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Research Development in the Glass Fiber
Sodium-Sulfur Battery

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SUMMARY

I. Technical Problem

The sodium-sulfur battery based on hollow glass fibers as the
electrolyte has been shown to have outstanding characteristics
as a rechargeable cell. It should be capable of 100 watt hours
per pound at over 80 watts per pound, and not be damaged by
charge/discharge cycling.

The major problems are to obtain increased lifetimes, to demonstrate
non-variance in its electrochemical characteristics over thousands
of cycles, and to assemble the cells into metal envelopes and
into high voltage batteries. The batteries, like the cells, must
be capable of long-lived non-variant operation.

II. General Methodology

The problems are being defined and attacked by building and
operating various size hollow fiber cells. These cells range from
single fiber cells to cells containing many thousands of fibers.
When these cells fail, the failure mode is analyzed. Small
assemblies are designed and built that can test specific parts
of the cells which may be involved in the failure. For example,
single fibers or small bundles of fibers can be assembled and
used as a Na anode discharging and charging into a sodium or a
sulfide pool to test the effect of passage of sodium ions on the
glass lifetime.

As improvements are made, the cells are scaled up to confirm
the improvements and to see if scaling up introduces new factors
affectin the cell lifetime.

III. Technical Results

During this period, the effects of impurities in the sodium on
the glass fiber were determined and methods of removing the harmful
impurities were developed. Removal of these impurities greatly
improved the lives of the fibers.

Calcium in the sodium at the 0.04% level is very bad. It causes
the resistance of the glass to increase, probably due to strains
set up as the calcium ion enters the glass network. When enough
calcium has entered the glass matrix, the fiber breaks. Potassium
in the sodium also leads to increased glass resistance and strain.
It is very bad at over the 1% level. At lower levels of 140 to 600 ppm,
the resistance build-up is linear with K content. The effect of

potassium is reversible. On charging the fiber from pure Na_2S_4, the resistance drops as K is removed from the glass. With 140-160 ppm of K in the Na, no decrease in fiber lifetime is seen.

Various oxides or hydroxides of sodium cause damage to the glass fiber. They seem to corrode the glass in areas where they concentrate, e.g., the bottom sealed tips of the fibers.

These impurities are removed to a satisfactorily low level by adding one volume of oxygen to the molten sodium to form Na_2O + digesting the sodium at 300°C to get

$$Na_2O + Ca \longrightarrow CaO + Na.$$

Filtering at about 110°C gets rid of CaO and most of the Na_2O. The "purified" sodium is then treated at $\sim$500°C with Zr/Ti alloy to remove the final oxides to "a few" ppm or less.

Using this sodium, no glass fiber failures are seen even when over 20 ampere-hours of Na per cm^2 of fiber are passed through the glass. This would correspond to a coulomb passage of 10,000 hours at the design rate of 2 ma/cm^2.

High current densities do not seem to shorten fiber lifetimes when the clean sodium is used. Current densities of up to 150 ma/cm^2 were used in dianode assemblies and in cells. Failure is tube sheet related whether the current density is high or normal. Since failure at the present time is not coulomb or rate dependent, high current densities are not a useful means of running accelerated tests on the overall cell.

The only impurity in the sulfur that we have so far found to be a problem is Mg. This is introduced from the 5005 alloy aluminum used as a cathode foil. On extended testing of cells, it causes increasing glass resistance and may contribute to shorter lifetimes. Other non-Mg containing Al alloys can be used if they are coated with a 1000 Å layer of molybdenum. With this foil, no resistance increase with extended cell operation is seen. There is, however, a rather strange resistance increase during a discharge cycle which disappears during the charge cycle. When clean sodium is used, contrary to our previous report, H in the sulfide (from spiking with NaH) does not cause increased cell resistance on discharging the cell. Small amounts have no effect.

Cell lifetime tests using the clean sodium are in progress. The first cells put together, whether they were 0.5 A-hr., 1000 fiber cells or 6 A-hr., 3000 fiber cells, failed in 23-30 days. The failure mode, however, instead of being fiber related, was tube sheet related. Apparently the clean sodium wets the tube sheet and spreads more readily than the standard sodium. It penetrates pores in the tube sheet that were small enough to be ignored previously. The tube sheets are now being fused at a higher temperature to close up the pores.

A 1000 fiber cell has had no resistance increase in 21 days of operation. So far, it has undergone 500 C/D cycles and the glass has passed over 500 ampere-hours at 12 ma/cm^2 (6 times the design rate).

A dianode assembly, using the standard sodium is still operating at 7 months of charge/discharge cycling where only 1-2 column volumes of sodium are passed in and out of Na_2S_4 per cycle. This shows that with <u>small</u> amounts of sodium passed, the impurities are not limiting.

When large amounts of Na are passed with impure sodium, the cell lives are shortened. A single fiber cell broke in the fiber after 4 Ampere-hours per cm^2 was discharged through the glass when the sodium had calcium scavenged but not the oxides. A similar single fiber cell, still in operation, with clean sodium, has passed over 20 ampere-hour per cm^2 in 1200 C/D cycles. This cell is being run at a very high rate. It is sodium limited and passing 5-6 column volumes of Na on each cycle--comparable to full size cell design.

Lifetime of the 6 A-hour cells (3000 fibers) using Ca-scavenged sodium is about 25-30 days. These are run at >85% depth of discharge based on the sulfur. Failure is due to fiber degradation-- probably the oxide content of the sodium. The cell resistance increases about 30% in the first 3 weeks. The same life is seen at designed rates (6 hours) or 2.5 times the designed rate. In these cells, with the unscavenged sodium, use of the molybdenum-aluminum foil instead of the carbon on Mg-containing Al foil, did not improve lifetime.

The first thermal cycling of the cells has begun. Charged 1000 fiber cells have been cooled to 120°C and reheated to 300°C several times with no failure. When cooled to room temperature, however, they could not be reheated and started.

Mock-ups of the 40 Ampere-hour cell have been made but not started. They have 15000 fibers. The fiber-foil roll is 1.4" in diameter.

Spinning has been improved in this period. A spinnerette with a protruding central needle helps in giving a more stable fiber pick-up and assembly. With this spinnerette it seems possible to use N_2 as a cooling gas instead of helium. Better temperature control at the spinnerette has helped greatly. The temperature is now held to 0.1°C.

Scanning electron microscope studies of the glass fiber have shown bad pits and scratches in the glass after fiber lay-down. Another later study, probably after the lay-down pulleys were cleaned showed no damage from pitting and scratching.

Cutting the fibers to length and sealing them with hot N_2 uniformly is still a problem. Improvements were made in the hot N_2 jet assemblies by changing the insulation and by chamfering the needle jet. When helium was tried as a cutting gas, control was very critical.

The tube sheet paste, made up of 46% 200-325 mesh glass spheres, 46% "fine" glass particles, and 8% cumene, is not reproducible. Studies have been started to define the "fine" glass particles as far as particle size and size distribution is concerned. Preliminary glass grinding trials to make the "fines" have been started using a Sweco Vibro-mill Grinder rather than ball-milling.

Fibers stored over molecular sieves at room temperature for over 3 months have shown no loss in tensile strength from the original strengths.

A battery test facility has been designed and is being built. The first control module is under test.

IV. Implications for Further Research

Now that the Na and S purity have been defined and attained, degradation and breakage of the fiber is currently not a problem. The clean Na does, however, penetrate the tube sheet pores and methods of sealing these pores are being tried. Lifetime studies and analyses for modes of failure will be continued.

The composition of the cathode foil will have to be further defined. The "carbon on 5005 aluminum", is less expensive than the "molybdenum on aluminum", but the role of the Mg in the 5005 Al must be clarified.

The larger 40 Ampere-hour cells will be built and started. We will try to define any harmful effects in scaling up the 6 A-hour cell to 40 Ampere-hour. We intend to put these cells in metal cases rather than using the pyrex envelopes. Corrosion and impurity studies of these metal cases will be started.

Process development is a very important part of the continued research. The effect of variables on glass fiber spinning quality needs looking at. We need to understand and control the make-up of the tube sheet paste so that we can reproducibly assemble cells.

We would still like to develop accelerated test methods for the Na-S glass fiber cell.

INTRODUCTION

This is a report on the Development of the Hollow Fiber Sodium-Sulfur Battery covering the period July 1, 1975 to December 31, 1975. Much effort has gone into finding the causes of cell failure, and removing or mitigating these causes.

The hollow fiber sodium-sulfur cell has been shown to be capable of reproducible voltage characteristics over several thousand charge/discharge cycles at high efficiencies. It is potentially an inexpensive lightweight rechargeable energy storage device. The targets for the development effort are to improve the lifetime of the cell and to scale up to larger sizes.

During the previous reporting period, cell failure due to weakened fibers at the tube sheet-fiber interface were corrected. At the beginning of this period, the cell failure mode seemed to be degradation of the glass fibers during cell operation. The main thrust of the effort for this reporting period was to identify those agents causing this degradation and find ways to remove them or mitigate the causes.

Other parts of the program include improving the methods of making the cell components, evaluating working cells, and their failure causes, and determining the effects of very high discharge rates.

RESULTS

I. Effect of Impurities in Sodium

Most of this work was done using the dianode assembly shown in Figure 1.

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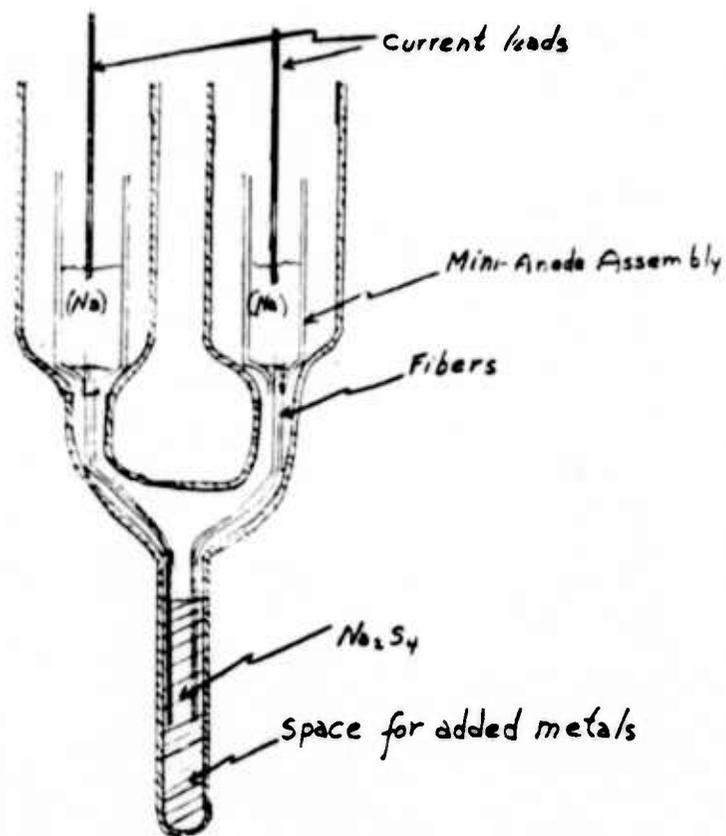
Di Anode Assembly

Large quantities of sodium can be passed from one reservoir into
the other, going as an ion through the glass walls of the capillaries
and through the molten sulfide. The effects of impurities are
magnified because the amount of sodium passing through the glass in
one direction can be hundreds or thousands of times that normally
passed through the glass during a discharge or charge cycle.

The effect of calcium was determined and discussed in the previous
report. Calcium from the sodium deposits as an ion in the glass
matrix and causes fiber failure. Before failure, the resistance
of the glass rises, probably due to strains in the glass matrix.
When the calcium content of the sodium was reduced to 15 ppm,
little resistance increase was seen and fiber life was greatly improved.

Some glass resistance increase was still seen on extended discharge. This was due to the potassium content of the sodium. Figure 2 shows the effect in a dianode assembly which was equipped with a reference electrode. The resistance rose during an extended discharge. It increased by about 30% during the first 325 ma-hr/cm^2. (In an ordinary cell, discharge is stopped at about 12 ma-hr/cm^2.) It rose another 14% in the next 2665 ma-hr/cm^2 of discharge. The first rapid resistance rise is considered due to potassium. The potassium reaches a steady state in the glass and further glass resistance increase is due to something else. Since in a normal working cell, current is reversed after the passage of about 12 ma hr per cm^2, these data suggest that when using sodium containing 130 ppm K, the final glass resistance will not be greater than about 20% higher than the original glass.
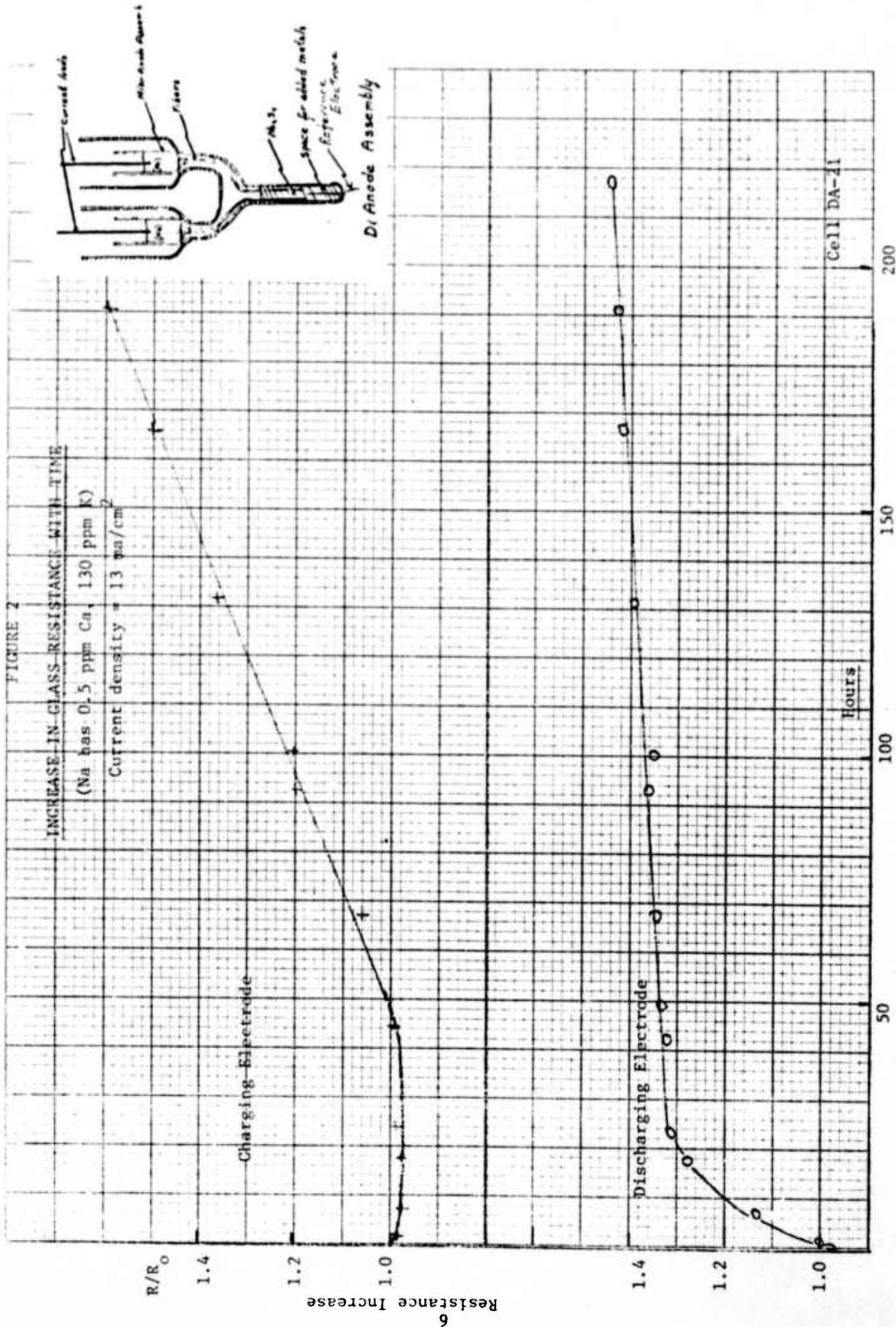
This rise in resistance due to potassium in the sodium is directly proportional to the amount of potassium present. Figure 3 shows how the glass resistance increases with time for K levels of 130, 220 and 650 ppm in the sodium. At 130 ppm, there does not seem to be enough strain in the glass to cause fiber weakening.

Attempts were made to get K-free Na by electrolysis of K-free NaOH. These failed due to improper design of the electrolysis cell. Some low-potassium sodium was finally made by distilling off K along with about 50% of the original sodium charge. The potassium content was reduced to about 20 ppm. The lower curve in Figure 3 shows how the resistance increase in the glass due to the K was lowered.

Even after removing the calcium from the sodium, fiber failures eventually occurred in the dianode assemblies on prolonged dishcarge. The failures were always near the bottom sealed end of the fibers. Examination of the broken fiber ends revealed a badly pitted internal surface of the fiber. Further up from the end, the interior surface of the fiber looked pristine. Apparently, as the sodium was passed down and through the fiber during discharge, a material concentrated at the lower end of the fiber that pitted the glass. It was assumed that the material was "oxides of sodium" (Na_2O, NaOH?).

Some of the calcium-free sodium was, therefore, treated at 500°C with a powder of zirconium-titanium alloy to lower the sodium oxide content from 10-20 ppm to "less than a few" ppm. This is termed "gettered" sodium. When this sodium was used in the diancde assemblies, the resulting lifetimes were greatly improved. Table I shows some results.

It is interesting to note that over 25,000 ma-hr/cm^2 of sodium could be passed through the glass without any evidence of fiber failure. At the design current of 2 ma/cm^2, this corresponds to an active life of more than 12,000 hours or 500 days.

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FIGURE 2

INCREASE IN GLASS RESISTANCE WITH TIME

(Na has 0.5 ppm Ca, 130 ppm K)

Current density = 13 ma/cm^2

R/R_o

1.4

1.2

1.0

Charging Electrode

Discharging Electrode

Hours

Cell DA-21

50   100   150   200

Resistance Increase

Di Anode Assembly

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FIGURE 3

EFFECT OF POTASSIUM IN SODIUM

Increase in Glass Resistance vs. Time
(Discharging Electrode)

650 ppm K

220 ppm K

130 ppm K

approx. 20 ppm K

R/R_0

Resistance Increase

2.5

2.0

1.5

1.0

Hours of Discharge

50   100   150

Di Anode Assembly

Current leads
Mika Anode Assembly
Fibers
Na_2S_4
Space for added metals
Reference Electrode

TABLE I

LIFETIME OF CYCLING DIANODE ASSEMBLIES

Ungettered Na (0.6 ppm Ca)		Life	
Cell No.	Current Density	Days	$ma-hr/cm^2$
DA-30	28.5 ma/cm^2	9	6,150
DA-31	26.6 ma/cm^2	10	6,400
DA-33	25.8 ma/cm^2	10	6,200

(All failures are fiber failures)

Gettered Na (0.6 ppm Ca)		Life	
Cell No.	Current Density	Days	$ma-hr/cm^2$
DA-51	47.4 ma/cm^2	17	19,400
DA-52	52.0 ma/cm^2	20	25,600
DA-54	55.0 ma/cm^2	21	28,150

(No fiber failures; all failures are in the tube sheet region)

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II. Effect of Impurities in the Sulfur

Some experiments were run in which the Na_2S_4 used in the dianode assemblies was doped with likely contaminants. This work was done before the effect of sodium oxides in the sodium was determined and corrected, so the results are suspect and the work needs to be repeated.

The sulfide in various dianode assemblies was spiked with small amounts of MgS, ZnS, Al_2S_3, and H (from $NaHSO_4$ or NaH). Changes of glass resistances were determined on both charging and discharging electrodes during extended operation. Figure 4 shows the resistance increase where MgS was used as a dopant compared to an undoped system. There is no apparent difference seen. It is possible, however, that differences may be obscured by the variability in the sodiums used.

Similar results were found for the Zn^{++}, Al^{+++}, and H from NaH. When $NaHSO_4$ was used as a source of H, there was a rapid increase in resistance of the glass at the discharge electrode. This may have been due to an impure Na. The experiment needs to be repeated.

Only one experiment has been run so far in which the purified "gettered" sodium was used and the sulfide was spiked with NaH. In this experiment, it appeared that the charging electrode increased in resistance over that of the non-spiked dianode assembly, and the discharging electrode had no change (Figure 5).

Work with actual running cells (as opposed to dianode assemblies) has suggested that Mg impurity does affect the glass resistance. Parallel experiments have been run using single fiber cells having cathode foils of either carbon coated 5005 aluminum alloy or molybdenum plated 1100 aluminum alloy.

The compositions of the aluminum alloys are listed with maximum impurities.

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
5005	0.4	0.7	0.2	0.2	.5-1.1	0.1	.25	remainder
1100	(1. total)		.2	.05	--	--	.1	99.0

Figure 6 shows the change in resistance with time for 4 cells, 2 of each cathode foil composition. Those having the carbon coated 5005 alloy develop more resistance. The increase in resistance is attributed to an increase in glass resistance. A possible mechanism is that Mg from the foil gets into the glass structure as Mg^{++}, and causes strain.

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FIGURE 4

EFFECT OF MgS IN Na₂S, CATHOLYTE

FIGURE 5

EFFECT OF NAH IN NA₂S₄ CATHOLYTE

(Na is purified, "gettered")

Discharging Electrodes

Undoped

doped with NaH

Charging Electrodes

doped with NaH

Undoped

R/R_o

Resistance Increase

1.5

1.0

1.5

1.0

Hours of Operation, 50 ma/cm²

10   20   30   40   50

Cells DA-50
      DA-55

Di Anode Assembly

Current leads
Main Anode Assembly
Sleeve
Na₂S₄
Space for added metals
Reference Electrode

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FIGURE 6

EFFECT OF CATHODE FOIL ON CELL RESISTANCE:

CELL RESISTANCE VS. TIME

(Na is purified "gettered")

Cathode is carbon on 5005 Al

Cathode is Mo on 1145 Al

(10 min. charge - 10 min. discharge)
(10 column volumes/cycle)

Cathode is carbon on 5005 Al

Cathode is Mo on 1145 Al

(0.5 hr. charge/0.5 hr. discharge)
(30 column volumes/cycle)

Single Fiber Cells MP-1
MP-2
MP-4
MP-5

ma-hours/cm² of Fiber

R/R₀

1.2
1.1
1.0
1.2
1.1
1.0

2000   5000   10000

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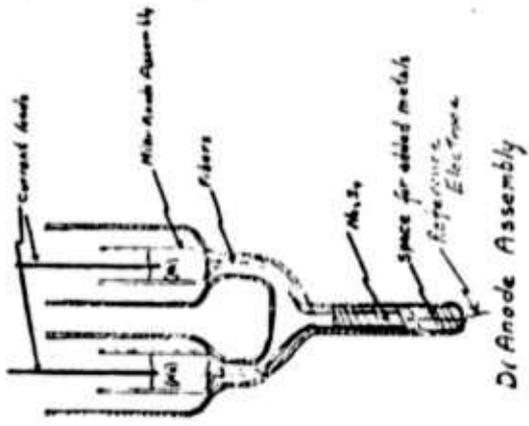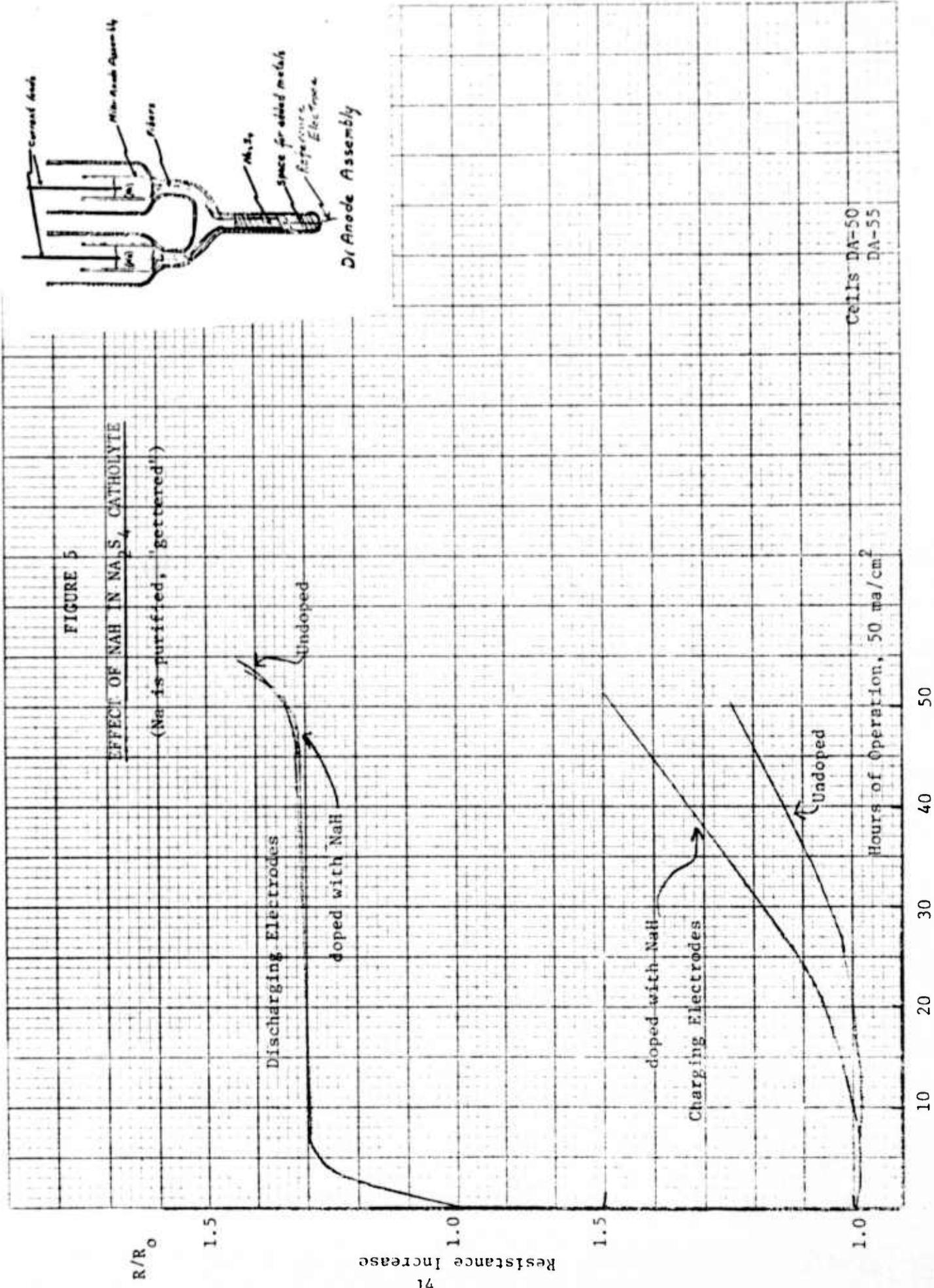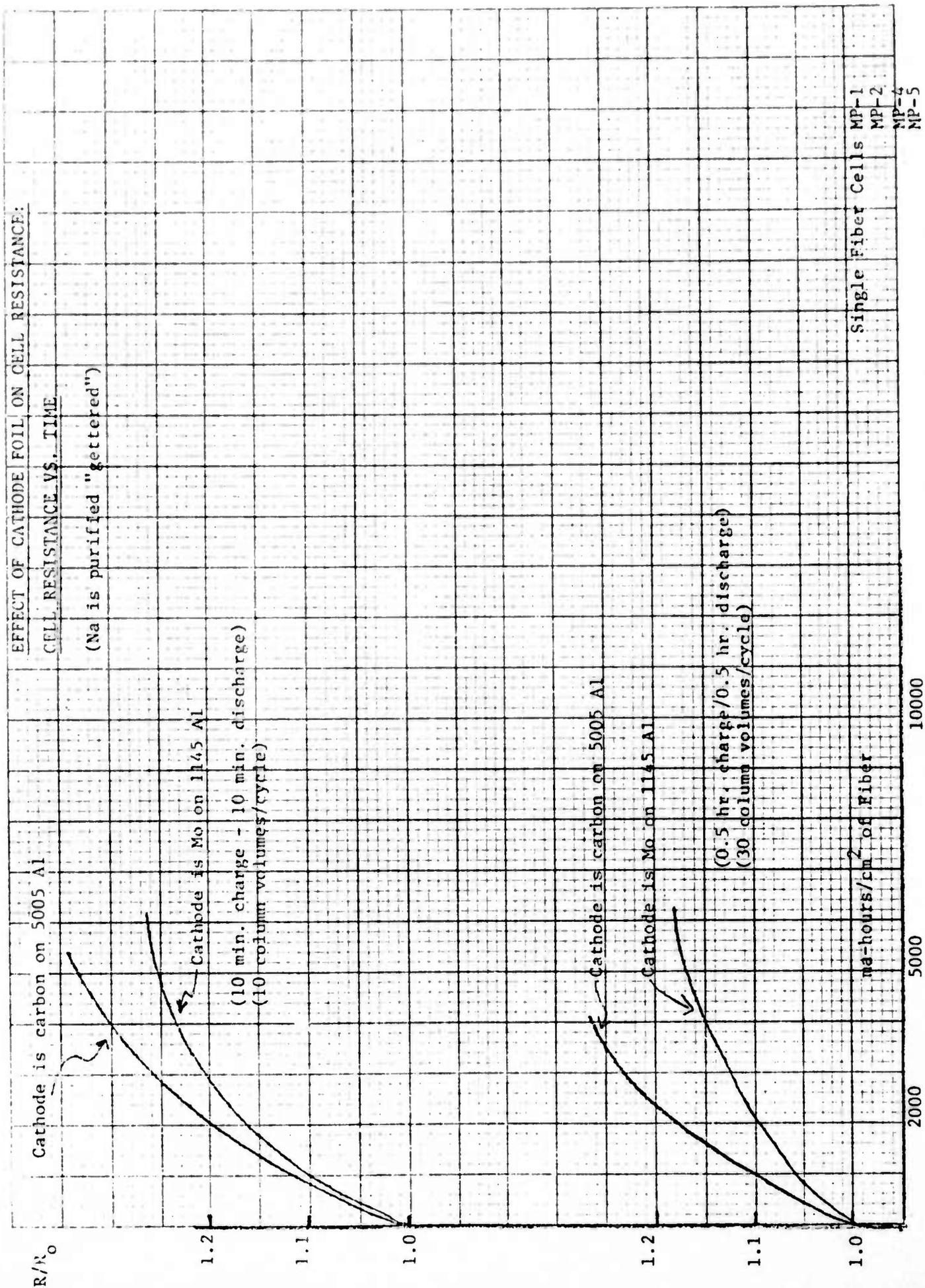
These results are confirmed with multi fiber cells. Figure 7
shows the change in resistance with time of cells having 3 types
of cathode foils. That with 1000 angstroms of molybdenum on
1145 aluminum shows no resistance increase.

III. Cell Operation

Lifetime: Purification of the sodium led to increased lifetimes
and a change in the mode of failure of operating cells. Before the
sodium was freed of calcium and sodium oxides, cells usually failed
by fiber failure. The time to failure was somewhat coulomb dependent---
the more strain put into the glass by the foreign ions, the more likely
was failure to occur. After use of the purified "gettered" sodium
began, failure of the fibers was rarely seen. Most failures are
taking place at the tube sheet-fiber interface, just under the tube
sheet.

The stability of the glass to the passage of sodium ions is demonstrated
by experiments done with the single fiber cells and dianode assemblies.
In these experiments, very high charge/discharge rates can be attained
and many coulombs of sodium ions can be passed through the glass in a
relatively short time. In a normally operating cell, about 5-6
column volumes of sodium will be discharged through the glass at about
2 ma per cm^2 and then the current will be reversed for charging.
In the dianode assemblies we can discharge 10-30 column volumes
or more (thus concentrating the impurities) and operate at various
rates up to 150 ma per cm^2.

Some of these dianode assemblies as shown in Figure 1 have passed over
20,000 ma-hours per cm^2 with current reversed after 10-30 column
volumes of sodium have been passed. This corresponds to 10,000 hours
at 2 ma per cm^2. Failure is at the tube sheet, not in the glass
fibers.

Three types of real cells are made and operated. They are single
fiber cells, 1000 fiber cells (0.5 A-hr.), and 3000 fiber cells
(6 A-hr.).

Before using the purified "gettered" sodium, the 6 A-hr. cells
lasted about 18 days when continuously cycled at >80% depth
and lasted almost 80 days when continuously cycled at 10-25% depth.
Failure was almost always in the fibers. After we began to use
the purified sodium, cells lasted about 30 days whether they were
run at the 6 hour rate (1 Ampere), the 3 hour rate (2 Amperes), the
2.4 hour rate (2.5 Amperes) or left on open circuit. The failure
mode changed from fiber failure to a penetration of the tube sheet
by the molten sodium. Apparently the clean sodium wets the tube sheet
sufficiently so that it penetrates pores that were previously
inconsequential. We are now fusing the tube sheets at higher temperatures
to get rid of the pores.

The internal resistance of these cells increased slowly to about
30% over the first 3 weeks of continuous operation. As mentioned
elsewhere, we believe this is due to the Mg in the aluminum cathode
foil.

FIGURE 7

EFFECT OF CATHODE FOIL ON CELL RESISTANCE

CELL RESISTANCE VS. TIME

(1000 Fiber, 0.5-A-hour Cells)

Cell No.	Cathode Foil
1	Mo on 1145 Al
2	Mo on 1145 Al plus a small piece of 5005 Al
3	Carbon on 5005 Al
4	MoS_2 on 1145 Al

Total Ampere-hours passed

100   300   500

.5   .4   .3

Many 0.5 A-hr. (1000 fiber) cells were built and run under
different conditions. Those using the most advanced conditions
(purified sodium, cathode foil of 1000 angstroms of Mo on
aluminum) show no increase in cell resistance in 21 days of
continuous operation and after over 500 deep charge-discharge
cycles. These cells were run at 12 Ma per cm^2, about 6 times
design rate. Over 500 ampere hours were passed before failure
at the tube sheet. The cells were run at over 85% depth of discharge.

Figure 8 shows the effect of using the cathode foil consisting of
1000 Angstroms of Mo on 1145 aluminum rather than the carbon coated
5005 aluminum. Resistance of the 0.5 A-hour cell remained constant
for its lifetime of about 30 days operated at 6 times current
density. Resistance of the cell using a piece of carbon coated 5005
aluminum adjacent to the glass increased about 20%.

Although the gross cell resistance remains constnat in time,
the cell resistance during a charge or discharge cycle is not as
uniform when the Mo-coated foil is used. Figure 9 shows some
typical plots of cell resistance with state of charge for the two
types of cathode foils. Although the curve for carbon on 5005 Al
is fairly reproducible from cell to cell, the slope of the curve
for Mo on 1145 Al varies somewhat, as shown in Figure 10.

The single fiber cells have been run at very high current densities--
up to 70 ma/cm^2 of fiber. As long as the purified sodium is used,
we do not see glass breakdown with increased current density. Of
course, to date we are limited to the lifetime governed by the tube
sheet mode of failure. Using these high current densities, we run
such cells for over 20 ampere-hour/cm^2 of fiber. This corresponds
to 10,000 operating hours at normal current density. On each charge
or discharge cycle, 5-6 column volumes of Na was passed through the
glass. The catholyte was a large excess of Na_2S_4. Over 1200
cycles were performed.

Cells of all sizes are now being tested in which higher temperatures
were used to fuse the tube sheet. This should prevent the "tube
sheet" mode of failure if the mechanism is really penetration of
micro-pores by the sodium.

Thermal Cycling of Cells

The first controlled experiments on thermal cycling were started.
A fully charged 1000 fiber cell was cooled to 130°C from 300°C,
held at that temperature for several hours, and then reheated. The
cell characteristics during charging and dishcarging were the same
as before cooling.

The cell was then cooled to room temperature and reheated to 300°C.
The cell failed. Failure occurred either during solidification or
during remelting of the solids.

FIGURE 8

EFFECT OF 5005 AL ALLOY
CHANGE OF CELL RESISTANCE VS. TIME

1000 fiber, 0.5 A-hr. cells
Purified Na
Cathode foil is Mo-coated 1145 Al

Piece of 5005 Al (0.5% Mg)
adjacent to glass fibers

No doping

Total Ampere-hours

Ohms

0.5

0.4
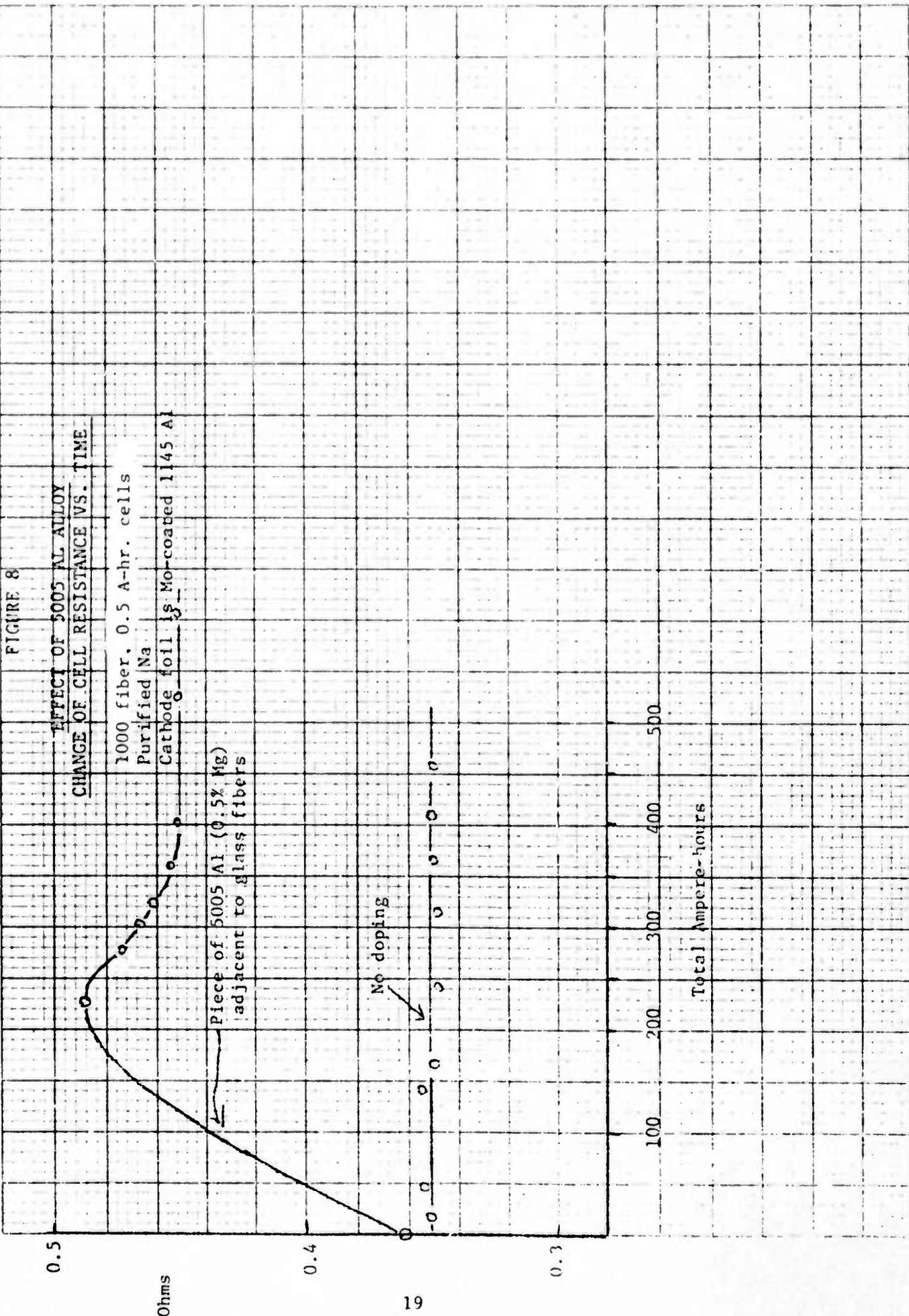
0.3

100   200   300   400   500

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FIGURE 9

EFFECT OF CATHODE FOIL:

CHANGE OF CELL RESISTANCE DURING A CHARGE - DISCHARGE CYCLE
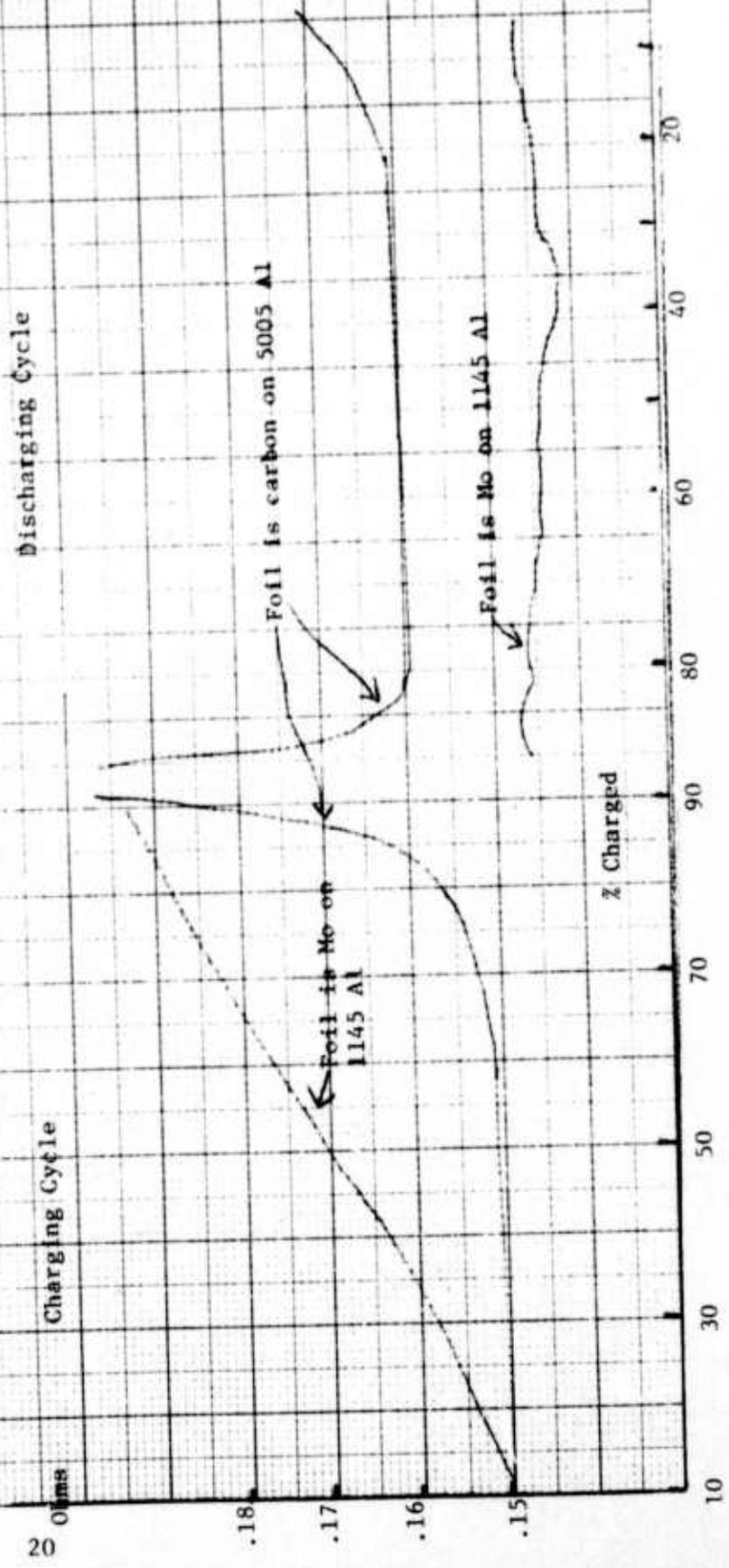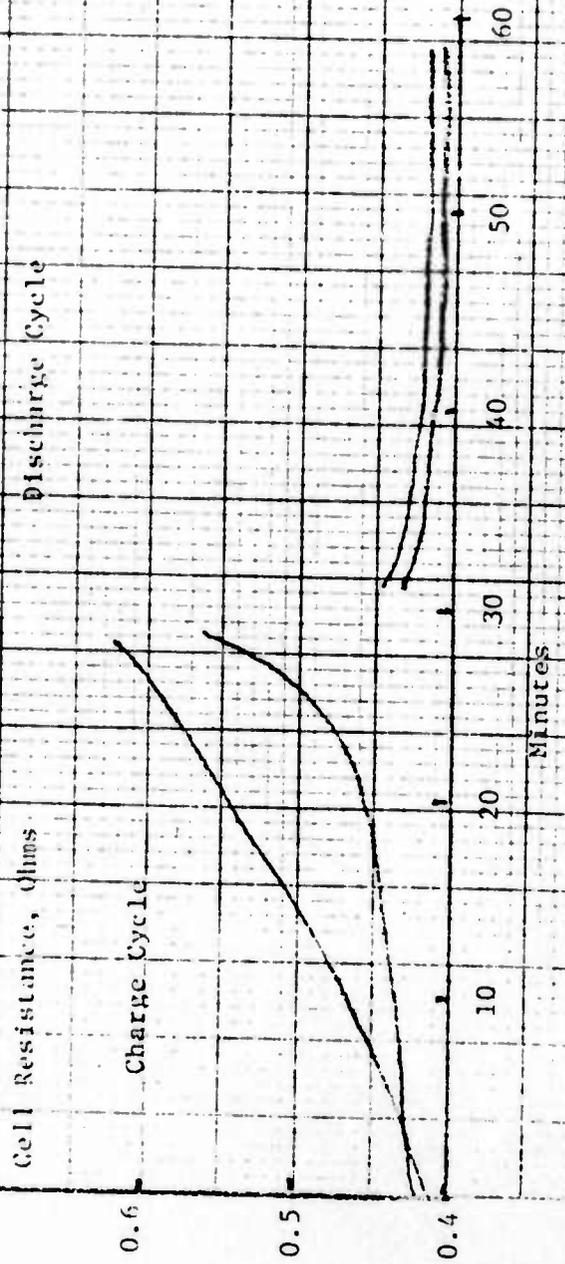
(3000 fiber, 6 A-hr Cells)

FIGURE 10

CHANGE OF CELL RESISTANCE DURING A CHARGE-DISCHARGE CYCLE:
COMPARISON OF "IDENTICAL" CELLS

(1000 fiber, 0.5 A-hr. cells)
Cathode Pot. is Mo on 1145Al

IV. Back-up for Fabrication Operations

Fiber Glass Spinning Much more work has been done on the operations
of spinning the glass fibers and cutting them to length. Stability
of drawing the glass through the platinum spinnerette has been
greatly increased by recognition of the importance of spinnerette
temperature and by close control of this temperature. In the
temperature range of 790°-810°C, there is a viscosity change of the
molten glass of nearly 3% per degree. When the temperature at the
spinnerette changes 1.2°C, the fiber size changes from 50 x 90
microns to 90 x 100 microns. A better temperature control was put
on the spinnerette heater. The temperature is now controlled to
0.1°C.

An improved version of the platinum spinnerette is now in use. The
central core gas needle protrudes beyone the annulus from which the
molten glass flows. This new design increases the stability of the
molten "bubble" at the spinnerette and results in a more uniform
lay-down of the cooled fiber. With the protruding needle it is
possible to cool the emerging stream of glass with jets of N_2
rather than using He for the quenching gas.

Two studies were made of the surfaces of the glass fibers using
scanning electron microscope techniques. In the first study,
fibers were taken after passing over the lay-down pulleys. Figures
11 and 12 are typical pictures of the fiber surface. There were
extensive scratches and pits--some microns deep. There were large
areas of general roughness. In some of the scratches, the debris
causing the scratch could be seen at the end of the scratch. In
the second study, fibers were taken both directly after emerging
from the spinnerette and after going over the lay-down pulleys.
All of these fibers showed essentially no scratches--the surfaces
were almost pristine. We have not yet investigated the reasons for
the different results in the two studies. Possibly it has to do
with the cleanliness of the lay-down pulleys.

There was some concern about the effect of the rapid quenching of
the fiber as it is drawn. If strains are built into the fibers,
they should show a drop in tensile strength when they are annealed.
Thin wall 50 x 70μ fibers had no drop in tensile strength when
annealed at 375°C for 1-1/2 hours. Thicker walled 90 x 50μ fibers
had a 25% drop in tensile after annealing. Quenching does put
surface strains in the larger and thicker walled fibers.

Getting proper lay-down of the fibers, cutting them to length, and
sealing the ends is still a tricky proposition. The fibers are cut
with jets of N_2 which pass through small heaters and platinum
hollow needles. These N_2 heaters were burning out after a few days
operation. The needles were getting gunked up with globules of
glass which distorted the flow of N_2. Better insulation on the
heaters has increased their lifetimes. The heating wires are
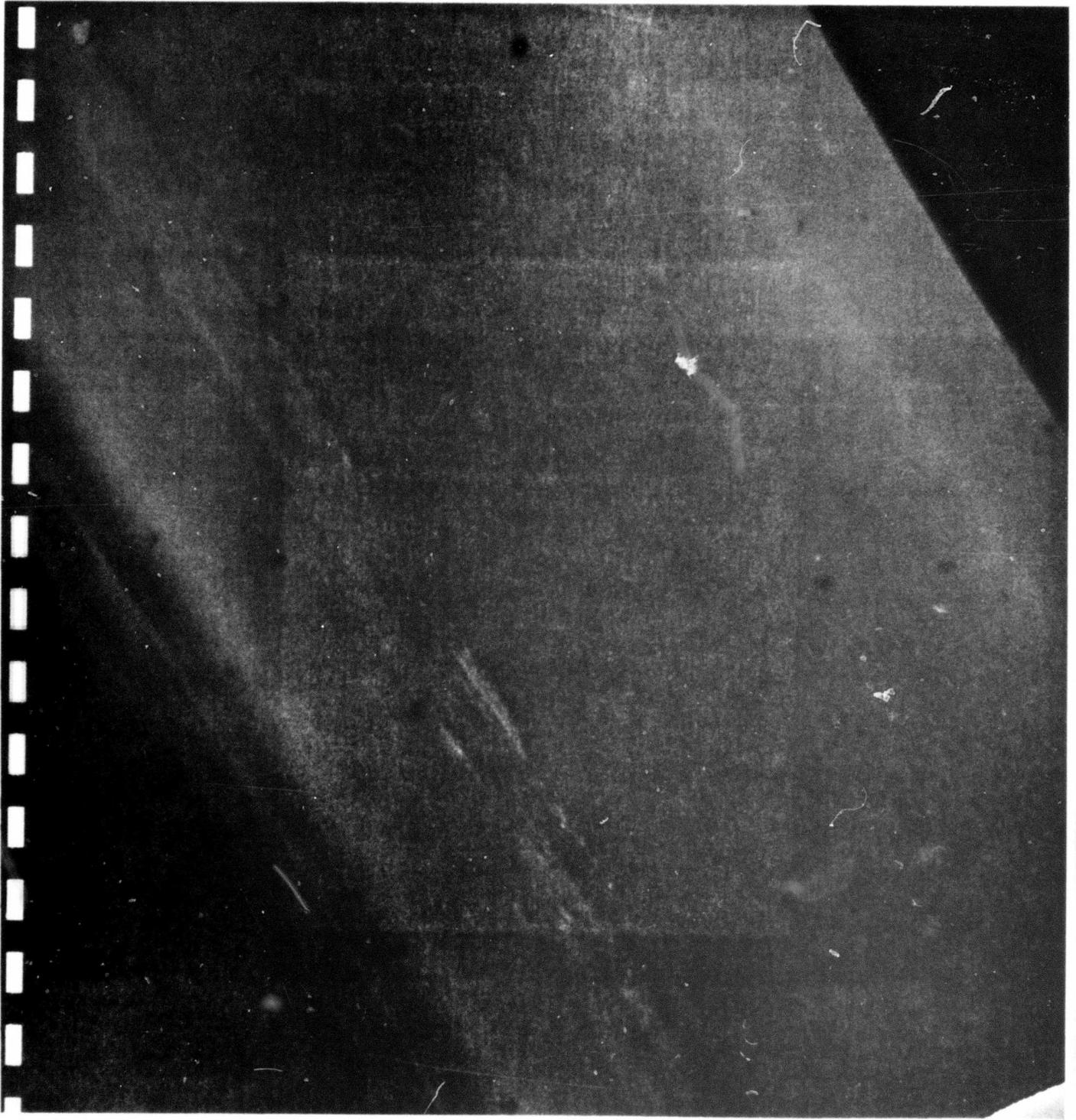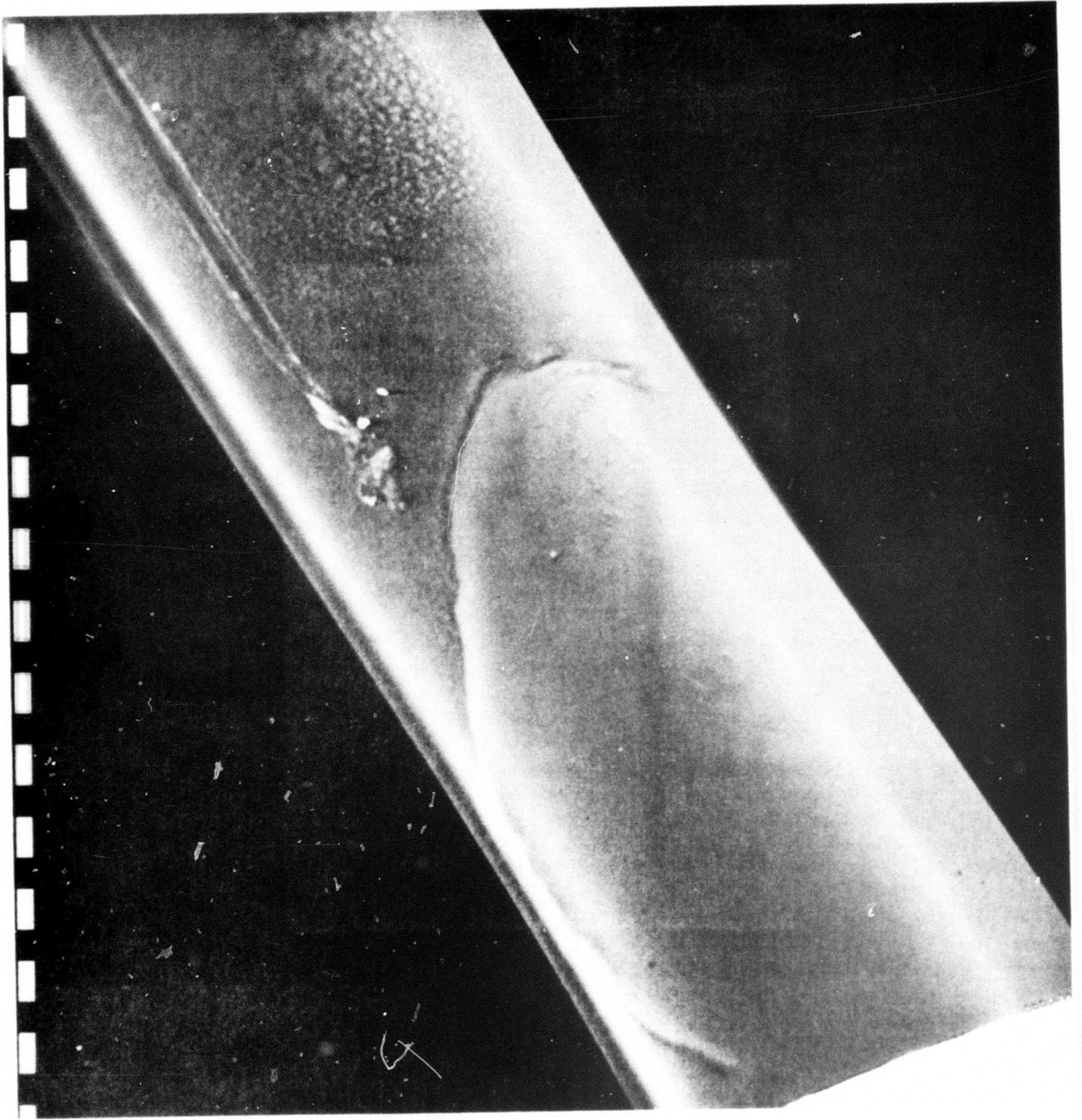covered with Alundum cement which in turn is covered with Sauereisen

FIGURE 11

FIGURE 12

cement. Previous types of insulation caused cracking and crazing
of the N_2 feed tube and hence a non-consistent flow of N_2 gas to
the hollow needle.

If the end of the hollow needle (.028" OD x .015" ID) is chamfered
to look like this:

it is not as likely to pick up globules of glass during operation.

Helium was tried as a cutting gas rather than N_2. The flow rates
and temperature settings were very critical. With too much heat a
large ball would form on the sealed end of the fiber, while too
little heat gave erratic sealing.

A batch of glass used for the fibers was made for us by Corning
Glass Works. It contained only 2.1% Si rather than the standard
2.52%. Although this substantially decreased the viscosity of the
melt, fibers could be readily drawn. Another type glass which was
drawn into fibers was identical with the standard 406 glass, except
for omitting the NaCl content. These Cl^--free fibers were made
into cells and the cells operated to see if the $^-$Cl anion had any
affect on the lifetime of the glass. None was detected.

A test was made to determine whether the glass fibers deteriorated
on standing. Fibers taken from storage after 4 months had tensile
strengths of 85000-95000 psi roughly the same as freshly drawn
fibers.

A big improvement in the uniformity of fiber lay-down was made by
making sure the thin aluminum tapes used for glueing the fibers in
correct juxtaposition to each other were flat. Previously, these
glue tapes had edges that had been wrinkled in the process of
cutting them. These wrinkled edges prevented the fibers from being
laid down and glued perfectly parallel to each other.

Cell Assembly - Making the glass powders to be used in the
tube sheet is still a big problem. It is important that the
paste made from the powders be of high solids content and be
reproducible in viscosity. The high solids content is important
for minimum shrinkage when the paste is later fused to a
solid disk. The reproducibility of viscosity is important
in trying to repeat and scale up cell assembly procedures.

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The glass powders are made by grinding glass cullet of the composition needed for the tube sheet. This glass is 95.5% B_2O_3 and 4.5% Na_2O. As mentioned in the previous report, the paste is made by mixing 46% (by weight) of fine glass powder, 46% glass spheres (200-325 mesh), and 8% cumene. Even though two batches of glass are ground in identical manners to make the "fines", the pastes made from these glasses may have very different qualities. A program was started to define the "optimum" glass particle sizes and size distributions for a high solids content paste. It has become apparent that both particle size and particle surface are extremely important.

A batch of "fines" that make a good paste has 64% of the particles less than one micron in diameter and only 9% of the particles greater than 2 microns. Other particle size distribution counts indicate that this is sufficient grinding. Even though the particles are fine enough, it may not be a sufficient condition. The particles are ground in an atmosphere of amine vapor to prevent re-agglomeration. The amount of this amine and the amount of moisture picked up during grinding by this very hygroscopic glass are very important. Studies to define these variables are continuing.

In order to grind the large quantities of glass needed to make quantities of 6 A-hr. and 40 A-hr. cells, we are trying out a Sweco Vibro-mill for grinding instead of using the ball mills. First results on promising. This mill takes a charge of 20 pounds of glass rather than the 1/4 pound taken by the ball mill.

The glass spheres (200-325 mesh) used in making the paste have been made by dropping glass particles of the proper size through a $CO-O_2$ flame. A hydrocarbon or hydrogen flame imparts undesirable H_2O to the glass. This process is slow and uses expensive and dangerous carbon monoxide. Some progress has been made on spherodizing the particles by dropping them through a hot tube. Two important variables are the tube temperature and the gas pressure inside of the tube. If the glass particles get too hot and do not quench fast enough they will stick to each other. One big problem is that the particles stick to the wall of the tube if they come in contact with it. We will try lining the hot tube with graphite to prevent sticking.

Assembly of Larger Cells and Testing - We are getting ready to scale up to a 40 Ampere hour size. This cell will have 15,000 fibers and be from 1.4" to 1.8" in diameter. After a number of trials we have been able to repeatedly roll bundles of fibers, foil, and tube sheet for this size cell. We can cure the tube sheet without getting shrinkage cracks. The viscosity and thixotropic character of the tube sheet paste become very important as the larger cells are rolled.

A cell testing station has been designed. It will enable individual testing of 25 cells at up to 40 amperes each. The cells can be put on charge/discharge cycling controlled by either time cycles or output voltage sensing. They can be left on charge, discharge, or open circuit if desired. The first module of the test station has been "breadboarded" and is in test with a 6 ampere-hour cell.

A data acquisition system has been designed which will sample each of the 25 cells, and compute, and print out the cell resistance at each cycle.

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