AD-782 059

RESEARCH AND DEVELOPMENT ON THE GLASS FIBER SODIUM-SULFUR BATTERY

Charles A. Levine

Dow Chemical U.S.A.

Prepared for:

Advanced Research Projects Agency

1 May 1974

Semi-Annual Technical Report

May 1, 1974

Research and Development on the Glass Fiber Sodium-Sulfur Battery

Contract No. DAHC-15-73-C-0254

Sponsored by

Advanced Research Projects Agency

ARPA Order No. 2381

Submitted by

The Dow Chemical Company
Walnut Creek, California

Program Code D10
Effective March 27, 1973
Expiration Date June 30, 1974
Contract Amount $240,510

Charles A. Levine
Principal Investigator
Phone: 415-933-3100

This research was supported by the
Advanced Research Projects Agency
of the Department of Defense under
Contract No. DAHC-15-73-C-0254

TABLE OF CONTENTS

SUMMARY

I. Technical Problem

The research and development program under this effort is an attempt to evaluate, improve, and scale up the hollow fiber sodium sulfur secondary cell. Some of the goals include achieving at least 1000 cycles of charge-discharge operation, building larger cells capable of long lifetimes, determining operating parameters at various rates of charge-discharge, and determining conditions required for thermal cycling the cells.

II. General Methodology

It has already been demonstrated experimentally that under normal operating conditions the rechargeable cell operates with negligable polarization, reversibly, and with extremely high efficiency. The main effort of getting longer life and larger cells revolves around the questions of what causes cell failures and how to assemble cells in such a manner as to not cause mechanical damage.

The work on mechanisms of cell failure is mostly carried out using small cells containing a few to a thousand hollow fibers. These cells can be rapidly constructed with little cost in time and materials. With these small cells we can determine the effect of different glass compositions, surface treatments, sealing techniques, etc. The nominal five ampere-hour cell is then used to confirm the findings, to determine conditions needed for thermal cycling, and to test larger scale assembly techniques. Analyses of cell failures are used to determine changes necessary to build better performance into the cells.

Along with cell operation and analysis, a large effort must go into making the component parts of the cells. The lifetime of the completed cell is extremely dependent on the "quality" of the component parts.

III. Technical Results

Substantial progress has been made toward solving the problems. Small cells containing 100 fibers have operated as long as 85 days, charging and discharging at one hour per cycle for approximately 2000 cycles. This exceeds the 1000 cycle goal. Cells containing 1000 fibers have operated for as long as 24 days giving over 550 C-D cycles. Each cycle is about 60% of cell capacity. Larger size cells containing 3200 and 4600 fibers, operated for 14 days and 9 days respectively. The 4600 fiber cell gave 54 cycles at 4 hours per cycle, charging and discharging at 40% of capacity.

High rate charge-discharge cycling is very satisfying. Cells nominally designed for a one hour rate have been operated at 17 minutes charge - 17 minutes discharge at over 90% of cell capacity for up to 213 cycles before failure.

Causes of failure are still not adequately resolved. Cell lifetime is shorter if there are (1) more fibers, (2) poor quality fiber glass, and (3) thinner glass fiber walls. But the factors controlling why fibers fail is not known.

Early cells had increasing cell resistance starting after several days of operation. This problem was solved.

A study of conditions necessary to permit thermal cycling of the cells has just begun.

Interactions between the tube sheet glass and the glass fibers are extremely important to the cell lifetime. Several variations in compositions of these glasses have been made to minimize these interactions.

In spite of a large effort placed on the mechanical operation of spinning and assemblying the glass fibers from a glass melt, we still cannot do this routinely. In order to have bubble-free glass, we must use a new boron nitride spinnerette for each days run. Slight changes in glass viscosity drastically affect the uniformity of assembly of the fibers.

Mechanical damage during assembly of the 5 ampere-hour cells has been materially lessened by the use of special supports in the cell assembly. This unfortunately adds weight to the cell. We are still trying to develop alternate methods of cell assembly without mechanical damage.

IV. Implications for Further Research

We are still trying to pin down those factors that cause the glass fibers to eventually fail. Reproducible spinning of the glass fiber from the melt and its subsequent handling is probably very important. The lifetime of the larger cells must be materially increased and higher currents drawn.

Thermal cycling of the cell is anticipated to be a big problem. The expansions and contractions of different solids in contact with each other will cause tremendous mechanical strains. We must learn how to minimize these. The heating and cooling experiments must be done on the larger size cells to be meaningful.

INTRODUCTION

Development is proceeding on a high energy density sodium-sulfur secondary battery which uses the walls of fine hollow glass fibers as the electrolyte-separator. Use of thousands of these hollow glass fibers, bundled together in parallel and filled with sodium as the anolyte, result in a cell that has a very high energy per unit weight at a high power per unit weight.

This work is being done under a contract sponsored by the Advanced Research Projects Agency and jointly funded by the Advanced Research Projects Agency and The Dow Chemical Company.

This is a semi-annual technical report covering operations covering the time from the start of the contract to May 1st, 1974. Under the terms of the contract we are to try to make multi-fiber cells capable of at least 1000 cycles of charge-discharge, build larger cells capable of long life-times, scale up to a 5 ampere-hour cell, continue development of a 40 ampere-hour cell, determine operating parameters at different charge-discharge rates, and determine construction details necessary for thermal cycling.

We have made good progress under this contract. We have constructed 100 fiber cells that have operated over 2000 cycles and 85 days continuously. Cells containing 1000 fibers have operated continuously for over 3 weeks and 500 cycles. Progress is being made on scaling these up to 5 ampere-hour cells. An understanding of some of the factors affecting lifetime is being made. High rate charge-discharge cycling has been done. This is the only system the authors are aware of that is capable of being cycled at over 90% of cell capacity at a 17 minute rate for hundreds of cycles without failure.

RESULTS

I. Back-up for Fabrication Operations

Glass Making. The glasses used in making the fibers and the glasses used in making the solder glass are all made by mixing the raw materials and melting in platinum crucibles at 925° to 1000°C. The fiber glasses are fundamentally borates with various additions to improve conductance, control expansion coefficients, and prevent crystallization.

The T104 fiber glass used at the beginning of this report period is a fluoride containing borate. Variable results using this glass suggested that the fluoride component was vaporizing from the molten glass batch. To test this, samples were taken from the glass batch every half hour over a two hour period while the molten glass was held at 1050°C. Analytical results from neutron activation analyses are shown below. The fluoride content remained quite constant.

F^- Content of T104 Glass

	% F
Sample 1 hour after melting	3.22
" 1.5 " " "	3.37
" 2.0 " " "	3.19
" 2.5 " " "	3.17
" 3.0 " " "	3.48

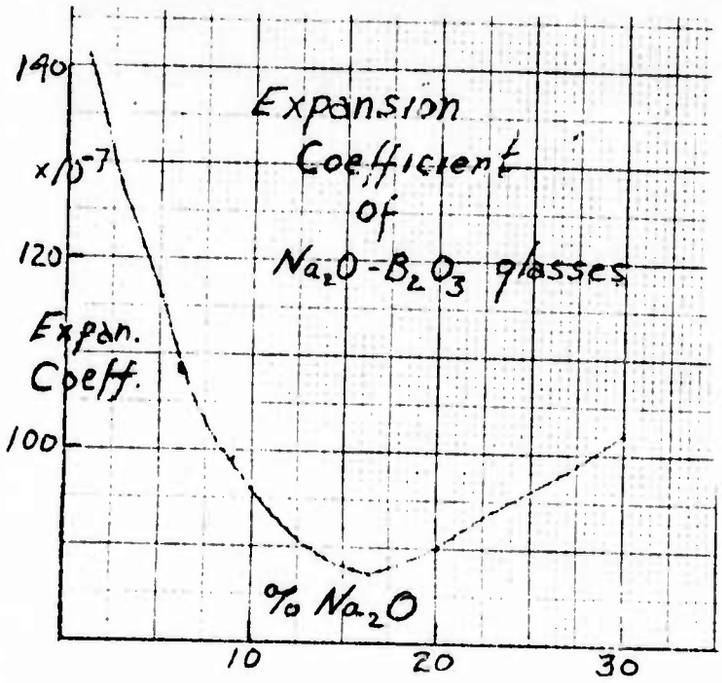
The glass was then loaded into the melt tank of the fiber drawing furnace, bubbled with dry nitrogen at 850°C for 16 hours to dry it, and then debubbled by evacuation for 1 hour. This glass was pulled into hollow fibers. Samples were taken during the 4 hour fiber pulling run. Again, no change in fluoride content was detectable.

The variable results obtained using this glass turned out to be due to a mismatch in expansion coefficient between the glass and the tube sheet glass. The apparatus used to determine expansion coefficients (Du Pont Thermal-Mechanical Analyzer) was rebuilt to give accurate and consistent results. The expansion coefficient of the T104 fiber glass was redetermined to be 130 x 10^{-7} per °C instead of 108 x 10^{-7}. An attempt was made to adjust the chemical composition of this glass to bring the expansion closer to that of the glass used for the tube sheet material. It was then found that the tube sheet glass--another fluoride containing glass--did change composition as the molten batch sat in the oven at 950°C. The analyses are shown below.

F^- Content of T162 Solder Glass

	% F-
16 minutes after melting	11.4
50 " " "	10.7
70 " " "	10.0
100 " " "	9.0
145 " " "	8.4
205 " " "	6.68
265 " " "	5.28

A somewhat different glass system was then substituted for the old solder glass system. Using a binary B_2O_3 - Na_2CO_3 mix, low melting solder glasses can be made with a wide variety of expansion coefficients. Also, the glasses are stable in composition during melting and processing. The expansion characteristics of the sodium borate glasses are shown.



Using this system we could pick a low melting solder glass with the same expansion as the fiber glass. A glass with the same expansion coefficient as the T104 fiber glass ($\alpha = 130 \times 10^{-7}$) would be about 2% Na_2O - 98% B_2O_3. Unfortunately this solder glass has an annealing temperature much below 300°C, the operating temperature of the finished cell.

The sodium borate solder glass system was still desireable from the standpoint of an adjustable expansion coefficient, but at least 4% Na_2O was needed to make the softening point high enough to be useable. Therefore, we decided to adjust the fiber glass composition to have a fiber glass expansion coefficient in the range of the useable solder glasses.

A fiber glass very similar to T104, but containing chloride instead of fluoride was developed. It was called T406. The expansion coefficients, transition temperatures, and softening points of some of these glasses are shown in the Table.

	Exp. Coeff. x 10^7	T_g	$T_{s.p.}$
T104 fiber glass	130	432°C	>460°C
T406 fiber glass	116	~450°C	>460°C
$91B_2O_3$:$9Na_2O$ solder glass	94	300-310°C	387°C
$94B_2O_3$:$6Na_2O$ solder glass	114	300-310°C	380°C
$94B_2O_3$:$6Na_2O$ (dried)	111	335°C	400°C

The T406 fiber glass and the $94B_2O_3/6Na_2O$ solder glass are a good match.

Solder Glass Making. The solder glass must be ground and made into a high solids content extrudeable paste so it can be applied and shaped into a tube sheet holding all the fibers. To make this paste with a high solid content, the glass particle must be properly sized for good packing. The solder glass cullett is broken up, ground and sieved. The 200-325 mesh portion is spheroidized by feeding it through a CO + O_2 flame. Since the $94B_2O_3/6Na_2O$ is water sensitive, a hydrocarbon flame cannot be used. The -325 mesh portion is ball-milled to a much finer powder. Equal weights of the spheres and the powder are suspended in cumene to give the paste.

A great deal of trouble was encountered in trying to ball mill the 94/6 to the proper fineness. "Proper fineness" is defined by its ability to be suspended and extruded in a small amount of cumene. Dry ball milling for up to 18 days gave only marginal performance. Attempts to wet grind in toluene, isooctane, or hexane were not successful. An investigation of particle sizes using electron microscopy indicated that after about 5 days, the rate of impact fusion of the glass particles equalled the rate of spallation. Ball milling at -17°C or with a surface active agent (hexadecylamine) did not help.

We finally discovered that the glass could be ball milled to a proper size by ball milling at 90°C in the presence of 1% hexadecylamine. Apparently, at 90°C, the vapor pressure of the amine is high enough so that freshly broken glass surfaces are covered with a surface layer of the amine. This prevents re-agglomeration. The standard method of grinding 94/6 now is to ball mill the -325 mesh fines for at least 7 days at 90°C in the presence of 1 1/2% hexadecylamine. The ball mill must be well sealed to prevent loss of amine. Other surface active agents tried included $C_{16}H_{33}CN$. This did not work. $C_{18}H_{38}OH$ gave marginal results.

During the attempts to suspend the poorly ground 94/6 solder glass, some suspending vehicles other than cumene were tried. Neither pyridine nor piperidine, which have higher dielectric constants, nor benzene, which has a lower dielectric constant, worked as well as cumene.

A low melting solder glass of $91B_2O_3/9Na_2O$ will grind by ball milling much more readily than the 94/6. The 91/9 has an expansion coefficient of 94×10^{-7} instead of the desired 114×10^{-7}. Adequate tube sheet glasses could be made by mixing 50% by weight of the 91/9 finely ground powder and 50% 200-325 mesh glass spheres of T104 glass ($\sigma = 130 \times 10^{-7}$). When we were finally able to grind the 94/6, this approach was abandoned.

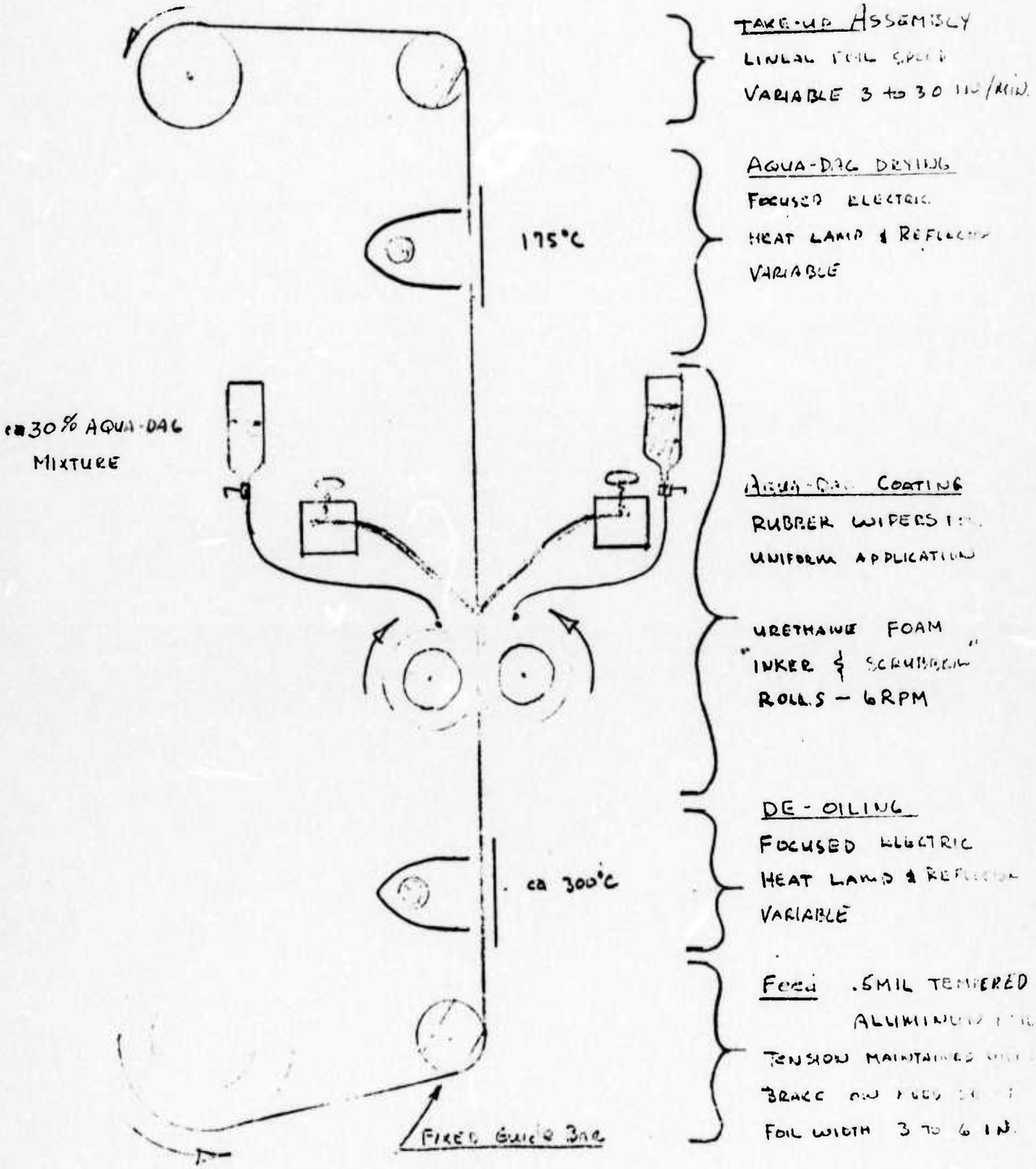
Preparation of Cathode Foils. The 0.7 mil thick aluminum foil used as the cathode collector must be coated with carbon before assembling the cell. This is done by cleaning the foil, painting it with aquadag, and then baking it to remove the binder. In the past, this cleaning and applying carbon has been done by hand. Strips of the foil, 15 cm by 300 cm were baked at 300°C in air to oxidize any oil on the surface, painted with a mixture of aquadag and water, dried by hot air, and then baked for one to two hours at 300°C to get rid of the binder. A device to coat the foil in a continuous manner was built.

The foil is unwound from a back tension roller and past a focused heat lamp (300 watt - 110 volt) to vaporize from the surface "ROLLING LUBRICANTS" which prevent the aquadag from wetting the foil surface. Tests have shown that heating the foil only slightly hotter than is necessary to remove the oils causes the foil to anneal partially and the resulting warps make the winding of the foil in a straight roll impossible. All attempts at completely annealing the foil at this time failed due to uneven roll-up problems. A gentle air current blown across the foil at the de-oiling section seemed to be beneficial, probably due to oil vapor being prevented from condensing on the cool foil directly above.

The aquadag is applied to the foil with two opposing rolls, each with a replaceable urethane foam sleeve. A certain amount of scrubbing is necessary to assure all surfaces are wetted with the aquadag mixture. Different roll materials and roll pressures were tried. The maximum pressure on the rolls that did not distort the foil was the better adjustment. It is also desireable to keep the rolls saturated with the aquadag mixture such that a small pool of the mixture is maintained at the foil roll junction. This was found easy to maintain with the foam urethane sleeves. Because the sleeves were "homemade" and somewhat less than round at the seams the coating was applied thinner at this position.

Two opposing rubber wiper blades distributed the mixture evenly on the foil, but with improved scrubber rolls, the wiper blades might not be necessary. The quantity of aquadag applied is related to the mixture concentration. It was noted that a relatively thick application of aquadag rubbed off more than a thinner application. The effect this may have on the end use of the foil is not known.

ALUMINUM FOIL AQUA-DAG COATING DEVICE



Drying the aquadag coated foil is easy provided there are no drops of liquid present, in which case the drying is too slow and the wet drops get rolled up. Correctly positioning of the rubber wiper blades prevented drop formation. On the inside foil surface there was a gradual build-up of graphite on the fixed guide bar. When this occurred, it distorted the foil and resulted in undesireable grooves or wrinkles in the foil. If a wet drop got to the guide bar this effect was immediate, otherwise, operation was satisfactory for about 70 to 100 lineal ft. The graphite build-up could be removed easily with 600 grade emery paper.

The aluminum foil feed stock was not rolled perfectly and the take-up assembly always rolled up somewhat more uneven than the feed roll. This limited the size of a finished roll wound in a desireable condition to about 30 to 50 ft.

A better feed roll or an automatic guide system would increase the size of the finished roll, however, the development cost of the latter might not be worth the benefits.

If the foil drive stops while the aquadag drying lamp is on the foil is immediately melted.

The finished roll is removed from the drive roll and placed in a 300°C oven for annealing.

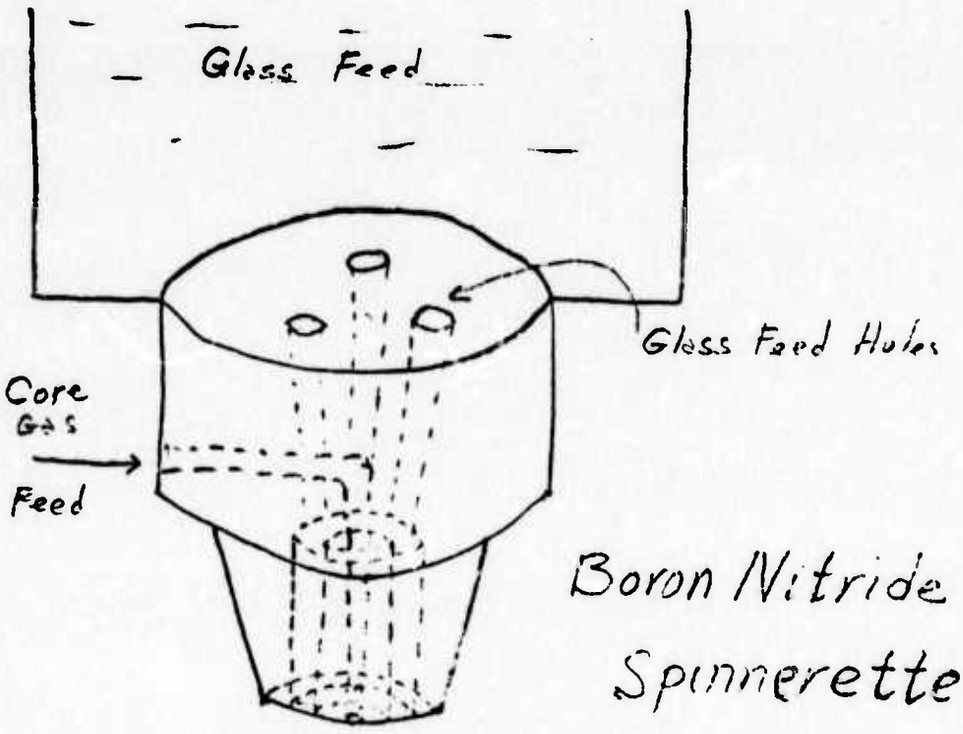
Preparation of Anode Cups. No changes have been made in the preparation of the anode cups other than to improve the technique. This operation is still done by hand. The 5 mil wall aluminum cup is degreased and dipped into a 750°C melt of the same glass that is used for the solder glass. Care must be taken to keep the

glass-melt free of bubbles. When the aluminum cup is withdrawn, a ledge of the glass is left around the lower lip of the aluminum cup. Excess glass is broken away and discarded. We have not yet begun the task of permanently sealing the top of the cup around an anode lead.

Purification of Reactants. The sodium metal is not purified. Sulfur is distilled at 800°C over a two foot Vycor bed in order to react any organic matter to CS_2 and H_2S. The distilled sulfur is then purged at 145°C with nitrogen for 4-5 days. The purity of the sulfur can be determined by the initial resistance of a newly filled NA-S cell.

II. Modification of Mini-Plants

Fiber Drawing and Assembly. To make the glass fibers, the fiber glass cullet is melted in a nickel furnace and extruded through a boron nitride spinnerette.



The glass is extruded at about 780°C. Boron nitride is used because it is not readily wettable by the molten glass. If the glass wetted the spinnerette, some glass would have a long residence time at a temperature that would allow crystallization. Crystal formation weakens the glass fiber.

At the beginning of this period we were experiencing a number of difficulties in drawing the hollow glass fibers. The dimensions of the hollow glass fiber did not stay constant. Pressure surges caused the glass to occasionally back up into the core gas needle. A new core gas pressure system was built to increase dimensional control.

The spinnerette itself received a fair amount of development work. In place of the one piece boron nitride spinnerette, a two piece spinnerette was constructed in order to make the machining easier. The two piece spinnerette gave great difficulties in alignment - in trying to get the hole in the fiber centered - and in leakage so it was abandoned.

There were bubbles in the glass fibers which seemed to come from reaction of the T104 glass with the boron nitride spinnerette. Bubble-free glass fibers were obtained during a 6 hour run only when we (1) used a new spinnerette and (2) a freshly cleaned fiber glass melting tube. A small amount of SiO_2 (.04 mole %) was added to the T104 glass to keep it from crystallizing and a platinum spinnerette was tried. This gave a great many bubbles in the glass and the platinum spinnerette turned black. Probably some sort of electro-chemical reaction took place in this system that included the platinum, a nickel furnace, gold washers, molten borate glass and possibly lots of stray currents.

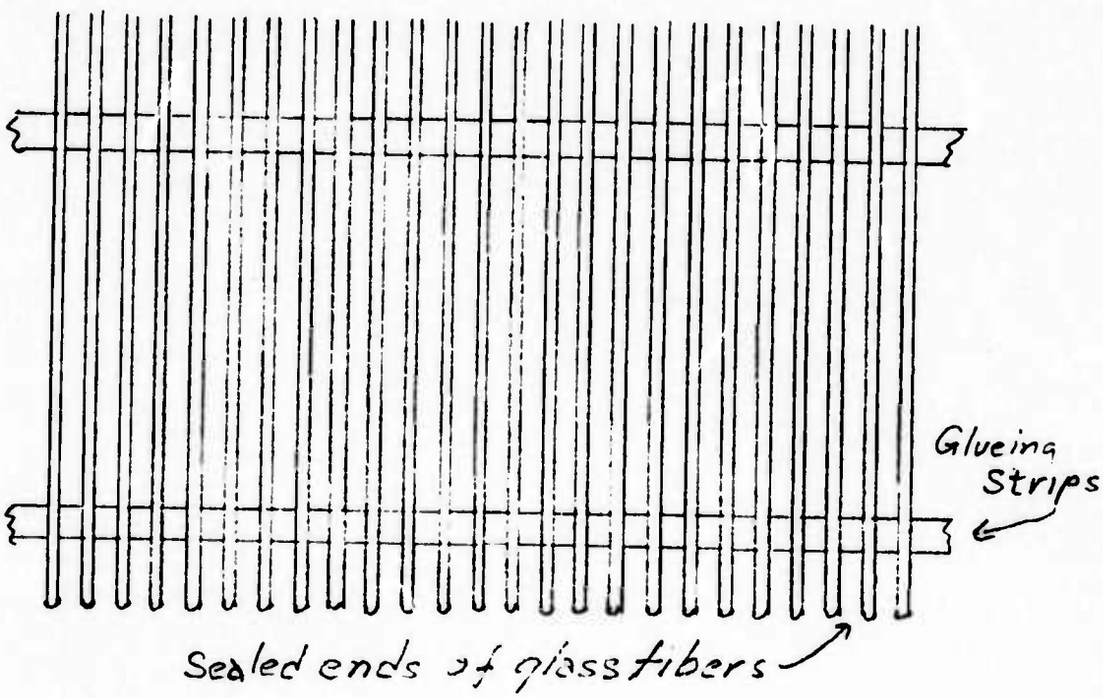
A platinum spinnerette and a platinum lined furnace were designed and are being built.

Thinking that perhaps the fluoride in the T104 glass was reacting with the boron nitride to form the bubbles, we substituted chloride for the fluoride in the glass cullet. We still obtained bubbles unless the two conditions mentioned previously were met.

The glass for the fibers is dried as thoroughly as possible before the spinning operation. After melting, dry nitrogen is bubbled through the melt for 16 hours. A vacuum is then applied for 1 to 2 hours. This dried glass is then spun directly from the tube in which it was dried.

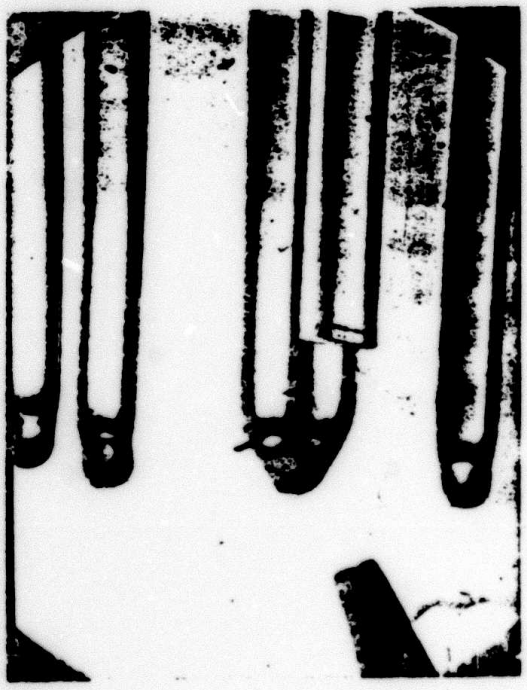
The "bubble problem" was <u>not</u> helped by pre-drying the raw materials that make the glass, by eliminating bi-metallic couples in the melt tank, or by "dry box" handling of the spinnerettes.

As the fiber is drawn, it is taken up on the fiber assembly machine where it is laid down in a parallel arrangement with a preset distance between fibers, cut to length, and one end sealed.



Laying the fibers down parallel with a pre-set distance between them has been and is a continuing problem. At the beginning of this period, tension pulleys were used between the spinnerette and the take-up reel. Unfortunately, the glass fiber would cut the rubber surface of the tension pulley and then get caught on snags. The tension pulleys were discarded and replaced with a series of 4 free-running pulleys which directed the fibers to the take-up belts. Surfaces on these pulleys have, at various stages of development, been aluminum, stainless steel, and lucite. The aluminum surface was probably bad because the aluminum oxide scratched the fiber. As yet, we do not have enough information to tell if the stainless steel is bad. The lucite tends to pick up a static charge and cause the fiber lay-down to be uneven.

When the lay-down of the fibers is uneven and the fiber to fiber spacing is not correct, the procedure of sealing the tiny fibers can seal two or more fibers together. This results in a weak area which may break.



Not only the lay-down pulleys, but also the glueing tapes affect the ability to space the fibers at proper intervals. These 0.5 mil aluminum tapes hold the fibers at the desired spacing. At the beginning of this period, the glueing tapes sometimes "wandered", dragging the fibers askew. The fiber assembly machine was modified so that these tapes run in grooves, forcing them to align properly.

Another modification of the fiber assembly machine followed the discovery that some of the glass fibers leaving the machine were broken at points where the fibers were glued to the glueing tapes. They had been broken by being forced against tiny pieces of broken glass that had collected on the take-up belts. Wiper pads of kerosene-treated polyurethane foam were placed against these take-up belts. This solved the problem.

A device was built to apply a coating on the fiber as it was drawn. This applicator was placed between the spinnerette and the fiber take-up pulleys. It was hoped that coating the freshly drawn fiber would prevent it from being scratched and keep it strong. A solution of 2% hexadecyl amine in xylene was applied to the fiber. Unfortunately, some of this coating came off on the take-up pulleys and caused static charge build-up. This caused a very bad non-uniformity of lay-down of the fibers so the coating step was discontinued.

III. Cell Assembly

Assembly of Fibers and Cathode Foil. The glass fibers and the cathode foil are rolled together, jelly-roll fashion, on the cell assembly machine as the tube sheet paste is applied. This is a straight forward process and there have been essentially no mechanical changes. The spacing between adjacent foils was increased from 100 microns to 175 microns for several cells by changing the thickness of the spacer

tape. The purpose was to see if the resultant cells were longer lived. The results were inconclusive.

Handling the rolled cell assemblies sometimes resulted in broken fibers on the outside of the roll.

To prevent this we used 65μ diameter rods (instead of hollow fibers) on the outer several layers of the roll.

As the fibers and foil are rolled up and the tube sheet paste is applied, it was found advantageous to vibrate the whole assembly to get good penetration of the tube sheet paste in amongst the fibers. The tube sheet paste is thixotropic and the use of vibration at this stage greatly reduces the leakage of the final cell. Minimum porosity of the final tube sheet was found if: (1) vibration was used; (2) the tube sheet paste was fairly fluid; and (3) the tube sheet was fairly thick.

Curing of the Tube Sheet. Little further work has been done on tube sheet curing and fusing conditions. We very rarely get cracks in the tube sheet during the fusion step.

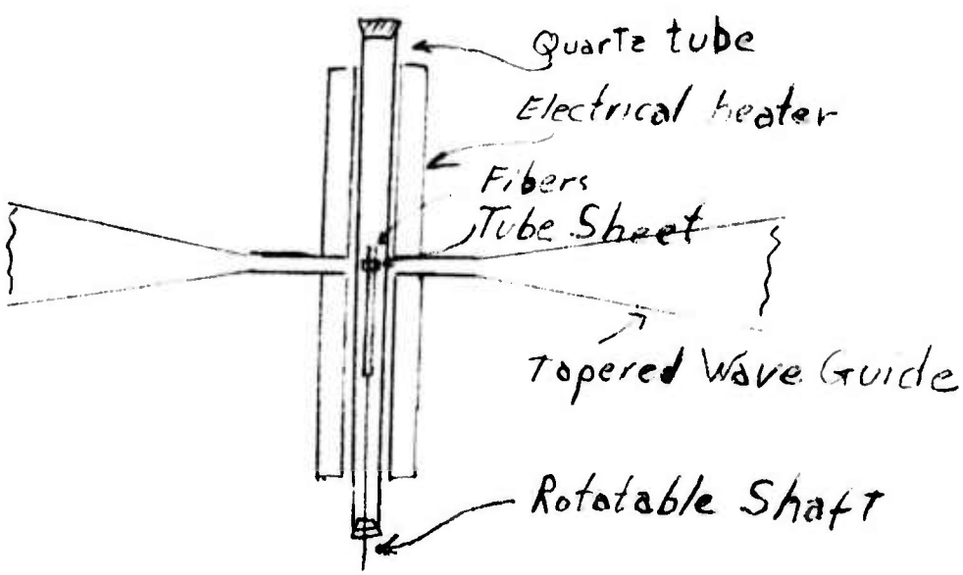
After rolling the cell assembly, the tube sheet is dried under a heat lamp for about 20-30 minutes, machined to size, placed in a vacuum, and then heated at about 5° C per minute to 394° C. For the 5 ampere - hr. size cell, the vacuum must be applied about 10 minutes before heating is started. This removes much of the cumene from the tube sheet. If this is not done, the tube sheet cracks. The assembly is held at 394° C for 1-1/2 hours to allow the tube sheet to fuse into a solid glass mass.

Attempts to place the assembly in a 394°C block immediately after the 10 minute vacuum treatment resulted in cracked tube sheets. In general, we know that higher temperatures and longer times weaken the fibers. The 0.4 ampere-hr. cells fuse satisfactorily at 384°C, but for some reason the larger cells need 394°C.

Attempts were made to fuse the tube sheet glass by means of microwave energy. If this could be done -- if we could get very localized heating -- we might be able to use as tube sheet glass the same glass composition used in the glass fibers. Expansion coefficient differences would be non-existing and there would be no weakening of the fiber walls due to fluxing by different glass. Since the tube sheet is made up of extremely fine particles, their high surface energy should permit them to fuse together under time-temperature conditions that would not cause the fibers to seal off. This approach would require that the tube sheet mass be heated rapidly throughout its depth until fusion occurs and then be cooled before appreciable glass flow takes place in the fibers.

Since the glass is a good ionic conductor, it was felt that microwave heating could accomplish the desired rapid and deep heating.

A special wave guide as shown in the sketch was built and coupled to a 918 megahertz microwave generator.



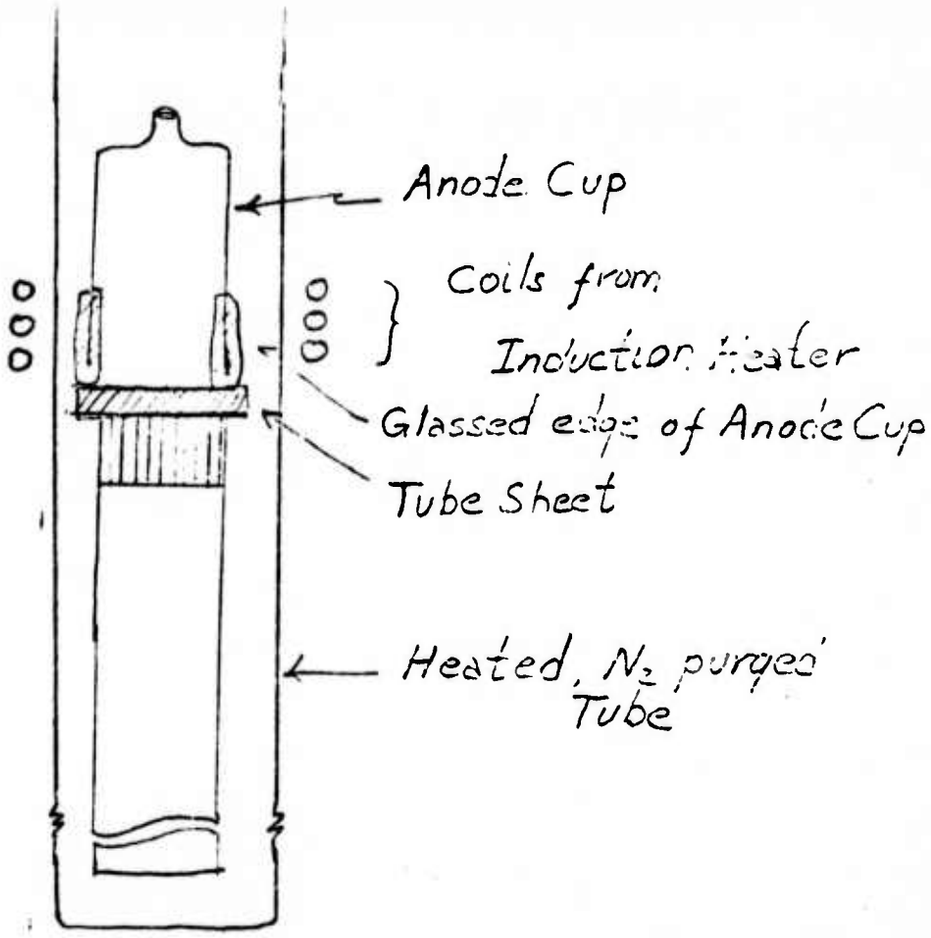
The specimen cell was placed in the heated sample port and positioned so that the tube sheet was centered in the narrowed microwave beam. It was then rotated while microwave energy was applied in short bursts of one to five seconds duration. A view port at the tube sheet level (not shown) permitted visual observation during the irradiation.

It was found that the glass was indeed rapidly heated by the microwave energy, but it was non-uniform. Hot spots developed almost instantly and these became energy sinks, preventing the surrounding material from receiving energy. This was due to the very great increase of ionic conductance of the glass with temperature. The hot spots could, and sometimes did, occur on the fibers. In this case the fibers were promptly melted off or grossly distorted.

The project was abandoned when it became obvious that rapid uniform heating of the tube sheet material could not be attained.

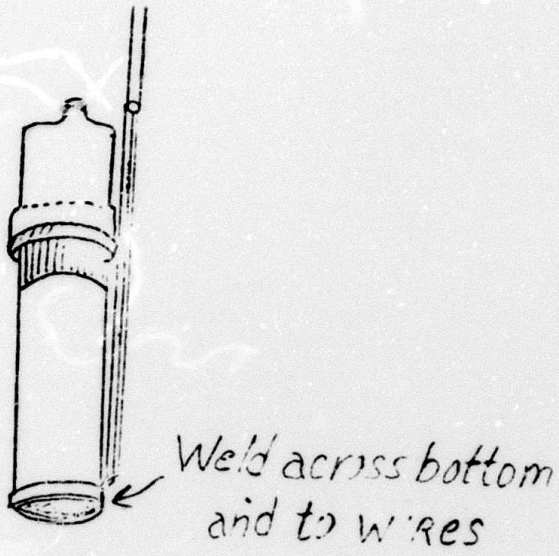
Applying the Anode Cup. The anode cup with its glassed edge is sealed on the glass tube sheet by fusing the glasses together. The assembly, at 350°C, is locally heated by an induction coil. The aluminum cup picks up the heat, the glass edge is melted; it sags into the tube sheet glass and they fuse.

We experienced some difficulty due to nonreproducibility of the induction heating step. After the heating coil was redesigned and all the contacts on the induction heater were cleaned, the operation became very reproducible. At the induction heater settings of 375 ma plate current and 50 ma grid current, good anode cup fusion to the tube sheet takes place in 60-80 seconds on the 5 ampere-hour assembly.



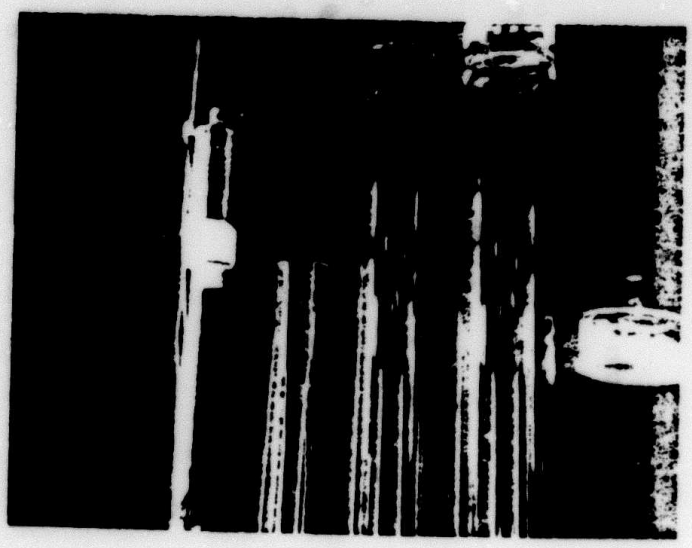
Applying Cathode Connector. A connection must be made from the cathode pick-up foil to an external cathode lead. In the final design of the sealed cell, the case will be the external cathode connector. In the laboratory cells, however, a lead heavy enough to carry 5 amperes with little voltage drop must be attached to the foils and extend externally from the cell. The lead must be flexible enough so the cell is not damaged due to mechanical strains during assembly.

For the 5 ampere-hour cell we are using an 18 cm length of four, .030" aluminum wires (in parallel) attached to a 14 cm length of .125" aluminum rod. The wires give flexibility. The wires are heliarc welded to the bottom of the foil-fiber assembly. Total resistance is about 0.0085 ohms.



Internal Jigs and Structure.

As the 5 ampere-hour cell is placed in its envelope and loaded with reactants, mechanical stresses due to handling are placed on the cell which sometimes break some of the glass fibers just below the tube sheet. In order to prevent this, some glass support "jigs" were designed. The figure shows the units.



The split cylinder supports the cell assembly from the collar on the tube sheet. The cell assembly therefore does not rest on the bottom of its own structure. The inner tube holds the cell assembly on its support. All handling of the cell assembly is done by means of this tube, so there is no movement of the anode cup relative to the fiber-foil part of the cell assembly. The larger glass tube is the outer envelope of the cell.

The 0.4 ampere-hour cell had a different problem. Being much smaller, it is not subjected to all the mechanical strains of the larger cell. However, on long term operation of the cell, sulfur catholyte slowly distills upward and condenses on cooler portions of the cell. Since only a small amount of sulfur is used in these cells, the loss is serious and shows up as rising internal resistance of the cell.

A "sulfur-trap" was designed to reduce the distillation rate of the sulfur. It is a little cup that is placed upside down over the cell assembly. It restricts the flow of sulfur vapor into the colder portion of the cell envelope. It solved the problem of large increases in cell resistance of the 0.4 ampere-hour cells which occurred after they have been in operation about a week.

Loading and Starting the Cells. Sodium and sulfur are loaded into the cells at about 150°C in an inert atmosphere box. The cell assembly, inside the inner glass tube, is heated to 150°C. Molten sodium at 150°C is poured into the anode cup. A vacuum is pulled on the whole assembly to evacuate the hollow fibers. When the vacuum is released sodium is forced into the open ends of the fibers.

Meanwhile, sulfur is placed in the outer envelope of the cell and heated to 150°C. This is approximately its lowest viscosity. The

cell assembly in its tube is then lowered into the sulfur. A hole in the bottom of the inner tube lets sulfur flow in and fill the voids in the fiber-foil roll. An anode lead is then inserted into the top of the anode cup, extending into the sodium and the cell is removed from the inert atmosphere box, placed in an auxiliary heater and taken to 300°C.

Since the catholyte is pure sulfur, the cell resistance is extremely high. Discharge is started and the cell resistance drops. It drops very rapidly at first, going from kilo-ohms to a few ohms in a matter of minutes. It does, however, take some hours to get down to its theoretical resistance.

IV. Testing and Evaluation of Cells

Two different type of cells are used in the testing and evaluation program. The smaller size is a 1.1 cm diameter fiber bundle and contains up to 1000 fibers 5 cm long. It is very easily assembled with a minimum of handling. Its disadvantage is that the cathode lead is a linear extension of the cathode foil and hence the foil has a non-linear voltage drop. It could not be scaled up directly to larger sizes because of very large voltage drops at high currents. Its advantage is that the assembly process creates very few strains on the fibers and few if any fibers are broken during cell assembly.

The larger size cell has a 1.65 cm diameter fiber roll and contains up to 5800 fibers 8 cm long. It is designated the "five ampere-hour cell". It is designed so that its construction details can be directly scaled up to larger sizes. One of the problems of this type of cell is that in assembly a few of the fibers can easily be broken at the juncture of the fiber bundle and the tube sheet. We are trying to learn how to assemble these larger sizes without this preliminary damage.

The small size cell is commonly used for most testing. It is used to test new glasses, new tube sheets, treatments of cell components, high rate discharges, etc. The larger size cell is used to confirm the findings on the smaller cells and to do the thermal cycling experiments.

At the beginning of this period we were using the fluoride containing T104 fiber glass and the fluoride containing T162 tube sheet glass. Lifetimes of the multi-fiber cells were limited, for the most part, to 10-12 days for the small size cells containing 100 fibers and about 2 days for the larger cells containing several thousand fibers.

When we switched to the chloride containing T406 glass for the fibers and the $94B_2O_3{:}6Na_2O$ tube sheet glass lifetime of the operating cells immediately increased.

The tables list pertinent characteristics of many of the cells which were run. The T-number cells are the smaller 1.1 cm diameter cells. The A-numbers are the larger 1.65 cm diameter cells. All of the listed cells except T59 and T60 are with the T406 fiber glass and the $94B_2O_3{:}6Na_2O$ tube sheet glass.

From the tables, several things are apparent. The cells last longer if (1) they have thicker walls, (2) they are made with fiber glass that is "non-bubbly" (good quality), and (3) they have fewer fibers. Cell T10 ran 56 days (1300 cycles) with 600 fibers having 22μ walls. It stopped operating when it ran out of sodium. The longest 1000 fiber 10μ wall cells ran 23 to 24 days. Only one 100 fiber 10μ wall cell operating on deep charge-discharge ran longer (T27 - 85 days, $\sim$2000 cycles).

CELL OPERATION

Cell	No. of Fibers	Wall Thickness	Cell Current	Life, Days	Conditions	Failure Mode
T9	600	22μ	70 ma	20		Shorted
T10	600	22	70	56		Ran out of Na
T17	100	10μ	20 ma	32		Fiber Failure
T18	"	"	10	49	Resist increased 140%	Lead Shorting (?)
T24	"	"	30	22		Anode Lead Broke
T27	"	"	30	85	Resist increased 500%	
T29	"	"	"O.C."	80	10 ma, 2% of the time. Resist increased 240%	
T11	1000	10μ	310 ma	16		
T14	"	"	"	10		Fiber Failure
T20	"	"	330	15		
T22	"	"	320	14		
T23	"	"	"O.C."	3	S° region	Fiber Failure
T28	"	"	320	16		" "
T32	1000	10μ	320	16	Ba^{++} treated foil	Probable fiber failure
T33	"	"	"	17	" " "	Failure between foil & T.S.
T40	"	"	180	14	" " "	?
T34	1000	10μ	1 Amp.	7	Not deep discharge, Ba^{++} treated foil	Solid formed (?)
T35	"	"	"	2	Deep discharge, " " "	" " "
T36	"	"	"	2	" " " " "	" " "
T48	"	"	"	8	Has S° trap, silicone stopper. Ran 213 cycles.	Fiber Failure

CELL OPERATION (cont.)

Cell	No. of Fibers	Wall Thickness	Cell Current	Life, Days	Conditions	Failure Mode
T37	1000	10μ	300 ma	15	S^{o} trap, Ba^{++} treated foil	
T38	"	"	320	24	" "	Failed between foil & T.S.
T44	"	"	320	23	" " ⟶	No resistance increase!
T42	1000	10μ	330	6	S^{o} trap, Cs^{++} treated foil	Fiber failure
T45	"	"	-	1	" "	
T46	"	"	320	16	" " , silicone stopper	
T47	1000	10μ	320	14	S^{o} trap, silicone stopper, foil baked 1 hr. ⟶	No resistance increase!
T49	"	"	310	22	" , rubber stopper (cold), " " " ⟶	" " "
T50	"	"	340	18	" , silicone stopper, foil baked 24 hr. ⟶	" " "
T53	"	"	310	23	" " " " ,	Resist increased 10%
T54	"	"	310	21	" " " " ,	Resist increased 70%
T56	"	"	330	18	" " " " ,	Resist increased 4%
T59	1000 ($non\text{-}Cl^{-}$)	10μ	310/800	7	", foil baked 4 hrs; 2 days @ 300°C, 2 days @ 330°C, 36 deep cycles	
T60	" "	"	300	7	", " " " ⟶	Resist increased 10%

CELL OPERATIONS

Cell	No. of Fibers	Fiber Size	Cell Leak Rate Bubbles/Min.	Current	Cell Resistances	Life	Remarks
A-59	60	35 x 55	10	20 ma	Incr. 220%	33 Days	Slow increase in resistance.
A-61	4000	30 x 80	12	Disch.	0.1 (theo)	1 Day	Bubbly glass; failed by short.
A-62	1600	30 x 80	48	.2-.4 Amp	0.2 (theo)	3 Days	Bubbly glass; failed by short.
A-64	3700	33 x 78	16	.5-.7 Amp	0.1 ⌐→ .2 (6 Days)	9 Days	Erratic on 9th day.
A-68	3200	33 x 78	20	.2-.5 Amp	0.15→ .3 (13 Days)	14 Days	Shorting in roll.
A-69	5800	50 x 70	84	2.-3. Amp	0.04, Constant	4.5 Days	Possible disch. to solid. Shorted.
A-71H	5800	50 x 70	42	Disch,.02A	Constant	4 Days	Short in roll (?)
A-73	3400	33 x 78	27	.3 Amps	0.2, Constant	8 Days	Machine treated Al foil.
A-76	3500	50 x 70	9	.7 Amp	Constant	5 Days	Failure above foil roll.
A-77	3500	50 x 70	60	.05 Amp	Constant	2 Days	Failure near tube sheet.
A-78	6960	50 x 70	28	2.0 Amp	Constant	3 Days	Shorted in foil wrap, 3 shrt.
A-81	4080	33 x 78	34				
A-82	4080	33 x 78	66	Temperature Cycling Experiments			
A-83	4080	33 x 78	60				
A-85	5800	50 x 70	60	3.0 Amp	0.05, Constant	1 Day	Short in foil roll, btoom of fibers.
A-87	4600	50 x 70	40	1.0 Amp	0.06, Constant	9 Days	54 cycles at 40% of capacity, failure mode ?

Almost all charge-discharge cycling of the T-cells was done between 60 and 90% of full capacity of cells. Cycles were either 80 minutes or 2 hours for the full cycle except for the high rate experiments where the cells were operated on 17 minute charge and 17 minute discharge.

There seemed to be little difference in lifetime between "stand-by" operation and normal one hour rate. Cell T-29, left mostly on open circuit in the one phase sulfide region of catholyte lasted 80 days, while T-27, operating on charge-discharge, ran 85 days. Similarly, cell T-23, left on open circuit with the catholyte in the two phase sulfur region, failed in 3 days while its sister 1000 fiber cells generally lasted about 2 weeks. The cell failure mechanism seemed to be the same--fiber failure.

A theory was proposed that the fibers were weakening in operation due to removal of H^+ which was in the glass due to its original water content. It was suggested that Ba^{++} on the foil, adjacent to the fibers, might enter the surface layer of the glass, put the glass structure under compression, and hence, strengthen the fibers. The results from cells T32, 33 and 40 show that it did not work.

As the lifetimes of the cells reached 2 weeks and increased beyond that, the internal resistance of the cells began to increase drastically. Cell T18, at 49 days, had an increase of resistance of 140%. Cell T-27 had 300% increase in 35 days and 500% increase in 85 days. In these T-cells, during long runs, sulfur from the catholyte distills up and condenses on cold portions of the cell assembly. We installed an inverted cup "sulfur trap" to reduce the amount of sulfur escaping from the working portion of the cell assembly. The resistance increase was drastically reduced. In cells T37, 38 and 44 we saw very little or no resistance increase in over 3 weeks of operation.

Since most of the cell failures seem due to weakening and failure of the glass fibers, a search for causes of such possible weakening was made. One possible cause could be H^+ impurity in the catholyte. It is possible that it could displace Na^+ in the glass, weakening the glass. The odor of H_2S was often noticed after a cell failure. Possible sources of the H^+ were residual binder on the coated aluminum foil and degradation products from rubber stoppers used to seal the small T-cells. Changing rubber stoppers to silicone stoppers did not reduce the problem. Neither did baking the foil out for 24 hours at 300°C rather than one hour.

Another possible cause of weakening could be removal of the chloride content of the fiber glass by migration during cell operation. We developed a chloride-free glass to test this possibility. So far, only two cells (T59, T60) were run. Unfortunately, the fiber glass used for these cells was of poor quality (bubbly) and this may be the cause of the short lifetimes (7 days) of the cells. This work is continuing.

Some of the cells were run at very high rates. Instead of the designed one hour rate, they were run at a 17 minute rate. Charge and discharge was at over 80% of cell capacity. The cell characteristics during the cycles were invariant. Resistances and capacities were exactly reproduced over hundreds of cycles. Two of the cells (T35, T36) failed in 2 days of such operation. It is presumed that they were discharged too far and solid sulfide formation crushed some fibers. One high rate cell (T34) was only cycled at about 60% of its capacity and lasted 7 days. Another high rate cell that was cycled at over 90% of capacity at the 17 minute rate lasted 8 days and 213 full cycles ! Failure mechanism, again, seemed to be fiber failure.

There seems to be at least two kinds of fiber failures. In one, the fibers fail inside of the fiber-foil roll. In the other, fibers fail between the bottom of the tube sheet and the top of the fiber-foil roll. The second type of failure may be partially due to weakening of the fiber by the amine present on the solder glass during cell assembly. Experiments are underway to determine this and to determine if the fibers weaken with time at 300°C even in the absence of sodium and sulfur.

The 1.65 cm diameter A-cells in general have shorter lifetimes than the T-cells. It is not known for sure whether this is always due to the more difficult mode of assembly, or whether it is sometimes due to the fact that they have many more fibers. The A-cells almost invariably have a leak rate after assembly corresponding to one or more broken fibers. If the assembly is made using 70μ rods instead of glass fibers, there is no leak.

One cell (A-59) was assembled with about 6000 rods taking the place of hollow fibers and 60 working fibers. It operated, charging and discharging at a very low percent of capacity but at designed current density for a one hour cell for 33 days (650 cycles). The internal resistance of the cell increased by 20% in 1 week, 40% after two weeks and 60% after 3 weeks. It is not known whether this increase is associated with breaking of fibers or something else.

The longest-lived of these larger cells were A-64, 8 and 73 with 8, 9, and 14 days. They all had fibers with 22μ walls. The longest lived of the 10μ wall cells were 4 to 5 days (A-69, 71H, 76) except for one cell (A-87) that operated continually at 1 ampere for 9 days. It cycled at 2 hour charge - 2 hour discharge using 40% of the cell capacity. It ran 54 cycles with the cell internal resistance remaining constant at 0.06Ω throughout the run.

Cell failures happened both in the foil-fiber roll and above the roll but below the tube sheet. After the discovery that scraps of glass were scratching and cutting the fibers during the spinning operation, and correcting this problem, almost all failures have been above the fiber-foil roll. If the cell is assembled and loaded so that the sulfur liquid level is some distance below the tube sheet, we sometimes see cell failure at the same time that the sulfur has wicked up the outside of the fiber and contacted the tube sheet. This indicates that many failures are due to fibers breaking off just below the tube sheet.

Only three runs have been made to determine the effects of temperature cycling. These were cells A-81, A-82 and A-83. No design changes were made even though we believe some will have to be to compensate for cooling strains. Cell A-81 was charged until the catholyte was almost pure sulfur. The internal cell resistance went from 0.3 Ω to 67 Ω. It was then cooled from 300°C to 235-240°C, left there 45 minutes, and then re-heated. All liquid components should have stayed liquid. The cell then discharged normally except that about 2 hours after initial discharge the cell failed, shorting at the top of the foil roll.

In cell A-82 the experiment was repeated except that the catholyte was initially charged only to a cell resistance of 4.9 Ω. It was cooled to 235°C for 2 hours. It was then reheated and operated in discharge-charge cycling, 80 minute cycles, for 11 1/2 hours before failure. This heating and cooling probably did not contribute to failure.

Cell A-83 was charged to a catholyte composition of Na_2S_{20} and cooled to 225°C from 300°C over a one hour period. At this point fibers directly beneath the tube sheet cracked and broke. The catholyte level was below the place where the fibers broke. It is probable that some sodium polysulfide had been isolated on the

fibers above the main bulk of the catholyte and it solidified there, breaking fibers. Further heating-cooling experiments are being done.

To date, then, our longest lived A-cell with 3000 to 5000 fibers is 14 days. This has 22μ walls. Unfortunately the thick walls mean increased cell resistance. Our longest lived cell with 10μ walls is a 4600 fiber cell at 8 days and 54 cycles. We are trying to define causes of failure and improve on this performance.

CAL:pr