AD 731029

NOLTR 71-81

DEVELOPMENT OF LONG LIFE ZINC-OXYGEN CELLS

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By
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30 JUNE 1971

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NOLTR 71-81

46

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Commander Naval Ordnance Laboratory Silver Spring, Maryland 20910	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

DEVELOPMENT OF LONG LIFE ZINC-OXYGEN CELLS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Progress

5. AUTHOR(S) (First name, middle initial, last name)

Richard D. Weller

6. REPORT DATE 30 June 1971	7a. TOTAL NO. OF PAGES 44	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. b. PROJECT NO. Task No. ORD 531 215/UF17-351-503 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NOLTR 71-81 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES Details of illustrations in this document may be be studied on microfiche	12. SPONSORING MILITARY ACTIVITY Naval Ordnance Systems Command

13. ABSTRACT

The feasibility of using zinc-oxygen batteries for long-term discharges has been investigated with the objective of attaining a one-year discharge lifetime and a five-year storage lifetime at uncontrolled temperatures. Zinc and oxygen electrodes were developed at the Naval Ordnance Laboratory and used to construct zinc-oxygen cells for discharge testing. Cell testing lifetimes ranged from two to six months with zinc conversion efficiency falling between 70 percent and 90 percent on the two-month tests. Zinc conversion efficiency was reduced to 40 percent on the six-month tests due to the use of nickel as the zinc electrode current collecting screen material. Cell lifetime was limited by premature oxidation of the zinc electrode due to corrosive chemical reactions set up by the nickel.

The five-year storage requirement dictates the use of a reserve configuration with electrolyte kept in individual cell reservoirs during storage. Preliminary designs of the electrolyte storage and activation systems were done based on the electrode and cell designs developed.

DD FORM 1 NOV 65 1473 (PAGE 1)
S/N 0101-807-6801

UNCLASSIFIED
Security Classification

UNCLASSIFIED
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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Zinc-Oxygen Battery Oxygen Electrode Fabrication Teflon Bonded Electrodes						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

UNCLASSIFIED
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DEVELOPMENT OF LONG LIFE ZINC-OXYGEN CELLS

Prepared by:
Richard D. Weller

ABSTRACT: "Ready-round" underwater mines require electric power supplies capable of long-term uncontrolled storage with subsequent reliable discharge at the one year rate. A reserve zinc oxygen battery is considered as a possible candidate to obtain the reserve feature, increase the energy density per unit weight, and match the energy density per unit volume of the Leclanché cells traditionally used for the bulk of the underwater mine batteries. Porous sintered zinc and silver-catalyzed Teflon on porous stainless steel oxygen electrodes were constructed and tested in 12 to 14 ampere-hour cells at discharge rates ranging from six days to six months. Zinc conversion efficiencies of 70 to 90 percent were obtained at the two-month discharge rate. The six-month discharge rate conversion efficiency was reduced to 40 percent due to the corrosive chemical reactions induced by the presence of nickel in the support and current collecting screen used in the zinc anode. The reserve battery concept applied to the zinc-oxygen system requires that both the potassium hydroxide electrolyte and the oxygen be withheld from the cell during storage. Two reserve battery concepts are presented. Neither design was constructed.

Methods of anode, cathode, and cell fabrication avoided the use of any known industrial proprietary or patented data.

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DEVELOPMENT OF LONG LIFE ZINC-OXYGEN CELLS

Future underwater mines will probably require application of the "ready-round" concept of operational readiness. Thus the Naval Ordnance Systems Command authorized a study of the zinc-oxygen reserve battery concept as a possible solution to the uncontrolled storage and one-year discharge life problem imposed by the "ready-round" mine concept. Under this program zinc-oxygen cells were developed that worked well for up to four months of discharge life. Also, two complete reserve battery systems were designed, but not constructed. The program was terminated on 30 June 1970, without a conclusive demonstration of the feasibility of utilizing the zinc-oxygen reserve battery systems in underwater mines, as funds were insufficient to cover all mine programs.

The work was performed for the Naval Ordnance Systems Command as Task No. ORD 531 215/UF17-351-503.

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Captain, USN
Commander

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ALBERT LIGHTBODY
By direction

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INTRODUCTION

The objective of this effort was to investigate the feasibility of using zinc oxygen batteries for long-term discharges of up to one year at low continuous current drains. One of the main requirements was to build the battery in a reserve configuration (electrolyte stored separately) so that long shelf life at higher temperatures could be achieved. A summary of the desired battery characteristics follows:

Discharge Time: 1 year

Power: 100 milliwatts continuous with occasional "spike" loads of 1 millisecond duration

Voltage: 15 volts nominal

Storage Time: 5 years at uncontrolled temperature

A more detailed mission requirement list is given in the appendix.

The approach taken was to develop zinc and oxygen electrode structures, fabrication methods, and methods of cell construction that were completely disclosed and government owned. Cells fabricated from these electrodes would be tested for operating life on low rate discharges to determine the zinc electrode conversion efficiency and the ability of the oxygen electrode to operate for extended periods. The life tests would also determine the ability of the cell structure to withstand KOH leaks. Preliminary designs of the electrolyte storage and activation system and the overall battery arrangement would be done based on the cell structure developed.

In the actual course of the project, zinc and oxygen electrode structures were developed at the U. S. Naval Ordnance Laboratory as well as a method for constructing cells with plastic frames and parts. Cell life tests of two to six-month duration were successfully performed and a preliminary design of the electrolyte storage and activation system was completed. Figure 1 is a picture of a typical test cell, as constructed, which would produce 12 to 14 ampere-hours at 1.4 volts. In the early tests on this project, cell lifetime was limited by the method of cell construction which allowed KOH electrolyte to leak from the cell. In later tests, lifetime was limited (six months maximum achieved) by corrosion effects on the zinc electrode.

Zinc-oxygen (air) cells have been in practical use since the early 1930's. Reference 1 describes a type of zinc-air cell manufactured by the Union Carbide Corporation in 1932 intended for use as a radio and general purpose battery. This cell utilized flat plate cast zinc electrodes and was therefore limited to low current density discharges to prevent zinc passivation. NaOH electrolyte was used in sufficient quantity to dissolve all of the zinc oxide produced (3.3 cc of NaOH per ampere-hour). The cell used a porous, activated carbon cathode and would operate successfully for periods of up to a year at energy densities of 40 to 45 watt-hrs/lb.

Modern versions of the zinc oxygen cell have utilized porous zinc battery electrodes so that high currents can be drawn. The electrolyte is usually KOH in the quantity of .5 to 1.5 cc/amp-hr of zinc with the zinc oxide reaction product appearing in the electrolyte as a solid precipitate. The modern cells also utilize the recently developed fuel cell oxygen electrodes with Teflon bonded catalysts (Reference 2). This type of cell will produce well over 100 watt-hrs/lb used as an air battery (Reference 3). Thus far, practical applications have been limited to air batteries with discharge times in the range of a few hours to one week.

In the oxygen configuration, with high pressure oxygen storage, and electrolyte stored in a separate reservoir for added shelf life, the zinc-oxygen battery should produce 60 to 65 watt-hrs/lb. Table 1 gives an estimated weight breakdown of such a system and also includes the weight of a similar cadmium-oxygen system, both batteries assumed to supply 100 milliwatts for one year at 15 volts.

According to Dirkse (Reference 4) the reaction taking place at the zinc electrode during discharge in KOH is the conversion of zinc metal to $Zn(OH)_4^{--}$ ions, which later decompose to form ZnO. The oxygen electrode promotes the breakdown and recombination of O_2 molecules to OH^- ions which are ultimately available for reaction at the zinc electrode by ionic transport. The overall cell reaction then is:

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

The theoretical open circuit voltage (E_0) for this reaction is 1.65 V (room temp, 30 percent KOH, saturated with ZnO). In practice, with mercury amalgamated zinc electrodes, 1.40 to 1.45 volts open circuit is actually obtained.

Many references on the theory of oxygen electrode operation are available and a few are listed here for the convenience of the reader (References 5, 6, and 7). Austin (Reference 5) classifies the theoretical problems as falling into three general areas: electrocatalysis, electrokinetics, and mode of operation (the mechanism by which a reactant gets to a site where it can react electrochemically, and the description of physical models of the electrode structure). No further discussion of oxygen electrode operating theories will be undertaken herein since the oxygen electrode work on this project was restricted to the practical development and testing of electrodes.

ELECTRODE DEVELOPMENT

Oxygen Electrodes

The function of the oxygen electrode is to maintain a stable three-phase mixture of solid catalyst, liquid electrolyte, and gaseous oxygen. The three components in contact with one another will promote the reduction of O_2 gas to OH^- ions with the resultant flow of electrons into the oxygen electrode. The electrode must also perform the mechanical functions of keeping the bulk electrolyte contained and simultaneously preventing the oxygen gas from bubbling through the electrode into the inside of the cell. The electrode must also provide electrical conductivity from the oxygen reaction sites to the external circuit.

There are several dozen (Reference 8) known catalysts which will promote the reduction of oxygen. Some of the more common ones which came under consideration for this project are platinum black, palladium black, activated carbon, raney nickel powder, and silver powder. Platinum and palladium blacks are the fastest rate catalysts known, but are very scarce and expensive for applications where the highest rate discharges are not needed. Activated carbon is cheap and readily available, but problems were encountered in electrode fabrication attempts because of mechanical weakness and poor electrical conductivity in the finished electrodes. Raney nickel is a cheap, plentiful catalyst but was discarded because of its tendency to ignite spontaneously in air during electrode fabrication attempts. Fabrication of electrodes in a glove box or other inert atmosphere device was an unwanted complication.

The final choice of catalyst material was silver powder, moderately plentiful and inexpensive, which has none of the above mentioned difficulties.

Teflon Bonded Electrodes

In its final configuration, the oxygen electrode that was developed was a three-layered structure consisting of a layer of porous stainless steel, a second layer of catalyst material (Teflon bonded silver powder), and a third layer of unsintered Teflon sheet. Figure 2 is a microphotograph of a cross section of an oxygen electrode.

The porous stainless steel base material (Union Carbide, Stock No. SA 259) is a sintered sheet from .007 to .009 inches thick and has an overall porosity of 50 percent. It serves as a mechanical support for the rest of the electrode and as a current collector for the catalytic layer. Figure 3 is a microphotograph of the porous stainless steel sheet. The stainless steel forms the electrolyte side of the electrode and KOH penetrates the pores of the steel sheet to reach the second layer.

The second layer is the silver-Teflon catalyst region which maintains a three-phase mixture in which the oxygen reacts. Silver powder (Metz Refining Co. "C-18 Fine Silver") is mixed with a PTFE suspension (Dupont, Teflon 30-B) in water to form a mixture of paint-like consistency which is applied to the stainless steel layer with a paint brush. The electrode is then heated in air at 600°F for ten minutes driving off the water and sintering the Teflon and silver layer. The amount of Teflon in the original mixture is adjusted so that the silver-Teflon layer is 80 percent silver and 20 percent Teflon by weight (45 percent silver and 55 percent TFE by volume). The painting-heating process is repeated 10 to 15 times to build up a catalytic layer of .008 to .012 inches thickness with a 1000 PSI press between two plastic plates after every third coat. Figure 4 is a microphotograph of the catalytic layer showing the porous nature of the silver-Teflon mixture. After a few hours or days, some KOH will soak completely through the catalyst layer forming drops of liquid on the oxygen side and eventually dripping into the oxygen gas space. This tendency for the electrodes to "weep" is the reason for the third layer, consisting of pure Teflon in a porous form, referred to as "unsintered" Teflon.

Unsintered Teflon sheet is commercially available from several sources in varying widths and thicknesses. In this case, a .010 inch thick sheet was used and applied to the electrode by simple pressing at 6000 PSI. Unsintered Teflon sheet will allow passage of oxygen but the pores are small enough (.05 to .5 microns) to effectively block the passage of KOH. A layer performing this function is often referred to as a "wet-proofing" layer.

After the wet-proofing layer was applied, a 1/8 inch wide strip of wet-proofing and catalyst layers was removed to expose the stainless steel surface and a copper lead wire was spot welded in place on one side. Figure 5 is a photograph of two finished electrodes showing the gas and electrolyte sides.

Figure 6 shows the electrical performance of one of the oxygen electrodes operating in a zinc-oxygen cell with KOH electrolyte. Figure 7 is a schematic drawing of the apparatus used to obtain the electrical performance data incorporating removable electrolyte and gas chambers so that a large number of cathodes can be tested against one zinc electrode. The cell was held together sometimes with bolts and sometimes with a large wooden clamp. The performance curve (Figure 6) shows that most of the voltage drop in the lower current regions is due to the oxygen electrode. Therefore a logical cell arrangement is to sandwich a zinc electrode between two oxygen electrodes, providing more oxygen electrode surface area and cutting down the cell voltage drop on load. This effectively cuts the oxygen electrode current density in half compared to an arrangement with one oxygen electrode per zinc electrode.

Electrodes Made by Chemical Deposition of Silver

Attempts to deposit silver directly onto porous Teflon sheets by chemical deposition were largely unsuccessful due to poor mechanical adherence of the silver to the Teflon and unsustained electrical performance. The silver was deposited onto porous Teflon sheets (pore size 2 to 10 microns) by precipitation from the silver-ammonia complex solution by the addition of sugar (electrode treatment procedure listed in the appendix). Electrodes were made in three ways:

a. Floating the Teflon sheet on the surface of the liquid while precipitation was taking place, depositing .3 mg/cm^2 of silver metal onto the Teflon.

b. Holding the Teflon sheet on the bottom of the precipitating liquid, depositing 1 to 3 mg/cm^2 of silver metal onto the Teflon.

c. Pulling the precipitating solution through the porous Teflon sheet, depositing 10 to 20 mg/cm^2 of silver metal in the pores and on the surface of the sheet.

Figure 8 shows the apparatus used in this procedure.

Figure 9 shows the performance of cells constructed by electrodes made by each of these procedures compared to the performance of a TFE bonded silver electrode. The TFE bonded electrode shows better performance in all ranges of current density. The TFE bonded electrodes also show more consistent voltage levels as the time of discharge increases.

Zinc Electrodes

Several methods of making porous zinc battery electrodes are known including electrolytic conversion of zinc oxide plates (Reference 9), electroplating zinc from a ZnO saturated KOH solution, pressing zinc powder into the desired electrode shape, and sintering of zinc powders into a mechanically stable structure. A new method of sintering zinc powder into a high coulombic efficiency electrode was developed on this project.

The new sintering method is described in a recent publication (Reference 10) and a complete description of the zinc electrode development work can be found there. Briefly the new method involves the melting of zinc powder inside a matrix of NaCl particles after the zinc oxide coating has been cleaned off with dilute HCl. The molten zinc runs together into a coherent structure, and after cooling, the NaCl is soaked out with water. The porosity and pore size in the electrode can be varied by changing the NaCl amount and particle size. These electrodes gave excellent results on discharge tests of up to two months duration with coulombic efficiencies falling generally in the range of 70 percent to 90 percent in well constructed cells. Coulombic efficiencies fell to the 40 percent range for six-month life tests due to the corrosion effect of nickel screens which had been included in the electrodes as current collectors. Figure 10 shows one of the finished zinc electrodes.

The zinc electrodes were amalgamated with mercury in a solution of mercuric acetate so that two percent of the electrode weight was mercury. This is done to inhibit the corrosion of zinc by the electrolyte and the associated production of hydrogen gas. The zinc electrode was wrapped in a polypropylene fabric (Kendall Grade H470) separator as pictured in Figure 11. The zinc and oxygen electrodes were assembled into cells as described in the next section. Originally, the zinc electrode current collecting screen was silver, but it was found that silver deteriorated badly during the melting phase of electrode manufacture usually breaking off at the edges of the electrode. Nickel screens survived the heating cycle well but led to the corrosion problems discussed in detail in the next section.

CELL CONSTRUCTION AND TESTING

The zinc and oxygen electrodes were incorporated into cells for life testing and the determination of electrical performance characteristics. The cells utilized lucite frames to mount two oxygen electrodes per cell, one on each side of a zinc electrode. The zinc electrode current collector extended through a slot in the side of the frame and was sealed with epoxy. Figure 12 shows a cross section of the original cell design. The oxygen electrodes were held to the sides of the frame by the plastic electrode retainers shown in Figure 12. Retainers and electrodes were sealed in place with epoxy or ethylene dichloride. Sealing of the oxygen electrode to the shoulder of the lucite block was the most critical aspect of the cell design. A KOH proof seal was never attained with the design of Figure 12.

Figure 13 shows a schematic of the cell design which produced an oxygen electrode seal that withstood KOH penetration. The plastic cell frames were made in two pieces, one for each cathode. The cathodes were installed first with a bead of epoxy (3M Co., Resin #4) around the edge from both the inside and the outside of the cell. This allowed the cathode seal to be examined from both the inside and outside for cracks, holes, and unsealed areas. After the cathodes were installed on each frame and inspected, the two frames were clamped together around a wrapped zinc electrode and sealed by the epoxy placed in the mating tongue-groove arrangement on the inside of the frames. Figure 14 is a photograph of the frames used.

After the cells were constructed, electrolyte (31 percent KOH) was placed into the cells with a hypodermic needle through the electrolyte fill holes shown in Figures 12 and 13. The fill holes were then filled with epoxy producing a completely sealed cell in which electrolyte had no direct access to the outside. The typical cell constructed was 3 x 3 x 1/2 inches, weighed 80 to 110 grams, contained 15 to 20 cc of electrolyte, and would produce 12 to 14 ampere-hours at 1.4 volts at the most efficient operating conditions (2-month discharge). Figure 1 is a photograph of one of the cells. A total of 42 cells was built and placed on discharge test with 33 tests completed at the time of this report, and nine cells remaining on long-term discharges.

The discharge tests were conducted with the cells in oxygen chambers as shown in Figure 15. The oxygen chambers were made of two circular discs with a 1/2-inch cavity in each one clamped together with a rubber "O-ring" seal around the edge. The 1/2-inch cavities in each block formed a one-inch wide gas tight space containing the cell. Gas tight electrical leads came through the front of the chamber to allow the cell to discharge through a constant resistance. Voltage measurements were made periodically. Knowing the cell voltage and discharge resistance, the total amount of current produced by the cell could be calculated. The coulombic efficiency of the zinc electrode could then be calculated by using the previously recorded weight of the zinc electrode, Faraday's laws of electrochemical equivalents, and the known amount of current produced. Table II summarizes the results of the cell discharge tests. Table II is divided into four groups of cells constructed consecutively.

Group I, Cells 1 through 12, was the initial construction effort built with a single lucite frame in the manner illustrated in Figure 12. The cell parts in this group were all made of lucite and the cathodes were fastened to the lucite frame by gluing with ethylene dichloride, a lucite solvent. Early in the tests, it became apparent that an adequate seal had not been achieved between the stainless steel cathode base and the lucite frame since KOH could be observed leaking from the cells around the edges of the electrodes. Cells on shorter term tests (175Ω discharge and less) achieved zinc utilization in the range of 40 to 60 percent, but the longer term cells achieved only 15 to 40 percent due to the loss of electrolyte, allowing oxygen gas to have direct access to the zinc electrodes.

After the electrolyte leaks in Group I became obvious, the cells of Group II were constructed trying various methods of electrode sealing with different epoxies, silicone rubber cement, and cell frame variations. Most of the attempts to seal the electrolyte in were unsuccessful in Group II, but the experiments led to the cell construction illustrated in Figure 13 and used to construct the cells of Group III.

In Group III, high discharge efficiencies were obtained from Cells 25, 26, 32, 33, and 34 on 175Ω loads (approximately two month discharge) with a group average of 78.4 percent. Figure 16 shows the cell voltage versus time plot for Cell No. 32. Some electrolyte could be observed leaking from the cells but the rate of leakage was slow enough to allow normal operation. The electrolyte appeared not to come around the edge of the oxygen electrode, but possibly through the zinc electrode screen seal or directly through the cathode itself. The longer lived cells of Group III on 1000Ω discharge achieved an approximate six-month lifetime at a zinc utilization of 40.8 percent group average. Figure 17 shows the voltage-time plot for Cell No. 30. The reason for the drop in zinc utilization from 78.4 percent to

40.8 percent was the use of nickel as the zinc electrode current collecting screen. An investigation of the six-month cells to determine the reason for the drop in zinc utilization was performed and reached the following conclusions:

a. The cells failed due to complete oxidation of the zinc electrodes. The oxygen electrodes performed normally when fresh zinc was inserted into the cell after the removal of the ZnO mass from the cell cavity. Since only 40 percent of the electrode was used electrically, 60 percent was oxidized by unwanted parasitic chemical reactions.

b. One of the parasitic reactions definitely shown to exist was the dissolving of nickel by the electrolyte to form nickel hydroxide, $Ni(OH)_2$, and the subsequent oxidation of zinc metal by the $Ni(OH)_2$:

$$Zn + Ni(OH)_2 \rightarrow ZnO + H_2O + Ni.$$

The evidence for this reaction was the presence of nickel metal in the ZnO mass obtained from the discharged cells. Nickel can be dissolved from two sources in the cell: the zinc electrode supporting screen (100 percent Ni) and the stainless steel backing of the oxygen electrode (8 percent Ni).

c. Chromium metal present in the oxygen electrode stainless steel (18 percent Cr) was also dissolved by the electrolyte. It is uncertain whether the dissolved chromium was in the ionic form of CrO_2^- or $CrO_4^=$. If the chromium is in the $CrO_4^=$ state, it will react with the zinc as follows:

$$2CrO_4^= + 3Zn + H_2O \rightarrow 2CrO_2^- + 2OH^- + 3ZnO$$

oxidizing the zinc electrode. If the chromium is in the CrO_2^- state, there will be no reaction with the zinc electrode. Therefore, it is uncertain whether or not the chromium contributed to the parasitic oxidation of the zinc.

d. Some iron in the oxygen electrode was oxidized by the electrolyte and remained as a thin coating of rust on the electrolyte side of the cathode. Iron evidently did not contribute to the oxidation of zinc.

e. The silver metal oxygen catalyst material was either undissolved or dissolved in undetectably small amounts and did not contribute to the oxidation of zinc. No silver was found in the electrolyte or the zinc-oxide mass.

The results of Group III showed that nickel screen is a suitable choice of zinc electrode current collector for discharges in the range of two months duration or less. Nickel is a poor choice, however, for discharges of six months or longer. The cells of Group IV were constructed in an attempt to solve the corrosion problems by plating the nickel screens with a more stable metal.

Electrodes incorporating gold, silver, and chromium plated nickel screens (three each) were incorporated into the nine cells of Group IV which are still undergoing discharge testing at the time of this report.

ELECTROLYTE RESERVOIR AND ACTIVATION SYSTEM DESIGN

Designs of electrolyte storage and activation systems were studied for the electrode and cell models developed and previously discussed. The use of a single, central electrolyte reservoir with tubes leading to each cell was ruled out for long term-discharges because of the probability of current drains between cells through a common electrolyte trapped in the tubes after activation. This problem becomes more critical with longer discharges where small currents through an electrolyte path from cell to cell can use up a significant fraction of the cell capacity as time progresses. Therefore the reservoir designs were based on the concept of having an individual reservoir for each cell eliminating the chance of an electrolyte path between cells.

A basic problem with the automatic activation of a zinc-oxygen cell is the trapping of a residual gas bubble inside the cell during electrolyte injection. When electrolyte is forced into the cell interior, the residual gas inside the cell will be compressed into a smaller bubble in the top of the cell. This would prevent the complete wetting of the zinc and oxygen electrodes allowing direct access of oxygen gas to the zinc and only partial performance from the oxygen electrodes. This problem was approached by making the residual cell gas CO_2, which would be absorbed by the KOH electrolyte as K_2CO_3, a solid material dissolved into the liquid electrolyte. This would leave no gas bubbles in the cell after activation. Furthermore, absorption of the CO_2 gas will cause a vacuum inside the cell providing a driving force for the electrolyte injection.

The design shown in Figure 18 is based on the use of CO_2 gas as the cell filling gas for storage. In this design the electrolyte is contained in a reservoir, the bottom half rigid and the top half consisting of a flexible plastic bag lined with metal foil on the outside to prevent CO_2 absorption from the atmosphere during storage. The electrolyte reservoir is sealed at the bottom by a metal diaphragm. When cell activation is desired, a voltage is applied to lead wires connected to the ends of a piece of nitinol wire wound around a drum. The nitinol wire is in a stretched condition and will remain so at room temperature indefinitely. However, the passage of electrical current through the nitinol wire will cause the wire to be heated above the critical temperature chosen in the 230 to 250°F range. When this happens, the wire will return to its original length with considerable force (100,000 PSI stress generated inside the wire). When the wire shortens, it rotates the drum moving a cutter against the metal foil diaphragm allowing the electrolyte to contact the CO_2 gas inside the cell. Part of the CO_2 gas will immediately be absorbed causing a pressure decrease inside the cell. The pressure difference between the inside and outside of the cell will start to collapse the flexible bag forcing KOH into the cell cavity and allowing further absorption of CO_2. Finally, the flexible bag will be turned inside out, collapsed to the position illustrated in Figure 18b, with the cell completely filled with KOH and ready for discharge. This design allows the flexible bag to reexpand during the cell discharge to compensate for expansion of the cell contents due to conversion of zinc to zinc oxide.

Figure 19 shows the details of the nitinol wire arrangement for activation.

It should be remembered that the design described above has not been experimentally tested and several areas of uncertainty exist which need investigation:

a. KOH proof seals are needed at various places in the reservoir-cell assembly. Critical areas will probably be the sealing of the flexible electrolyte container to the rigid reservoir frame (Point A in Figure 18), and the sealing of the metal foil diaphragm to the reservoir frame(Point B in Figure 18). Sealing, along with resistance to KOH corrosion, will be the overriding factors governing the choice of plastic materials to construct the cell-reservoir assembly.

b. Provided sealing can be achieved, polyethylene would be a good material to use for the flexible electrolyte container because of its flexibility and resistance to KOH corrosion. A thin, metal foil covering over the outside of the polyethylene would probably be needed to prevent CO_2 diffusion through the polyethylene into the KOH while the cell is stored or handled in air.

c. reliminary experiments with the nitinol wire indicate that the wire is very stiff and difficult to wind around a drum if stretched in a line. The nitinol wire should be annealed in a spiral form, wound around the cylinder, and stretched by rotating the cylinder backwards. Preliminary tests show that nitinol gases visibly when immersed in KOH so a Teflon or other plastic coating over the wire will probably be necessary.

d. Activation requires a pressure difference buildup between the inside and outside of the cell. Therefore a pressure difference will exist across the oxygen electrodes which are porous by nature allowing gas to diffuse through. It is believed that the gas diffusion rate through the cathode is slow enough to allow a sizable pressure difference for long enough to obtain activation but this point must be experimentally established.

In the event that the above described electrolyte storage and activation system proves impractical, Figure 20 shows a schematic of an alternate approach. In this design, the electrolyte is stored in a long cylinder with smooth walls fitted with a piston. The cylinder is sealed by thin metal on plastic diaphragms on both ends. When activation is desired, oxygen gas from the high pressure storage tank is allowed to go through a pressure reducing valve to the reservoir breaking the diaphragms on both ends. The gas then pushes the piston to the other end of the reservoir injecting electrolyte into the cell. Again, the cell is filled with CO_2 gas to prevent bubbles from being trapped inside.

Figures 21 and 22 show schematics of overall battery systems based on the cell and activation systems discussed above. Figure 21 is a battery design utilizing the first activation system described with nitinol wire activators. In this case, the cell electrolyte cavities and the oxygen gas space are filled with CO_2 gas for storage purposes. The cell activation nitinol wires are all wired in parallel and heated from a single, outside electrical source. After the time required for the electrolyte to flow into the cells (to be determined experimentally), current is applied to the oxygen release squib valve providing oxygen to the gas space for cell operation. The CO_2 gas inside the cell cavities will be absorbed rapidly by the electrolyte coming into the cell. The CO_2 gas in the oxygen space outside the cells will be absorbed slowly by the electrolyte as the CO_2 diffuses through the cathode wet-proofing layer. Eventually all the CO_2 in the gas space will be absorbed leaving a pure oxygen atmosphere for cell reaction.

With the alternate method of activation, the overall battery design would be that shown schematically in Figure 22. In this case, activation is accomplished by oxygen gas from the high pressure storage tank. Firing the first squib valve allows oxygen to come into the activation system manifold at a pressure (determined experimentally) higher than that of the CO_2 filled cells and gas space. This breaks the diaphragms in all the reservoirs forcing KOH into the cells. The second step in activation is to electrically fire the second squib valve allowing oxygen to come out of the manifold into the gas space for cell operation equalizing the pressure on the inside and outside of the cell. As before, the CO_2 in the gas space will be slowly absorbed by the KOH through the cathode.

SUMMARY AND CONCLUSIONS

Zinc electrodes and oxygen electrodes have been developed and used in the construction and performance testing of long life zinc-oxygen cells. The basic design and methods of manufacture of both the zinc and oxygen electrodes are completely government owned. The zinc electrode developed is a new type of sintered structure which in two-month discharge tests has achieved a 70 percent to 90 percent coulombic conversion efficiency. Six-month discharge tests showed an average conversion efficiency of 40 percent due to the inclusion of a nickel current collecting screen in the zinc electrode. The nickel has a detrimental effect on the zinc electrode setting up a corrosive chemical reaction with nickel metal being deposited on the zinc electrode. The oxygen electrode developed is a three-layered structure consisting of a porous stainless steel base, a second layer of Teflon bonded silver powder, and a third layer of pure Teflon wetproofing. The overall thickness of the electrode is .020 to .025 inches. The oxygen electrodes have performed well in tests of up to six months duration.

Since cell lifetime is presently limited by the zinc electrode, further work on this project should include the development of a replacement for the nickel screen in the zinc electrodes, with the consideration of plated nickel screens as well as amalgamated copper or brass. Experimental development and testing of the electrolyte storage and activation methods outlined in this report should be performed.

The zinc-oxygen cell probably can attain a one-year operating lifetime at low currents if parasitic chemical effects can be completely eliminated from the zinc electrode.

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8. Austin, L. C., Fuel Cells, A Review of Government Sponsored Research, 1950 - 1964, Chap. 17, NASA SP-120, 1967.
9. Shepard, C. M. and Langelan, C. H., "Formation of Porous Metal Plates by Electrolytic Reduction," Journal of the Electrochemical Society, August 1962.
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TABLE I

ESTIMATE OF ZINC-OXYGEN AND CADMIUM-OXYGEN SYSTEM WEIGHTS

100 milliwatts, 15 volts, one year

	Weight -- Lbs.	
Component	Zinc Oxygen	Cadmium Oxygen
Anode Metal	2.2	5.1
Cathodes	.5	.75
Electrolyte (1 cc/amp-hr)	2.9	3.2
End Plates	.4	.4
Can	1.25	2.7
Epoxy and/or Cell Support	.4	.9
Electrical Leads and Connections	.5	.5
Total Cell Stack	8.15	13.55
Oxygen	.57	.77
Oxygen Tank and Support	1.7	2.3
Pressure and Flow Regulator	.3	.3
Piping and Fittings	.5	.5
Pressure Transducer and Wiring	.2	.2
Total O_2 System	3.27	4.07
Extra Electrolyte	.2	.2
Tank and Liner	.5	.5
Controls, Piping and Valves	1.0	1.0
Total KOH System	1.7	1.7
Total Battery	13.1	19.3
Watt Hrs/Lb	66	45
No. of Cells	11	15
Operating Volts/Cell	1.4	1.0

TABLE II

SUMMARY OF ZINC-OXYGEN CELL DISCHARGE TESTS

Cell No.	Discharge Lifetime hrs.	- mos.	Discharge Load Ω	Average Cell Voltage	Current Density ma/cm²	Theoretical Capacity amp-hrs.	Zinc Conversion Efficiency %
Group I, Cells 1-12, Initial Test Group with Large, Early Electrolyte Leaks							
1	156	6½ days	15.7	1.20	4	14.4	84
2	1222	1.7	500	1.39	.14	15.3	22.2
3	1490	2.1	1000	1.40	.073	14.3	14.6
4	480	.6	20 ma	1.34	1.0	15.0	64
5	360	.5	20 ma	1.35	1.0	15.0	48
6	576	.8	175	1.37	.41	14.9	30.3
7	3310	4.6	750	1.40	.10	15.5	39.1
8	1370	1.9	500	1.36	.14	14.9	25
9	1175	1.6	175	1.35	.41	14.9	61
10	912	1.3	175	1.35	.41	14.7	48
11	1080	1.5	175	1.36	.41	14.6	57.5
12	744	1	175	1.37	.41	14.1	41.5
Group II, Cells 13-24, Experiments in Different Methods of Cell Sealing							
13	288	.4	750	1.37	.10	14.9	3.5
14	1128	1.6	1000	1.41	.075	14.9	10.7
15	480	.6	175	1.38	.41	14.7	25.8
16	1680	2.3	500	1.40	.14	15.0	31.3
17	264	.4	175	1.34	.41	15.0	13.5
18	72	.1	500	1.42	.14	15.1	1.3
19	72	.1	1000	1.45	.075	15.1	.6
20	1440	2.0	500	1.40	.14	14.9	26.9
21	Damaged during construction						
22	816	1.1	175	1.38	.41	14.8	43.5
23	2040	2.8	750	1.39	.10	14.4	26.2
24	792	1.1	175	1.36	.41	14.6	42.2

TABLE II
(Cont'd)

Cell No.	Discharge Lifetime hrs.	Discharge Lifetime mos.	Discharge Load Ω	Average Cell Voltage	Current Density ma/cm^2	Theoretical Capacity amp-hrs.	Zinc Conversion Efficiency %
Group III, Cells 25-34 with Improved Cell Sealing Techniques							
25	1608	2.2	175	1.39	.41	14.9	86
26	1175	1.6	175	1.38	.41	15.1	61.5
27	3840	5.3	500	1.38	.14	15.1	70.2
28	3860	5.3	1000	1.44	.075	14.3	39
29	3940	5.5	1000	1.44	.075	14.0	40.6
30	4250	5.9	1000	1.44	.075	14.2	43
31*	1320	1.8	500	1.42	.145	14.9	25.1
32	1490	2.1	175	1.42	.42	15.1	80
33	1655	2.3	175	1.42	.42	15.3	88
34	1415	2.0	175	1.42	.42	15.0	76.5

*Cell 31 Developed Early Leaks.

Cell No.	Discharge Lifetime hrs.	Discharge Lifetime mos.	Discharge Load Ω	Average Cell Voltage	Current Density ma/cm^2	Theoretical Capacity amp-hrs.	Zinc Conversion Efficiency %
Group IV, Cells 35-43 with Silver, Gold, or Chromium Plated Nickel Screens							
35	Group IV Cells still on test		2500	1.46	.03	12.7	Group IV Cells still on test
36			1500	1.47	.05	9.75	
37			2500	1.47	.03	10.2	
38			1500	1.46	.05	14.9	
39			1500	1.47	.05	11.5	
40			1500	1.47	.05	14.0	
41			2500	1.46	.03	15.0	
42			1500	1.46	.05	14.9	
43			1500	1.46	.05	12.7	

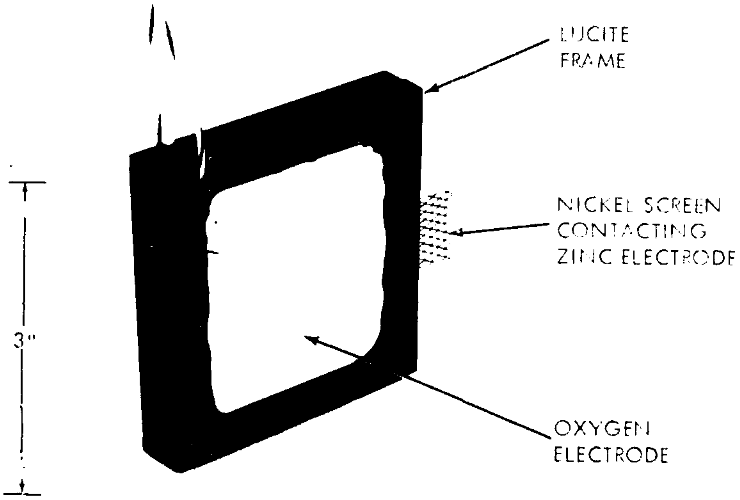


FIG. 1 FINISHED ZINC-OXYGEN CELL

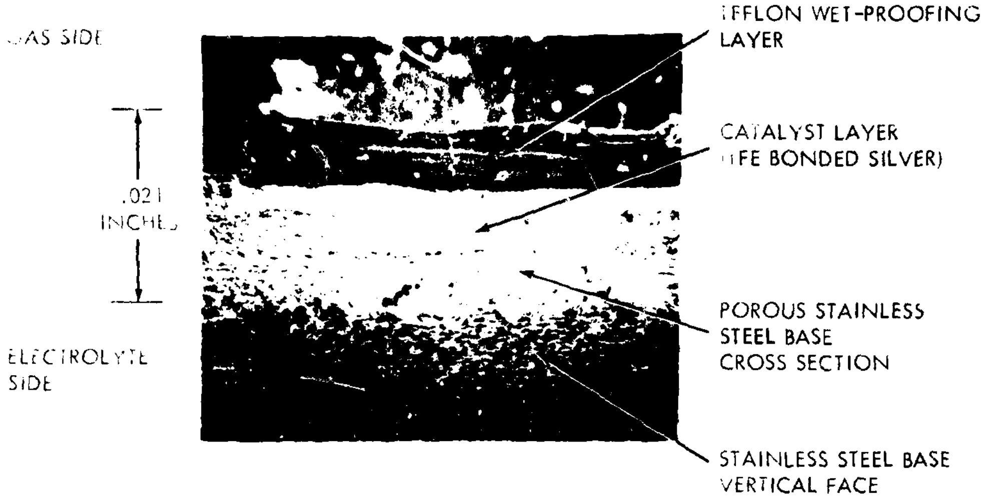


FIG. 2 70 X MICROPHOTOGRAPH OF AN OXYGEN ELECTRODE CROSS-SECTION

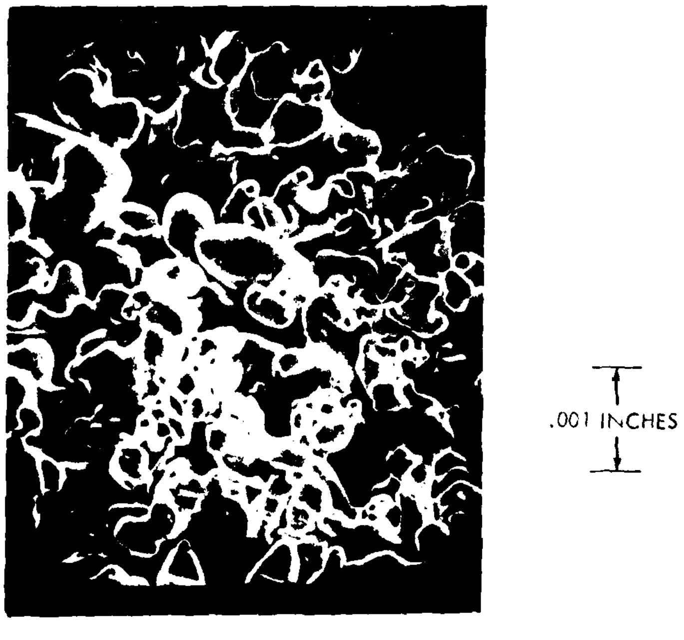
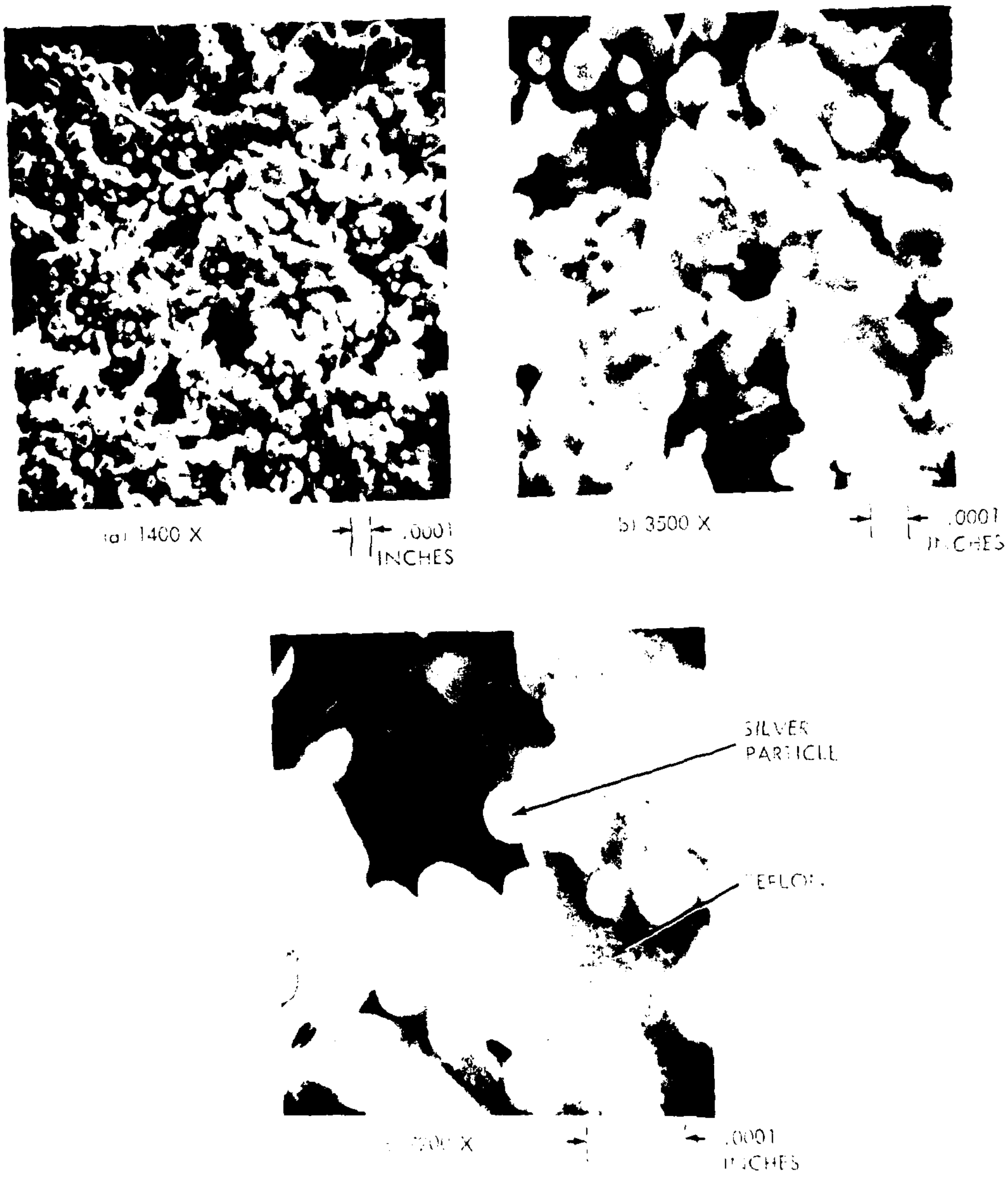


FIG. 3 700 X MICROPHOTOGRAPH OF POROUS SINTERED STAINLESS STEEL BASE MATERIAL



(a) 1400 X

(b) 3500 X

(c) [illegible] X

FIG. [illegible] MICROPHOTOGRAPHS OF THE TFE-SILVER CATALYST LAYER

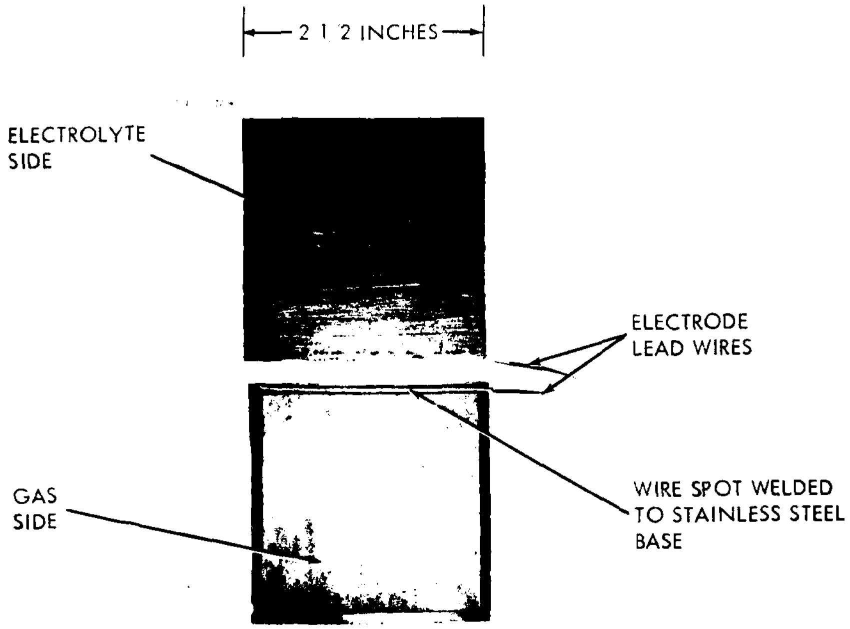


FIG. 5 FINISHED OXYGEN ELECTRODES

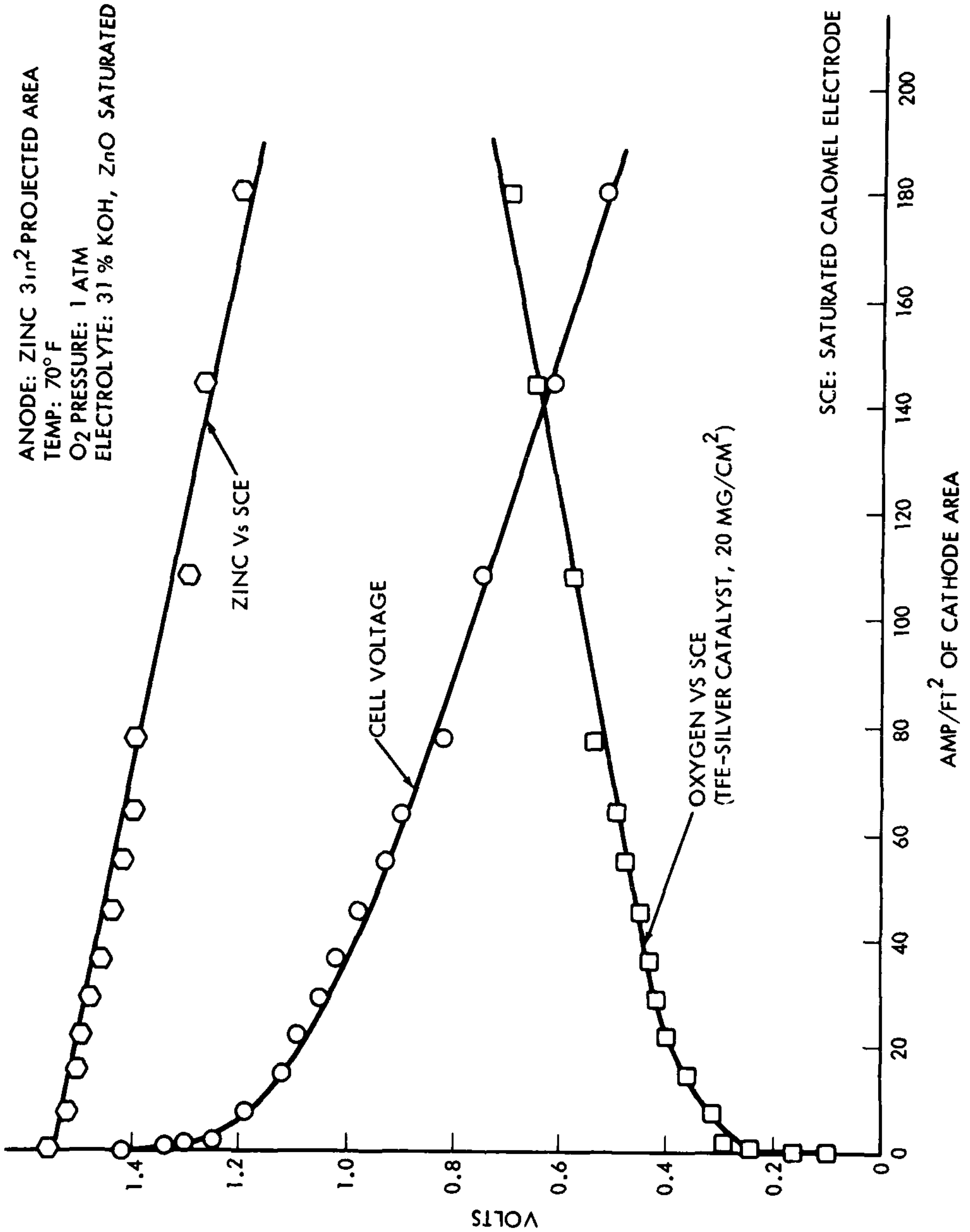


FIG. 6 PERFORMANCE OF OXYGEN ELECTRODE

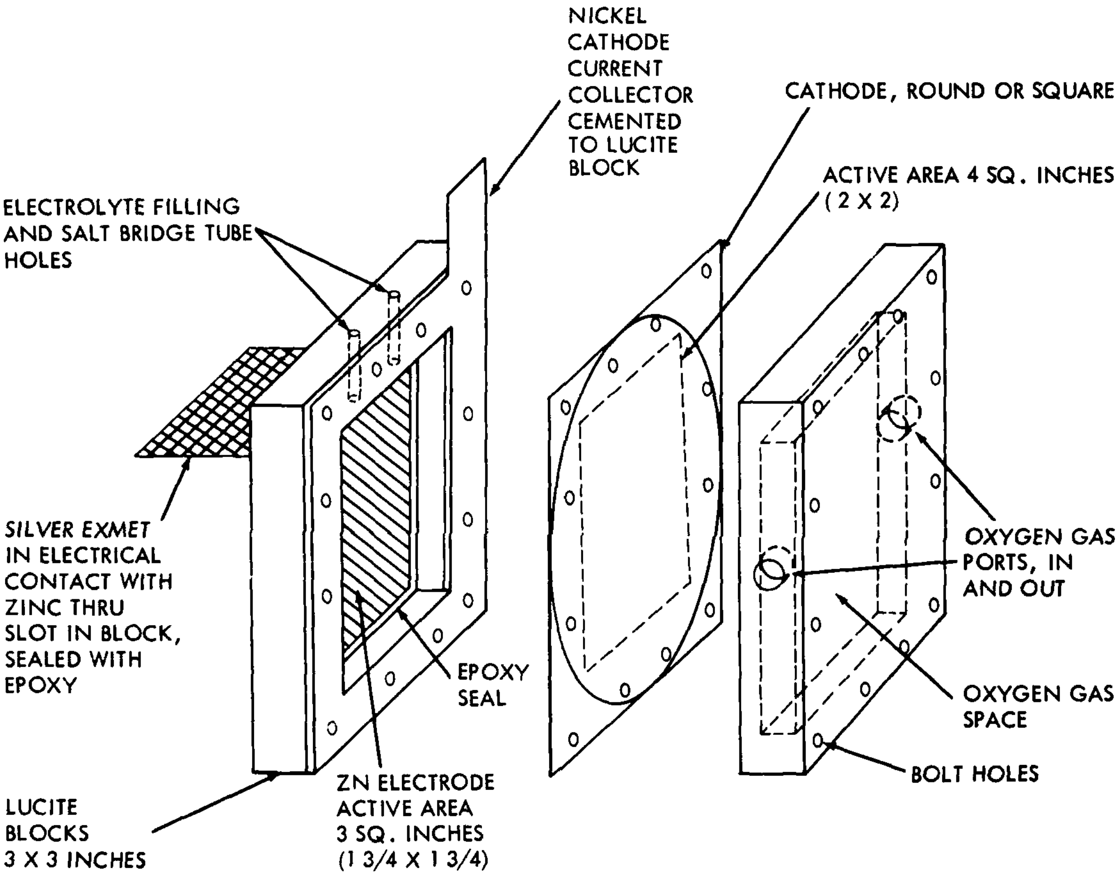


FIG. 7 APPARATUS FOR ELECTRICALLY TESTING OXYGEN ELECTRODES AGAINST ZINC PLATES

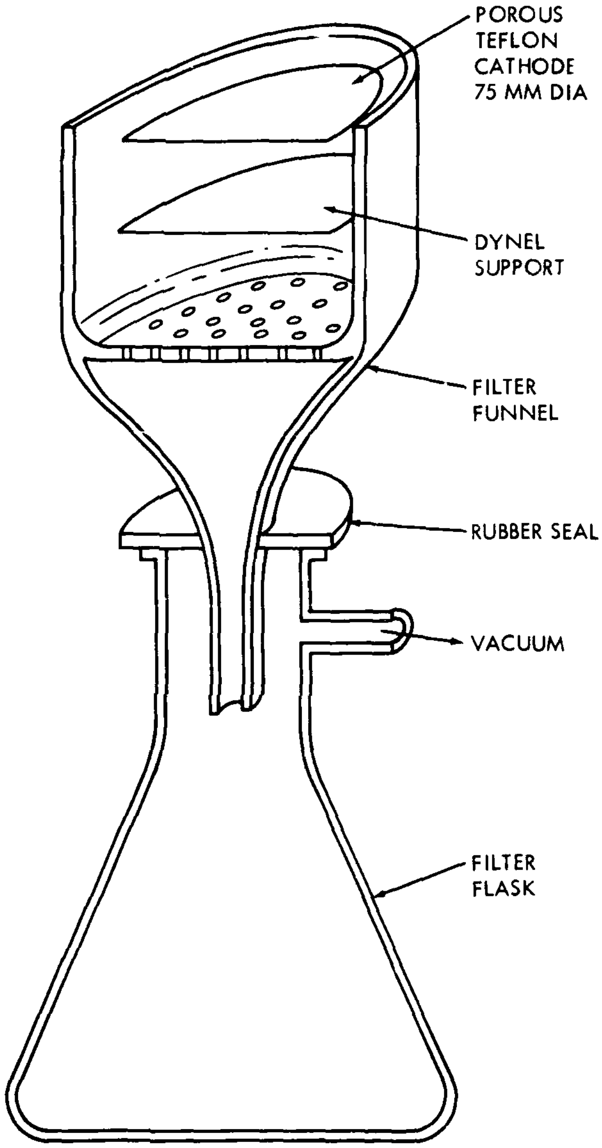


FIG. 8 APPARATUS FOR MAKING OXYGEN ELECTRODES FROM POROUS TEFLON

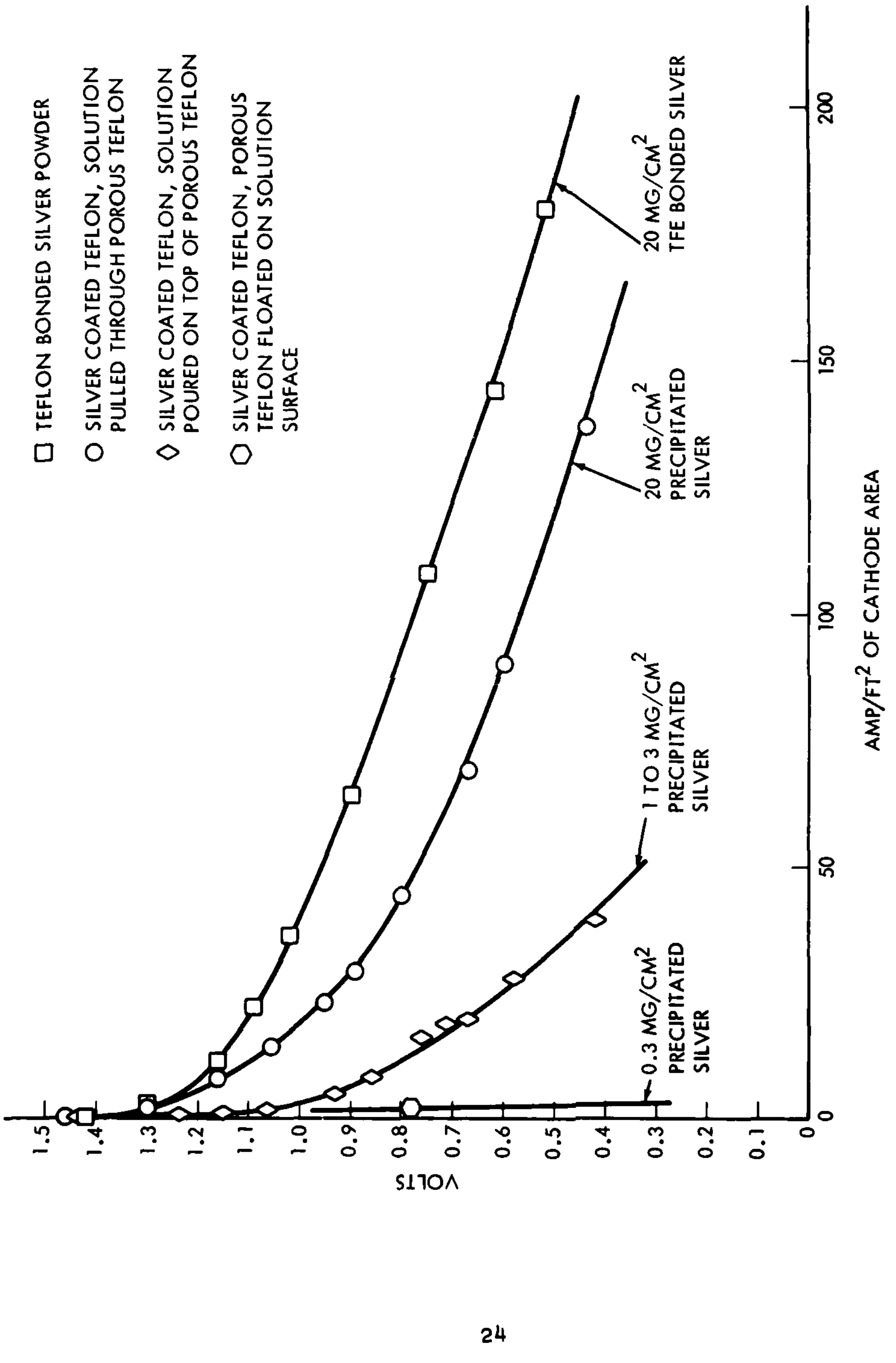
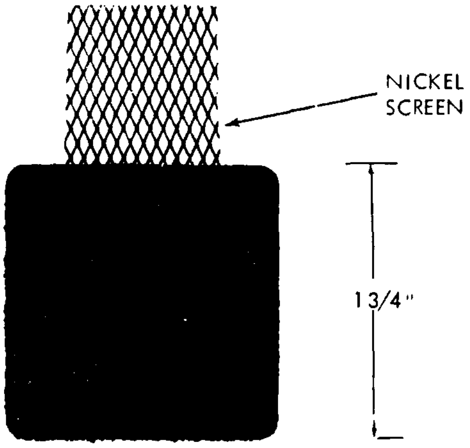


FIG. 9 PERFORMANCE OF ZINC-OXYGEN CELLS WITH PRECIPITATED SILVER CATHODES AND TEFLON BONDED SILVER CATHODES



STARTING ZINC PARTICLE SIZE: 60 TO 180 MESH RANGE
NaCL PARTICLE SIZE: 5% > 30 MESH
59% 30 TO 40 MESH
33% 40 TO 60 MESH
3% 60 TO 80 MESH

FIG. 10 FINISHED ZINC ELECTRODE

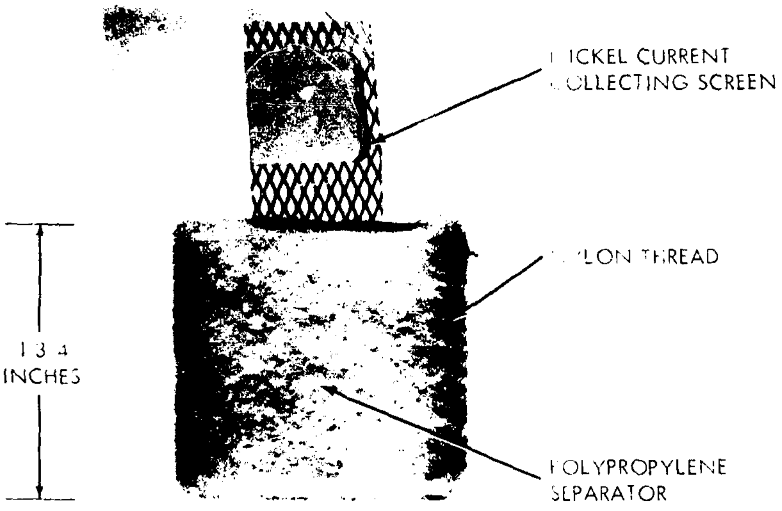


FIG. 11 ZINC ELECTRODE WRAPPED IN POLYPROPYLENE SEPARATOR

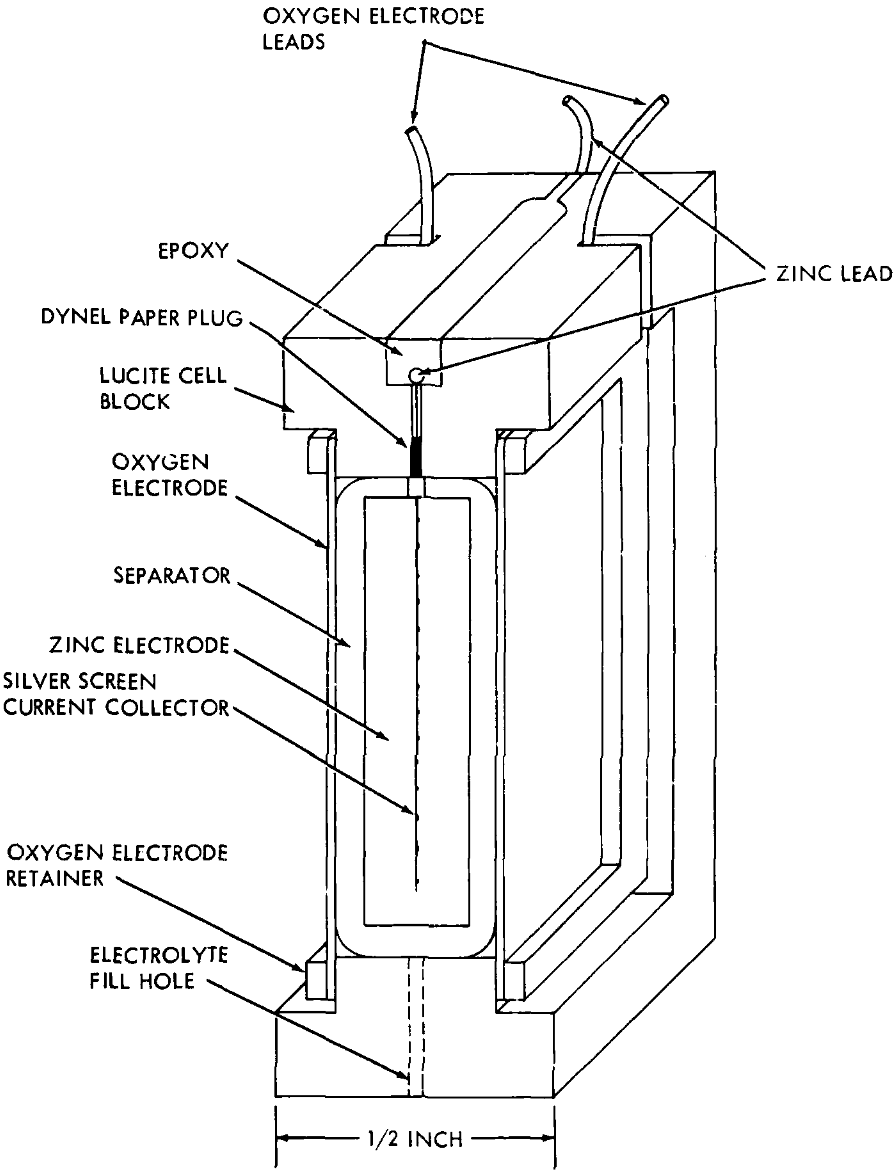
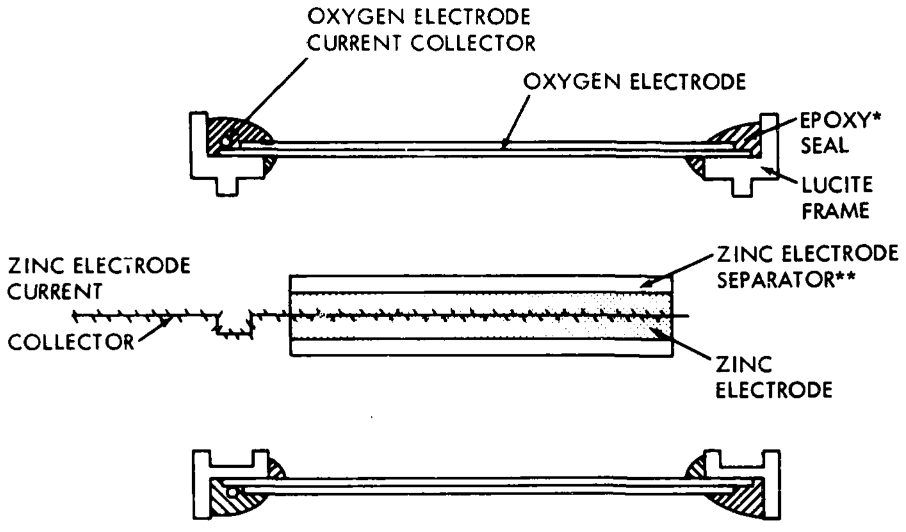
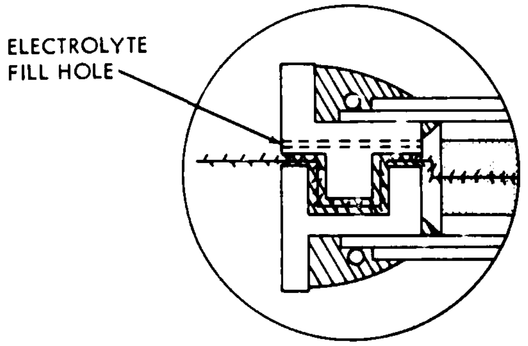


FIG. 12 CROSS SECTION OF THE ORIGINAL CELL DESIGN



a) BLOW-UP VIEW OF CELL CONSTRUCTION



*3-M ELECTRICAL RESIN "

**POLYPROPYLENE KENDALL GRADE H476

b) DETAILS OF FRAME AND ZINC ELECTRODE CURRENT COLLECTOR, ASSEMBLED

FIG. 13 SCHEMATIC OF SPLIT FRAME CELL DESIGN

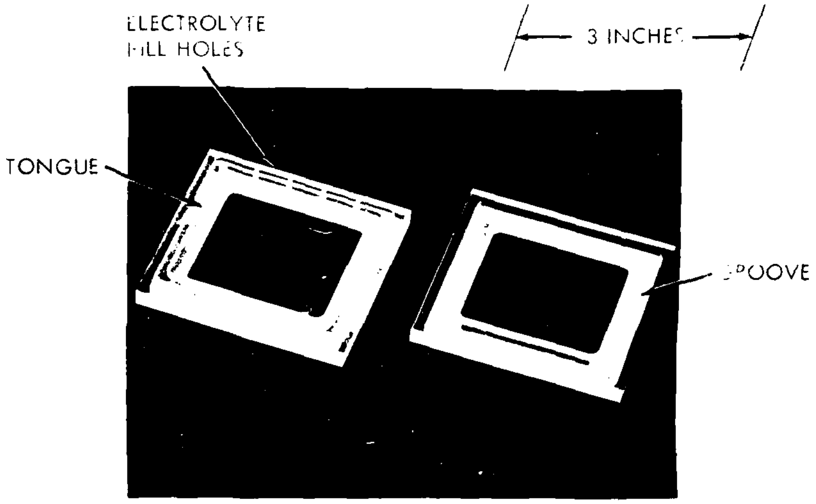
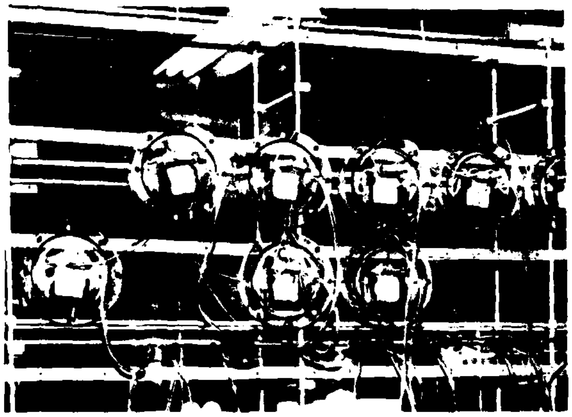
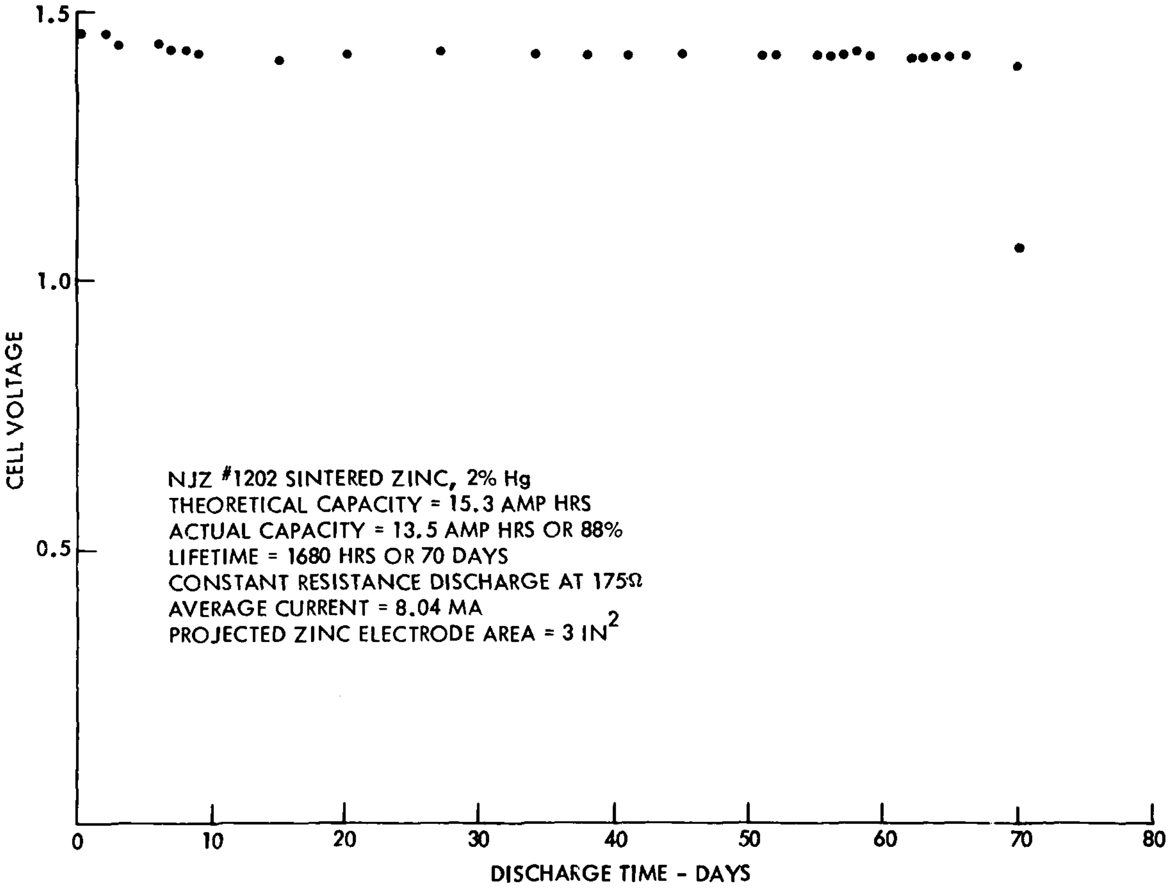


FIG. 14 LUCITE FRAMES USED IN SPLIT FRAME CELL DESIGN



SQUARE CELLS AS SHOWN IN FIGURE 1 ARE INSERTED IN DISC SHAPED OXYGEN CONTAINERS CONTINUOUSLY SUPPLIED WITH OXYGEN THRU THE PLASTIC TUBING AT 1 TO 3 INCHES OF WATER ABOVE ATMOSPHERIC PRESSURE

FIG. 15 ZINC OXYGEN CELLS ON DISCHARGE TEST



NJZ #1202 SINTERED ZINC, 2% Hg
THEORETICAL CAPACITY = 15.3 AMP HRS
ACTUAL CAPACITY = 13.5 AMP HRS OR 88%
LIFETIME = 1680 HRS OR 70 DAYS
CONSTANT RESISTANCE DISCHARGE AT 175Ω
AVERAGE CURRENT = 8.04 MA
PROJECTED ZINC ELECTRODE AREA = 3 IN^2

FIG. 16 TWO MONTH CELL DISCHARGE TEST

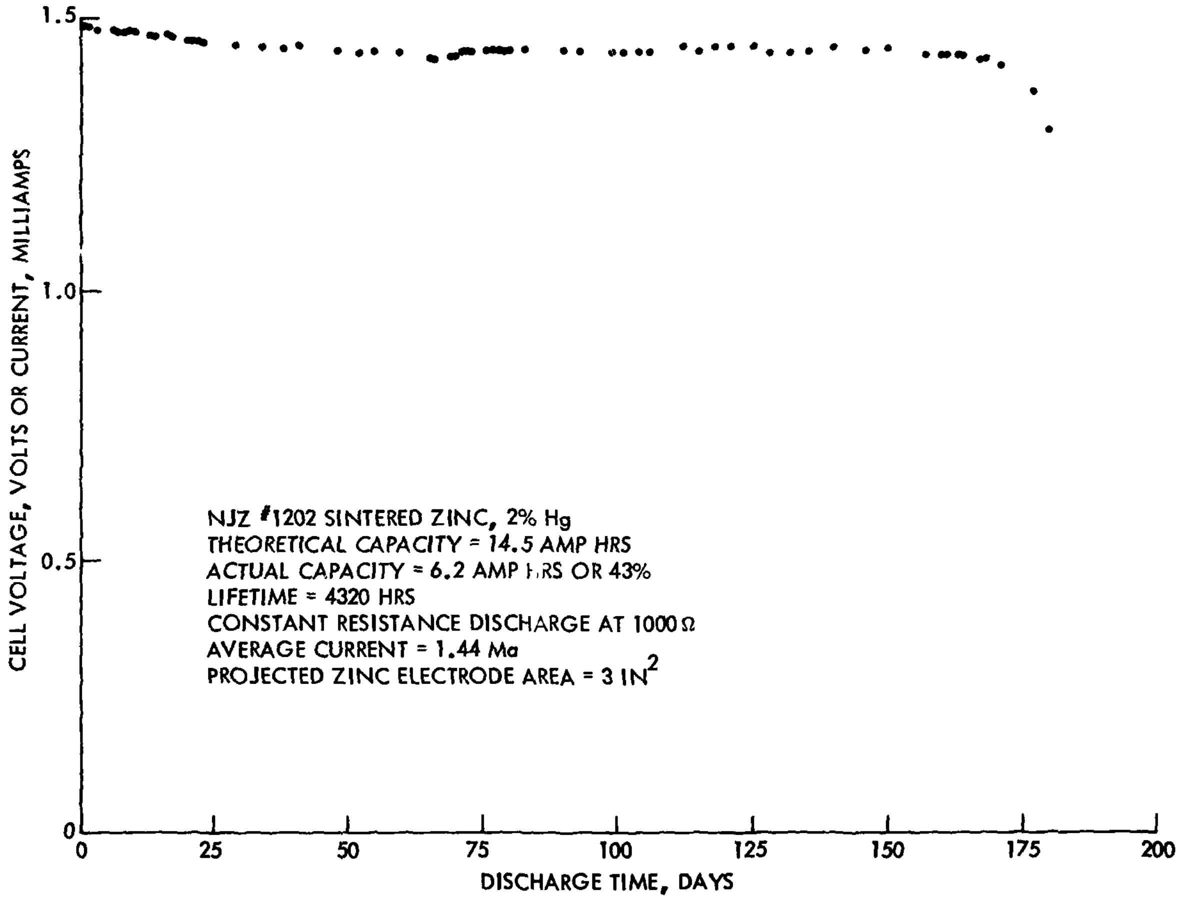
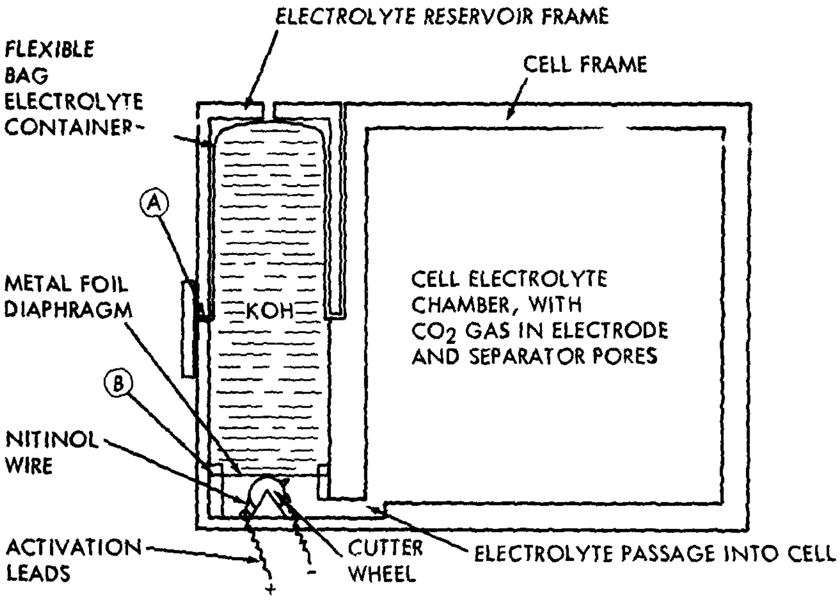
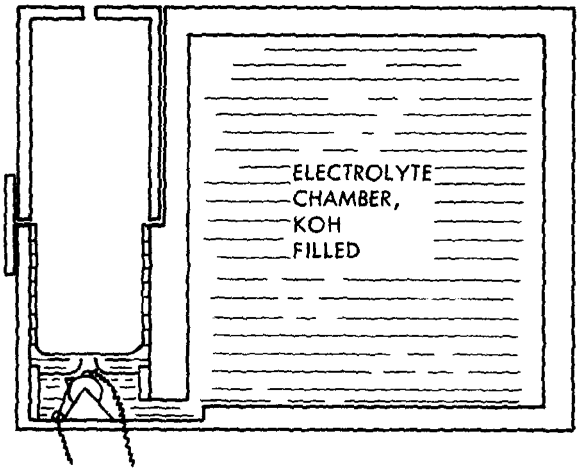


FIG. 17 SIX MONTH CELL DISCHARGE TEST

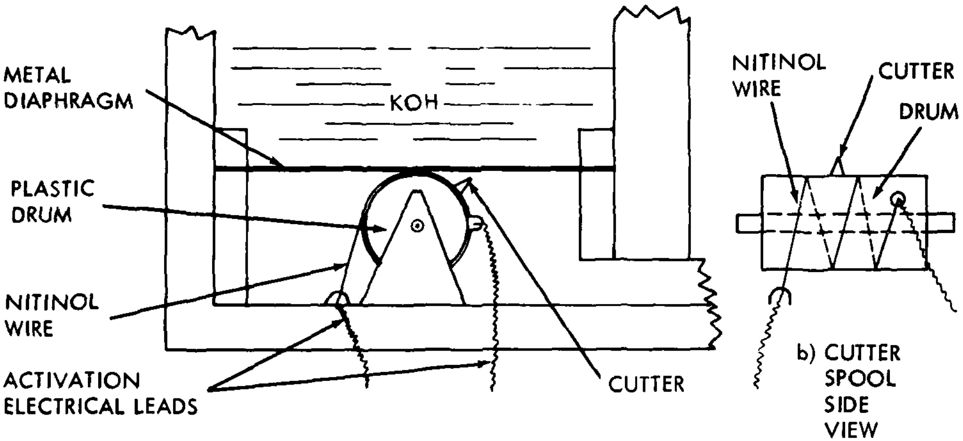


a) UNACTIVATED CELL IN STORAGE CONDITION CROSS SECTION



b) ACTIVATED CELL READY FOR DISCHARGE, CROSS SECTION

FIG. 18 SCHEMATIC OF CELL RESERVOIR AND ACTIVATION DESIGN



A) SCHEMATIC OF ACTIVATION SYSTEM MECHANISM

FIG. 19 DETAILS OF ACTIVATION SYSTEM DESIGN

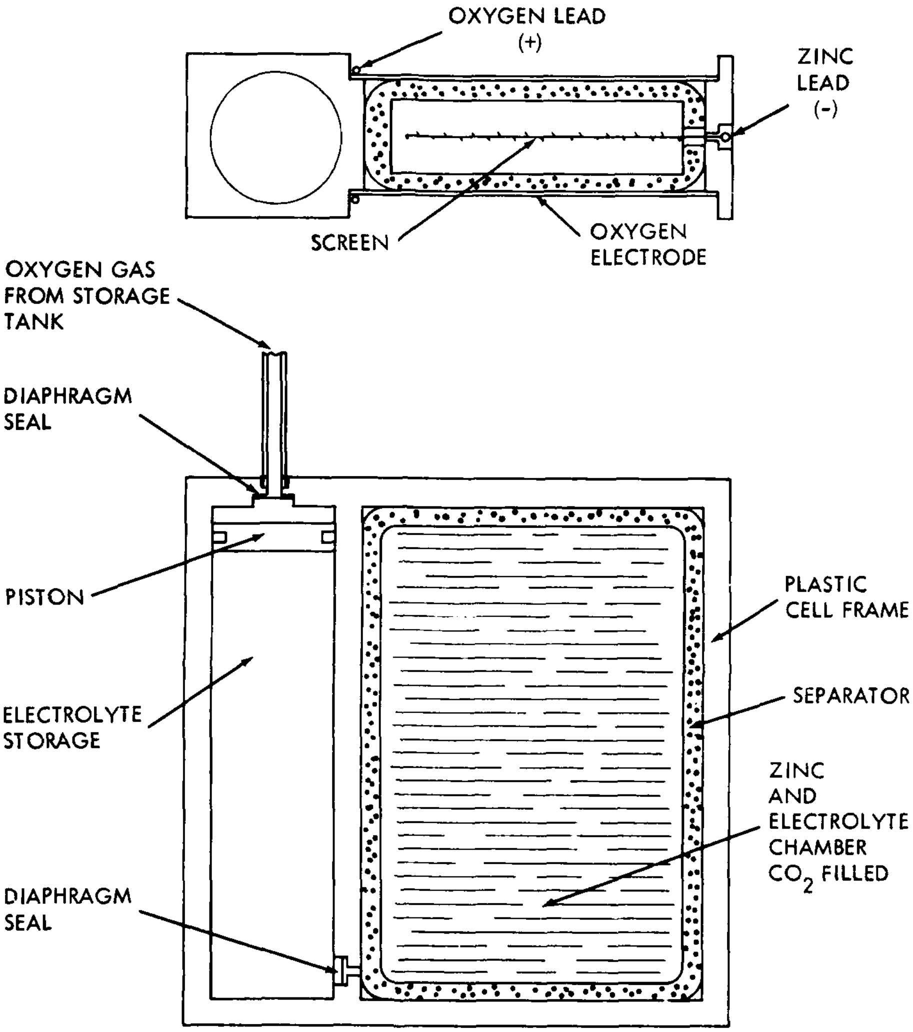
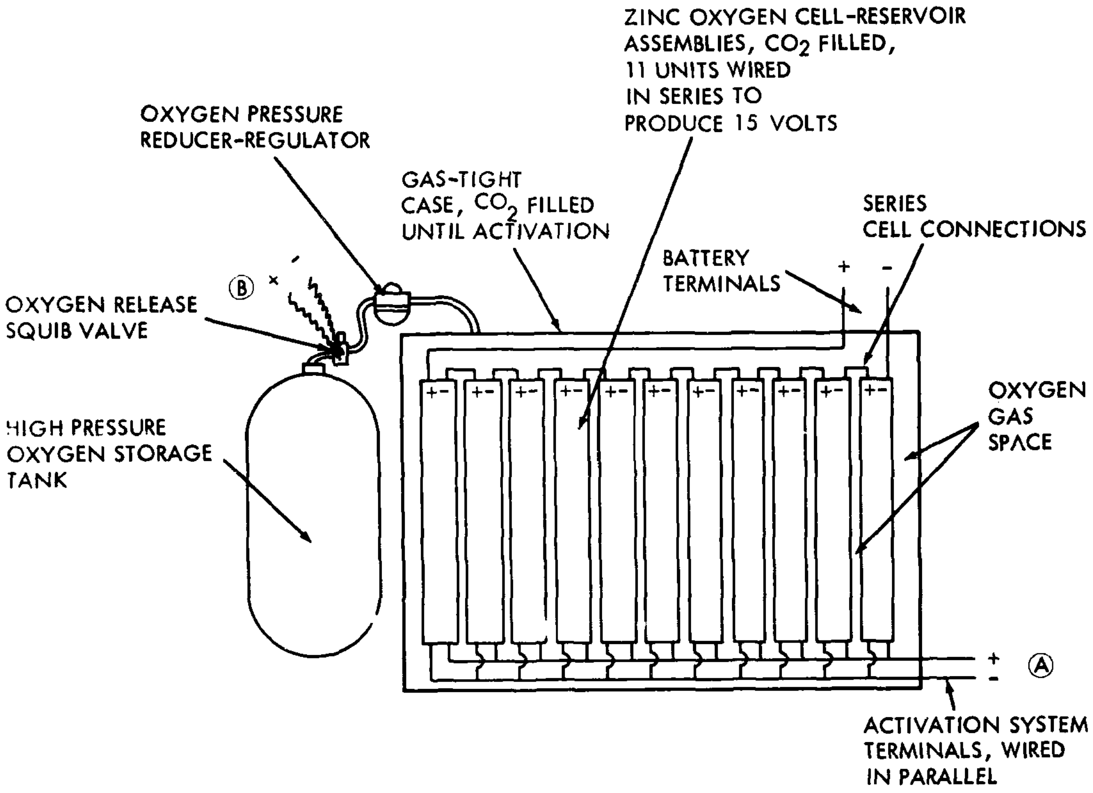


FIG. 20 SCHEMATIC OF ALTERNATE ELECTROLYTE STORAGE AND ACTIVATION METHOD

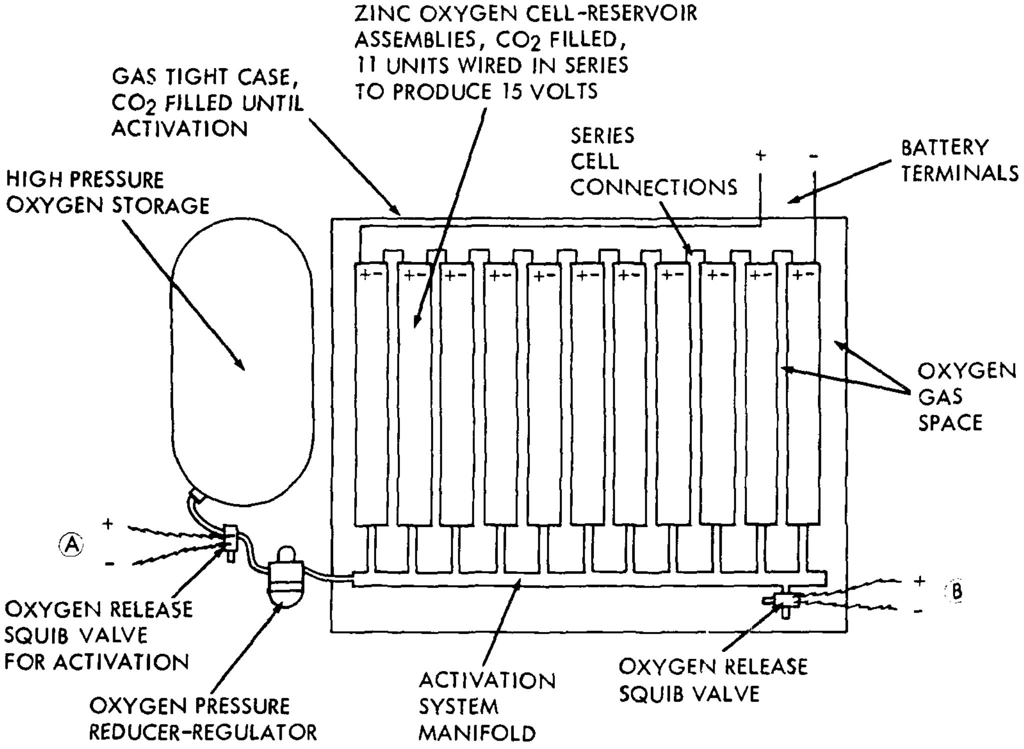


ACTIVATION SEQUENCE:

A. APPLY CURRENT TO CELL ACTIVATION SYSTEMS, POINTⒶ HEATING NITINOL WIRES, PUNCTURING DIAPHRAGMS, AND ALLOWING ELECTROLYTE TO RUN INTO THE CELLS.

B. AFTER A FEW MINUTES, APPLY CURRENT TO OXYGEN RELEASE SQUIB VALVE, POINTⒷ, PROVIDING OXYGEN FOR CELL OPERATION.

FIG. 21 SCHEMATIC OF OVERALL BATTERY SYSTEM



ACTIVATION SEQUENCE:

A. APPLY CURRENT TO SQUIB VALVE, POINT A, ALLOWING OXYGEN GAS TO RUPTURE THE METAL DIAPHRAGMS IN THE ELECTROLYTE RESERVOIRS, FORCING ELECTROLYTE INTO THE CELLS.

B. AFTER A FEW MINUTES, APPLY CURRENT TO SQUIB VALVE, POINT B, PROVIDING OXYGEN FOR CELL OPERATION.

FIG. 22 SCHEMATIC OF OVERALL BATTERY SYSTEM, ALTERNATE ACTIVATION METHOD

APPENDIX A

DETAILED MISSION REQUIREMENTS

Voltage: 15 volts nominal ± 10 percent.

Capacity: 100 milliwatts for one year continuous service to 85 percent of nominal voltage. In addition, intermittent loads of 400 milliwatts for not more than two percent of the total discharge time shall drop the voltage not more than 20 percent of nominal during the loaded period. The system should be capable of supplying spike loads and short overloads of 10 to 20 watts.

Operation: Discharge Time: 1 year continuous
Discharge Temp.: 28°F to 90°F
Discharge Orientation: must operate in any orientation with respect to 1-g.

Storage: 5 years in an uncontrolled environment
Storage Temp.: -65°F to +160°F

Activation: Minimum preparation for use is desired. An electrical signal or mechanical force will be available for actuation. The activation time is not to exceed one hour in any circumstances. One to five minute activation times are desirable. The battery should contain its own electrolyte and oxygen storage and distribution systems.

Weight and Volume: No specific requirements but weight and volume shall be minimized.

Vibration and Shock: Vibration and shock testing should be conducted to determine the compatibility of the cell and system structure with the following environments:

Vibration

a. Low frequency vibration, to simulate transportation by rail, truck, ship, or aircraft.

Simple harmonic excitation is applied parallel to each of the three principal axes of the device. The frequency range is covered by cycling at a logarithmic rate between the limits or by at least 24 discrete frequency steps which have a logarithmic distribution.

Frequency range (cps): 10-60

APPENDIX A
(Cont'd)

Amplitude, Peak to Peak: .10 ± .01 inches, or

2.0 ± .2g, whichever is less

Duration: 4 hours in each orientation

b. High frequency vibration, to simulate high speed aircraft delivery.

Simple harmonic excitation is applied to each of the three principal axes of the device. The frequency range is covered by cycling at a logarithmic rate of one octave per minute.

Frequency range (cps): 10-2000

Amplitude, Peak to Peak: .15 ± .02 inches, or

5.0 ± .5g whichever is less

Duration: 30 minutes per orientation

Shock

To simulate water entry at 750-800 FPS
Impact phase ΔV (FPS): 18-20
Impact phase time (MS): .1 to .3
Drag phase: duration 25 to 50 ms.

Average "g": 350 to 380
Peak "g": 500 to 550

APPENDIX B

METHOD OF DEPOSITING SILVER ONTO POROUS TEFLON SHEETS

Make the following solutions:

A. Sensitizing Solution

Stannous Chloride	10 g
HCL (12M)	40 ml
Distilled Water	1 liter

Dissolve the stannous chloride and mix the HCL into the cloudy solution to obtain a clear solution.

B. Reducing Solution

Sucrose	90 g
Nitric Acid (70%)	4 ml
Distilled Water	1 liter

Dissolve the sucrose in water and add the nitric acid. Bring solution to a boil and allow to cool to room temperature.

C. Silver Solution

Silver Nitrate	20 g
KOH (85%)	10 g
Distilled Water	400 ml
NH_4OH (30%)	50 ml

Dissolve silver nitrate in distilled water. Add KOH to form a dark brown precipitate. Add NH_4OH until brown precipitate dissolves. This mixture should be used as soon as possible after mixing, and no later than four to five hours after mixing.

To deposit silver on Teflon, first sensitize the Teflon surface by dipping it in Solution A for one minute. To four parts of Solution C, add one part of sugar Solution B. This will start the precipitation of silver from the solution. Place the Teflon in the solution in the manner desired, either floating on the solution or weighted to the bottom of the solution, or allow the precipitating solution to flow through the pores of the Teflon.