NASA CR-72636
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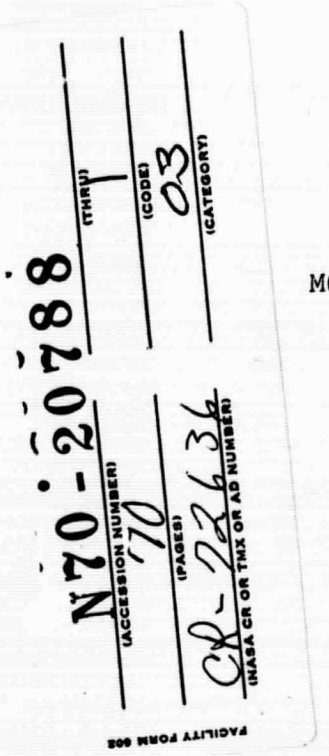
DEVELOPMENT OF A RECHARGEABLE ZINC-OXYGEN POWER SYSTEM

FINAL REPORT
Covering Period June 1968 through October 1969

by

H. A. Frank



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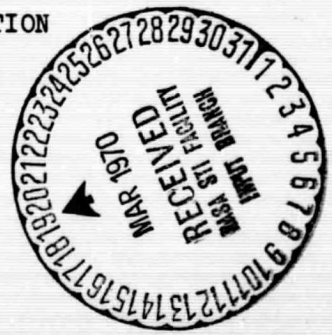

NASA Lewis Research Center
Contract NAS 3-11832

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McDonnell Douglas Astronautics Company
Western Division
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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
William A. Robertson, Project Manager
Direct Energy Conversion Division

FOREWORD

The work described herein was done at the Astropower Laboratory, McDonnell Douglas Astronautics Company, under NASA Contract NAS 3-11832 with Mr. William A. Robertson, Direct Energy Conversion Division, NASA Lewis Research Center, as Project Manager.

DEVELOPMENT OF A RECHARGEABLE ZINC-OXYGEN POWER SYSTEM

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ABSTRACT

This report describes the performance of rechargeable zinc-oxygen cells employing "Astroset" inorganic separators. Experimental cells were evaluated at 500 p.s.i.g. (35.1 kg./sq. cm.) and at ambient temperature on a continuous 6-hour cycle regime at 25% depth of discharge. Cells with the most promising components operated effectively for over 200 cycles (1200 hours). A hydrogen problem was noted and is discussed in detail.

TABLE OF CONTENTS

FIGURES

TABLES

DEVELOPMENT OF A RECHARGEABLE ZINC-OXYGEN POWER SYSTEM

by H. A. Frank

Astropower Laboratory
McDonnell Douglas Astronautics Company
Western Division

SUMMARY

The ultimate goal of this work is to develop a rechargeable zinc-oxygen cell employing proprietary "Astroset" separators. These are semiflexible separators made from inorganic materials. Major emphasis in the evaluation was on cycle life.

The first phase of the program consisted of designing and fabricating test rigs to permit completely sealed operation of the experimental cells. The second phase consisted of performance evaluation tests designed to yield the most promising cell components and configuration. The third and final phase consisted of statistically designed cycle life tests on cells with the most promising design features.

The experimental cells had a capacity of 4 amp. hr. These were run on continuous cycle regimes at ambient temperature. No special effort was devoted to minimizing size and weight of the cells but they were operated at a sufficiently high pressure, 500 p.s.i.g. (35.1 kg./sq. cm.), which would be required in a compact assembly.

Maximum operating life of the cells on this program was found to be between 200 and 300 cycles on a 6-hour regime. This consisted of a 4-hour charge period and a 2-hour discharge period at 25% depth, based on the total weight of the zinc electrode. Zinc penetration was found to be the ultimate cause of failure on those cells with extended operating times.

Statistical analyses revealed that the most important factors affecting cycle life were the type of separator, as well as interactions between the separator and matrix materials. The most promising separator was based on a formulation involving magnesium and chromium (type 4669-31). This gave the best results when used in conjunction with a special matrix based on potassium titinate (RKT/SKT) in 40% KOH electrolyte. Use of anodes containing increased amounts of zinc was found to be very beneficial in extending cycle life.

Overall results of this program were reviewed with the Project Manager at the completion of the technical effort. It was mutually agreed that there were three remaining problem areas which should receive further study before continuing with advanced cell development. The first and perhaps most serious problem is that of evolution and accumulation of hydrogen within the cell. This results in the formation of an explosive H_2-O_2 mixture which is a threat to safety and reliability. Methods of solving the problem are discussed below. Two other problem areas are the zinc electrodes and separators as failure in either one or both of these components ultimately limits cycle life. Either the zinc electrode limits life by losing capacity or the separators limit life by permitting internal short circuits. The best electrodes and separators employed to date permitted effective operation for appreciable operating times of 200 cycles or 1200 hours. This level of performance must be increased even more however to be suitable for synchronous satellites which are expected to function for years instead of months.

The hydrogen problem was studied quite extensively by Astropower Laboratory on an internal program, and it has made significant progress in solving it. We do not believe that hydrogen can be eliminated entirely from this system, but we do believe that it can be kept at a low, safe level at all times.

Our approach involves application of the two techniques, charge control and recombination surfaces. Charge control is used to prevent overcharge and thereby eliminate the hydrogen that is evolved in that process. The quantities of hydrogen involved here are quite appreciable and constitute a major factor in the buildup of concentration of this gas. Our proposed method of charge control is based on a proprietary hydrogen gas sensing element. This gives a strong signal at fast response times when exposed to hydrogen, and it has functioned well in an actual Zn-O_2 cell at elevated pressure. The second approach involves the use of recombination surfaces which consume hydrogen via catalytic recombination with surrounding oxygen. These surfaces, thereby, act as hydrogen "scavengers" or "getters." These could be most effectively incorporated into an actual Zn-O_2 system by application to the inside walls of the O_2 storage vessel. These surfaces are used to consume the small amounts of hydrogen that are normally evolved from zinc electrodes in alkaline systems. We believe that this twofold approach can maintain hydrogen concentration at extremely low levels, well below the explosive limit. This would eliminate explosive hazards, and greatly improve reliability of the system.

INTRODUCTION

The zinc-oxygen (ZnO_2) system is interesting for space applications because of its high theoretical energy density. Primary Zn-O_2 units have received a great deal of attention and have been brought to an advanced state of development (refs. 1, 2). Projected energy outputs of these units are in excess of 100 w. hr./lb. (0.22 kw. hr./kg.). However, secondary or rechargeable Zn-O_2 units have not been carried to this advanced state of development. All prior work with secondary Zn-O_2 systems as well as the work on this program has been concerned only with experimental laboratory cells (ref. 3).

It is not possible to make a reliable estimate of the actual energy density that could be delivered by a secondary $Zn-O_2$ unit. However there is no reason to believe that one cannot develop a secondary $Zn-O_2$ unit which delivers at least a sizeable fraction of the energy output projected for the primary $Zn-O_2$ units. A practical goal might be 50 w. hr./lb. (0.11 kw. hr./kg.). When such a secondary unit is developed and shown to exhibit long cycle life, this will represent an important advance in spacecraft battery technology. This is based on the fact that the only existing long life and reliable spacecraft battery is the nickel-cadmium system. Actual energy densities of this system are relatively low and in the range of 8 to 12 w. hr./lb. (0.018 to 0.025 kw. hr./kg.). In actual spacecraft applications the energy output may be derrated below 8 w. hr./lb. (0.018 kw. hr./kg.) to account for control circuits (ref. 4).

The number of investigations on secondary $Zn-O_2$ systems has been rather limited and developmental progress has been quite slow. One of the major problems has been the lack of an effective separator. Most conventional separator materials are not applicable to this system because they are made from organic materials which can be readily attacked by oxygen, especially at the high pressures required in this system. A prime requirement is, therefore, a separator material that is inert to high pressure oxygen.

Astropower Laboratory believed that it could make a significant contribution in this area by application of its "Astroset" separators. These are made from inorganic materials that are inert to oxygen under all conditions. These separators have been used quite extensively in AgO-Zn cells and have proven quite effective, especially for high temperature environments. Application of these separators to $Zn-O_2$ cells appeared quite logical. Therefore, Astropower Laboratory set out to establish this point on an internal program. Preliminary results of this investigation were encouraging and provided the basis for the present program.

The purpose of the current effort was to determine the most important factors that affect cycle life of the $Zn-O_2$ system, and to establish the upper limits of cycle life with the most promising candidate materials and construction. These objectives were to be accomplished by fabricating and testing experimental $Zn-O_2$ cells. No special effort was to be devoted to minimizing size and weight of experimental cells, as this could be done more effectively on future scaled-up systems. However, an important restriction was that the tests be carried out under a high pressure oxygen environment, because this would be essential for practical cells. Figure 1 indicates that the $Zn-O_2$ system must employ a pressure of at least 200 p.s.i.g. (14.1 kg./sq. cm.) before it is competitive with the Ni-Cd system on a volumetric energy density basis. Furthermore, the $Zn-O_2$ system must employ a pressure of at least 500 p.s.i.g. (35.1 kg./sq. cm.) before it is competitive with the most compact of all existing systems, the AgO-Zn system. Therefore, it was decided that the cells should be run at 500 p.s.i.g. (35.1 kg./sq. cm.) on this program.

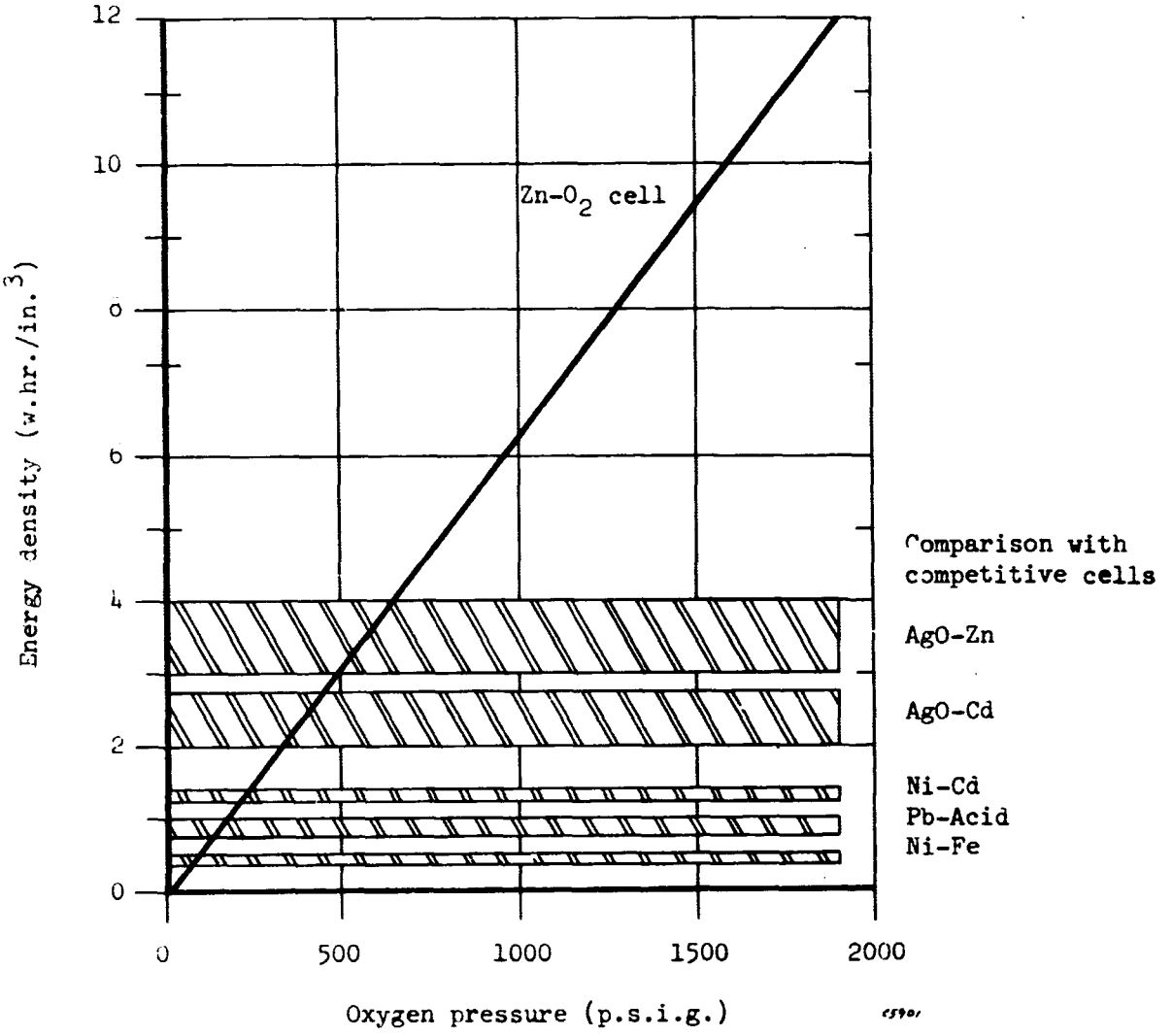


Figure 1. - Pressure vs. Volumetric Energy Density - Zn-O_2 System

WORK PERFORMED

Results and discussion of all work performed on the contract are presented here. These results are organized and presented in accordance with the program tasks given in the original work statement.

Task 1; Basic Cell Design

The object of this phase of the program was to design and fabricate suitable test rigs for the experimental cells. These rigs were to contain all the components necessary for operating the experimental cells in the completely rechargeable manner and in the completely sealed condition. Results of this study are shown in figures 2 through 4 and are discussed below.

Figures 2 and 3 show the test cell body and cover designed to contain the cell assemblies. These parts were machined from Type 316 stainless steel bar stock. The cover was secured to the body with eight equally spaced bolts. The top of the body was machined to accommodate an O-ring for sealing. A Viton O-ring was selected because this is one of the few elastic materials that is stable in the highly corrosive alkaline environment. The cover had two parts to accommodate electrical feed-through terminals. These terminals contained a ceramic insulator and were cemented to the lids with epoxy as shown in figure 4. The terminals, as well as the O-ring described above, proved to be quite reliable and leak free at the 500 p.s.i.g. (35.1 kg./sq. cm.). The cover was also machined to accommodate two Swagelock fittings. These were identical and were connected to a section of 1/8" stainless steel tubing used to flush and fill the assembly with O_2 at the start of each test. These fittings proved reliable and leak free at 500 p.s.i.g. (35.1 kg./sq. cm.) when their threaded ends were wrapped with Teflon tape sealant. Twenty of these body and cover assemblies were fabricated and used throughout the program. The inner walls were coated with a 10 mil. (0.025 cm.) layer of Teflon before initiating the life tests. This prevented accidental shorts and possible electrolysis of water.

Initial program plans called for operating the cells at three different pressures, 50, 100, and 500 p.s.i.g. (3.5, 7.0, and 35.1 kg./cm. sq.). These were to be the maximum pressures attained inside the body at the end of a charge period, with atmospheric starting pressure at the beginning of charge (or end of discharge). In other words, the oxygen pressure was to increase linearly with time from zero to the preset maximum pressure during the charge period and was to decrease linearly with time from the maximum to atmospheric pressure during the discharge period. In a similar manner, the pressure in such an assembly varies with constant current cycling and with no side reactions.

It was initially planned that this operation be achieved by adjusting internal volume of the body assembly with shims. These were Lucite discs with a variety of thicknesses and with slightly smaller diameter than that of the body. A sufficient number of these shims were to be added in each test setup to give the desired pressure, as calculated by the perfect gas law and the electrochemical equivalent of oxygen.

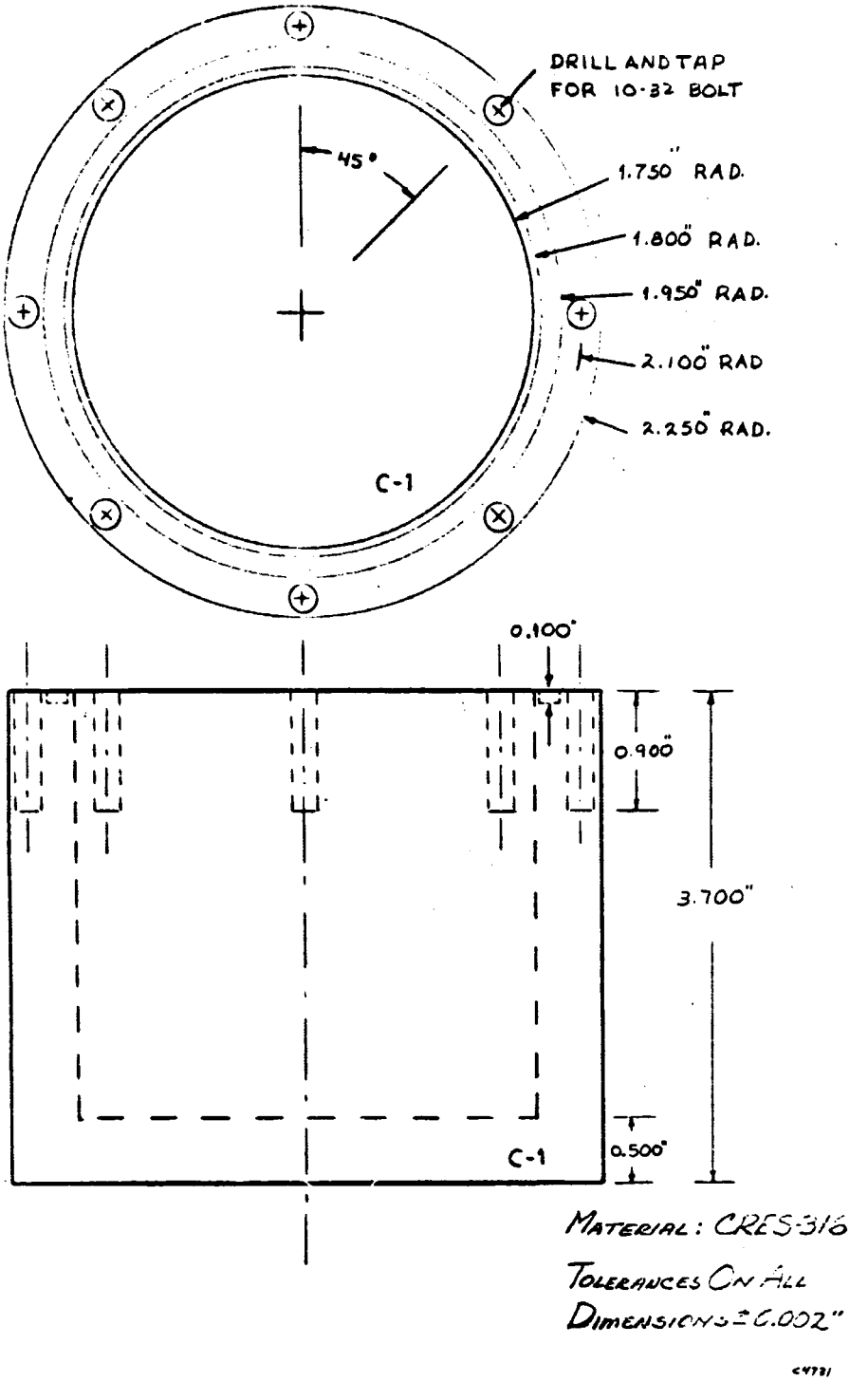


Figure 2. - Test Cell Body

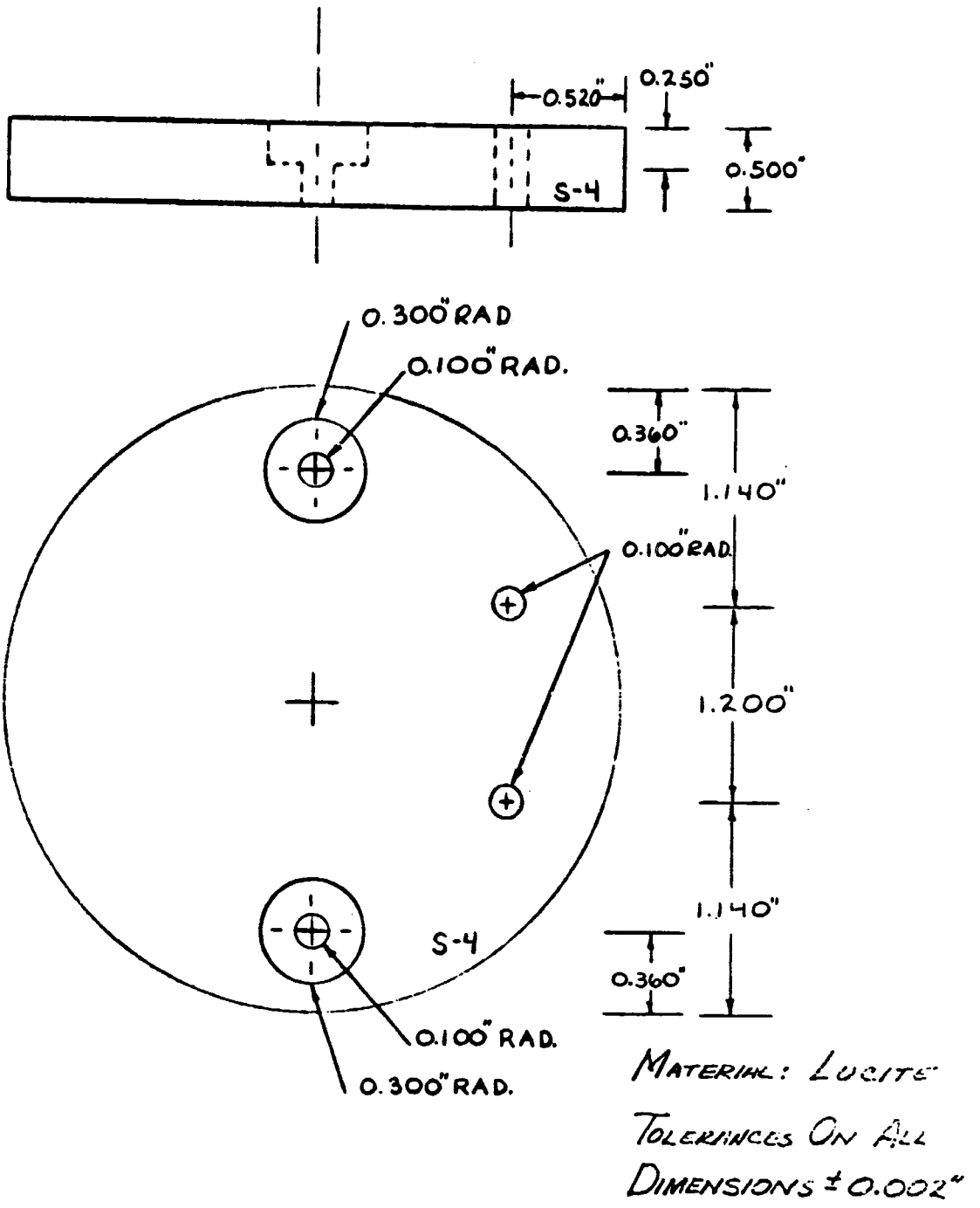


Figure 3. - Cell Case Cover

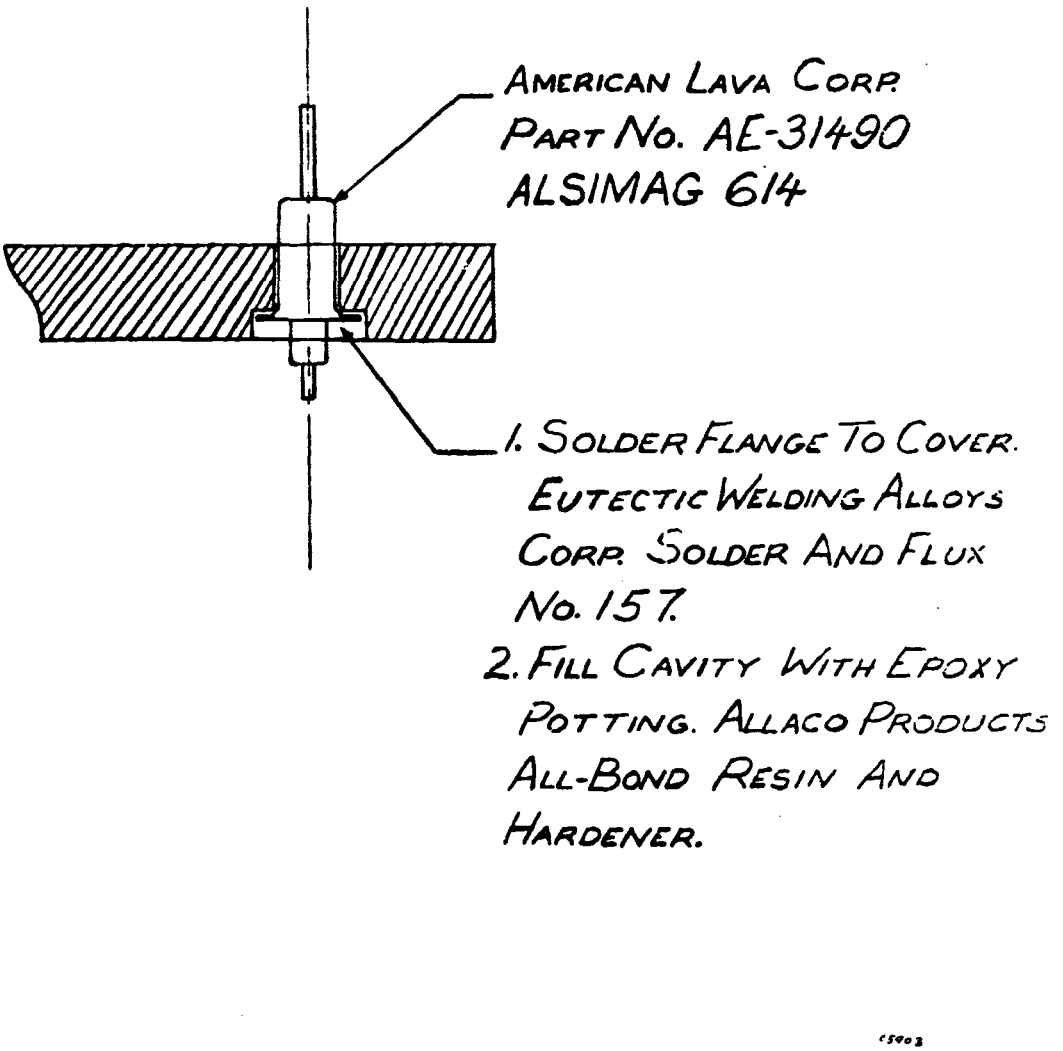


Figure 4. - Feed Through Terminal

This mode of adjusting pressures was abandoned shortly after beginning the experimental program when it was decided to operate at the 500 p.s.i.g. (35.1 kg./cm. sq.) level. It was decided that the shims be eliminated and the pressure adjusted by the initial oxygen fill. This was to be carried out by installing the $Zn-O_2$ cell in the test cell body and pressurizing with oxygen to such a level that pressure would reach 500 p.s.i.g. (35.1 kg./cm. sq.) at the end of charge.

Details of the $Zn-O_2$ case assembly are shown in figures 5 through 9. This assembly was designed to accommodate a range of anode-matrix thicknesses, as required in the work statement. Lucite was selected as the construction material for the initial tests, but this was later changed to "Kel-F" to avoid use of combustible materials. The assembly consisted of three major parts — left and right-hand case halves and the frame-spacer. The frame-spacer was designed to position the anode assembly and contained a small hole in its top through which the anode lead was passed. The case halves were made with one recessed surface which contained a series of holes, as shown in figures 6 and 7. These holes provided a path for transporting oxygen to the cathodes. Pack tightness or thickness of the assembly was varied by inserting a number of shims inside the recessed areas of the case halves. These shims were made of Teflon and were drilled with the same hole pattern as the case halves. A layer of screen was also used in the recessed area of each cell half between the Teflon shims and the cathode. These served to stiffen the electrode and to distribute the oxygen over the surface of the cathodes as it entered from the inlet holes. Vexar (polypropylene) was used initially as the screen material, but this was later changed to nickel Distex.

Four through holes were drilled in the corners of each of the cell halves and also the frame spacer. The assembly was held together by screws and nuts.

The two cathode terminals were twisted together to form a single cathode lead. Short segments of thin Teflon tubing were passed over both the anode and cathode leads to prevent accidental shorting between the two or between either one and the metal body. These leads were soldered to the feed through terminals of the cover with indium alloy solder. External ends of the feed through terminals were clearly and appropriately marked "Positive" and "Negative" to avoid possible errors in electrical hook-up.

Task 2; Single Cell Performance Tests

This task was subdivided into parts consisting of single cell construction and performance tests and single cell life tests. The former were designed to determine the most promising cell configurations and were to be of relatively short duration. However, to obtain the most meaningful data all cells were cycled to failure. The latter were designed to determine the most significant factors that effect cycle life and to determine the upper limits of cycle life for this system. The life tests were to use the most promising configurations that were determined from the construction and performance tests and were to be carried out in accordance with a full or fractional factorial experimental design.

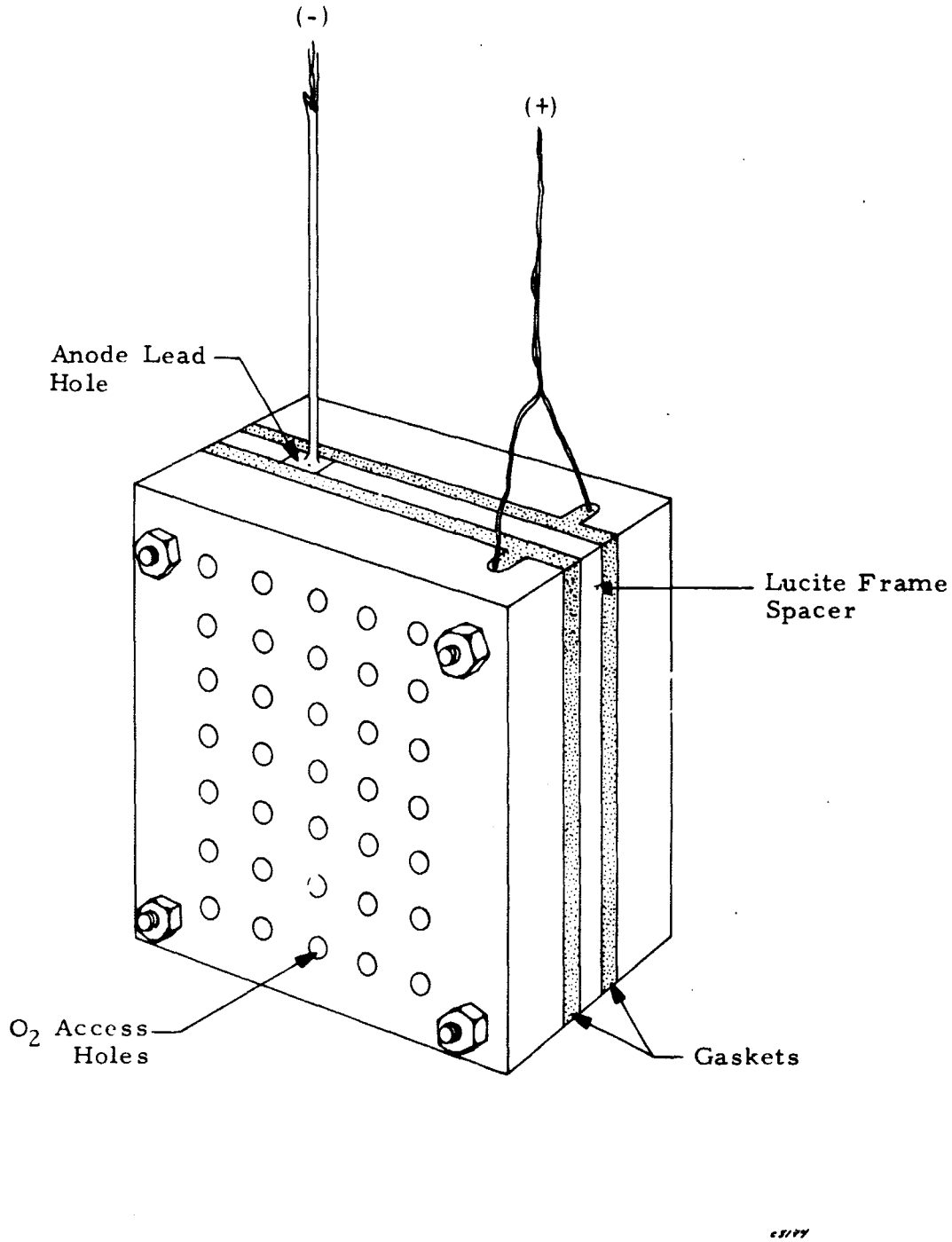


Figure 5. - Sealed-Frame Zn-O_2 Cell Design

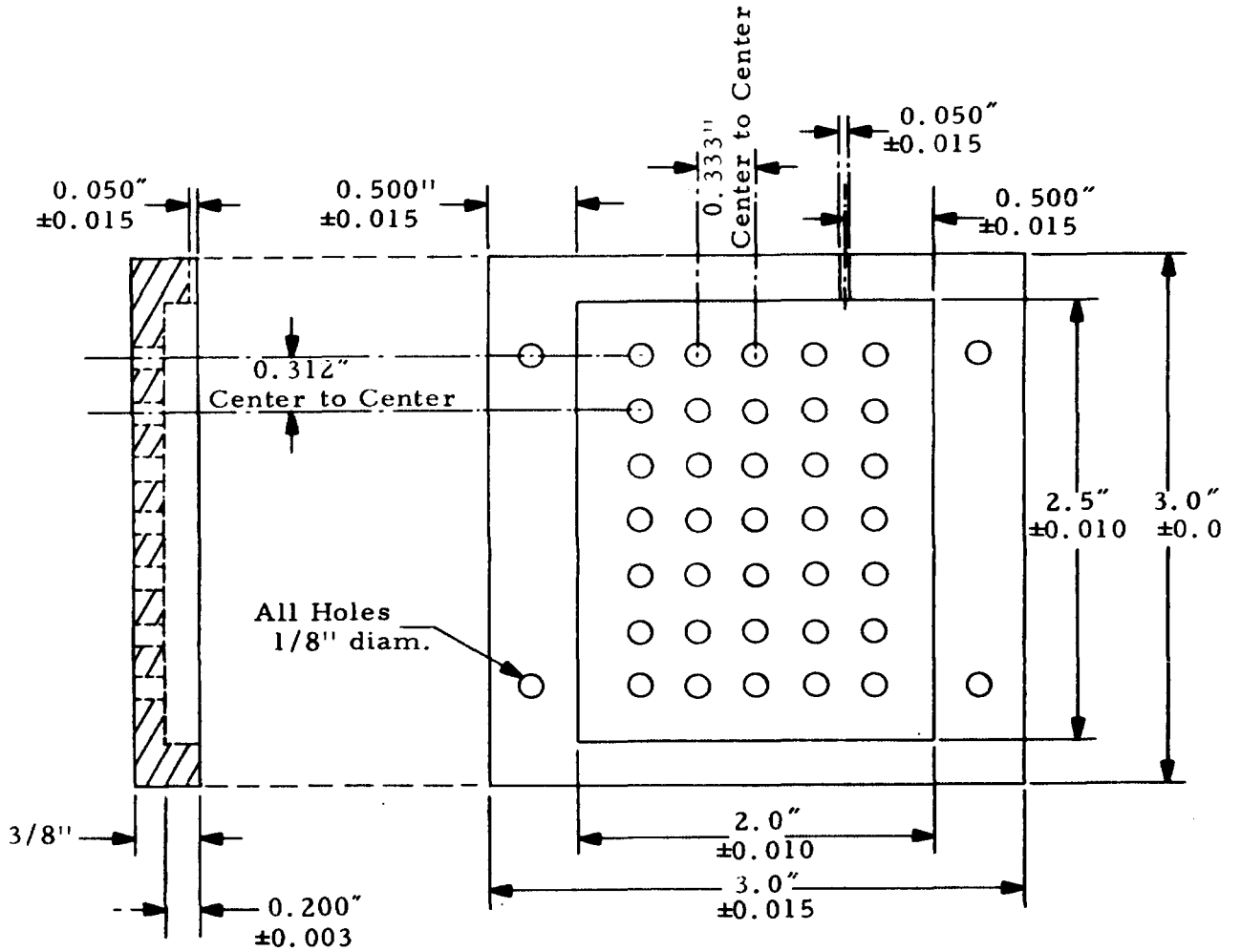


Figure 6. - Left Case Half

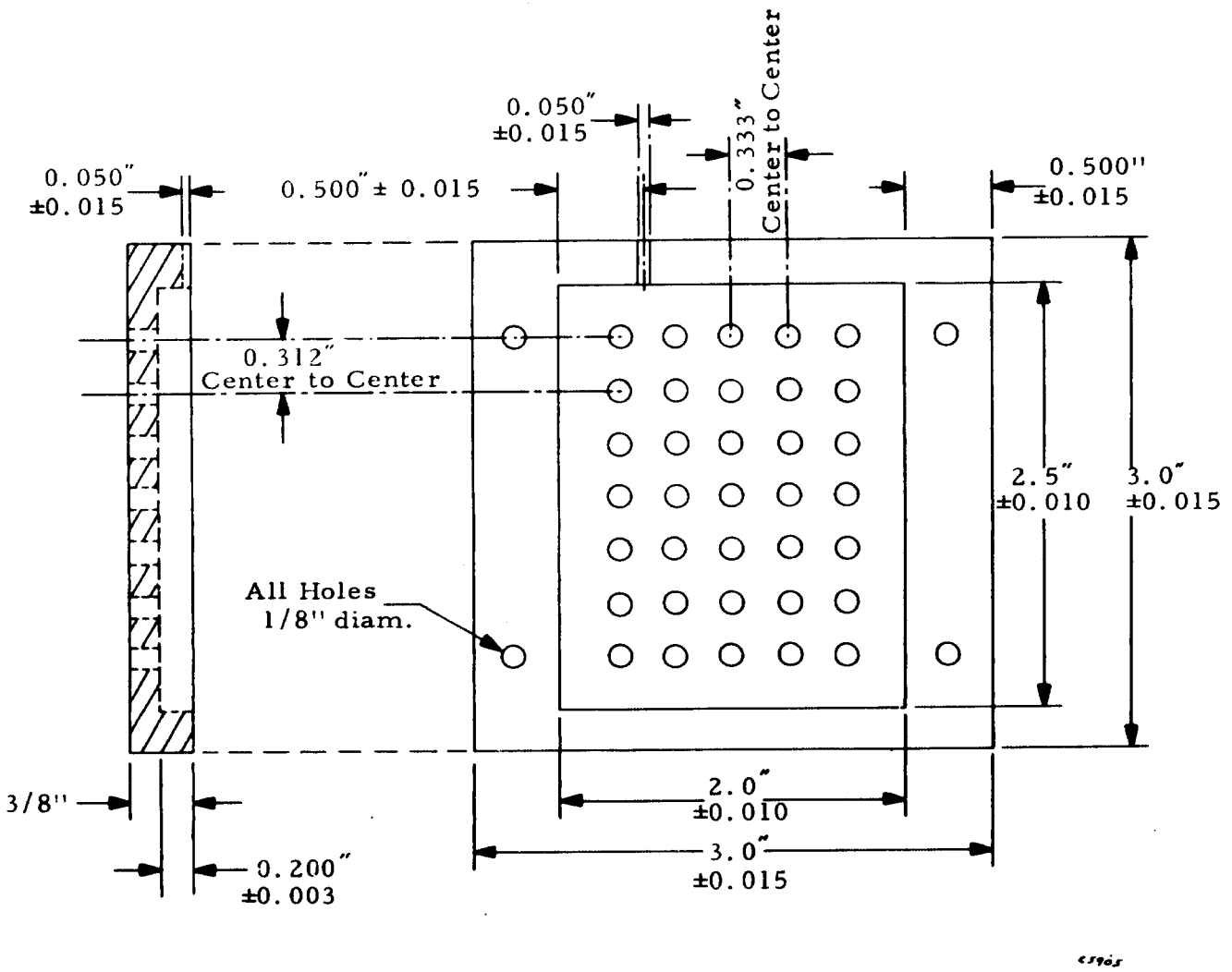


Figure 7. - Right Case Half

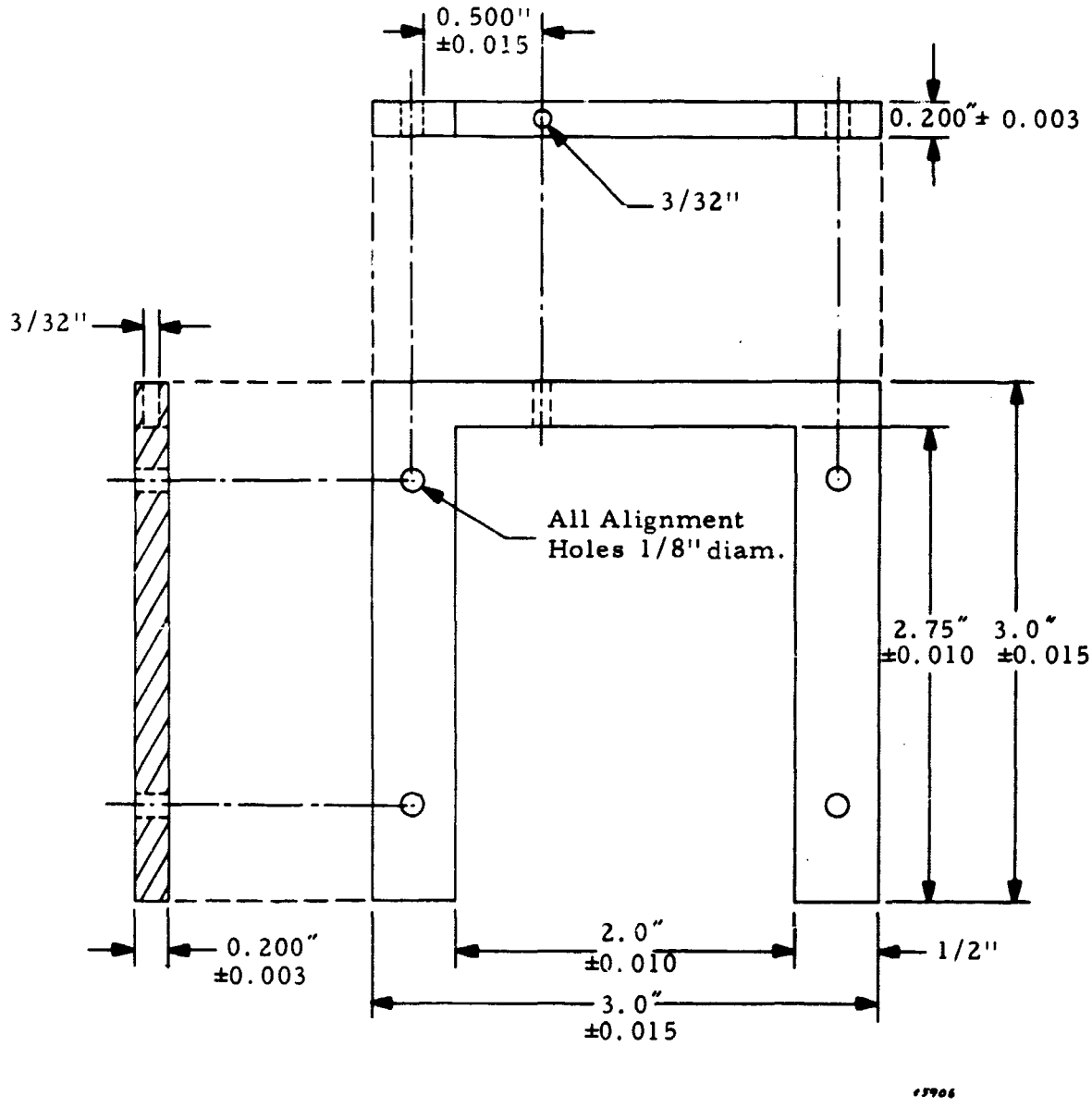


Figure 8. - Frame Spacer

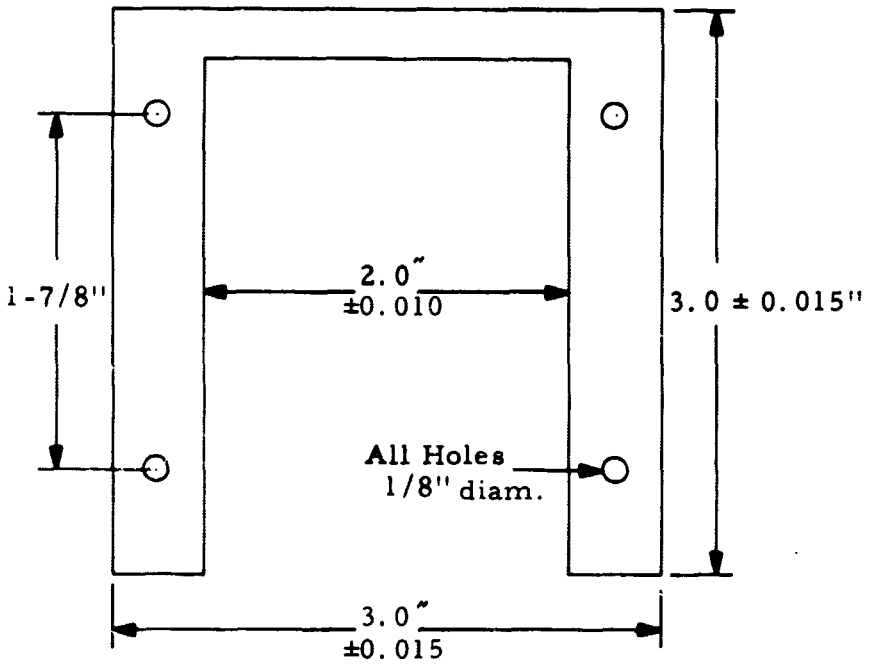


Figure 9. - Gasket

Single Cell Construction and Performance Tests

A total of 175 cells were built and tested under this phase of the program. Each of these was designed to test the effect of one or more constructional or operational variables on performance. These variables included such items as the type of separator, the type and amount of matrix materials, the method for maintaining a moisture balance, etc. A tabulation of these tests is given in the appendix.

Oxygen Cathodes. - Only one type of oxygen cathode was used on this program. This was American Cyanamid Type AB-6 Fuel Cell Electrode. Original program plans had called for evaluation of two other types of oxygen cathodes but these tests were abandoned later in the program in lieu of additional work.

The AB-6 material was received in the form of a square sheet, with length and width of 12 in. (30.5 cm.) and thickness of 0.010 in. (0.025 cm.). This was cut into rectangular pieces with dimension of 1.9 in. x 2.1 in. (4.9 cm. x 5.3 cm.). Two of these pieces were used in each cell with one on each side of the anode assembly (see fig. 10). With one exception regarding the method of current collection (see below), there were no variations in the cathode throughout this phase or in the life tests.

It should be pointed out that these electrodes served the dual function as cathodes during discharge and as anodes during charge. No auxiliary or charging electrodes were used in any of the cells. Use of auxiliary electrodes has been proposed by other investigators because they noted a degradation in the activity of the catalytic electrodes for reducing oxygen after they had been used for extended periods on charge (ref. 3). This type of degradation was not noted on any of the cells in this program, at least for the indicated operating times which extended beyond 1200 hours.

Cathode Current Collectors. - The original method of collecting current from the cathodes was to use metal grids located behind each of the AB-6 electrodes. These collectors were in firm contact with the cathodes, and were held in place by the pressure exerted between the cell half-cases. Wires were spot welded to the corners of these screens and were taken out the top for external electrical contact. This arrangement was found to provide adequate current collection for all of the initial test cells in this phase. Internal resistances of the cells were not measured during this time but the actual values must have been quite low. This was evidenced by the relatively low charge voltages and high discharge voltage and the slope of the E/I curve. Therefore, the method of current collection did not contribute any excessive IR drop with corresponding loss in efficiency.

The method of current collection was modified slightly at the end of this phase. The purpose of this change was not necessarily to improve electrochemical performance but rather to improve reliability. The metal grids were changed to gold plated nickel screen 60 mesh, made from 0.0045 in. (0.0114 cm.) diam. wire. The screen was plated with gold to a thickness of 100 microinch (2.54×10^{-4} cm.) to prevent corrosion. Gold-plated nickel wires, 0.020 in.

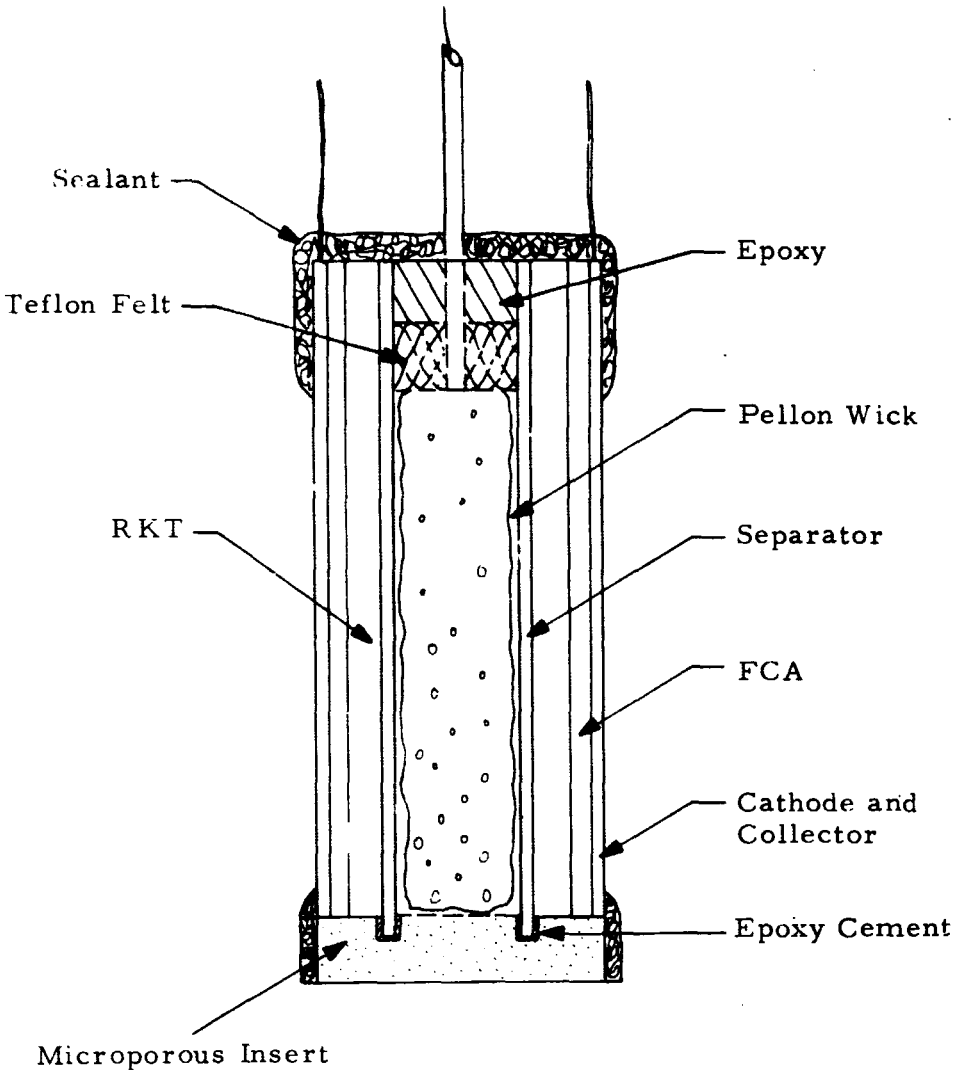


Figure 10. - Electrode Assembly

(0.051 cm.) diam. with 100 microinch (2.54×10^{-4} cm.) of gold, were spot welded to these screens for external electrical contact. In addition to the above, lead wires were spot welded directly to the AB-6 electrodes and were taken out with the other wires for external electrical contact. These wires were gold-plated nickel, and were spot welded along two edges of the AB-6 electrodes.

It was anticipated that these changes would provide for more positive uniform, electrical contacts than the single metal grids described earlier. This would avoid uneven current distribution and resultant local hot spots that could occur at the point contacts of single grids. These hot spots may have played a part in one or more of the explosions as an ignition source.

This method of current collection proved to be effective from an electrical point of view. Total internal cell resistances were generally well below 0.1 ohm with these collectors. A few cells that used these collectors did explode. This collector therefore did not eliminate all possible sources of ignition. Use of these collectors could, and probably did prevent additional explosions, aside from those noted later.

Electrode Stiffeners and Gas Distributors. - The AB-6 electrode material is a very thin and flexible material and offers very little mechanical strength. If employed directly in a cell without support, it could readily become bent and wrinkled. For this reason it was necessary to employ some type of electrode stiffeners. In addition to providing electrode support the candidate material must also provide for effective gas distribution acorss the surface of the electrode. This required use of porous materials. Other requirements were that the material be stable in an oxygen environment and be thin and lightweight in order to minimize size and weight of the complete assembly.

The first material to be examined for this application was Armalon Felt. This material is made from fluorocarbon fibers and was obtained from E. I. DuPont de Nemours & Co. It was cut into strips and placed behind the oxygen current collectors. It was anticipated that the material would be sufficiently stable and porous for this application and would keep the electrodes flat in conjunction with pressure applied from the case halves. The material met most of the above requirements but was apparently not stiff enough for this application. This was evidenced by the warped electrodes which were found in cells that employed this material.

The second material to be evaluated for this purpose was Vexar mesh. This was made from polypropylene and was obtained from E. I. Dupont de Nemours & Co. It was sufficiently stiff to provide uniform pressure over the entire electrode surface. Moreover, it had a very open structure and provided little resistance to oxygen flow. Electrical performance of several cells which employed Vexar appeared promising. However, Vexar was abandoned because it was readily ignited in a high pressure oxygen environment. This was evident from examination of the components of cells which had exploded. The Vexar may not necessarily have initiated these explosions, but it undoubtedly contributed a great deal to the explosive force. This was deemed sufficient to rule out its use in this application.

The third and final material evaluated for this application was Distex. This was a new grid type material from Exmet Corporation, Bridgeport, Conn. and was designated as type 5Ni30-1/0. It was made from pure nickel in the form of an open screen with 0.060 in. (0.152 cm.) thickness. After receipt, it was plated with 100 microinch (2.54×10^{-4} cm.) of gold. The purose of the gold was to prevent corrosion as in the case of the nickel screen and wires described earlier. This material met all of the required specifications for a noncombustible stiffener and gas distributer.

Anodes. - Flat plate anodes were used throughout this program. With a few exceptions, these contained 7 g. of an active ZnO-HgO mix in the proportion of 98 g. ZnO and 2 g. HgO. The mix was evenly distributed on both sides of a silver grid with dimensions of 1.9 in. x 2.1 in. (4.84 cm. x 5.34 cm.). This was then pressed to a total thickness of 0.060 in. (0.152 cm.). The grid was Exmet type 3 Ag 10-3/0 and contained three 7 in. (17.8 cm.) lead-wires spot welded to one corner. A piece of KT paper with the same length and width as above and with thickness of 0.20 in. (0.508 cm.) was then pressed onto each surface of the anode.

The higher weight anodes were prepared in a similar manner except that the weight of mix was 6 g. Overall length and width of the electrode were the same and thickness was increased to 0.067 in. (1.7 cm.) to maintain the same packing density.

Ion Transport Matrices. - The Zn-O_2 cell employed on this program did not contain free electrolyte between its plates as do most types of batteries. Instead, the cell employed an immobilized electrolyte between its plates as found in some fuel cells and a few types of batteries. Examples of cells with this type of electrolyte containment are a regenerative hydrogen-oxygen fuel cell (ref. 5), and sintered plate type nickel-cadmium cells (ref. 4). In these cases the electrolyte is held by capillary forces in the matrix between anode and cathode. This matrix has been labeled the ion transport matrix (or ITM), since it serves as a medium through which the ions of the electrolyte may migrate. This approach for fuel cells and hybrid metal-air/O_2 cells avoids the problem of electrode flooding which is associated with the cells containing free electrolyte. Moreover, the use of the matrix permits gravity-free operation, since all liquid is held by capillary forces. This is essential for space applications.

Several materials were examined for use as ion transport matrices in this phase of the program. These consisted of Pellon, fuel cell asbestos, potassium titinate, and a specially processed form of potassium titinate. All but the last of these materials was commercially available, and all of these, including the special form of KT, were characterized by being highly absorbent materials stable in a KOH environment.

Pellon was one of the first materials to be examined. This is supplied by the industrial division of Pellon Corporation, Lowell, Mass. as nonwoven polyamide fibers. The material has been successfully employed as a separator in AgO-Zn cells and Ni-Cd cells (ref. 4). Two stock sizes were available with thicknesses of six and ten mils. The former was designated as P-6 and the latter as P-10. Pellon Corporation designated these as types 2505 ML and 2505 K

respectively. Pellon was abandoned after noting that it contained leachable organic impurities. This was pointed out on another program (ref. 6) where it was found that some lots of the material contained small amounts of wetting agents used in the manufacturing process. Although the presence of this impurity could not be rigorously proven for all batches of Pellon, the possibility of its occurrence was sufficient to rule it out as a candidate matrix material.

Potassium titinate was an effective ion transport matrix and was used quite extensively on this program. This material in fibrous form, made by E. I. DuPont de Nemours & Co., was processed in paper form by Hurlbut Paper Co., Div. of Mead Corp., South Lee, Mass. The material is referred to as "RKT" in this report. Only one thickness (0.02 in.) was available.

Early in the test program, it was found that improved cycle life could be obtained by incorporating a layer of RKT inside the anode compartment. The RKT was sandwiched firmly between the anode and the adjacent separator. Two such layers were employed for each anode with one on each face as shown in figure 10.

RKT was effective as an ITM outside the anode assembly (between the separator and oxygen electrodes). Multiple layers of it appeared more promising than one layer in regard to cycle life. Combinations of RKT with other matrix materials also appeared promising.

Although RKT was a promising matrix material early in the program, it was thought advisable to examine other candidate materials for two reasons. First, the RKT was quite fragile and could be torn readily. Second, the RKT was only produced in one thickness, which limited design freedom.

In order to improve the properties of the existing RKT material Astropower undertook an investigation of it under an internal program. This study resulted in an improved type of semiflexible film matrix based on the original KT. The resultant film is referred to as "special potassium titinate" or "SKT" in this report.

The potential of SKT was recognized early in the test program and the project officer gave his approval for its incorporation in experimental cells. Initial results appeared very promising in regard to cycle life and also ease of assembly. The SKT was used in a manner similar to the regular KT. It was cut into rectangular pieces and installed between the separators and cathodes on both sides of the anode assembly. Once again it was found that multiple layers of SKT as well as combinations of SKT with other matrices gave promising results for extended cycle life. These possibilities were explored in subsequent tests. The SKT had a resistance slightly higher than KT paper. However, the additional IR drop never exceeded 50 mv. under the most adverse operating conditions. The added resistance of this material was undesirable, but it was by no means a major limitation.

The last material to be examined as a matrix was fuel cell asbestos. This is made by Johns Manville in the form of a mat with a wide range of available

thicknesses. It is made from pure asbestos fiber without any binders. The thickness employed on this program was 0.011 in. (0.028 cm.). This material is referred to as "FCA" in this report.

The FCA was also a good ion transport matrix. It absorbed large quantities of KOH, which resulted in low cell resistances and appeared suitable for extended operation. Most important it appeared that FCA served well when used in conjunction with one of the RKT materials described above. When employed in this manner the FCA was located on the outside layers adjacent to the cathodes while the RKT layers were located on the inside between the FCA matrices and the separators. This arrangement is shown in figure 10.

Separators. - Original program plans specified a maximum of three types of separators to be evaluated in conjunction with the $Zn-O_2$ cells on this program. Two of these were to be proprietary Astroset separators as approved by the project monitor and one was to be a commercially available material. These plans were revised somewhat during the course of the program and resulted in evaluation of a few more separators than were originally planned. This additional work was considered a worthwhile trade off for other scheduled work.

Initial consideration was given to use of a material from Southwest Research Institute as the commercial separator. This was their radiation grafted separator, type SWRI-GX. However, use of this material was abandoned in a Technical Direction which specified an alternate from RAI Research Corporation designated as type "RAI-1770-C." This was described as a cross-linked, low density, polyethylene-acrylic acid graft material. Evaluation of this material was rather short lived because it was subsequently discovered to be a potential safety hazard for this system. This followed from the fact that one of the first cells to use this material exploded during initial oxygen filling. For this reason it was mutually decided to discontinue use of this material.

Aside from these initial tests with the RAI material, all other tests used the proprietary Astroset separators. Altogether, a total of five different types were examined on this program. All of these were similar, in that they consisted of an inorganic substrate that was coated with an inorganic film. The substrate was the same in each case but the films were made of different materials. Two of these separators had been employed on both CRAD and IRAD programs dealing with AgO-Zn and $Zn-O_2$ (ref. 6). The remaining three had been used only on an IRAD program for $Zn-O_2$ cells. Properties of these separators and preliminary evaluation of their merits for the $Zn-O_2$ system are discussed below.

Separator type 3420-09 was used quite extensively in the early stages of this program. The material itself was found to have acceptable properties as shown in Table I. Performance of the separator in actual $Zn-O_2$ cells also appeared promising. Its contribution to internal resistance was not excessive, as evidenced by the fact that cells which employed it exhibited relatively low charge voltages (1.9 to 2.1 volts) and high discharge voltages (1.2 to 1.3 volts) in the early stages of cycling. The separator also appeared to resist zinc penetration and permit extended cycle life. This was evidenced by the fact that the cell which operated the longest at this early stage (243 cycles on a 2 x 4 hr. regime) employed this type of separator. Even though these early

TABLE I. - PHYSICAL PROPERTIES OF SEPARATORS

Description	Resistivity (ohm.-cm.)		Zn penetration rate (hrs./mil.) [hrs./cm.]		% weight loss after 24 hours in 30% KOH — 100°C (ceramic material only)	Pore volume (cc./g.)
	30%	45%	30%	45%		
Flexible 3420-009	0.3	12.0	(0.15) [5.90]	(0.19) [7.50]		
Flexible 3420-25	7.0	11.0	(0.18) [7.10]	(0.17) [6.70]	2.0%	0.44
Flexible 4669-31	7.3	9.0	(0.12) [4.60]	(0.11) [4.30]	27% wt. gain	0.45
Flexible original 036-011	8.7	9.4	(0.10) [3.90]	(0.09) [3.50]	21%	0.47
Flexible modified 036-011	6.5	7.2	(0.07) [2.80]	(0.10) [2.90]	29.5%	0.54

results appeared promising, the use of this material was abandoned later on in the program. The reason for this decision was not based on any of the above results but rather on independent studies of this material on another program (ref. 5). Here it was found that a related type of separator was found to cause gassing (hydrogen evolution) in AgO-Zn cells. This separator was the rigid form of the 3420-09 and contained the same type of ceramic component that was used in the semi-flexible type. The gassing was subsequently found to be caused by a component in the ceramic which formed a local couple with the zinc electrode. It was reasonable to assume that the same ceramic in the semi-flexible material could also cause hydrogen evolution in a $Zn-O_2$ cell. Although this point was not rigorously demonstrated it was deemed important enough, for safety reasons, to rule out the use of this separator. No further tests were carried out with this material in the following test study.

Separator type 3420-25, based on entirely different ceramic components, was also used quite extensively in the early stages of this program as well as on several of the life tests. Physical properties of the material itself appeared quite suitable for this application and comparable to those of type 3420-09 as shown in Table I. Cell test results indicated good electrochemical performance of this separator at least in the early stages of cycling as with type 3420-09. Finally, since the material presented no gassing problem, it was selected as one of the separators for the life test cells.

Separator type 4669-31 was found to be one of the most pormising materials for $Zn-O_2$ cells on an internal program. This was based on yet another ceramic composition. Physical properties of the material were found to be quite similar to types 3420-09 and 3420-25 at least in regard to conductivity and zinc penetration. The compatibility test of this material with KOH gave a positive gain in weight as indicated in Table I. In the case of the 4669-31 material, the KOH probably reacts with one or more of the components and forms an insoluble species which stays as a part of the structure. This phenomena is not necessarily undesirable except that one might speculate that it could adversely affect the pore structure. However, this was obviously not the case as there was little change in conductivity (which is directly related to pore properties) of cells with these separators for extended periods. In accordance with a request from the Technical Monitor a special test was carried out on this material to examine its gassing characteristics. This involved periodic sampling and analysis of gases from a continuously cycling cell containing this separator. Results indicated less than 0.006% wt. % H_2 (0.096 vol. %) after 20 and 50 cycles. This result was deemed sufficient to establish that type 4669-31 separator did not cause an appreciable hydrogen problem in this cell. With approval of the Technical Monitor it was therefore decided to employ the 4669-31 material as the second type of separator instead of the 3420-09 material.

Two other types of separators were evaluated on this program. These are designated as "Original Type 036-011" and "Modified Type 036-011." Although these were not actually employed in this phase of the program they are discussed here for the sake of organization. Both of these separators were of the flexible type as the others described above and both employed the same

substrate as the others. Their films contained some clay-type materials. The original and the modified types both contained the same chemical species but differed from one another in the ratios of their species. The modified type was formulated so as to contain less of a leachable component and was thereby anticipated to have more stable properties.

The reason for selecting these types of separators was based on the results of prior programs that Astropower Laboratory carried out for NASA/Lewis Research Center (refs. 7, 8). Here it was found that the rigid form of the 036-011 material was very effective as a separator for AgO-Zn cells. The rigid form appeared to hold up well and prevent shortening in these cells for extended periods even at elevated temperatures. It was reasoned therefore that the flexible form might be equally effective for the $Zn-O_2$ cell of this program.

Resistivities of these separators was found to be quite comparable to the others and were in the range of 6 to 9 ohm-cm. as shown in Table I. Zinc penetration resistances of these separators were also quite comparable to the others and in the range of 0.07 to 0.10 hrs./mil. (27.5 to 39.4 hrs./cm.). Although these preliminary test results on the 036-011 separators suggested that they should perform as well as the above separators, this was not confirmed in subsequent cycle tests as described below. Apparently there were other factors which limited life of cells with 036-011 separators. Compatibility tests with KOH indicated an appreciable loss in weight of both the original and modified. This was not as anticipated especially in the case of the modified type which supposedly contained less leachables. The most likely explanation for this was in the processing of this material. Apparently the formulation was not fired to a high enough temperature to cause the desired reaction. No attempts were made to improve this material because of lack of time and funds.

Samples of each of the materials were sent to the American Instrument Company, Silver Springs, Maryland, for determination of porosity and pore size distribution by the mercury intrusion method. Porosities of all of the separators were found to be very close and in the range of 0.44 to 0.54 cc./g. See Table I. Pore size distribution characteristics of all the separators were also found to be quite similar. These are shown in figure 11 through 14. Each of the separators was found to have a small but finite fraction of pores with diameters from 0.01 to 0.1 microns and from 10 to 100 microns. In all cases, however, the majority of the pores had diameters within the range of 0.1 to 1.0 microns. It seems that the pores larger than 1 micron are associated with the substrate, and that the finer pores are principally associated with the coating. Original test data are given in the appendix.

Wicks. - Early in this phase of the program it was apparent that drying of the anode was a serious problem and one which limited cycle life. This was evident from inspection of several cells which had failed after only a few cycles. Anodes of these cells were noted to be very dry and quite hard. Moreover, it was found that these cells could be restored essentially to their original condition by reactivating them in KOH and giving them another formation charge.

Cat. No. 5-7135

POROSITY DETERMINATION

(By 5-7107 or 5-7108 Aminco—Winslow Porosimeter)

DATE September 9, 1969

SAMPLE # 3420-25 Paper Measured Pore Volume: 0.44 cc/g.

WT. OF SAMPLE, G. 0.3048

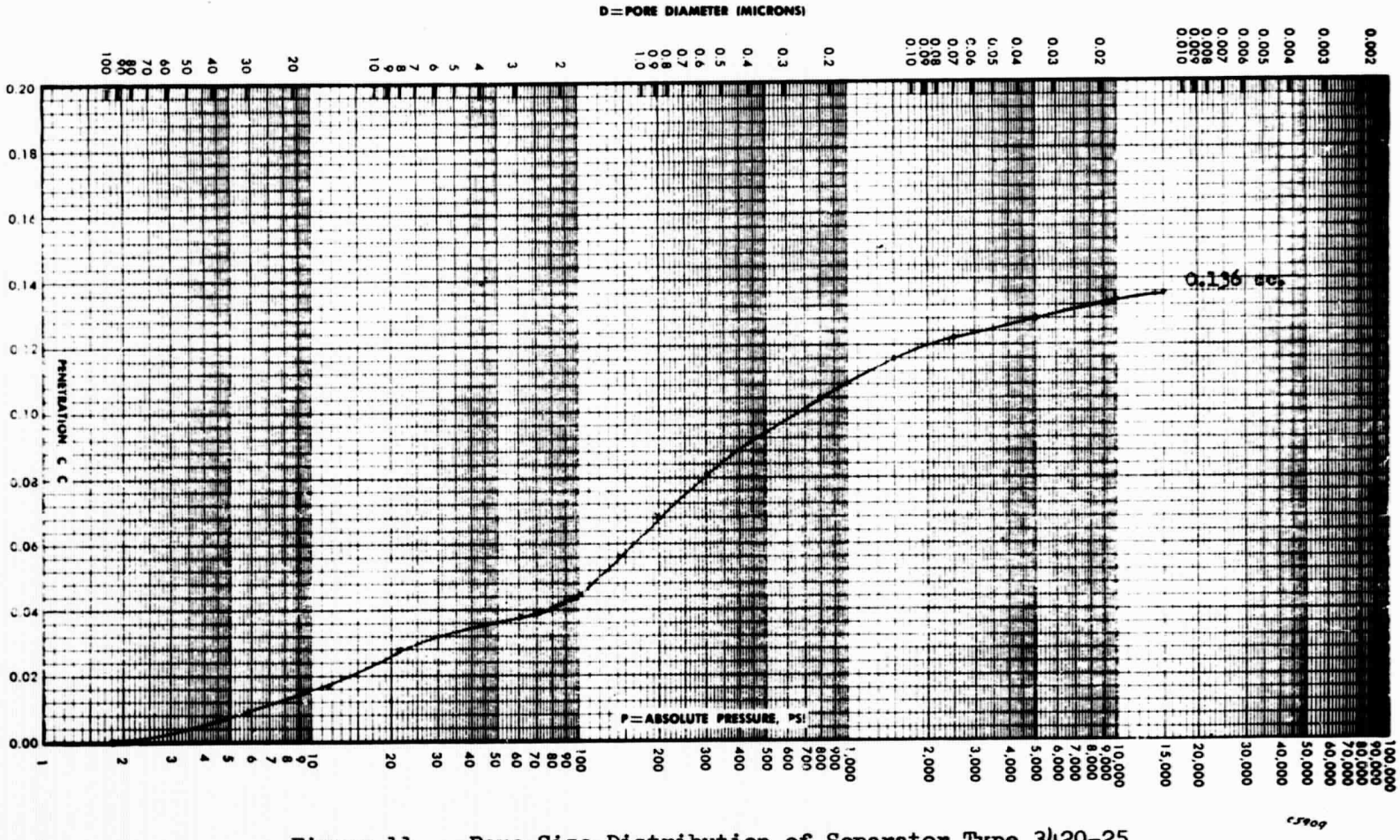


Figure 11. - Pore Size Distribution of Separator Type 3420-25

Cat. No. 5-7135

POROSITY DETERMINATION

(By 5-7107 or 5-7108 Aminco—Winslow Porosimeter)

DATE September 9, 1969

SAMPLE # 4669-31 Paper Measured Pore Volume: 0.45 cc/g.

WT. OF SAMPLE, G. 0.3306

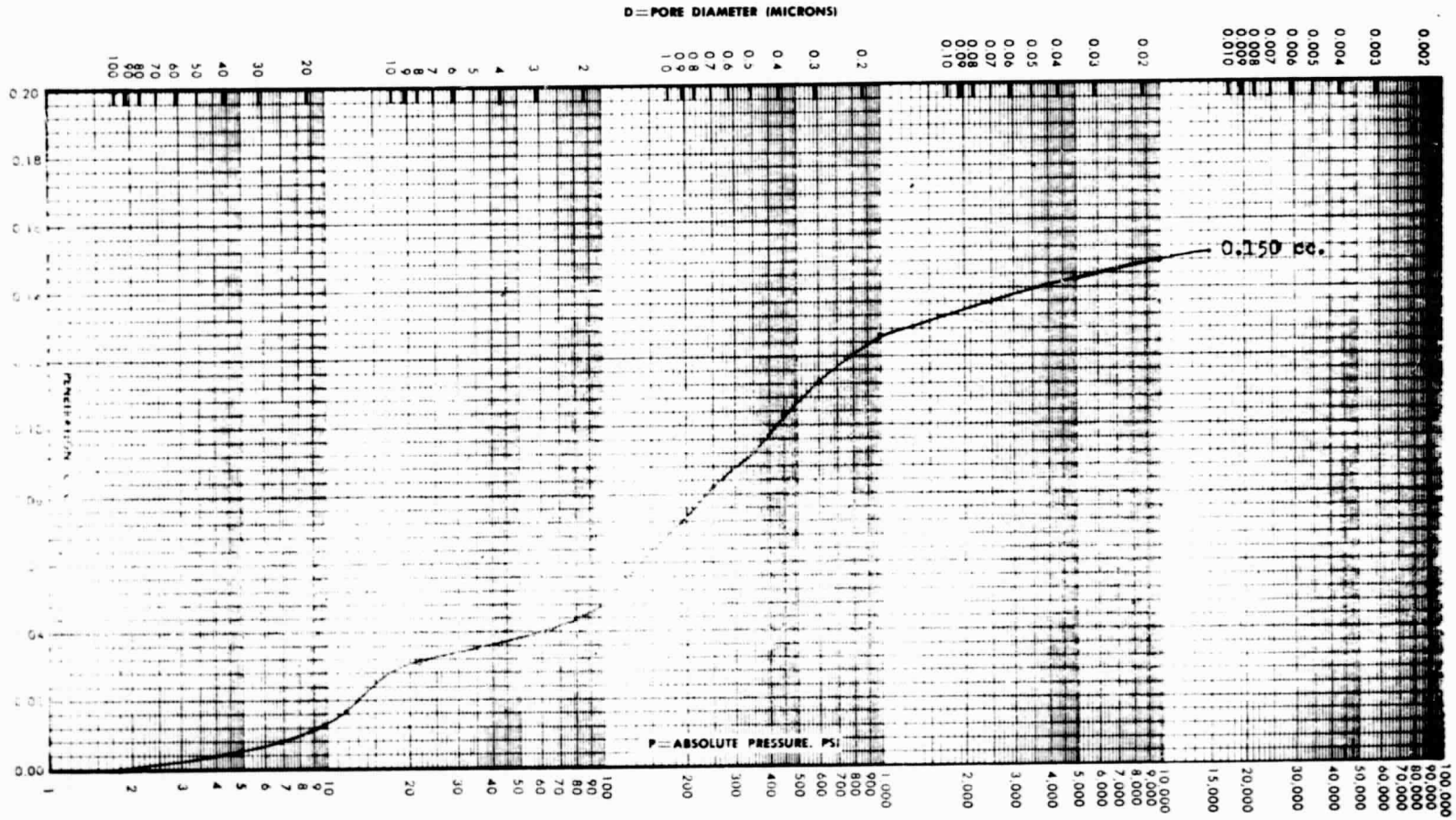


Figure 12. - Pore Size Distribution of Separator Type 4669-31

Cat. No. 5-7135

POROSITY DETERMINATION

(By 5-7107 or 5-7108 Aminco—Winslow Porosimeter)

DATE September 9, 1969

SAMPLE # 036-11 (Original) --Paper Measured Pore Volume: 0.47 cc/g.

WT. OF SAMPLE, G. 0.3506

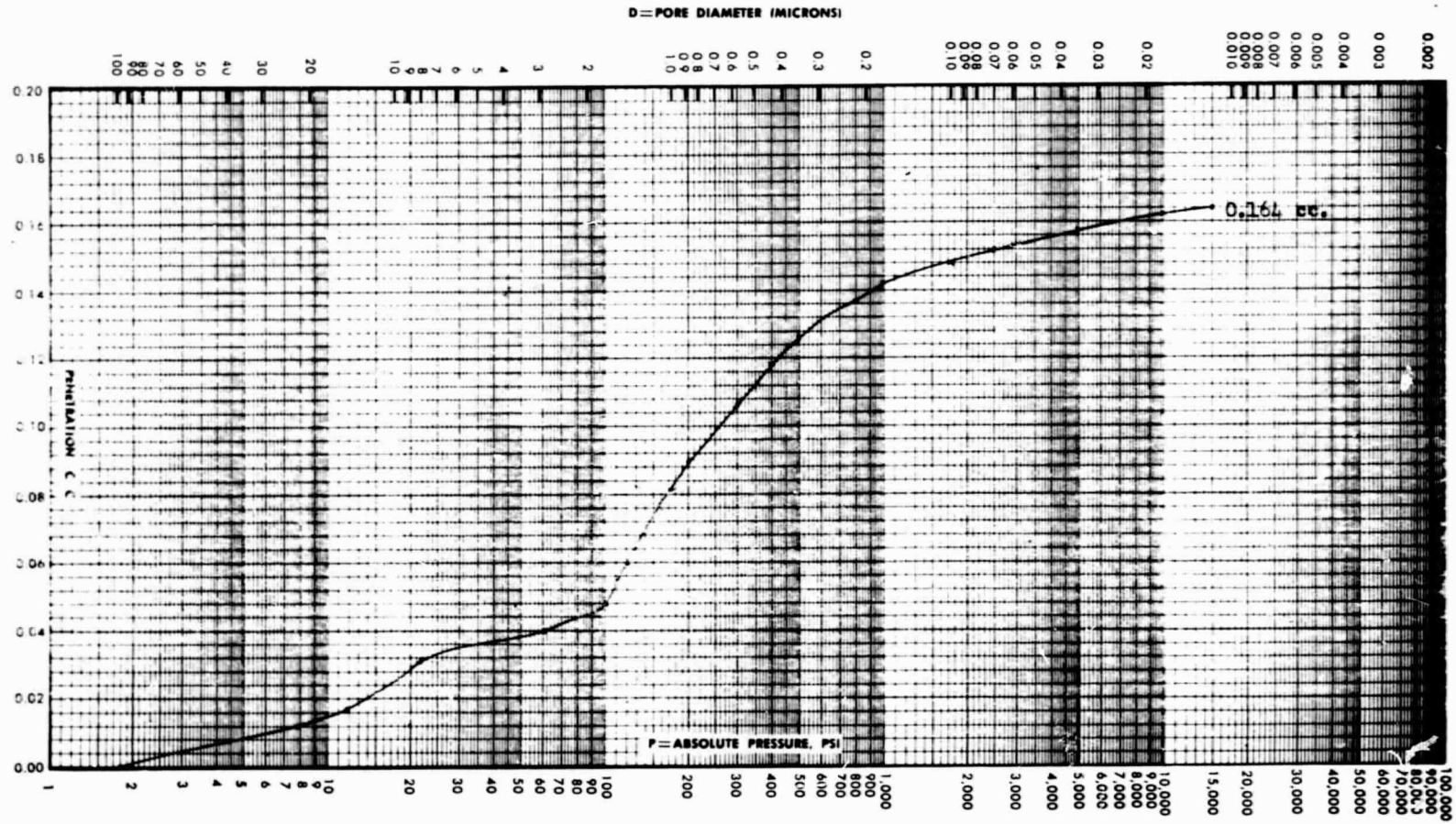


Figure 13. - Pore Size Distribution of Separator Type 036-011 (Original)

Cat. No. 5-7135

POROSITY DETERMINATION

(By 5-7107 or 5-7108 Aminco—Winslow Porosimeter)

DATE September 10, 1969

SAMPLE # 036-11 (Modified) --Paper Measured Pore Volume: 0.54 cc/g.

WT. OF SAMPLE, G. 0.3626

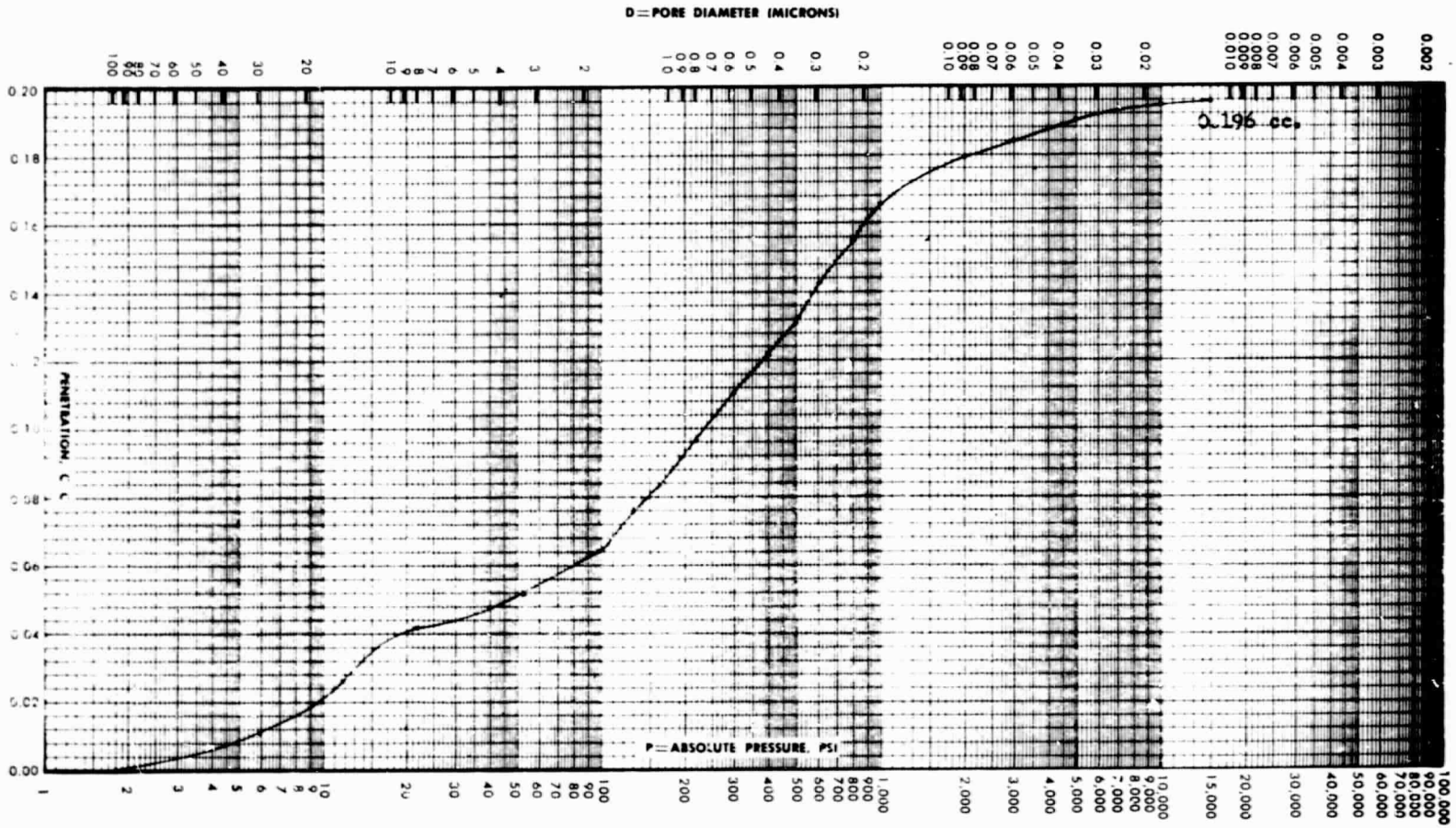


Figure 14. - Pore Size Distribution of Separator Type 036-011 (Modified)

These results pointed to the need for keeping the anodes wet at all times with KOH. The original cell configuration was obviously lacking in this capacity. It provided sufficient electrolyte for short term initial performance, but it did not contain the electrolyte for long periods or provide a means for replenishing the supply of electrolyte. What was obviously lacking was an effective wicking arrangement to keep the anode in the saturated state at all times.

Several wicking configurations were examined in this phase of the program. The most promising one used a porous ceramic insert as described below. This was used in all of the life test cells.

The first configuration to be examined made use of Teflon felt wicks. This material was cut into long strips which were wrapped around the periphery of the zinc electrode and passed through the bottom of the anode assembly as shown in figure 15. The ends of these wicks were immersed in a small pool of KOH electrolyte at the bottom of the steel chamber. This configuration showed some promise in that it permitted a cell to operate effectively for 44 cycles on a 2 x 4 hour regime without drying or need of servicing.

A second configuration made use of Pellon (P10) as the wicking material. A schematic of this arrangement is given in figure 16a. This design consisted of inverted "U" wraps of Pellon which were in contact with the anode surfaces and extended downward on the outside of the anode assembly. The bottoms of these Pellon sheets were immersed in a pool of KOH electrolyte. This configuration also appeared promising in that it provided for effective operation for at least 20 cycles on the 2 x 4 hr. regime given above.

The third and most successful configuration employed a microporous ceramic insert as shown in figure 16b. This was cemented into the bottom of the anode compartment and extended to the bottom of the cell case. The cell was positioned inside the steel assembly in such a manner that its ceramic insert was partially immersed in the pool of electrolyte at the bottom. In this manner the electrolyte supply within the anode was continuously replenished by wicking action of the ceramic insert. The original design employed Pellon strips to aid the wicking process. These were located on either side of the zinc anode and were in contact with the ceramic insert (see fig. 10). It was believed that these would be necessary for distributing electrolyte over the surfaces of the anode. These Pellon strips were later found to be unnecessary and were not employed in the life tests. One additional feature, which was retained, was a strip of Teflon felt across the top of the anode assembly. This appeared to aid in the retnetion of electrolyte.

As will be subsequently described, this method of wicking appeared the most promising of all those that were examined, and the method was subsequently applied to the cells on life test.

Electrolyte Purification. - At the request of the technical monitor an exploratory and short term test was carried out to give some indication of the purity of the electrolyte that was employed in the experimental cells. This test involved overnight electrolysis of a small quantity of electrolyte in a 100 ml.

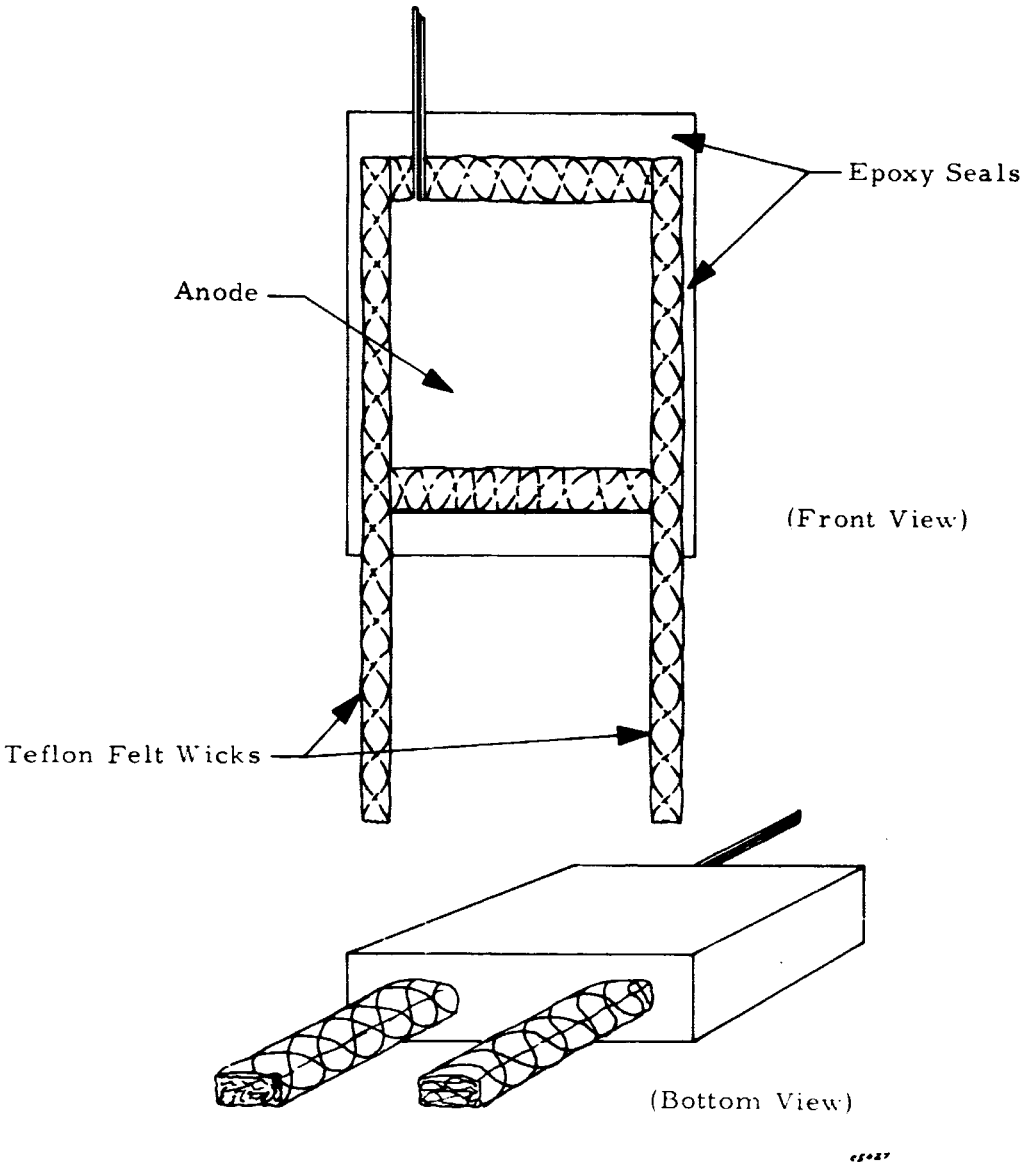
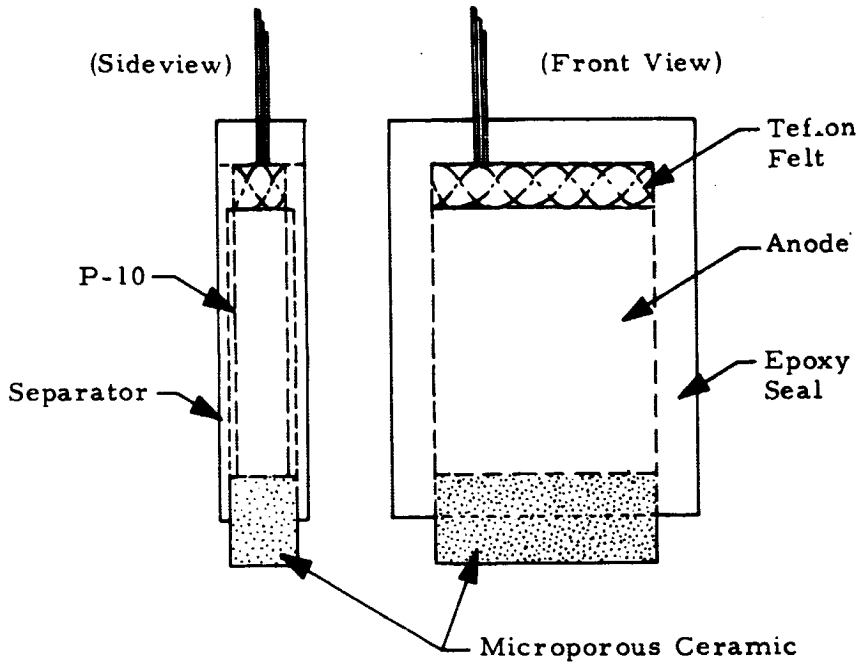
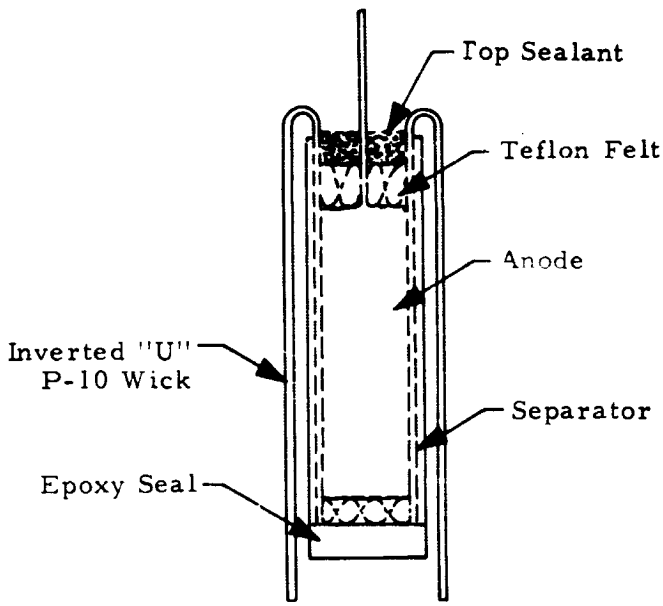


Figure 15. - Cell 9617-13 Anode Compartment "Wick Design"



16B "Microporous Wick Concept"



16A "Inverted 'U' Wick Design"

Figure 16. - Anode Design Modifications

polyethylene beaker. Anodes and cathodes were identical in this unit and consisted of square 1 in. x 1 in. (2.54 x 2.54 cm.) pieces of nickel screen. These were placed parallel to one another and separated by a distance of approximately 1/4 in. (0.63 cm.). Electrolysis was carried out overnight at a current of approximately 10 ma./sq. cm. At the end of a 16-hour period, the anode was removed from the electrolyte without turning off the current, as recommended by the monitor. Examination revealed that the anode had turned quite dark and had increased in weight approximately 6 mg. The cathode on the other hand was noted to retain its shiny metallic appearance and its weight did not change. These results signified that there was indeed some sign of impurity. This was speculated to be iron based on the use of iron storage containers but this was not rigorously proven. Regardless of the type of impurity, its presence was undesirable, because it could contaminate the zinc electrode and cause hydrogen evolution.

Based on these findings it was decided to purify all forthcoming batches of electrolyte that were to be employed on this program. This was carried out in a bank of electrolyzers which were operated in a manner similar to that described above. Each electrolyzer consisted of an array of six nickel screen anodes and cathodes with overall dimensions of 3 x 5 in. (7.6 x 12.6 cm.). These were housed in rectangular polysulfone cases in a parallel plate arrangement found in most batteries. Anodes and cathodes were separated by Vexar plastic mesh. The units were filled with 300 cc. of raw electrolyte and inserted in a plastic desiccator to avoid contact with ambient air. The units were then charged overnight at a current density of 10 ma./sq. cm. as above. A small vent on the desiccator was opened slightly to permit escape of H_2 and O_2 gases. The purified electrolyte was then transported to sealed polyethylene containers. This process was carried out on both the 30% and 45% types of electrolyte used.

Sealing Anodes. - The initial experimental cells employed an open type anode construction that is commonly found in AgO-Zn or Ni-Cd cells. This permitted direct contact of oxygen with the top of the Zn anode and thereby provided a situation which was conducive to chemical reaction between the Zn and O_2. This of course resulted in self-discharge of the cell.

This problem was resolved by sealing the anode compartment in the manner shown in figure 10. This involved use of an epoxy seal around the periphery of the anode compartment, including the terminal lead. Improvements in cycle life were noted immediately upon adoption of these seals. It was realized that these seals could not be expected to entirely eliminate contact of oxygen with the anode because smaller amounts of this gas could reach the anode via absorption in the electrolyte and diffusion through the separator. The rate of self-discharge sustained by this latter mechanism however must have been very low because large amounts of overcharge were unnecessary for extended operation of the cell.

Pack Tightness. - Cell components including anode, cathodes, matrices, and collectors were contained within the cavities provided in the case halves. The amount of compression applied to these components was controlled by the use of shims which were inserted inside these cavities. These shims were made in

a variety of thicknesses and with the same hole pattern as the case halves to permit oxygen transport to the electrodes. The appropriate number of shims were selected to give the desired degree of compression. In a prior internal program, the optimum compression was about 0.050 in. (0.126 cm.) for the particular cell design employed there. For the design employed on this program, the amount of compression was varied from 0.010 to 0.060 in. (0.025 to 0.152 cm.) depending upon the number of layers of matrix material and other components. In general, however, there were two values of compression used on most of these cells and the life test cells. The first value was 0.030 in. (0.076 cm.), which was applied to cells with "High" volume. This amount of compression was provided by installation of two 15 mil. (0.038 cm.) shims, one in each cavity. The second value was 0.020 in. (0.051 cm.) for cells with "Low" volume and was provided by two 10 mil. shims as above. Although distribution of this compression among the various compressible components was not established the overall changes in dimensions were as given below. The total reduction in thickness was noted to be approximately 14% in both cases.

"Hi" Volume Thicknesses

1 anode @ 0.060 in.	0.060 in.	0.153 cm.
2 separators @ 0.013 in. each	0.026 in.	0.066 cm.
4 layers KT @ 0.020 in. each	0.080 in.	0.204 cm.
4 layers FCA @ 0.011 in. each	0.044 in.	0.112 cm.
Total Original Thickness	0.210 in.	0.535 cm.
Amount of Compression	0.030 in.	0.763 cm.

"Low" Volume Thicknesses

1 anode @ 0.060 in.	0.060 in.	0.153 cm.
2 separators @ 0.013 in. coil	0.026 in.	0.066 cm.
2 layers KT @ 0.020 in.	0.040 in.	0.102 cm.
2 layers FCA @ 0.011 in.	0.022 in.	0.559 cm.
Total Original Thickness	0.148 in.	0.880 cm.
Amount of Compression	0.020 in.	0.058 cm.

Electrolyte Volume. - The amount of electrolyte that a cell picks up during its activation process was determined as a function of time under vacuum. This involved taking weights of cells in the dry form as initially assembled, and at various intervals of time during the vacuum impregnation process. When results were plotted, it was found after 4hours, that the rate of increase in weight was essentially zero. Therefore, after this time, the cells had become saturated and would not absorb any more electrolyte. A four-hour vacuum impregnation process was employed for all cells on this program. The total amount of electrolyte that a cell absorbed was dependent upon the amount of matrix

materials and the compression. In general, the values ranged from 15 to 20 g. With 30% KOH, this corresponded to a volume of 11.6 to 15.5 cc. and with 40% KOH, this corresponded to a volume of 10.3 to 13.7 cc.

Extended Test. - Although this phase of the program was not necessarily concerned with "Life Tests" it did include a few tests which could be considered in this category. These involved cells which exhibited high level and stable performance in their early stages of cycling. These were purposely left on continuous cycling in order to obtain an early indication of the upper limits of operational life of this type of cell.

One test in particular deserves special mention in that it demonstrated capability of achieving 243 cycles on a 6-hour regime at 50% depth of discharge. Performance characteristics of this cell near the end of the test (cycle #235) is given in figure 17. Results show that even in this latter stage of testing the cell's voltage was above 1.2 V. for the complete 2-hour dischcarge period at 0.6 amp. Charge voltage was also noted to be below 2.2 V. for the complete 4-hour charge period at 0.33 amps. The distinguishing feature of this cell was that it was one of the first to contain the microporous insert for wicking.

Single Cell Life Tests

The objective of this phase of the program was to evaluate the effects of four factors on cycle life. These consisted of electrolyte volume, electrolyte concentration, separator material, and matrix material. Effects of these factors were to be determined by full or fractional factorial experiment designs. The test cell design, as well as the most promising components and conditions, were to be selected on the basis of the "Performance and Construction" tests of the preceeding phase. A minimum of 40 and a maximum of 80 tests were to be carried out in this phase.

As will subsequently be pointed out, a total of 53 life tests were carried out in this phase. Several significant results, both positive and negative, were obtained during this phase. The most encouraging was that two types of cells operated effectively for more than 200 cycles on a 4-hour regime. This represents attainment of one of the major milestones of this program.

Experimental. - The test cells in this series were fabricated in accordance with the designs discussed earlier. All parts were kept clean at all times and handled in accordance with procedures for items to be used in an oxygen environment. Components were first assembled in the Kel-F cases and dry weights of the case assembly were determined. The case assembly was then placed in a small polyethylene container which was filled with purified electrolyte of either 30 or 45% KOH. The immersed assembly was then removed from vacuum, and excess electrolyte was drained off for 10 minutes. The assembly was then reweighed and electrolyte absorption was calculated. Impedance of the assembly was then measured at 1,000 cycles.

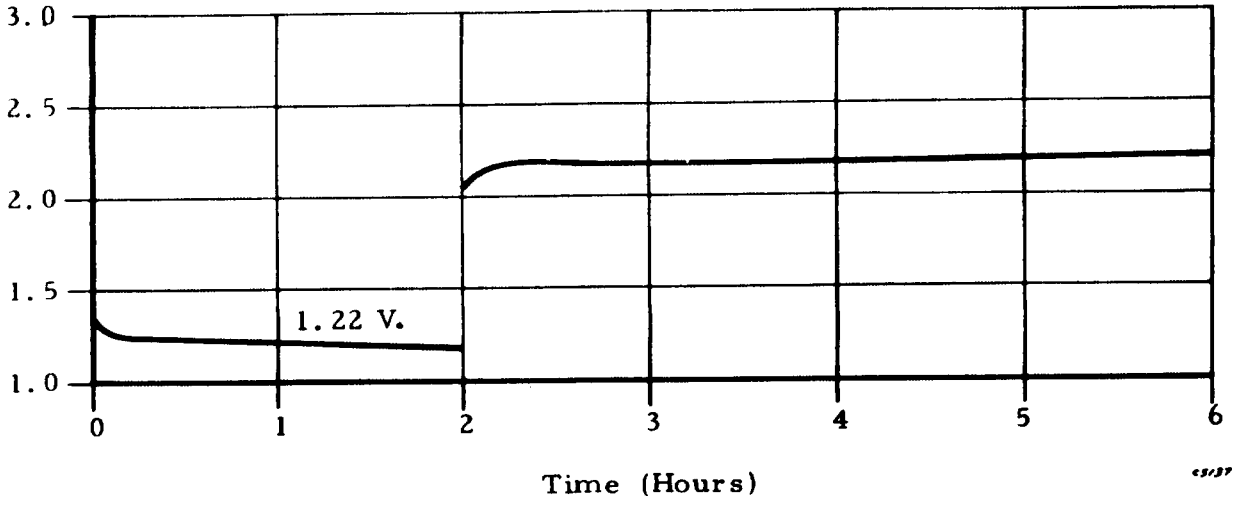


Figure 17. - Cycle Performance of Cell 9617-15 After 235 Cycles Regime: 2 Hours Discharge at 0.6 A. x 4 Hours Charge at 0.33 A.

The cell assembly was then installed in the Teflon-lined steel vessel and its leads were soldered to the lid of the vessel. The lid was then secured with eight bolts which were tightened evenly with a torque wrench set at 20 in.-lbs. (23 kg.-cm.). The vessel was then installed inside a steel enclosure within a test bay. Four electrical leads (two for power and two for voltage sensing) were then appropriately connected to the lid and were routed to a remote test station. A copper-constantan termocouple was taped to the wall of the vessel and was routed to a cold junction and multichannel recorder in the test area. A 1/16 in. (0.158 cm.) stainless steel pressure line was connected to the lid and routed to the test area. This line was not sealed off in the test area at this stage.

The cell was then placed on overnight formation charge at constant current. Charge current was selected to given an input of 85% of theoretical capacity over a 15 hour period. For cells with 7 g. anodes, the current was 254 ma. for an input of 3.8 amp. hr. For cells with 8 g. anodes, the current was 290 ma. for an input of 4.3 amp. hr. The voltage at the end of formation was noted and recorded, as well as the cell impedance at 1,000 cycles.

The assembly was then purged with nitrogen several times at low pressure to rid it of any hydrogen that might have accumulated during formation. The assembly was then pressurized with oxygen to 500 p.s.i.g. (35.1 kg./sq. cm.) and sealed off.

At this point, the assembly or assemblies were ready for automatic cycling. The assemblies were cycled independently of one another except for the fact that they were all triggered for charge and discharge by a common clock timer. Each cell was discharged across a fixed load which had been previously adjusted so that average current was 500 ma. for the 2 hr. discharge period. Each cell was charged separately by its own regulated power supply. A charge period lasts 4 hours at a current of 270 ma. to give a nominal 10% overcharge.

Current limiting devices were employed on some of the initial tests to avoid overcharge and resultant hydrogen evolution. These caused charge current to taper sharply when cell voltage reached a present maximum at which it was speculated that hydrogen could be evolved. These voltages were estimated on the basis of theoretical open circuit voltages, cell impedance, and polarization characteristics. In order to be on the conservative side, the upper limits of the initial cells were set in the range of 2.1 to 2.2 volts. This avoided hydrogen evolution but also resulted in insufficient input in some cells which developed higher internal resistances. Performance of these cells degraded rapidly, and it was necessary to reform them and raise their upper voltage limits before they could be given a "fair" test. These cells are designated appropriately. Subsequent cells were also equipped and run with the charge control devices. All of these received adequate input, because their upper voltage limits were adjusted on a daily basis to maintain the required charge input.

Voltages of each of the cells was recorded continuously with minature 0-3V. d.c. Rustrak recorders. Manual voltage and current readings of each cell were recorded at least once a day from precision Weston 911 voltmeters and ammeters. These recordings were usually at the end of a charge or discharge

period. Manual pressure readings of each assembly were also taken at these times from 0-600 p.s.i.(42.2 kg./sq. cm.) pressure gages ± 2 p.s.i. (± 0.041 kg./sq.cm.). External cell temperatures of each of the steel chambers were recorded on a multichannel 20-point recorder. This was not necessarily used to gather accurate operating data, but rather to observe trends in performance and hopefully to detect signs of internal combustion.

After a cell had failed on its regime, it was disconnected and disassembled for examination. The first step involved analysis of residual gases. This was carried out by first venting the cell from the 500 p.s.i. level to the 300 p.s.i. level in order to flush out the lines of stagnent gas, and obtain a true representative sample. A sample was then taken at this point with a syringe and run on a gas chromatograph (Beckman GC-2A). The test cell body and cell assembly were then carefully removed and given visual and other tests as recommended by the Technical Monitor.

Results of Life Tests. - A total of 53 cells were subjected to life tests on this phase of the program. All of the cells were similar, in that they were housed in the same cases and pressure vessels. All employed the same cathodes and current collectors, all were run at the same pressure. All were run on the same cycle regime. The only differences among these cells were their types of separators and matrices, electrolyte volume, and concentration. From a statistical point of view the tests may be divided into four groups. Each of these is reviewed separately below.

The first group was the most extensive and consisted of a full replication of four factors at two levels each. Two cells were to be constructed and tested for each treatment (type), and three cells were to be tested at eight of the treatments. This required a total of 40 tests. All of these tests, in addition to one repeat test, were carried out giving a total of 41 tests. The four factor levels were as follows:

a.	Electrolyte volume	Low and High
b.	Electrolyte concentration	30%, 40%
c.	Separator materials	3420-25, 4669-31
d.	Matrix materials	RKT/FCA, RKT/SKT

The relationship of electrolyte volume-matrix materials with the number of layers of each was as follows:

a.	Low electrolyte volume	RKT/FCA, RKT/2SKT
b.	High electrolyte volume	2RKT/2FCA, 2RKT/4SKT

Details of the construction of each cell are given in Table II under tests 1 through 41. All of these contained 7 g. anodes and the indicated level of each of the four factors as shown. Initial properties of these cells before and after formation are given in Table III. The amount of electrolyte pickup of all cells was noted to be in the range of 16 to 24 g., and the amount was noted to correspond in general to the level of the volume factor. Impedances of the cells were noted to be relatively uniform and in the range of 0.1 to

TABLE II. - CONSTRUCTION OF CELLS ON LIFE TEST

Test no.	Cell no.	Electrolyte volume		Electrolyte composition		Matrix Materials				Separation Type				Anode weight	
		Low	High	30%	40%	RKT/ FCA	2 RKT/ 2 FCA	RKT/ SKT	2 RKT/ 4 SKT	3420-25	4669-31	036-011 Original	036-011 Modified	7 g.	8 g.
1	1-1	X		X		X				X				X	
2	1-2	X		X		X				X				X	
3	1-3	X		X		X				X				X	
4	2-1		X	X			X			X				X	
5	2-2		X	X			X			X				X	
6	2-3		X	X			X			X				X	
7	3-1	X			X	X				X				X	
8	3-2	X			X	X				X				X	
9	3-3	X			X	X				X				X	
10	4-1	X		X		X					X			X	
11	4-2	X		X		X					X			X	
12	4-3	X		X		X					X			X	
13	5-1	X		X				X		X				X	
14	5-2	X		X				X		X				X	
15	6-1		X		X		X			X				X	
16	6-2		X		X		X			X				X	
17	6-3		X		X		X			X				X	
18	7-1		X	X			X				X			X	
19	7-2		X	X			X				X			X	
20	7-3		X	X			X				X			X	
21	8-1		X	X					X	X				X	
22	8-2		X	X					X	X				X	
23	9-1	X			X	X					X			X	
24	9-2	X			X	X					X			X	
25	9-3	X			X	X					X			X	
26	10-1	X			X			X		X				X	
27	10-2	X			X			X		X				X	

(continued)

TABLE II (concluded)

Test no.	Cell no.	Electrolyte volume		Electrolyte composition		Matrix Materials				Separation Type				Anode weight	
		Low	High	30%	40%	RKT/ FCA	2 RKT/ 2 FCA	RKT/ SKT	2 RKT/ 4 SKT	3420-25	4669-31	036-011 original	036-011 modified	7 g.	8 g.
28	11-1	X		X				X			X			X	
29	11-2	X		X				X			X			X	
30	12-1		X		X		X				X			X	
31	12-2		X		X		X				X			X	
32	12-3		X		X		X				X			X	
33	13-1		X		X				X	X				X	
34	13-2		X		X				X	X				X	
35	14-1		X	X					X		X			X	
36	14-2		X	X					X		X			X	
37	15-1	X			X			X			X			X	
38	15-2	X			X			X			X			X	
39	16-1		X		X				X		X			X	
40	16-2		X		X				X		X			X	
41	16-3		X		X				X		X			X	
42	17-1		X		X		X					X		X	
43	18-1		X		X		X					X		X	
44	19-1		X		X				X			X		X	
45	20-1		X		X				X			X		X	
46	21-1		X		X						X				X
47	21-2		X		X		X				X				X
48	22-1		X		X				X		X				X
49	22-2		X		X				X		X				X
50	23-1		X		X		X						X	X	
51	23-2		X		X		X						X	X	
52	24-1		X		X				X				X	X	
53	24-2		X		X				X				X	X	

TABLE III. - INITIAL PROPERTIES OF CELLS PLACED ON LIFE TEST

Test no.	Cell no.	Electrolyte absorption (gms.)	Activation impedance (ohms.)	Voltage at end of formation (volts)	Formation impedance (ohms.)
1	1-1	21.1	0.125	2.02	0.07
2	1-2*	18.6	0.13	2.04	0.10
3	1-3	16.9	0.14	2.00	
4	2-1	19.5	0.195	2.00	0.03
5	2-2	23.2	0.13	2.06	0.10
6	2-3	19.8	0.14	2.02	0.09
7	3-1	20.3	0.155	2.05	0.10
8	3-2*	18.2	0.13	2.03	0.10
9	3-3	18.5	0.17	2.04	0.09
10	4-1	18.0	0.15	2.02	0.05
11	4-2*	16.2	0.13	2.17	0.06
12	4-3	18.1	0.21	2.02	
13	5-1	16.9	0.30	2.18	0.11
14	5-2	19.8	0.165	2.02	0.07
15	6-1*	22.2*	0.295	2.18	0.17
16	6-2*	21.7	0.18	2.04	0.10
17	6-3	22.7	0.25	2.10	0.11
18	7-1	21.0	0.17	2.03	0.07
19	7-2*	21.0	0.14	2.08	0.06
20	7-3	20.5	0.20	2.05	
21	8-1	22.4	0.10	2.12	0.10
22	8-2	19.9	0.26	2.01	0.10
23	9-1	18.9	0.22	2.06	0.05
24	9-2*	19.9	0.22	2.10	0.07
25	9-3	19.3	0.22	1.98	
26	10-1	16.5	0.40	2.12	0.10
27	10-2	22.2	0.185		
28	11-1	16.3	0.3	2.18	0.13

(continued)

TABLE III (concluded)

Test no.	Cell no.	Electrolyte absorption (gms.)	Activation impedance (ohms.)	Voltage at end of formation (volts)	Formation impedance (ohms.)
29	11-2*	15.1*	0.23	2.18	0.20
30	12-1*	29.6*	0.73	2.28	0.13
31	12-2*	21.6*	0.19	2.12	0.07
32	12-3	24.2	0.20	2.03	0.10
33	13-1	19.9	0.30	2.11	0.15
34	13-2	23.2	0.31	2.14	0.20
35	14-1	20.6	0.20	2.39	0.20
36	14-2*	19.2*	0.25	2.18	
37	15-1	17.7	0.30	2.24	0.10
38	15-2*	19.5*	0.33	2.14	
39	16-1	19.3	0.50	2.32	0.37
40	16-2*	22.7*	0.48	2.24	
41	16-3	22.8	0.13	2.15	0.10
42	17-1	19.1	0.15	1.95	0.08
43	18-1	22.6	0.22	2.03	0.10
44	19-1	20.5	0.15	1.98	0.08
45	20-1	23.2*	0.30	2.08	0.12
46	21-1	21.8	0.17	1.98	0.09
47	21-2	22.1	0.18	2.00	
48	22-1	21.0	0.18	2.04	
49	22-2	22.7	0.20	2.13	
50	23-1	21.1	0.18	1.98	0.08
51	23-2	22.1	0.18	1.99	0.09
52	24-1	21.2	0.21	2.06	0.10
53	24-2	19.5*	0.20	2.03	0.09

*These cells given one extra hour of vacuum impregnation in electrolyte

0.3 ohm. after activation. A few cells exhibited somewhat higher impedances with initial values close to 1.0 ohm. These were given additional activation treatment by soaking them another hour in KOH under vacuum. This treatment reduced impedances, in most cases to values below 0.73 ohm. There was no apparent correlation between cell construction and activation impedance. End of formation voltages of most cells were noted to fall in a range of 2.0 to 2.2 volts. There were a few exceptions to this trend, with one cell reaching a level of 2.39 volts. This was apparently not indicative of any forthcoming problems in this particular cell, since it operated as effectively as most others in this group. There were no apparent correlations between end of formation voltage and cell construction, at least in this group. However, it was noted in subsequent groups that cells with type 036-011 separators, did exhibit consistently lower end of formation voltages close to the 2.0 V. level. Impedances of the cells after formation were relatively uniform and close to a level of 0.1 ohm. in most cases. Cell #16-1 was an exception, exhibiting an impedance of 0.37 ohm. This result must be attributed to faulty materials or assembly procedures, as cells with similar construction exhibited impedances near 0.1 ohm. As will subsequently be pointed out, cell 16-1 was one that exploded. On this basis, one might speculate that formation impedance might give some indication of a cell's reliability.

Operating times of the 41 cells in this group are given in Table IV. These values are noted to range from a low of 3 cycles (18 hours) to a high of 214 cycles (1284 hours). The latter result represents the longest operating time of any cell in this series, and is one of the most promising results of this program. The particular cell which achieved the result was #7-1. This was characterized by its type 4669-31 separator, 30% KOH, high electrolyte volume and the RKT/FCA type of matrix. The cell with the next highest operating time was #12-3 with 148 cycles (592 hours). This cell was similar to cell 7-1 and contained the same type of separator. The only difference was that it contained 45% KOH instead of 30% KOH.

Test results, from this first group, were analyzed statistically by the Project Monitor and personnel of NASA/Lewis Research Center. They employed an analysis of variance technique to determine the significance of each of the four factors on cycle life.

The formula employed is given below.

$$Y = b_a + b_1X_a + b_2X_b + b_3X_c + b_4X_d + b_5X_aX_b$$
$$+ b_6X_aX_c + b_7X_aX_d + b_8X_bX_c + b_9X_bX_b$$
$$+ b_{10}X_cX_c + b_{11}X_aX_bX_c + b_{12}X_aX_bX_d$$
$$+ b_{13}X_aX_cX_d + b_{14}X_bX_cX_d + b_{15}X_aX_bX_cX_d$$

TABLE IV. - OPERATING TIME OF SINGLE CELLS ON LIFE TEST

Test no.	Cell no.	Number of cycles to 1.0 volt
1	1-1	10
2	1-2	28
3	2-1	40
4	2-1	10
5	2-2	48
6	2-3	8
7	3-1	30
8	3-2	40
9	3-3	24
10	4-1	20
11	4-2	9
12	4-3	40
13	5-3	11
14	5-2	36
15	6-1	40
16	6-2	48
17	6-3	40
18	7-1	214
19	7-2	64
20	7-3	32
21	8-1	29
22	8-2	8
23	9-1	30
24	9-2	10
25	9-3	36
26	10-1	29
27	10-2	12
28	11-1	29
29	11-2	34
30	12-1	40
31	12-2	56
32	12-3	172
33	13-1	33
34	13-2	7
35	14-1	58
36	14-2	92
37	15-1	88
38	15-2	96
39	16-1	3
40	16-2	72
41	16-3	9
42	17-1	23
43	18-1	30
44	19-1	26
45	20-1	44
46	21-1	31
47	21-2	42
48	22-1	167
49	22-2	217
50	23-1	18
51	23-2	20
52	24-1	2
53	24-2	6

where

Y = number of cycles

λ_a = volume of electrolyte

λ_b = concentration of electrolyte

λ_c = type of separator

λ_d = type of matrix

The coefficients were determined by regression analysis in a computer run, wherein the appropriate values of cycle life were substituted in the above equation with the corresponding cell construction factors. Several significant results were obtained from this study as described below.

First, it was found that 78.9% of the total variability could be explained by the four terms listed above. This signified that a relatively small amount of the variability could be attributed to other factors such as faulty materials or construction.

Second, these results established that the type of separator as well as interactions between separator and other factors have a pronounced effect on cycle life. This was shown by application of the "t" test to the coefficients as determined above. Results were as follows:

Coefficient	Probability of Significance
b_1	0.922
b_2	0.922
b_3	0.999
b_4	0.479
b_5	0.280
b_6	0.956
b_7	0.758
b_8	0.808
b_9	0.154
b_{10}	0.996
b_{11}	0.653
b_{12}	0.938
b_{13}	0.530
b_{14}	0.742
b_{15}	0.832

These results indicate that the term "b_3", which is a function of the type of separator, is most significant as its probability of significance exceeds 0.999. Therefore the type of separator plays the most important role in determining cycle life. The next most significant factor is the separator-matrix interaction, which is associated with term "b_{10}". This has a probability of 0.996. The separator-volume interaction, associated with term "b_6", is also noted to be significant with a probability of 0.956. Electrolyte volume and concentration, associated with terms b_1 and b_2 respectively, are also significant and both have probabilities of 0.922.

Although these results specify which factors and combinations of factors are significant, they do not define which level of each factor is the most promising, or if the levels should be extended for more promising results. This type of projection cannot be reliably made with the above data. It is possible to make some speculations by comparing average cycle lifes of groups of cells with different constructions. On this basis one arrives at the following conclusions regarding cycle life.

a. Type 4669-31 separator is more effective than type 3420-25 separator.

b. The combination of SKT matrix with 4669-31 separator is more effective than the FCA matrix with 4669-31 separator.

c. The combination of 40% KOH with type 4669-31 separator is more effective than 30% KOH with 4669-31 separator.

d. The combination of high electrolyte volume with type 4669-31 separator is more effective than low electrolyte volume with 4669-31 separator.

These results may be summarized by indicating that the most promising cell is one that employs type 4669-31 separator, with SKT matrix, a high electrolyte volume, and with 40% KOH. Review of the cycle life data of Table IV tends to confirm these conclusions, at least on a statistical basis.

Results of cell failure analyses are given in Table V. These analyses were conducted as soon as possible after a cell had failed the cycle regime. The residual gas was analyzed in most cases, and then the cell was subjected to visual as well as other types of examinations as requested. Several significant observations and conclusions are discussed below.

First, it was found that most of the cells contained at least some hydrogen in varying amounts ranging from less than 1% to a high of 15.3% (by volume). This is a most significant observation in that it shows that hydrogen can and is indeed evolved in a cell of this type, and that the concentration of this gas can reach significant levels in relatively short periods of time. The presence of hydrogen does not necessarily affect electrical performance, at least at the indicated levels, but does present a serious explosive hazard. This is attributed to the fact that the explosive limit of hydrogen in oxygen under the conditions within the cell is close to 6%. The possibility of explosion is real, as demonstrated by the fact that three of the cells in this series resulted in failure by explosion. The causes for hydrogen evolution

TABLE V. - FAILURE ANALYSIS OF LIFE TEST CELLS

Test no.	Cell no.	Overall moisture condition		Zinc penetration			Residual gas analysis		End of charge voltage	Most likely causes of failure			Additional notes (impedance values measured after failure)
		Wet	Dry	Severe	Mild	None	% H_2	% O_2	Volts	Zn Penetration	Drying	Other	
1	1-1		X		X				2.20	X	X		
2	1-2		X			X			2.15		X	X	Faulty anode seal and some Zn growth out top, Z = 0.12
3	1-3	X		X			3.3	96.7	2.30	X			
4	2-1		X		X				2.20	X	X		
5	2-2	X		X			1.9	98.1	2.35	X			Z = 0.38 Ω
6	2-3					X	0.0	100.0	2.17				Z = 0.04 Ω
7	3-1	X			X				2.17	X			
8	3-2	X			X		0.0	100.0	2.13	X			Z = 0.16 Ω
9	3-3	X					0.0	100.0	2.20	X			Z = 0.06 Ω
10	4-1		X		X				2.21	X			
11	4-2		X			X	8.5	91.5	2.12		X		Z = 0.11 Ω
12	4-3	X			X		0.0	100.0	2.38	X			
13	5-1		X			X			2.17		X	X	Anode slumped
14	5-2		X			X			2.11			X	Cell exploded
15	6-1		X						2.22	X	X		
16	6-2	X		X					2.21	X			Z = 0.28 Ω
17	6-3		X	X			1.5	98.5	2.34	X	X		Z = 0.25 Ω
18	7-1	X			X		0.5	99.5	2.30	X			
19	7-2		X	X			4.9	95.1	2.41	X	X		
20	7-3	X				X	4.5	95.5	2.36			X	Ceramic insert was cracked and had Zn growth through it

(continued)

TABLE V (continued)

Test no.	Cell no.	Overall moisture condition		Zinc penetration			Residual gas analysis		End of charge voltage	Most likely causes of failure			Additional notes (impedance values measured after failure)
		Wet	Dry	Severe	Mild	None	% H_2	% O_2	Volts	Zn penetration	Drying	Other	
21	8-1		X			X			2.26		X		
22	8-2		X			X			2.14		X		
23	9-1	X			X				2.17	X			Anode had blue-green color
24	9-2		X			X			2.15				Z = 0.12 Ω
25	9-3	X		X			1.8	98.2	2.36	X			
26	10-1	X		X			1.6	98.4	2.25	X			
27	10-2	X				X	0.0	100.0	2.16			X	Faulty anode in initial construction
28	11-1		X		X				2.23	X	X		
29	11-2	X					9.1	90.9	2.17	X			
30	12-1	X		X					2.20	X			
31	12-2	X			X		2.3	97.7	2.22	X			Z = 0.33 Ω
32	12-3	X					0.0	100.0	2.20	X			Z = 0.34 Ω
33	13-1	X		X					2.23	X			
34	13-2	X			X				2.20			X	Cell exploded
35	14-1		X	X			7.0	93.0	2.42	X	X		Spectrographic analysis of anode indicated 0.06% by weight
36	14-2		X				15.3	84.7	2.37	X	X		Z = 0.21 Ω
37	15-1		X	X			0.0	100.0	2.32	X	X		Z = 0.33 Ω
38	15-2	X		X			1.1	98.9	2.27	X			Z = 0.19 Ω

(continued)

TABLE V (concluded)

Test no.	Cell no.	Overall moisutre condition		Zinc penetration			Residual gas analysis		End of charge voltage	Most likely causes of failure			Additional notes (impedance values measured after failure)
		Wet	Dry	Severe	Mild	None	% H_2	% O_2	Volts	Zn penetration	Drying	Other	
39	16-1	X				X			2.20			X	Cell exploded
40	16-2	X		X			2.0	98.0	2.39	X			Z = 0.46 Ω
41	16-3						5.1	94.9	2.16				
42	17-1	X		X			1.7	98.3	2.28	X			Spectrographic analysis of anode yielded trace <.005% pt
43	18-1	X		X			2.9	97.1	2.30	X			Same as above
44	19-1	X			X		2.9	97.1	2.20	X			
45	20-1								2.31				
46	21-1	X				X			2.19			X	Z = 0.19 Ω, faulty anode
47	21-2	X		X					2.34	X			Z = 0.59 Ω
48	22-1		X		X		2.5	97.5	2.35	X	X		Z = 0.49 Ω
49	22-2	X		X			9.4	90.5	2.36	X			Z = 0.30 Ω
50	23-1		X			X	0.5	99.5			X		Anode dark blue in color
51	23-2		X						2.13				Z = 0.18 Ω
52	24-1					X			2.08				
53	24-2						3.1	96.8	2.14				

and means for minimizing it and preventing accumulation are presented later under "Recommended Future Efforts."

Disregarding the explosions, two major factors caused, or at least contributed to a large extent, to most of the cell failures. These were zinc penetration and drying of the anode. Zinc penetration was the predominant mode of failure for most of the cells. This caused relatively early failures in several of the cells with the 3420-25 type of separator. Zinc penetration also caused failure in most of the cells with 4669-31 separators but after somewhat longer operating periods. The combination of 4669-31 separator in conjunction with the SKT matrix appeared to be the most promising configuration for resistance to zinc penetration. The cells with this combination ultimately failed by penetration, but did so after accumulating a significant number of cycles. Several cells which had failed by anode drying contained SKT. This correlation did not hold in all cases however.

A few cell failures were attributed purely to mechanical or construction faults such as cracked ceramic insert or faulty zinc anode. These are designated in Table V.

One final and significant result of these analyses concerns a platinum determination. This was done spectrographically on a sample of the anode from cell 14-1. Cell 14-1 operated effectively for 58 cycles (232 hours) and accumulated an appreciable amount of hydrogen (7%). The analysis indicated a platinum content of 0.06% by weight. This amount of platinum was not appreciable in terms of the total anode weight, but it could have contributed to hydrogen build up. This metal is known to cause H_2 evolution via formation of a local couple when present in very small amounts. The same test was applied to the anodes of cells 17-1 and 18-1. The analyses indicated trace amounts of platinum in both cases as indicated in Table V.

The second group of cells on life test was characterized by the use of a new type of separator. This decision was based on the statistical study of the first group of cells, wherein it was shown that the separator was the key component in regard to cycle life. It was logical therefore to evaluate alternative separators in order to obtain longer cycle life than obtained with 4669-31.

The separator was designated as "original-flexible-type-036-011. This was the flexiblized form of a rigid type separator which had shown a great deal of promise on preceding AgO-Zn cell programs (refs. 7, 8). Other components of these cells were made in accordance with the construction of prior cells 12 and 16 which had shown good performance on a statistical basis. These had employed "High" electrolyte volume and 40% KOH. A total of four cells were built and tested in this series. Cells 17-1 and 18-1 were identical and similar to cell 12 except for the separator. Cells 19-1 and 20-1 were also identical and similar to cell 16 except for the separator. All four contained 7 g. anodes.

Initial properties of these cells were in the same range as those of preceding cells as shown in Table III. Perhaps the only distinguishing feature, noted at this stage, was a tendency for slightly lower end of formation voltages which ranged from 1.95 V. to 2.08 V.

Test results shown in Table IV were not very encouraging as it was noted that operating times ranged from only 23 to 44 cycles. Disassembly and examination of these cells revealed extensive zinc penetration through the separator and throughout the cells. This was the obvious cause of failure in all four cells. Residual gas analyses again revealed some hydrogen in the range of 1 to 3%.

Consequently, it was decided to abandon any further use of this separator. Even though the rigid form of this separator appeared to offer good promise, it was apparent that the flexible form was not suitable. An attempt was made at the end of the program to modify this separator and re-evaluate it on these cells. This is described at the end of this section.

At this point in the program, it was decided to introduce one new variable, the amount of active anode material. The incentive for this decision was based on the known improvements in life of AgO-Zn cells that can be derived by use of higher weight anodes which is equivalent to operation at lower depth of discharge (1). It was speculated that with a small increase in anode weight it might be possible to operate the $Zn-O_2$ cells for longer periods than achieved in prior tests.

Therefore, it was decided to increase anode weight from 7 to 8 g. of ZnO mix. Four cells were fabricated with 8 g. anodes. The first two were identical and were similar to cell 12. These were designated cells 21-1 and 21-2. The second two were also identical and were similar to cell 16. These were designated cells 22-1 and 22-2. As shown in Table II all four cells contained 4669-31 separator, 40% KOH, and high electrolyte volume. The only difference between them was that the former two contained the RKT/FCA type matrix, whereas the latter two contained the RKT/SKT type matrix. Initial characteristics of these cells were in the same range as prior similar cells (see table III).

Results of this test series were indeed significant, as shown by the cycle life data of Table IV. The first two cells 21-1 and 21-2 with RKT/FCA matrices did not exhibit appreciably more cycle life than the corresponding cells with 7 g. anodes. However, the latter two with RKT/SKT matrices were noted to operate extremely well in comparison to the corresponding prior cells with 7 g. anodes. Cell 22-1 operated effectively for 167 cycles while cell 22-2 operated effectively for 217 cycles. Both cells displayed some capacity at the indicated number of cycles but not sufficient capacity to meet the requirements of the regime. Performance characteristics of each of these cells during the latter stages of cycling are given in Figures 18 and 19. In both cases the discharge voltages were noted to average near 1.2 volts and to remain above 1.0 volt for the complete two hour discharge period. These characteristics were taken at 150 cycles for cell 22-1 and at 200 cycles for cell 22-2. These results tend to confirm that increased anode weight will improve cycle life of $Zn-O_2$ cells. The results also give additional support to the prior conclusion that the RKT/SKT type matrix is more effective than the RKT/FCA type matrix in terms of extended cycle life.

A final life-test series was carried out with another type of separator, designated as modified-flexible type 036-011. This material contained the

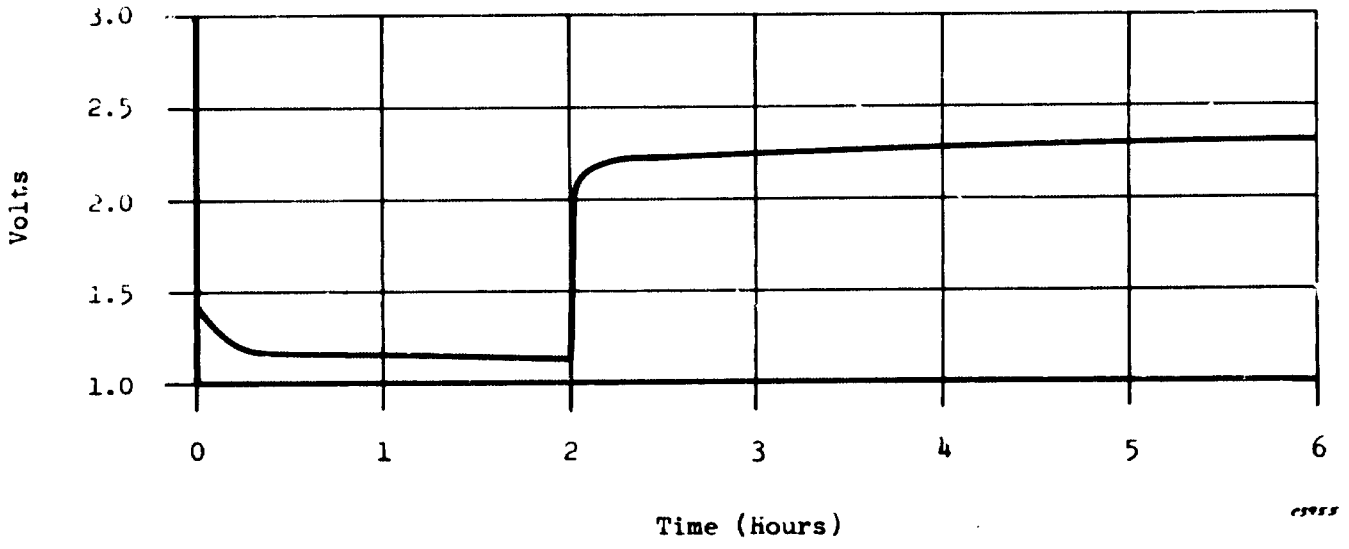


Figure 18. Cycle Performance of Cell 22-1 After 150 Cycles on 6 Hour Regime (discharge at 500 m.a. and charge at 260 m.a.)

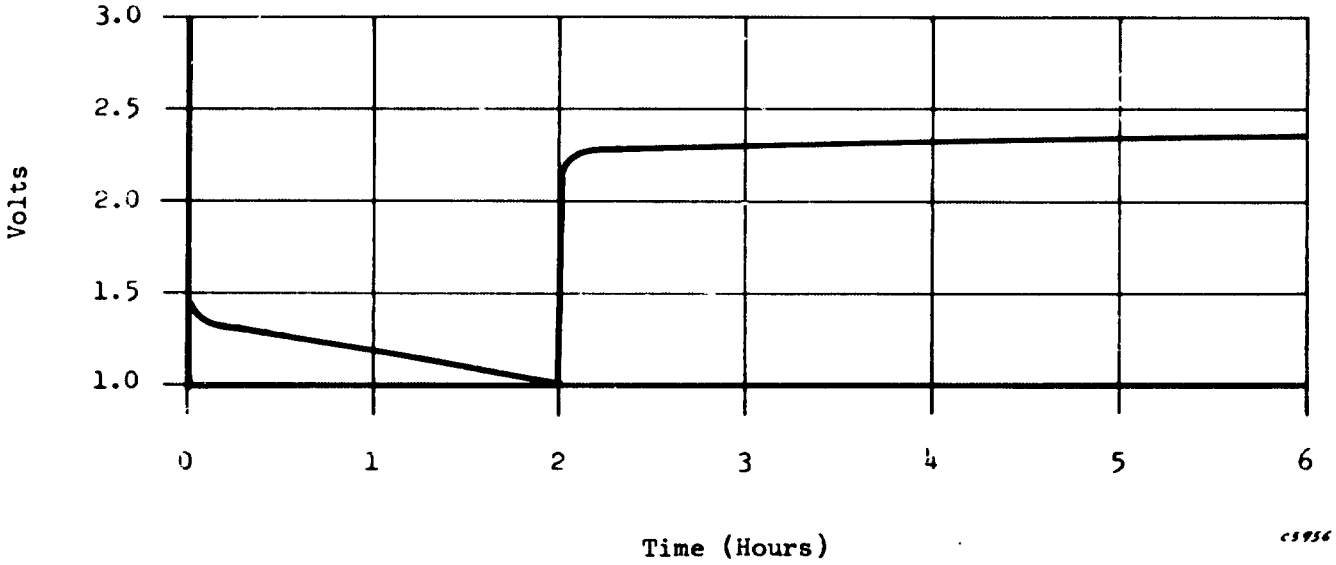


Figure 19. Cycle Performance of Cell 22-2 After 200 Cycles on 6 Hour Regime (discharge at 500 m.a. and charge at 260 m.a.)

same types of chemical species that were employed in the original 036-011 material but in a different ratio. It was hoped that the change in ratio of components would immobilize the leachable components of the original 036-011 material, and thereby improve stability and resistance to zinc penetration. Four cells were fabricated with this separator material. All of these contained 7 g. anodes for comparison with prior cells. All of these contained 45% KOH and high electrolyte volume. The first two were identical and contained the RKT/FCA type matrix. These were designated cells 23-1 and 23-2. The second two were also identical and contained the RKT/SKT type matrix. These were designated cells 24-1 and 24-2.

Results of this final test series were quite negative and inconclusive. As noted in Table IV, the operating time of three of these cells ranged from only 6 to 20 cycles. The fourth one exploded on its second cycle. This occurred during the middle of its second discharge period. Disassembly and examination of these cells revealed their anodes to be dry and to have a blue cast which signified probable passivation. There were no signs of zinc penetration in any of the cells. These results show that the modified flexible type of 036-011 separator is unsuitable for $Zn-O_2$ cells. The modified 036-011 material might have an advantage over the original 036-011 material in regard to resistance to zinc penetration. The tests however did not last long enough to establish this point. Failures at a very early stage in cycle life were brought about by other characteristics possibly attributable to the separator.

APPENDIX A

CELL IDENTIFICATION FOR PRELIMINARY CELL CONSTRUCTION AND PERFORMANCE TESTS

Cell No.	Cell No.	Cell No.	Cell No.	Cell No.	Cell No.
9542-12	9573-10	9574-1	9574-32	9575-23	9617-14
-13	-11	-2	-33	-24	-15
-14	-12	-3	-34	-25	-16
-15	-13	-4	-35	-26	-17
-16	-14	-5	9575-36	-27	-18
-17	-15	-6	-37	-28	-19
-18	-16	-7	-38	-29	-20
-19	-17	-8	-39	-30	-21
-20	-18	-9	-40	-31	-22
-21	-19	-10	-1	-32	-23
-22	-20	-11	-2	-33	-24
-23	-21	-12	-3	-34	-25
-24	-22	-13	-4	-35	-26
-25	-23	-14	-5	-36	-27
-26	-24	-15	-6	-37	-28
-27	-25	-16	-7	-38	-29
-28	-26	-17	-8	-39	-30
-29	-27	-18	-9	-40	
-30	-28	-19	-10	9617-1	
-31	-29	-20	-11	-2	
-32	-30	-21	-12	-3	
-33	-31	-22	-13	-4	
9573-1	-32	-23	-14	-5	
-2	-33	-24	-15	-6	
-3	-34	-25	-16	-7	
-4	-35	-26	-17	-8	
-5	-36	-27	-18	-9	
-6	-37	-28	-19	-10	
-7	-38	-29	-20	-11	
-8	-39	-30	-21	-12	
-9	-40	-31	-22	-13	

APPENDIX B

DESCRIPTION AND RESULTS OF POROSITY TESTS PERFORMED ON SEPARATORS BY AMERICAN INSTRUMENT COMPANY

AMERICAN INSTRUMENT CO., INC. 3030 Georgia Avenue, Silver Spring, Maryland 20910 (Area Code 301) 589-1727
Laboratory and Scientific Instruments; Superpressure and Materials Testing Equipment

Materials Technology Laboratory

POROSITY & DENSITY DETERMINATIONS BY THE METHOD OF MERCURY INTRUSION

In making these determinations on the samples submitted, we have observed the following procedures:

1. All determinations have been made on standard model Aminco Porosimeters, as specified.
2. Pore diameters have been calculated on the basis of the following values:

   mercury surface tension ..... 473 dynes/cm ;
   mercury contact angle..... 130°

3. Pressure readings have been corrected for the height of the mercury column in the penetrometer.
4. Mercury intrusion readings have been corrected for:
   a. The volume of residual air entrapped in the penetrometer at the time of filling with mercury. This correction is based upon an evacuation pressure of 0.05 torr and a filling pressure of 1.8 psia.
   b. The compressibility of mercury and variation of temperature. This correction has been empirically determined by a series of tests upon penetrometers filled only with mercury (no sample).
   c. The proportionality factor which converts capacitance, in picofarads, to intrusion, in milliliters, when using the 60,000 psi Porosimeter.

TWX: 710-825-9621
TELEX: 089-647
CABLE CODE: Aminco Silver Spring

AMINCO MATERIALS TECHNOLOGY LABORATORY POROSITY DETERMINATION

CUSTOMER McDonnell Douglas Aircraft Corp. DATE 9-9-69

SAMPLE # 4669-31 Paper BY C.C.B.

WEIGHT 0.3306 g PENETROMETER 6.1 ml., Short, Solid # 4

MEASURED PORE VOLUME 0.45 cc/g and DENSITY ---- g/cc at 15,000 psia

ABSOLUTE PRESSURE (psia)	INTRUSION (cc)	ABSOLUTE PRESSURE (psia)	INTRUSION (cc)
1.8	0.0000		
6.8	0.0080		
11.6	0.0170		
21.8	0.0314		
61.9	0.0408		
102.0	0,0486		
142.2	0.0610		
192.4	0.0720		
250	0.0820		
350	0.0921		
450	0.1031		
600	0.1130		
1000	0.1259		
2500	0.1368		
5000	0.1427		
10,000	0.1480		
15,000	0.1502		

AMINCO MATERIALS TECHNOLOGY LABORATORY POROSITY DETERMINATION

CUSTOMER McDonnell Douglas Aircraft Corp. DATE 9-9-69

SAMPLE # 3420-25 Paper BY C.C.B.

WEIGHT 0.3048 g PENETROMETER 6.1 ml., Short. Solid # 4

MEASURED PORE VOLUME 0.44 cc/g and DENSITY ---- g/cc at 15,000 psia

ABSOLUTE PRESSURE (psia)	INTRUSION (cc)	ABSOLUTE PRESSURE (psia)	INTRUSION (cc)
1.8	0.0000		
5.8	0.0090		
11.6	0.0170		
21.8	0.0286		
61.9	0.0387		
102.0	0.0451		
142.2	0.0563		
200	0.0681		
300	0.0811		
500	0.0941		
800	0.1045		
1500	0.1166		
2500	0.1225		
5000	0.1284		
10,000	0.1334		
15,000	0.1356		

AMINCO MATERIALS TECHNOLOGY LABORATORY POROSITY DETERMINATION

CUSTOMER McDonnell Douglas Aircraft Corp. DATE 9-9-69

SAMPLE # 036-11 (Original)---Paper BY C.C.B.

WEIGHT 0.3506 g PENETROMETER 6.1 ml., Short Solid # 4

MEASURED PORE VOLUME 0.47 cc/g and DENSITY ---- g/cc at ~5,000 psia

ABSOLUTE PRESSURE (psia)	INTRUSION (cc)	ABSOLUTE PRESSURE (psia)	INTRUSION (cc)
1.8	0.0000		
7.8	0.0120		
11.6	0.0170		
21.8	0.0311		
61.9	0.0402		
102.0	0.0482		
122.2	0.0601		
162.4	0.0779		
200	0.0895		
300	0.1057		
400	0.1180		
500	0.1257		
800	0.1370		
1000	0.1418		
2500	0.1521		
5000	0.1576		
10,000	0.1622		
15,000	0.1641		

AMINCO MATERIALS TECHNOLOGY LABORATORY POROSITY DETERMINATION

CUSTOMER McDonnell Douglas Aircraft Corp. DATE 9-10-69

SAMPLE # 036-11 (Modified)-----Paper BY C.C.B.

WEIGHT 0.3626 g PENETROMETER 6.1 ml., Short, Solid # 4

MEASURED PORE VOLUME 0.54 cc/g and DENSITY ---- g/cc at 15,000 psia

ABSOLUTE PRESSURE (psia)	INTRUSION (cc)	ABSOLUTE PRESSURE (psia)	INTRUSION (cc)
1.8	0.0000		
5.9	0.0110		
11.8	0.0260		
21.9	0.0417		
52.2	0.0520		
102.3	0.0653		
132.4	0.0760		
162.6	0.0836		
220	0.0970		
300	0.1110		
400	0.1216		
500	0.1312		
600	0.1427		
800	0.1552		
1000	0.1655		
2000	0.1795		
3000	0.1848		
5000	0.1900		
10,000	0.1950		
15,000	0.1958		