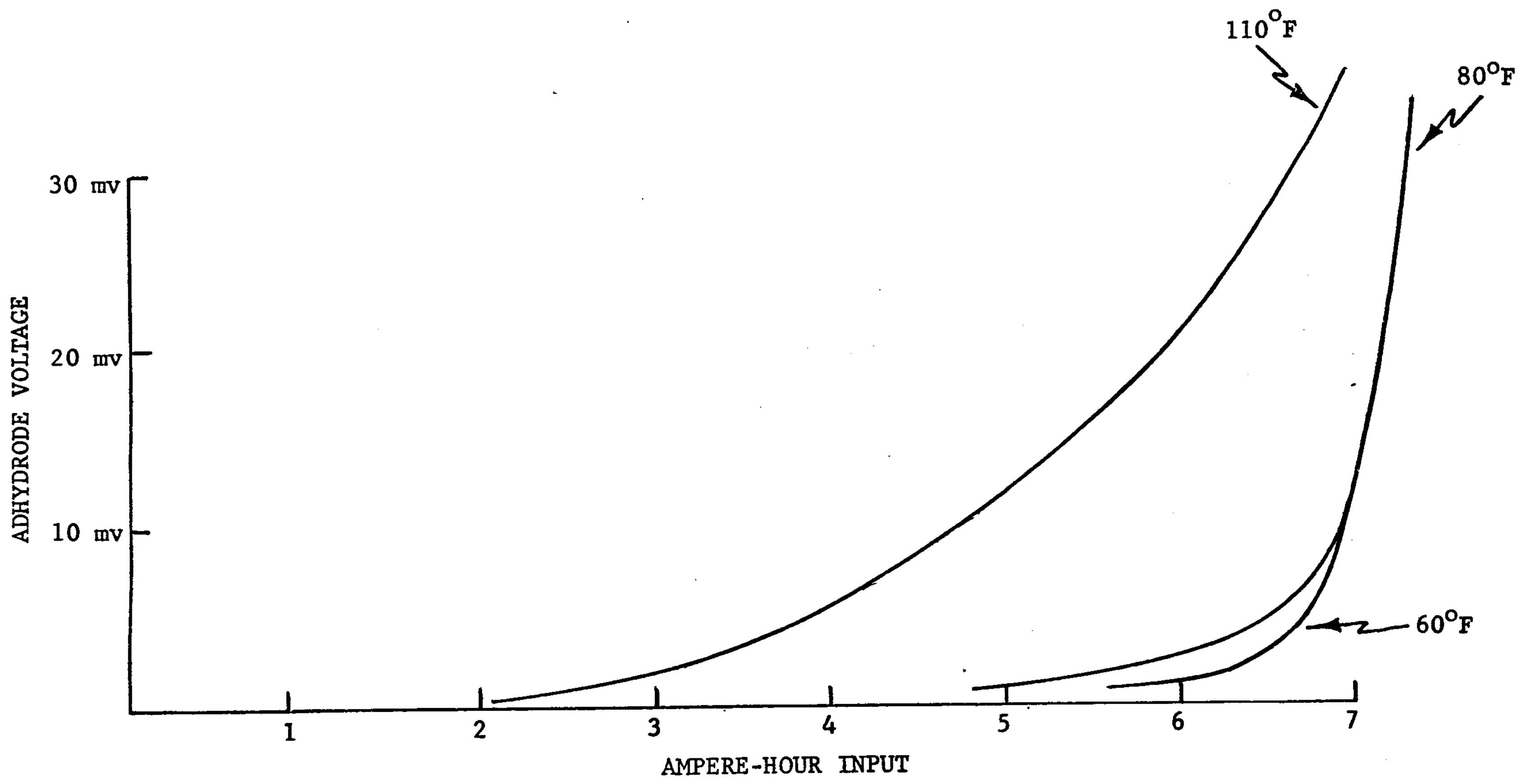


FIGURE 10. TEMPERATURE CHARACTERISTICS OF GULTON 6 AMPERE-HOUR ADHYDRODE CELL (3 AMPERE CHARGE RATE)

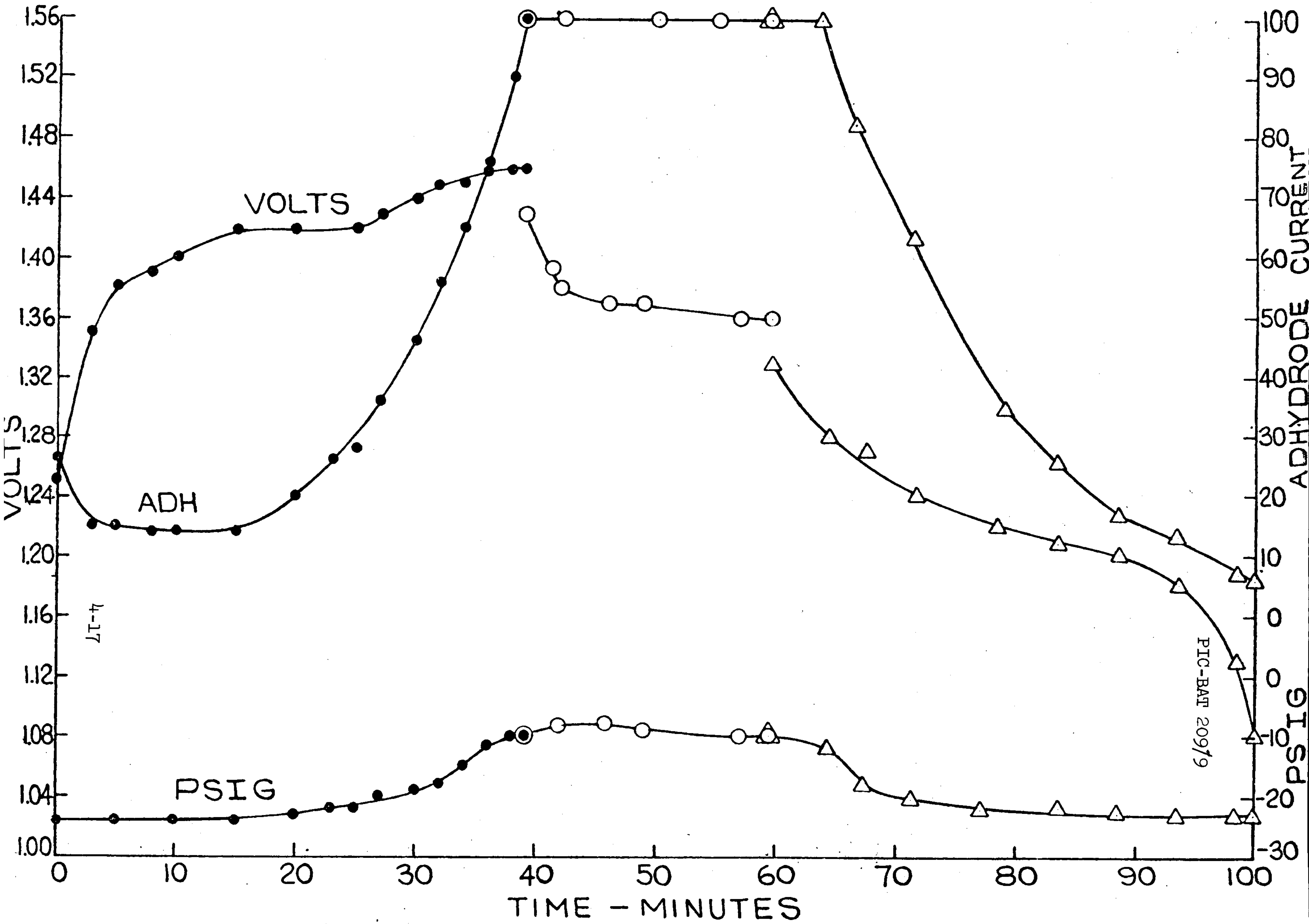


FIGURE 11. EXAMPLE OF VO-6 HSAD CELL IN CYCLE

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Section 5

A TECHNIQUE FOR OBTAINING REFERENCE POTENTIALS IN SEALED NICKEL-CADMIUM BUTTON CELLS

by

W. H. Dyson

The Electric Storage Battery Company

The Carl F. Norberg Research Center

Yardley, Pennsylvania

September 1965

A TECHNIQUE FOR OBTAINING REFERENCE POTENTIALS IN SEALED NICKEL-CADMIUM BUTTON CELLS

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At the present time, The Electric Storage Battery Company is investigating the use of gas recombination techniques for overdischarge protection in nickel-cadmium button cells. In order to obtain necessary single electrode data a stable reference electrode must be introduced into the cell.

The reference electrode chosen was amalgamated gold, which was anodized after installation to produce a Hg/HgO reference electrode. Because of the small size and limited capacity of these electrodes, all potential measurements were made using Keithley 610A electrometers having an input resistance of 10^{14} ohms. The voltage of these electrodes was found to differ somewhat from that of Hg/HgO electrodes produced by more conventional means.

The difference between the anodized amalgam and a paste-type Hg/HgO electrode was of the order of several millivolts and varied depending on the degree of amalgamation and age of the amalgamated gold electrode. For example, a freshly amalgamated electrode having a high degree of amalgamation (Hg content $> 90\%$) had, after anodization to the point of oxygen evolution, an equilibrium voltage of -.002 volts versus a paste electrode. At the opposite extreme, another electrode having 1.4% amalgamation which was anodized to oxygen evolution after two weeks' storage at room temperature showed an equilibrium voltage of +.050 volts versus a paste electrode. The differences between electrodes of any one treatment were of the order of millivolts. This could be tolerated, particularly in view of the convenience and ease of fabrication of the amalgam electrode. These variations are at present the subject of study by this laboratory.

In order to obtain valid data, it was necessary that the reference be installed in such a way that: (a) the geometry of the cell remained essentially unaltered, (b) the cell could be sealed using the same tooling used to seal the commercial prototype cell, and (c) the thermal and electrical properties of the cell remained essentially unaltered.

The cells are sealed by crimping the top edge of the cathode can around the rim of the anode cap, a nylon grommet acting as seal and insulator. All attempts to introduce the reference electrode through the insulating grommet were unsuccessful, for one or both of two reasons, i.e.:

1. the addition of the reference electrode lead and an insulator to the seal resulted in poor seals, since the tolerances of the closing die do not permit additional material.

2. the reference lead was cut or itself cut the insulation, a result of the force needed to crimp the cell.

The only way the reference was successfully installed was to have it entirely in the cell can at the time the cell is closed; contact was made with the reference after closure.

The method of doing this is as follows:

1. The cell container used is one size larger than the cell under study i.e., for studies of the 150 MAH cell the container for the 225 MAH cell was used. The increased volume is obtained by increasing the depth of the can; all other dimensions remain the same. This is of importance in retaining the same cell geometry.

2. The reference electrode, which is a strip of amalgamated gold foil, is bent into an "L". The base of the "L" is placed atop an insulator which has been tamped into the bottom of the cell can. The vertical of the "L" is close to, but insulated from, the wall of the cell can. The base of the "L" and the insulator are then encased in a layer of epoxy resin. The epoxy acts as (1) a sealant, (2) an insulator for the reference, and (3) a "false floor" which reduces the volume of the can to that of the cell under study.

3. A small hole is drilled through the bottom of the can, through the epoxy and insulator, to the amalgamated gold. A portion of the surface of the amalgamated gold is scraped clean; then, a small drop of mercury is put in contact with the amalgamated gold for later contact purposes. The small hole is filled with epoxy and the bottom of the can is smoothed with crocus cloth.

4. The cell parts are assembled into the can as they would be in the corresponding commercial cell. The only additions to the parts are (1) the reference electrode, and (2) insulators for the reference electrode. Those cell parts which would normally be in contact with a tab are brought through the insulating layer from the can bottom. Electrolyte is added and the cell is closed in the appropriate closing die.

5. After the cell is closed, a second hole is drilled through the epoxy plug in the first hole mentioned in step 3. This hole permits a contact wire to be inserted into the mercury drop previously put in contact with the gold foil. The contact wire is then sealed in place with a drop of epoxy.

This technique satisfies the requirements laid down for the reference installation as follows: (a) Except for the small additional volume of the reference electrode and its insulators, the internal geometry of the cell is unaltered; (b) The cell is closed by commercial cell closing tooling; the seal is undisturbed by any added material; and (c) The thermal properties of the cell remain substantially unaltered, the major change is that the heat which is ordinarily transferred directly to the cell bottom for subsequent radiation or conduction from the cell must now be transferred by the contact tab to the cell bottom. This indirect transfer is compensated by the mass of the sealant and the added surface area of the larger can.

Once the cell has been closed, it remains closed. The subsequent contacting of the mercury drop, if carefully done, does not open the cell. Figure 1 is a schematic drawing of the reference assembly; for clarity, the working electrodes are not shown.

Typical data obtained by this method are shown in Figure 2. This particular discharge-and-reversal occurred during the fourth cycle of a cell which had the following construction:

Positive electrode:	Nickel hydrate	-80%
	Graphite	-20%
Negative electrode:	$Cd(OH)_2$	-90%
	Carbonyl nickel	-10%
Separator:	Pellon 2505 (2 layers)	
Electrolyte:	KOH-LiOH 0.25cc	
Recombination electrode:	Woven nickel mat, attached to the positive	
Positive precharge:	27% (initial)	

The cell was discharged in series with 2.4 volts and 120 ohms, a circuit which simulated a three cell battery driving a 120 ohm load. The various voltage levels are marked with the reactions believed to be occurring at those levels. The oxygen recombination mechanism is believed to be the so-called perhydroxyl mechanism, (1) i.e., perhydroxyl ion formation

$$2O_2 + 2H_2O + 4e \rightarrow 2OH^- + 2HO_2^-, \; E_o = 0.076v$$

followed by perhydroxyl decomposition

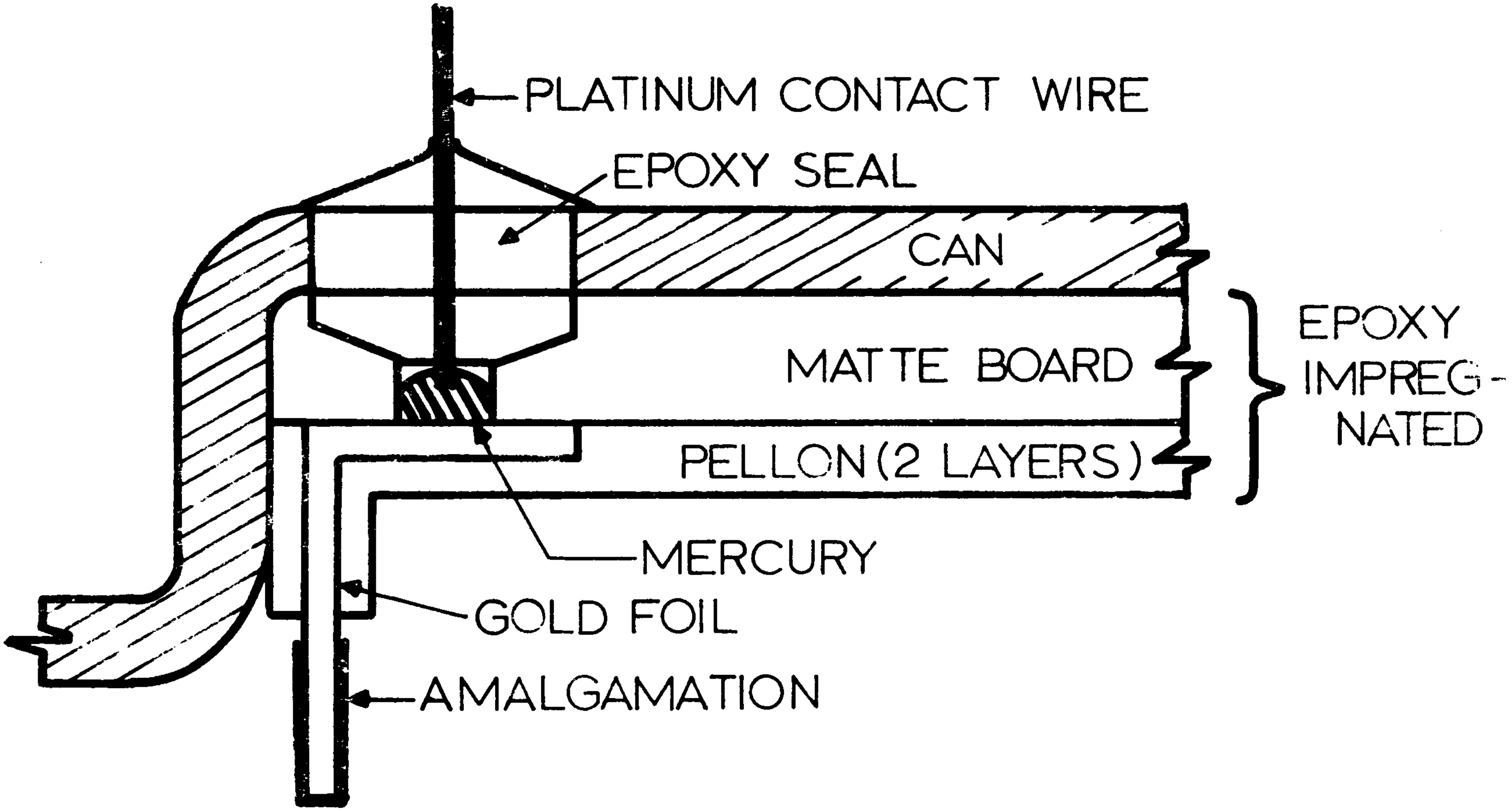
$$2HO_2^- \rightarrow 2OH^- + O_2$$

The net reaction is

$$O_2 + 2H_2O \rightarrow 4OH^-$$

References

(1) Baars, E. G., 12th Annual Power Sources Conference, 1958.



REFERENCE ELECTRODE ASSEMBLY

Fig. 1

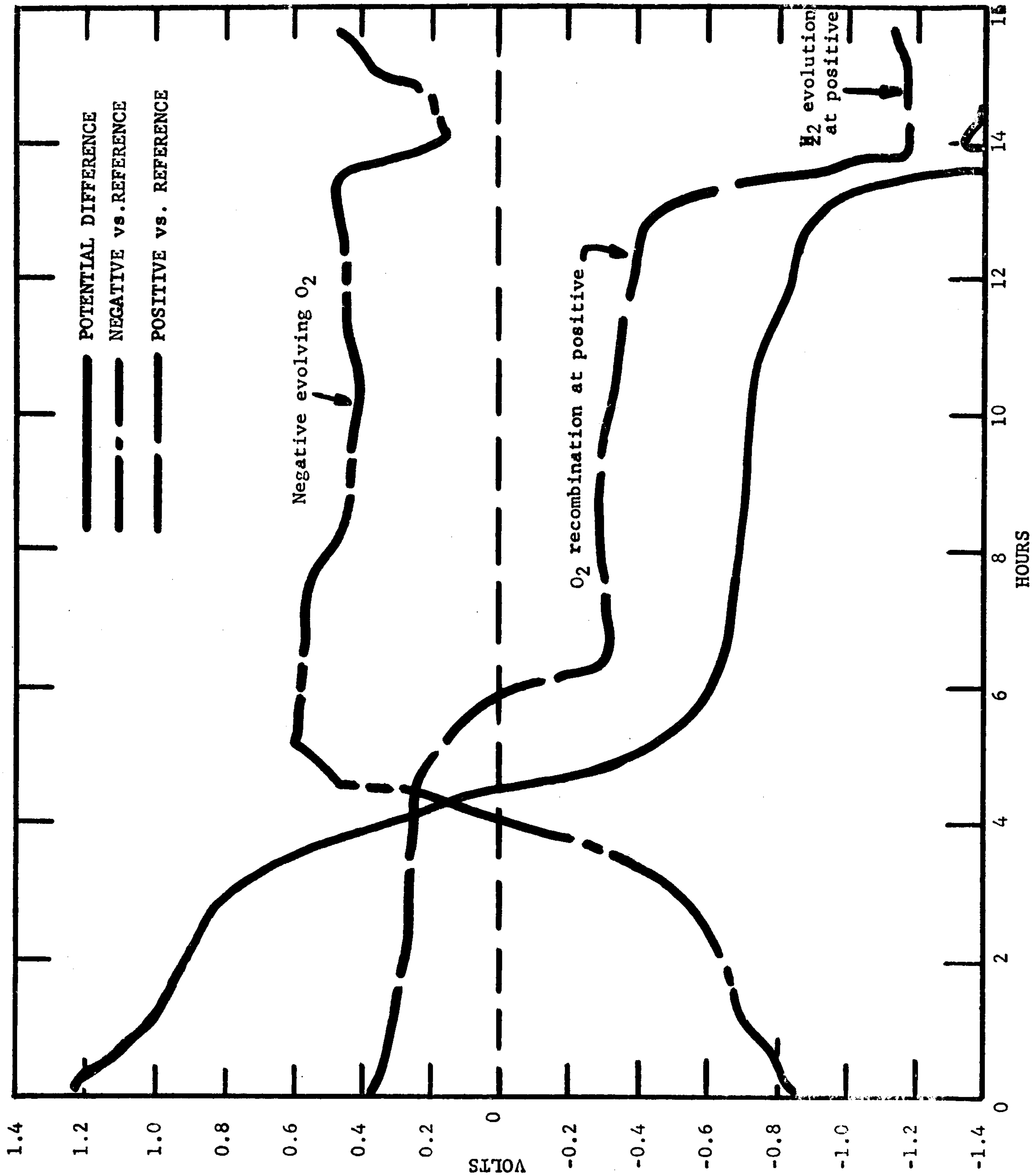


Figure 2

Potentials observed during discharge and reversal of a reference-equipped nickel-cadmium button cell. All reference potentials are versus amalgamated gold/HgO. The degree of amalgamation was sufficiently high to insure that the potential of the reference was within a few millivolts of a standard reference electrode.