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SODIUM-SULFUR BATTERY SYSTEM

Annual Report, May 19, 1975-May 19, 1976

November 1, 1976

Work performed under Contract No. EY-76-C-02-2565

Dow Chemical U.S.A.
Walnut Creek, California

ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION

Division of Conservation Research
and Technology

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Annual Report

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May 19, 1975 - May 19, 1976

Charles A. Levine, Principal Investigator

Dow Chemical Company
Walnut Creek, California

November 1, 1976

Contract EY-76-C-02-2565.*000

Prepared for

Energy Research & Development Administration

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ABSTRACT

The development of the hollow glass fiber sodium-sulfur battery has progressed significantly. Glass fiber quality has greatly improved and the fiber spinning and assembly machinery made capable of more uniform operation.

Impurities in the sulfur including H, C, Zn^{++} , and Al^{+++} , do not appear to affect cell lifetime, while impurities in the Na are important. The Ca and "oxide" contents of the Na must be held to low levels. Corrosion products of a 316 stainless steel case are harmless to at least 75 day lifetimes. The Mg content of aluminum alloys can leach out in the catholyte and cause cell resistance to increase. Lifetime does not seem to be a function of total current passed or current density across the fibers.

On 1000 fiber, 0.5 amp-hour cells, over 1400 deep charge-discharge cycles have been achieved in 75 days of operating life. A larger 5 amp-hour cell has gone through 130 cycles at over 80% depth. Cell resistance and capacity remain constant, even at the 1/2 hour rate. At lesser depths of discharge, the cells last longer. Failure was usually in the fibers when "dirty" Na was used, and usually just below the tube sheet when "clean" Na was used.

An updated estimate of "cost for sale" of the bare cell is approximately \$23.15 per kw hr. based on 0.8 kw hr. cells.

SUMMARY

I. Introduction

This is a research and development contract for work developing sodium-sulfur batteries suitable for use by electric utilities and for vehicular propulsion. The Na-S cell utilizing the walls of hollow glass fibers as the electrolyte has been demonstrated to have exceptionally good energy density characteristics. Projected costs look very low. This effort is aimed at increasing the cell lifetimes, determining some of the operating limitations, scaling up the cell in size and sealing it into a metal case.

The individual tasks are as follows:

Task I: Electrolyte Development and Evaluation

- a. Effect of sulfur impurities on glass and cell life.
- b. Effect of current and current density on glass properties.

Task II: Electrode and Cell Development

"Achieve 1000 cycles of charge-discharge operation, scale up to 5 ampere-hour cell, and build larger cells capable of long lifetimes. Determine cell construction details which may allow thermal cycling."

Task III: Develop and Evaluate Metal Alloys Suitable for Containers and Low-Cost Electrical Feed-throughs

Task IV: Evaluate Characteristics of Eight Hour Cell

Task V: Evaluation of Other Factors Affecting Cell Life

Task VI: Cost Estimate for Cell

II. Technical Results

A. Electrolyte Development and Evaluation

(1) Fiber Quality

Glass fiber quality has been greatly improved during this period. Electron microscopy studies early in the period showed many scratches and pits in the freshly drawn fibers, some as deep as several microns. The fibers now have essentially no defects on their surfaces.

The spinning system was improved to produce a more uniform fiber. The fiber quality control is now good enough so that fibers with thin 3μ walls can be made.

Relative fiber strengths are determined by tensile testing. Methods were developed to tensile test single 70μ O.D. fibers. The strength of the fibers is not degraded by up to three months storage under dry conditions. During cell assembly, however, if a poor vacuum is used during the tube sheet fusion, the fibers are substantially weakened.

(2) Effect of Sulfur Impurities on Glass and Cell Life

A definitive study has not been completed on the effects of common impurities in the sulfur catholyte on the glass fibers. The normal sulfur used in the cell has been distilled over Vycor chips at 950°C . If commercial "flowers of sulfur" is used without purification other than simple filtering, glass fiber life is not decreased and unusual resistance changes in the glass are not seen.

Extra C and H were added to the distilled sulfur catholyte in the form of lampblack. This added "impurity" showed no harmful effects over the 44 day life of the cell which was on deep and rapid charge-discharge cycles. Similarly H added by adding NaH to the Na_2S_4 had no detectable effect on the glass resistance.

The corrosion products of sulfur on 316 stainless steel do not affect the operating cell resistance over at least 75 days of rapid and deep charge-discharge. This is different from the results obtained by the Ford people with their $\beta\text{-Al}_2\text{O}_3$ cell, wherein the cell resistance increased due to the stainless steel corrosion products.

Addition of small amounts of MgS , ZnS , or Al_2S_3 to the distilled sulfur gave cell resistance increases that were identical to those seen with no additive. These experiments were run using sodium anolyte that had not been sufficiently purified, so cell resistance did increase. They need to be repeated with cells using the purified sodium.

It is possible that there is an effect on the glass from Mg migrating out of the cathode foil when aluminum alloys containing Mg are used as cathode foils. In identical 1000 fiber cells, cell resistance does not increase when foils of Mo on 1145 aluminum are used, but does increase if foils of carbon on 5005 aluminum (.5-1.0% Mg) are used or a piece of 5005 aluminum is inserted into the cell.

(3) Effect of Current and Current Density on Glass Properties

Although the cell design calls for a current density of about 2 ma per cm² on the glass fiber, rates up to 60 ma/cm² do not seem to cause degradation. At 60 ma/cm², over 30 ampere hours/cm² (coulomb equivalent to 15,000 hours at 2 ma/cm²) were passed with no apparent degradation. In large cells, of course, internal heating would be a problem at the high current densities. In a single fiber assembly, the fiber has passed over 175 ampere hours/cm² at 30 ma/cm².

Cycling current back and forth through the fiber does not harm the glass. One 1000 fiber cell has been charging and discharging at a 5.5% depth (around Na₂S₅ catholyte) and 8 ma/cm² for over 11,500 cycles. This is 2 minutes each charge and discharge.

B. Electrode and Cell Development

(1) Cell Life

Over 1400 deep charge-discharge cycles have been achieved on the 0.5 amp-hour cell, surpassing the 1000 cycle goal. The larger 5 ampere hour cell has been deep cycled through 190 cycles with no change in characteristics. Key to the longer lives were the discoveries that small amounts of oxide in the sodium causes glass fiber degradation and that the tube sheet had to be completely leak-tight when very pure sodium is used as the anolyte.

At lesser depths of discharge, the cells last longer. The 6 ampere-hour cell has lasted as long as 77 days (over 400 cycles) discharging to about 10% depth and recharging in 4 hour cycles. The smaller 0.5 amp-hour cell has gone over 82 days and 1800 cycles at up to 25% depth of discharge.

(2) Cathode Foil

The cathode foil of carbon coated 5005 alloy aluminum (.5-1.0% Mg) works satisfactorily but it may be the cause of a slow rise in cell resistance after several weeks of continuous operation. This slow resistance rise may be an indication of fiber damage with eventual fiber breakage. When a cathode foil of MoS₂ on 1100 alloy aluminum (no Mg) is used, no rise in resistance is seen, but final cell resistance is about 1 1/2 times normal. A 1000 Å thick plating of Mo on 1100 (or 1145) aluminum works fine with no resistance rise and no increased base-line cell resistance. A 50 Å layer instead of 1000 Å is not enough. Intermediate amounts are being tried.

The use of the cathode foil of Mo on Al causes an increased polarization of the cell during charge over that seen using the carbon on Al foil. This polarization is reproducible from cycle to cycle and is higher at higher current densities.

(3) Chloride-free Glass

The possibility of the chloride anion being mobile in the fiberglass was investigated. If mobile, strains could be formed. Cells made using fibers from a $\text{Na}_2\text{O} \cdot 2 \cdot \text{B}_2\text{O}_3 \cdot 2 \cdot \text{SiO}_2$ glass had the same lifetime as cells made from fibers of a similar glass containing 0.16 moles NaCl. The glass resistance and therefore the cell resistance, was about twice as high.

(4) Fusion of the Tubesheet - Tubesheet Material

With the extreme spreadability of the oxide-free sodium now being used as anolyte, minute pores or cracks in the tubesheet lead to cell failures. It is extremely important to completely fuse the tubesheet. Somewhat higher temperatures are necessary than those previously used.

For the 94% B_2O_3 - 6% Na_2O tubesheet material, a temperature of 405°C is necessary, and for the 95 1/2% B_2O_3 - 4 1/2% Na_2O , a temperature of 393°C is necessary. Poor vacuum during the fusion leads to weak fibers.

The criteria that are necessary and sufficient to give good "fines" for the tubesheet material are not yet defined. A particle size distribution of "good" material gave 64% of the particles less than 1μ and only 9% greater than 2μ . However, studies of other fines indicated that this particle size distribution by itself was not enough. Some condition of the "surface" of the fine particles is necessary. The effect of the humidity during the 12 days of ball-milling necessary to get the fine powder is important.

The tubesheet material "fines" can be made in a much shorter time by using a "Vibra-mill". Milling glass with 1 1/2% alkyl amine at $90-100^\circ\text{C}$ has given useable material in 48 hours in a preliminary run.

The 250-325 mesh glass spheres used in the tube sheet material mix has been made by dropping the glass particles through a $\text{CO} + \text{O}_2$ flame. A regular hydrocarbon flame would impart water to the glass. Unsuccessful attempts were made to use a hot tube for spherodizing the glass instead of the CO flame.

(5) Thermal Cycling of the Cell

The small 0.5 ampere hour, 1000 fiber cell in the fully charged condition could be cooled from 300°C to 120°C and reheated without harming the cell. When cooled to room temperature, the cell failed. A different design of the cell is proposed that should allow cooling to room temperature. It gives extra space into which the catholyte can be drained before cooling.

C. Metal Alloys Suitable for Containers

The only real testing of metal alloys to test for suitability as a container was done on 316 stainless steel. A stainless steel sleeve placed around the fiber bundle of a 1000 fiber cell and tied electrically to the cathode did not cause any resistance build up or appreciable shorter life than if the steel sleeve had not been there.

A number of metal cell cases of 316 stainless steel were made and welding techniques are being developed to seal them.

Work on aluminum cases has been halted until cell failure modes are determined. If the failure mode allows temperatures to rise above 600-700°C, aluminum cannot be used.

D. Evaluate Characteristics of Operating Cells

Operating characteristics of small cells should be the same as large cells since the electrode spacings, current densities, etc., are exactly the same. Cells operated at 2 to 3 hour rates (4 to 6 hour turn around cycles) have voltage curves which depend on the composition of the cathode foil.

Using cathode foil of carbon on 5005 Al and discharging or charging at a 3 hour rate, the terminal voltages on charge and discharge parallel the open circuit voltages except in the very high state-of-charge region. In this region, the high sulfur content of the catholyte adds appreciable resistance to the cell.

When the cathode foil is composed of Mo on 1145 alloy Al, the discharge terminal voltage more or less follows the open circuit voltage, but the charge voltage increases with state of charge. The amount of the increase is different for different Mo/Al foils. It can be as bad as increasing the charging voltage 25% almost linearly during a charge at the 3 hour rate.

Consecutive charge-discharge voltage curves or cell capacity curves are very reproducible. On the cell having 1400 deep charge-discharge cycles, the voltage characteristics and capacity have changed less than 10%.

E. Evaluation of Other Factors Affecting Cell Life

At the beginning of the year the resistance of the glass, and hence of the cell, increased with the passage of coulombs. Much of the increase was due to calcium in the sodium anolyte. When it was removed from the sodium, the resistance increase was less and the fibers had a longer life. At "less than 15 ppm" Ca, there appeared to be no problem.

The potassium content of the sodium causes increased glass resistance. With potassium as high as 1%, the fibers break on extended discharge. Up to 650 ppm K in Na, the resistance increase is proportional to the amount of K present. The use of Na containing 100-150 ppm K does not cause shortened lifetimes of the cell. This is the normal amount of K present in commercial Na.

Oxides in the sodium corrode the glass fibers and lead to fiber and cell failure. When the oxides are removed by cold trapping, cell lifetime improves. However, the remaining oxides still degrade the cell. The final oxides can be removed with a scavenger such as Zr-Ti alloy at 500°C.

After the Zr-Ti treatment to get rid of the final oxide, the mode of cell failure changed. Rather than by fiber breakage, cells began to fail by massive breakage just below the tubesheet. This was due to penetration of the micropores in the tubesheet by the sodium. The oxide-free sodium has a much greater degree of spreadability than the low oxide sodium. Fusing the tubesheet at a slightly higher temperature solved this problem.

Weak fibers, which lead to breakage on handling can result from a poor vacuum during the curing of the tubesheet. The normal tensile strength of the fibers. . .85,000 - 95,000 psi, does not degrade during a 3 month storage in a sealed container.

While wall thickness of the fiber is important from the standpoint of physical strength to allow handling during cell assembly, once the cell is successfully assembled, a thicker wall is not necessary for long life. Cells using fibers of 64 μ x 70 μ (3 μ wall) and 58 x 70 μ (6 μ wall) were built. The 3 μ wall fibers break during assembly, but several 6 μ wall fiber cells were started -- one lasting 82 days which is as long as 10 μ and 15 μ wall fibers lasted.

F. Cost Estimate for Cell

At the beginning of this period, a rough cost estimate gave a bare cell cost of between \$6 and \$18 per kwhr based on a production of 200 (10⁶) kwhr per year.

A more refined cost estimate, taking into account all the production facilities and back-up equipment needed turns out to be about \$23 per kwhr with a number of areas flagged for probable cost reduction.

The following is the cost break down for a 0.8 kwhr bare cell:

Raw Materials	\$6.48
Labor	3.92
Overhead (160% of Labor)	6.27
(10% of Raw Materials)	.65
Depreciation (10% of Capital)	.301
After tax return (15% of Capital)	.451
Income tax (15% of Capital)	<u>.451</u>
	\$18.52

This is based on 10^6 kwhr per year production. The labor for welding the stainless steel case is 53% of the total labor involved in the cell assembly. Using automated equipment for this will reduce the cost substantially. Spinning the fibers amounts to 20% of the labor and 48% of the capital cost. If fibers can be spun twice as fast as at present, the cost of the cell is reduced appreciably.

INTRODUCTION

The sodium-sulfur battery based on thin glass membranes as the electrolyte has the potential of furnishing energy at close to 100 watt-hours per pound at a power density of over 80 watts per pound. In addition, preliminary cost analysis indicate that the cost per kwhr should compete with lead acid batteries.

The relatively low costs and high energy densities suggest applications in both the off-peak power storage (load-leveling) application and the vehicular propulsion application.

The glass membranes are in the form of the walls of fine hollow fiber. Typically, the membrane is about 10μ thick, based on a hollow glass fiber having the dimensions of 50μ I.D. by 70μ O.D. Thousands of these fibers sealed at one end are bundled in parallel and the open ends fed from a common sodium reservoir. This gives a very large "anode" and electrolyte area in a relatively small volume. For a matching cathode area, metal foil is placed between the fibers. Figure 1 shows the arrangement.

At the beginning of this contract period, small Na-S hollow fiber cells had been built and operated at various rates of charge-discharge and various depths of charge. Small cells designed for the one hour rate had been charge-discharged to over 90% of capacity at a 20 minute rate (3 times the design rate) for up to 8 days and 213 cycles before failure. Another similar cell, charge-discharged at the high 20 minute rate, but to 12% depth of discharge, ran 9 days and gave 2300 cycles. The most prevalent mode of failure was by fiber degradation and breakage. Some cells lasted as long as 44 days under normal operation at low depths of discharge.

Another problem existing at the beginning of this contract period was a change in internal resistance of some cells during their lifetimes.

Equipment necessary to mechanically assemble the hollow fiber cell had been developed. The machinery necessary to spin the hollow glass fibers had been designed and built. At the beginning of this contract period, instabilities in this machine gave non-uniform fiber output. Other machines used to assemble the fibers with the cathode foil and the tube sheet also needed improvement.

THE DOW SODIUM SULFUR HOLLOW FIBER CELL

Fig. 1

The program for the year was divided into 7 tasks.

Task I - Electrolyte Development and Evaluation

Since cell failures were associated with failure of the glass fiber, a strong effort was made to determine the causes of fiber failure. These included looking at the effects of current and current densities, and determining the effects of impurities present in the sulfur on the fiber lifetime. The effects of impurities present in the sodium is being investigated in another effort financed by NASA.

Task II - Electrode and Cell Development

This task includes getting long-lived cells and larger cells. Goals were achieving 1000 deep charge-discharge cycles and scaling up to 5 ampere-hour and larger cells. It was hoped to define those conditions that would allow thermal cycling of the cells. This task, although reported here, was carried out under another effort jointly funded by Dow Chemical and the Advanced Research Project Agency.

Task III - Development and Evaluation of Metals for use as Containers

The cells, as built, have been housed in Pyrex envelopes. In practice, they will have to be encased in metal. This effort is to identify those metals suitable for the housing from the standpoints of corrosion resistance, strength, weldability, and non-interference with the performance of the operating cell. Preliminary work on putting the cell into the metal case will be performed.

Task IV - Evaluation of Eight Hour Cell Characteristics

Almost all the hollow fiber sodium-sulfur cells built prior to the contract period were designed for the one hour rate. The electrode-electrode spacing had been very close -- less than 50 microns. The designs for 8 hour cells suggest an electrode spacing of closer to 100 microns in order to get sufficient sulfur catholyte between the electrodes. The 50 micron spacing gave good charge characteristics up to catholyte compositions of $\text{Na}_2\text{S}_5 + 15\text{S}$ or so. This task was to demonstrate the charging parameters and other characteristics of a cell designed for approximately 8 hours.

Task V - Evaluation of Other Factors Affecting Cell Life

Besides those factors in Task I (current, current density, impurities), there are other factors which appeared to affect the life of the cell. Some of these were wall thickness, depth of discharge, rate of charge or discharge, etc. Also affecting lifetime are construction details of the cell. This task was to try to elucidate all possible factors which are important. This task was to be jointly funded by Dow Chemical, NASA, and ARPA, but is also reported here since it is an aid to the common goal.

Task VI - Cost Estimate

As development proceeds on the cell, any changes in materials, construction, or handling can drastically change the estimated cost-for-sale of the cell. We have, therefore, at the end of the contract period, using the best available data and guesswork, made an updated cost estimate for the hollow fiber sodium-sulfur battery.

Task VII - Coordination with Other Hollow Fiber Sodium-Sulfur Battery Research and Development Programs

This contract is being carried out alongside of two other R&D programs which are partially funded with Government funds. Continuous coordination of these programs prevents duplication of effort and results in faster progress toward the desired goal.

TECHNICAL RESULTS

A. Electrolyte Development and Evaluation

Fiber Quality

In a search for causes of short lifetimes in early cells, an electron microscopy study of the glass fibers was carried out. The surfaces of freshly drawn fibers were extensively studied in the scanning electron microscope using a variety of imaging and signal processing techniques. There were several categories of surface features.

- 1) Obvious refuse attached to the glass surface. This litter included pieces of glass fiber in significant numbers, dust, lint, pollen grains, etc.
- 2) Irregular protuberances from the surface that cannot be classified as either superficial refuse or actual surface features.
- 3) Small rounded protuberances on the surface from approximately 0.1μ to $5-10\mu$ in diameter. These are usually, but not always found in conjunction with the rubber cement or other surface refuse.
- 4) Large splotches with sharp contrast, even at high magnifications.

- 5) Areas of general roughness on the scale of 0.05 - $.5\mu$.
- 6) Scratches and gouges on the surface, some with the scratching material still on the surface at the terminus of the scratch. Some of these scratches were several microns wide and at least as deep. There were a large number of these scratches.
- 7) Holes and pits in the surface. Usually small ($0.5 - 2\mu$) in diameter, these features were definitely holes. They are deep enough so that no secondary electrons are observed coming from the bottoms. They must be at least as deep as they are wide. The surface density of these holes was fairly constant on all fibers studied at about one hole per 100μ of length.
- 8) Scaling or crystallization of the surface.

Figure 2 shows a low magnification (X1000) of a fiber. Figure 3 is a higher magnification (X2500) of a scratch.

The unknown character of some of the features led to further investigation with high voltage microscopy. The features described in 3, 4, and 5 are all caused by a general roughness of the fiber surface down to about the 0.1 scale. The variations seen are caused by variations of roughness.

The very worrisome features are the scratches and pits. In an effort to discover the causes of these scratches and pits, samples of the fiber were taken at various stages in the spinning operation. Samples were taken directly out of the spinnerette, after passing over various contact surfaces in the spinning apparatus, and at the final stage just before being rolled into the cell. Using the same examination techniques, all of these fibers had almost pristine surfaces. The different results may be due to a cleaning of the contact surfaces of the spinning apparatus before the second investigation was undertaken.

The effect of storage of glass fibers was determined. Fibers taken from storage after four months had tensile strengths of 85-95,000 psi -- roughly the same as freshly drawn fibers.

Fiber Tensile Testing

Glass fiber samples were loaded in tension to determine the effect of fiber size and age on ultimate tensile strength (UTS) and whether low UTS of a fiber batch could be correlated with early failure of cells made from that batch. Preliminary results exhibited little, if any, decrease in UTS of fibers stored for three months compared to fibers just drawn, and complete fiber UTS history will be recorded to confirm the preliminary conclusion that fiber UTS decreases very slowly with age. Fiber size also had little effect on UTS - mean UTS running between 85,000 - 90,000 psi. It appears cell failure may not be due to low UTS.

Fig. 2

Fig. 3

DI ANODE ASSEMBLY

Fig 4

The low rate of successful fiber breakage (approximately 25%; "successful" meaning the fiber broke in the middle rather than at the points where it was held) made evident the need for an improved tensile testing design, including an improved means of measuring the UTS, elongation, and strain rate. New methods of holding single fibers for ultimate tensile strength testing were examined. The most successful method was attaching thin strips of aluminum to each fiber end with a five-minute setting epoxy. The strips were then clamped into our tensile tester and the fiber loaded in tension until breakage occurred. Very few fibers broke unsuccessfully using this fiber holding method, and this method was used on an improved fiber tensile tester design. The change in fiber strength due to cell assembly conditions was investigated by tensile testing fibers annealed at 374°C for 1.5 hours. The fibers were rolled and cured similar to the methods of cell assembly, but the tube sheet and chemical treatment were not included. Relatively thin and thick wall fibers were each prepared. The thin wall fibers tested had no mean tensile strength decrease on annealing while the thick wall fibers exhibited a 25% drop in tensile strength, with test sample standard deviations ranging as high as 20%. The drop in tensile strength in the thick wall fibers might well be due to effect of a large compression layer which, when relieved on annealing, does not contribute to fiber strength.

Effect of Sulfur Impurities on Glass and Cell Life

In testing for the effects of impurities in the Na-S cell, a number of techniques are used. In some cases actual cells are built using anywhere from 10 to 6000 fibers. In "cells", the fiber to fiber distance and fiber to cathode foil distances can be controlled. A "cell" with 10 fibers could be made just like a cell of 3000 fibers with solid glass rods being used in place of most of the fibers. The cells can be assembled reproducibly and various impurity factors added or removed.

Another technique is using a "dianode assembly". This assembly is shown in Figure 4. Two "anodes" consisting of a bundle of 1-10 fibers potted into a sodium reservoir are immersed in a common molten catholyte. A reference electrode is also immersed in the catholyte. Large quantities of sodium can be passed from one reservoir to the other, going as the ion through the glass walls of the capillaries and through the molten catholyte. The effects of impurities are magnified because coulombs can be made to flow in one direction hundreds or thousands of times that normally used in an operating cell. The reference electrode permits monitoring and differentiation of any resistance rise on the "discharging" or the "charging" anode.

Some experiments were run in which the Na_2S_4 catholyte 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 not conclusive although the indications seem valid. The sulfides in various dianode assemblies were spiked with small amounts of MgS , ZnS , Al_2S_3 , and H (from NaHSO_4 or NaH). Changes in glass resistances were determined on both charging and discharging electrodes during extended operation. Figure 5 shows the resistance increase when MgS was used as a dopant compared to an undoped system. No apparent difference is seen. The resistance rises are probably due to the impure Na used.

FIGURE 5

EFFECT OF MgS IN Na_2S_4 CATHOLYTE - DIANODE ASSEMBLY

Similar results were found for the Zn^{++} , Al^{+++} , and H from NaH. When purified Na was used in the experiment, and the sulfide spiked with NaH, it did appear that the "charging" electrode had a resistance increase over the unspiked control. The discharging electrode had no change (Figure 6). The resistance increase could be caused by H migrating into the glass structure.

Work with actual running cells (as opposed to dianode assemblies) has suggested that Mg impurity does affect the glass resistance. Single fiber cells have been run using cathode foils of either carbon coated 5005 (Mg-containing) Al alloy, or molybdenum plated 1145 (no Mg) Al alloy. Figure 7 shows the change in resistance with time for four cells, two of each cathode foil composition. Those having carbon coated 5005 Al 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^{++} . These results are confirmed with multi-fiber cells. Figure 8 shows the changes in resistance with time for cells having 3 different types of cathode foils. That with 1000 Å of Mo on 1145 Al shows no resistance increase.

Since the dianode assembly (Figure 6) showed an increase in resistance on the charging electrode when H (from NaH) was added to the Na_2S_4 catholyte, it was decided to see the effect of adding H to a working cell. Lampblack (1% by wt. of S) was added to the sulfur charge in filling a 0.5 ampere-hour, 1000 fiber cell. This cell operated normally for 44 days, charging and discharging to about 85% depth, with no apparent increase in resistance. Any H present apparently did not lodge irreversibly in the glass. The only noted difference between this cell and one without lampblack is that the lampblack lowered the resistance of the initial charge of sulfur so that the initial discharge of the cell could be done rapidly.

The effect of "gross" sulfur purity was tested. Normally, the sulfur used in the Na-S cells is distilled over hot Vycor chips at 850°-900°C. This reacts carbon and hydrogenous impurities to CS_2 and H_2S which can be debubbled from the distilled sulfur. Several 1000 fiber cells (PS 58, PS 59) were started using as sulfur catholyte some crude "flowers of sulfur" that had been only melted and filtered. Normal lifetime for these cells on deep charge-discharge was over 60 days continuous operation. PS 58, using the filtered crude sulfur is still operating at over 50 days. PS 59, using filtered crude sulfur which had been purged with N_2 for two hours, failed in 15 days from fiber breakage.

1000 fiber cells - - - - usual life >60 days.

PS-58 - - - - filtered crude sulfur >50 days.

PS-59 - - - - filtered crude, N_2 bubbled sulfur. 15 days.

More work needs to be done on requirements for sulfur purity. It has been reported that 316 stainless steel case material adversely affects the performance of Na-S cells based on $\beta\text{-Al}_2\text{O}_3$. The hollow fiber cell with its lower current density and lower charging voltages may behave differently in the presence of the stainless steel. A 316 stainless steel sheath was placed surrounding the fiber bundle of a 1000 fiber, 0.5 ampere-hour

FIGURE 6

EFFECT OF NaH IN Na_2S_4 CATHOLYTE - DIANODE ASSEMBLY
(Na is purified, "gettered")

FIGURE 8

CATHODE FOIL EFFECT ON CELL RESISTANCE
1000 Fiber, 0.5 A-hour Cells

cell and electrically connected to the cathode foil. This cell (PS-40) was operated at 24 ma per cm^2 (12 times design current density), discharging to over 90% of its capacity in 1/2 hour and recharging in 1/2 hour and ran continuously 75 days. There was no evidence of any resistance increase during its lifetime. It had over 1650 cycles and failed due to fiber failure after passing the ampere equivalent of 900 days of normal operation. Apparently, 316 stainless steel is not harmful.

Effect of Current and Current Density on Glass Properties

The data on glass lifetime as a function of current passed and of current density has been gathered from lifetime results on single fibers, on the dianode assemblies, and on operating multi-fiber cells which range in size from 10 to 3000 fibers. The 3000 fiber cell is the 6 ampere-hour size.

Some typical data are shown:

<u>Cell No.</u>	<u>Current, Amps</u>	<u>Current Density (ma/cm²)</u>	<u>Life, Days</u>	<u>Amp-hr. cm²</u>	<u>Rate (hr.)</u>	<u>Depth, %</u>	<u>Notes</u>
PS-43	.8	8	>51	>9.4	.62	80%	6 μ fiber
PS-49	.5	5	>70	>8.2	1.0	50%	--
PS-40	1.0	10	75	17.5	.5	100%	
PS-54	.8	8	>34	>6.53	.62	5.5%	4 min. cycles
PS-57	1.0	10	59	13.7	.5	100%	
PS-53	.3	3	>62	>4.3	1.7	30%	
MP-9	3.5-4.5 ma	35-45	205	196.8	--	--	Single fiber
DA-52	6 ma	55	20	25.1	Dianode Assemblies, cycling		
DA-54	6.4 ma	58	21	27.8	10 Min. each direction, 30 column vols.		

Current densities have varied from 58 ma/cm² to 3 ma/cm² with no positive correlation of lifetime versus current density. In fact, most of the failures were due to failures near the tube sheet rather than fiber failures. The longest life and the most coulombs passed per cm² of fiber are with the single fiber "cell". At a normal current density of 2 ma/cm², the coulomb passage of 196.8 amp-hours per cm² corresponds to a lifetime of 11.2 years.

Although these data show that current densities up to 58 ma/cm^2 and total coulombs passed up to 196 ampere-hours per cm^2 are not the limiting factors in cell lifetime to date, such was not the case when impure Na was used. With calcium present in the sodium, lifetime was a function of total current passed in a discharge direction. The calcium ion entered the glass structure, caused strains, and broke the glass. With oxides present in sodium, fiber lifetime was a function of discharge depth and total current passed. The oxide would concentrate in the lower portion of the fiber during discharge, and cause corrosion of the glass. This data will be presented in more detail in a later section, Other Factors Affecting Cell Life.

B. Electrode and Cell Development

Cell Life

During the early part of this period, most cells were operated on shallow charge-discharge cycling. Generally they ran on 4 hour cycles, charging and discharging at 10 or 20% of capacity. Some cells were operated in the 2 phase ($\text{S} + \text{Na}_2\text{S}_5$) region and some in the one phase region.

Lifetimes of the early 6 ampere-hour, 3000 fiber cells were longer than the lifetimes of cells started later in this contract period. Table I lists most of the 6 ampere-hour cells reported in this period. Cells 184, TK 38, and TK 39 had operating lifetimes of 78, 60 and 55 days respectively. These cells operated on cycles of 2 hour charge and 2 hour discharge at about 0.25 amperes. This is only 8-10% of capacity. When cells were run to deeper depths of discharge, lifetime was shorter. Cells 185, 186 and 189, operating from 75% to over 80% of capacity at 1.0 to 1.5 amperes, lasted only 8, 8, and 6 days, respectively.

Concurrent research demonstrated that impurities in the Na were probably causing fiber breakage. Beginning with cell TK 64, Ca was removed from the sodium anolyte. No improvement of lifetime on shallow discharge was seen. The longest life was cell TK 71, 46 days charging-discharging on 4 hour cycles at 0.45 amperes (~15% depth). However on the shallow cycling, the mode of failure using the purer Na changed from predominately fiber failure to predominately failures happening just under the tube sheet. Lifetimes of those cells on deep charge-discharge cycling improved. Cells TK 85, TK 86, and TK 88, for example, cycled at 75-100% of capacity, had lifetimes of 23, 20 and 26 days. These operated at 1.0 to 1.8 amperes (6 hour to 3.3 hour rates). TK 88 ran over 130 cycles. Cell failures with these deep cycled cells were mostly due to fiber failure or failure due to air leakage into the cell. In some of these cells, the cell resistance was seen to increase during cell lifetime by factors up to 100%.

Work with dianode assemblies had shown the destructive effects of oxides in the sodium. Beginning with Cell TK 113, sodium was used that was "Ca-free" and that had been treated with a Zr-Ti alloy to scavenge out the remaining oxide. Cell lifetime was not improved. In fact, cell TK 119, left on open circuit, failed in 31 days. In these cells (TK 113 - TK 147) it is probable that air leaked into the assembly and reintroduced oxide into the sodium.

TABLE I

Cell No.	Fibers, μ	Wall, μ	Depth	Current, A	Life, Days	Leak Rate	Notes
184	50 x 90	20	11%	.27	78	0	- Constant resist., 2 phase region, violent failure below tube sheet.
185	50 x 90	20	80%	1.0	8	20	- 12 cycles, 7.5 hr. rate, failure under tube sheet.
186	50 x 90	20	76%	1.5	8	24	- 7-1/2 cycles, 4.8 hr. rate, ran out of Na.
189	50 x 90	20	--	1.0	6	20	- Weak fibers, ran out of Na?
190	50 x 90	20	50%	0.6	8	20	- 6 hr. rate, low capacity. Sudden high resistance
TK-38	40 x 90	25	10%	.24	60	0	- Sudden short to failure, tubesheet 7123, cured at 374°C.
TK-39	40 x 90	25	10%	.24	55	16	-
TK-49	40 x 90	25	12-24%	.3-.6	18	0	- Fibers broken at foil top; tube sheet 96/4, cured 386°C.
TK-50	40 x 90	25	12%	.3	13	7	- As above; in sulfur region.
TK-52	40 x 70	15	10%	.23	14	0	- Fiber failure; tube sheet 7123, cured 374°C.
TK-55	40 x 70	15	10%	.23	10	2	- Same as above, .004" spacer.
28 TK-54	40 x 70	15	13%	.32	30	1	- 156 cycles, failure below tube sheet, .005" spacer.
TK-60	50 x 90	20	--	--	2	12	- Short near bottom of fiber.
TK-62	50 x 90	20	15%	.35	17	2	- Sulfur region, failure under tube sheet.
TK-63	50 x 90	20	8%	.22	77	6	- Sulfur region, out of Na on 34th day, recharge some back, but high resist. Tube sheet 7123.
TK-64	50 x 90	20	20-25%	.5-.6	38 + 12	0	- Shorted and recovered, Na ₂ O added to Na, 7123 T.S.
TK-69	40 x 90	25	25%	.6	19	0	- Fiber failure: Use dry 7123 fines in T.S., Na ₂ O in Na.
TK-68	40 x 90	25	16%	.4	20	4	- Same as above.
TK-70	40 x 90	25	25%	.6	11	16	- Fiber failure, Ca-free Na, good T.S.
TK-71	40 x 90	25	18%	.45	46	6	- Failure under Tube Sheet, Ca-free Na.
TK-72	40 x 90	25	85%	.6	4	6	- 3 cycles, Ca-free Na. Possibly bad connection.
TK-73	40 x 90	25	80%	.8	4	18	- 3 cycles, probable short. 7123 T.S. fused 374°C.
TK-74	50 x 90	20	36%	.9	16	12	- Fiber failure, 1 and 2 phase sulfur, T.S. fused 374°C.
TK-75	50 x 90	20	28%	.7	8	6	- Failure under tube sheet. Ca-free Na, 7123 T.S.

TABLE I

Cell No.	Fibers, μ	Wall, μ	Depth	Current, A	Life, Days	Leak Rate	Notes
TK-78	50 x 90	20	40%	1.0	8	6	- Fiber failure, Ca-free Na, 7123 tube sheet.
TK-82	40 x 80	20	--	.5	1	32	- Shorting somewhere.
TK-85	50 x 90	20	85%	1.0	23	0	- 40 cycles to Na_2S_3 , 6 hour rate.
TK-86	50 x 90	20	85%	1.0	20	8	- Probable fiber failure, air leak into cell(?) - 26 cycles, probable tube sheet failure cell resist. constant. Probable air leak into cell.
TK-87	50 x 90	20	50%	1.2	12	3	- Failed under tube sheet. Resist. constant. Weak fibers.
TK-88	50 x 90	20	>80%	1.8	26	1.3	- 130 cycles. Failed under T.S., cell resist. increased 30% in 2 weeks.
TK-90	50 x 90	20	75%	1.0	17	0	- 26 cycles. Fiber failure, air leak(?)
TK-99	50 x 90	20	>75%	2.-3.	12	4	- Hole in Al cup. Air leak(?)
TK-100	50 x 90	20	80	2.0	11	1	- 33 cycles. Failed under T.S. Resistance increased.
TK-108	40 x 80	20	>75%	1.6	9	8	- 35 cycles. Fiber failure. T.S. OK. Al_2O_3 in Na. Resistance increased 100%. Air leak(?)
TK-109	50 x 80	15	>80%	2.0	12	2	- Tube sheet failure, resist. increased.
TK-111	50 x 80	15	30%	1.8	14.5	14	- 116 cycles, Mo-Al foil. High resistance.
TK-113	50 x 90	20	90%	1.2	4	0	- Failed at fiber ends. Na treated with Zr-Ti.
TK-115	50 x 90	20	>80%	.7	3	15	- After 3 days, ran 22 days at 10% depth. Na treated with Zr-Ti.
TK-116	50 x 90	20	60%	1.5	20	0	- Fiber failure. Cell resist. increases.
TK-117	50 x 90	20	10%	.23	24	0	- Mo-Al foil, low on Na, low capacity.
TK-119	50 x 90	20	open circuit		31	3	- 7123 tube sheet, fused at 374°C.
TK-121	45 x 80	17	>75%	2.0	7	8	- Failure through T.S. 7123 cured at 383°C.
TK-122	--	--	25%	.6	18	0	- Fiber failure, 7123 T.S. cured at 384°C.
TK-124	50 x 70-80	10-15	>75%	1.5	16	0	- Fiber failure, 7123 T.S. cured at 383°C.
TK-147	50 x 80	15	40%	1.0	8	0	- Fiber failure, 94-6 T.S. cured @ 390°C, air leak.

Greater lifetimes were achieved with the 1000 fiber, 0.5 ampere-hour assembly. Table II lists most of these cells which were started and failed during this period. On deep cycling to over 85% depth of discharge, 75 days of continuous operation was achieved (PS 40).

In this case, the 1000 fiber cell was cycling at 1.0 ampere, charging in 1/2 hour and discharging in 1/2 hour. Current density in the glass electrolyte was about 10 ma per cm², three times the design current density for the 6 μ wall fibers. Over 1600 complete cycles have been obtained with no change in cell characteristics. A number of other cells are deep cycling after over one month at the 1/2 hour rate (PS 51, PS 43, PS 52, PS 57, PS 55).

One cell (PS 43) has operated over 82 days. It was started at the 1/2 hour rate (1.0 ampere), but after 37 days it ran low on Na and partially lost contact at the anode. Recharging brought back partial contact, but the resistance remained high. From the 37th to the 82nd day, the cell has been operated to ~50% depth at the one hour rate (approximately 0.5 amperes).

As with the larger 3000 fiber, 6 ampere hour cells, the lifetimes of these 1000 fiber, 0.5 ampere hour cells fall into several categories. The early cells had shorter lifetimes due to the presence of Ca and oxides in the sodium. First Ca was removed giving somewhat longer lives, then the oxides were removed giving longer lives. Better sealing of the cell reduced air leakage into the running cell. Finally, getting rid of the residual oxide by Zr-Ti alloy scavenging at 500°C gives lives on deep cycling at high rates of well over two months.

One cell (PS 54) is operating on shallow cycling (5.5%) at a 37 minute rate (.8 amperes). It has a two minute charge and two minute discharge time at 8 ma per cm², four times the design rate. To date, it has gone over 34 days and 11,500 cycles without degradation. It is still operating.

Cathode Foil

Earlier in this report, mention was made of the effect of various cathode foils on the resistance change in single fiber cells and multi-fiber cells upon prolonged operation. Figures 7 and 8 illustrated these changes. When foils of 5005 Al (Mg-containing) were used, the cell resistances increased during the cell's life. These resistance increases were not seen in the 6 ampere-hour, 3000 fiber cell. This may be because the larger cell has not run long enough to see the resistance increase. The 100 ampere hours in the small cell would correspond to 1000 ampere hours in the larger cell for the same "amperes per cm²" across the glass and so far, the 6 ampere hour cells have not run that long.

TABLE II

Cell	Tube Sheet	Cathode	Depth	Life		Failure Mode	Remarks
				Days	A-days		
PS-13	94	MoAl	>95%	19	19	-at tube sheet	
PS-23	94	MoAl	80%	11	8	-at tube sheet	
PS-20	95-1/2	MoAl		Used in cooling experiments			
PS-16	95-1/2	MoAl	>90%	10	10	-at tube sheet	
PS-15	95-1/2	MoAl	>90%	9	9	-at tube sheet	
PS-24	95-1/2	MoAl	>90%	22	22	-at tube sheet	
PS-18	95-1/2	MoAl	>90%	18	18	-at tube sheet	
PS-21	95-1/2	CMoAl	90%	26	25	-fiber failure	
PS-27	95-1/2	CMoAl	95%	29	28	--	
PS-22	95-1/2	CA1	--	20	15	-at tube sheet. Took 2 weeks to reach normal cell resistance. T.S. cure at 405° instead of 397°C.	
PS-25	94	MoAl	90%	47	43		
PS-26	94	MoAl	>95%	14	14	-Al cup joint failure.	
PS-29	94	CA1	--	9	2	-Fiber failure. High internal resistance.	
PS-28	94	Al	--	--	--	-Ran out of Na. High resistance.	
PS-30	94	Al	--	32	--	-Tube sheet area. High resistance.	
PS-31	94	CA1 (Mg)	85%	15	12	-at tube sheet. Increasing resistance	
PS-32	94	MoS ₂ /Al	85%	20	16	-at tube sheet. Some resistance increase	
PS-35	94	MoAl	89%	49	43	-at tube sheet. Cured T.S. at 420°C	
PS-34	94	MoAl	--	41	30	-failed in prolonged charge to 40 volts	
PS-33	94	CA1	--	36		-at tube sheet. Decreasing resistance for 6 days. cycle 3x at 360°C. Resist. drops to near normal.	
PS-36	94	MoAl	>95%	27	27	-constant resistance	
PS-38	94	CA1	--	40	19	-at tube sheet. Slowly decreasing resistance	
PS-37	94	MoAl	>95%	20	19	-at tube sheet. Cure T.S. at 420°C.	
PS-39	94	CrAl	--	1	--	-at tube sheet.	
PS-40	94	MoAl	100%	75	70	-hrs. 316 S.S. insert	
PS-44	94	MoAl	90%	23	20	-low K in Na	
PS-45	94	MoAl		10		-impure sulfur	
PS-42	94	CA1	--	11	--	-fiber failure. High temp. to condition foil didn't work.	
PS-50	94	MoAl	--	19	--	-air leak	
PS-49	94	MoAl	55%	70	35	-T.S. cured at 420°C	

TABLE II

<u>Cell</u>	<u>Tube Sheet</u>	<u>Cathode</u>	<u>Depth</u>	<u>Days</u>	<u>Life</u> <u>A-days</u>	<u>Failure Mode</u>	<u>Remarks</u>
PS-51	94	MoAl	82%	>36	>28		1% lampblock to sulfur. Repid start.
PS-47	94	MoAl	60%	34	20	-tube sheet area	
PS-41	94	MoAl	100%	19	21	-tube sheet area. 6 μ wall fiber	
PS-43	94	MoAl	12%	>82	>47	-last elect. contact 37th day. Partially recovered. -6 μ wall fiber	
PS-46	94	MoAl	>95	6	11	-fiber failure. 3 μ wall fiber	
PS-54	94	MoAl	6	>34	>27	-high rate (.8 amp), shallow, 4 min. cycle.	
PS-53	94	MoAl	29	>62	>20		
PS-52	94	MoAl	78	>36	>30		
PS-56	94	MoAl	>95	26	29	-tube sheet area. More Zr-Ti added to Na, 6 μ wall	
PS-57	94	MoAl	91	59	57	-fiber failure. -no BCl ₃ treatment. Resistance constant	
PS-55	94	MoAl	73	>30	>25	-more ZrTi added to Na	
PS-59	94	MoAl	90	15	12	-fiber failure. crude filtered sulfur	
PS-58	94	MoAl	86	>24	>19	-fiber failure. crude filtered sulfur	
PS-60	94	MoAl	80	>8	>8	-crude filtered sulfur -distilled degassed sulfur.	

NOTE: Most PS cells cycled at 1/2 hour rate for charge and discharge.

Single Fiber Cells

- 0.95 MoAl 30-35 ma/cm², cycling at 6 column vols/cycle in Na₂S₄.
Lifetime = >47 days, >33.84 A hr/cm², >11,500 cycles.
- 95 MoAl same conditions as above.
Lifetime = >45 days

When foils of 1145 alloy aluminum (no Mg) were used, the increase in resistance during the lifetime of the cell was not seen. If uncoated 1145 Al is used, the cell resistance is, and remains high for at least 32 days. (Cells PS 28, PS 30.) If the 1145 Al is coated with carbon, the cell resistance starts out very high and slowly decreases. It takes almost two weeks of operation for the cell resistance to drop to normal (PS 22, PS 29, PS 33, PS 38). An attempt was made to decrease this "conditioning time" by heating the cell to 360°C for a total of 9 hours. No improvement was seen (PS 42).

When cathode foils of thin molybdenum coatings on the 1145 Al are used, cell resistances do not increase during the cell lifetime of up to 85 days. A large number of these cells in both the 6 ampere hour and the 0.5 ampere hour sizes were built. The effect of the Mg-containing foil is dramatically shown in Figure 9. This shows the resistance versus time curves for two 0.5 ampere hour cells identical except for a piece of Mg-containing Al foil adjacent to the fibers in one cell. The cell containing the piece of Mg-Al foil increases resistance about 20% while that with no Mg-Al foil has no change in resistance during its lifetime of about 30 days operated at 6 times design current density.

When the Mo coated 1145 Al cathode foil is used, however, a different phenomenon is seen. A polarization is observed that shows up as an increase in resistance during the charge cycle. This effect is seen by comparing the curves shown in Figure 10. These show cell resistances versus % charged or discharged. The data are from two 6 ampere hour cells, identical except for the cathode foils. Both cells were operated at about the same current. The cell having the cathode foil of carbon on 5005 (Mg-containing) Al shows the "good" characteristics of constant resistance until over 70% charged, where the resistance of the increasingly high sulfur content of the catholyte begins to be important. The cell with a foil of Mo on 1145 Al on the other hand, demonstrates a steadily increasing resistance during the charge cycle. The cell resistance is more or less constant and low on discharge.

This resistance characteristic is not the same for all cells. Figure 11 shows the resistance changes for two "identical" cells operated at the 1/2 hour rate (very high current densities). Preliminary results indicate the difference is probably due to differences of Mo thickness. Although these cells have a nominal 1000 Å of Mo, the thickness is not constant. Cells with thinner Mo platings do not show such large polarizations. One cell built with a cathode foil of 50 Å of Mo on Al had very high resistance. Cells with intermediate thicknesses are now being tried. Thicknesses of about 300 Å look good.

FIGURE 9

EFFECT OF 5005 AL ALLOY ON CELL RESISTANCE

1000 Fiber, 0.5 A-hour cells
Purified Na
Cathode: Mo on 1145 Al

Doping

--- Piece of 5005 Al (0.5% Mg)
adjacent to fibers
— None

FIGURE 10

CATHODE FOIL EFFECT ON CELL RESISTANCE DURING A CHARGE-DISCHARGE CYCLE

3000 Fiber, 6 A-hour Cells

Cathode

--- C on 5005 Al
— Mo on 1145 Al

FIGURE 11

COMPARISON OF "IDENTICAL" CELLS' RESISTANCES DURING A CHARGE-DISCHARGE CYCLE

1000 Fiber, 0.5 A-hour Cells

Cathode: Mo on 1145 Al

Since the Mo can be expected to change to MoS_2 in the cell, a cathode foil of MoS_2 spread on 1145 Al was tried. This cell (PS 32, Curve 4 of Figure 8) had a high resistance to begin with, but did not increase very much during operation. The MoS_2 used had large particle sizes, and the experiment should be run again with a finer grind of MoS_2 .

Chloride-free Glass

The possibility was considered that the chloride anion in the fiber glass might be mobile. If so, this would result in electrolysis of the glass as the sodium ion migrated one way and the chloride ion the other. It could be a cause for short lifetime and life would be a function of total current passed. Even though there is no indication that life is a function of total current passed, the possibility was investigated.

Glass of composition $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 0.2 \text{SiO}_2$ was made and drawn into fibers. This is the same composition as the normal fiber glass except that the normal fiber glass has 0.16 NaCl content in addition. Dianode assemblies as described earlier were used in this investigation. Up to 3.4 ampere hours per cm^2 of fiber were passed through these fibers at 13 ma per cm^2 and also through a similar dianode assembly using the normal chloride containing glass fiber. This is an equivalent current to 1700 hours at 2 ma/ cm^2 . The dianode assemblies behaved identically except for the three times higher resistance of the non-chloride containing glass. Therefore, within this amount of coulombs passed, any chloride migration is not important. The resistance slowly increased during the runs, but this is attributed to the calcium content of the Na used at that time.

Tube Sheet Material

The criteria that are necessary and sufficient to give "good" tube sheet material are not yet defined. The ground glass particles used in making the tube sheet must be of size, shape, and surface condition to form a high density flowable paste with a minimum of the cumene vehicle used.

A large effort has gone into this investigation. The tube sheet paste is made of 46% "fines" of tube sheet glass, 46% (-200 + 325) mesh spheres of tube sheet glass, and 8% by weight of cumene. If the "fines" are not properly made, the desirable flowable paste is not obtained. Instead, the mix resembles a moist sand.

The finely ground tube sheet glass particles have been made by ball-milling for up to 14 days at various temperatures a -325 mesh fraction of the glass. Usually hexadecylamine, up to 1 1/2%, is added as a grinding aid. In order to define what makes a "good" batch of fine particles, particle size distribution studies were done on various batches of "fines" which were characterized in performance as excellent to poor. Figure 12 shows % mass versus particle sizes. Samples 1 and 2 are different kinds of glasses that were included for comparison. All the rest are glass compositions 95 1/2% B_2O_3 - 4 1/2% Na_2O milled at different times, temperatures, or humidities. Table III lists the conditions for each sample. It is apparent that the "goodness" of the finely ground material is not entirely a function of particle size. Even sample 7, with a most populated particle diameter interval of 8 - 9 μ , worked OK. Obviously, as long as the particles are sufficiently fine, the surface character is of extreme importance.

The moisture content of the glass and the atmosphere during grinding seems to be very important. The hexadecylamine present during the grinding apparently keeps the freshly broken glass surfaces from re-agglomerating. It also acts to suspend the glass particle in the cumene. The presence of moisture can change the action of the amine during grinding. The physical presence of moisture on the fine glass particles also adversely affects the ability of the cumene to suspend the particles. Unsuccessful attempts were made to dry the "fines" after grinding with amine. The process of drying removed the amine so the glass particles would not suspend. Attempts at replacing the amine by ball-milling an additional two days in the presence of amine were unsuccessful.

A Sweco Vibra-Mill was obtained in order to have a higher grinding rate and greater production rate of "fines" than could be obtained from a ball mill. A number of grinding trials were made on the Vibra-Mill. The best results were obtained when the mill and the grinding media were pre-dried, and relatively dry glass was milled 48 hours. The milling is done at ~95°C in the presence of 0.5-1.5% hexadecylamine or a mixture of hexadecyl and dodecyl amines. The 48 hour milling is in contrast to the 8-12 days of ball milling necessary. The median diameter of the final powder was about one micron. Figure 13 shows the particle size distributions for the powder from the Sweco Vibra-Mill.

FIGURE 12 Percent Mass vs. Particle Size Curves

TABLE III

ASSORTED DATA FOR EIGHT TUBE SHEET GROUND GLASSES

	Sample Number and/or Description and/or Composition (e.g. 94-6 or 95.5-4.5)	Mill Jar Vol. Q = Quart G = Gallon	Time of Grind, Days	Temperature during milling, °C	Relative Humidity (%) around mill jar	Percent of Amine	Qualitative Usefulness of Ground Glass in Tube Sheet Extrusion Fabrication	S.E.M. Micrograph Magnification	Number of Grains Counted	Most Populous Particle Diameter Interval, μ m	Diameter Interval Containing Greatest Mass, μ m
1	T112S20, major fluoride in glass	1 G	1	~25	~2	1/2	Excellent	5000	1341	.265- .302	.78- .82
2	12/10/74; 94-6	1G, 1Q	1.5 + 2	25, 90	~40 ~40	1+, 1/2	Very Good	2500	1394	1.14- 1.31	6.00- 6.22
3	6/5/75; 95.5 - 4.5?	1 Q	10 + 2	90	Variable 2 to 40	1 + 1/2	Good	2500	1439	.38- .45	3.48- 3.54
4	12/5/75; 95.5 - 4.5	1 Q	8 + 2	90	<.01	1 + 1/2	Fair	2500	1789	.45- .53	2.04- 2.11
5	12/5/75; 95.5 - 4.5	1 G	5	90	<.01	1?	Poor	2500	863	.88- .96	3.5- 4.0
6	12/12/75; 95.5 - 4.5	1 Q	7 + 3	90	<.01	1 + 1/2	Poor	2500	1259	.49- .71	5.1- 5.3
7	12/2/75; 95.5 - 4.5	1 Q	6 + 2	90	<.01	1 + 1/2	Good	500 & 2500	3052	.82- .90	8.5- 8.9
8	12/5/75; 95.5 - 4.5	1 Q	8 + 2	90	<.01	1 + 1/2	Poor	500 & 2500	1180	.49- .71	13.5- 14.5

FIGURE 13- Original Data Points for Particle Populations in Sweco Run #5, showing variability and "best fit" curves.

SWECO RUN #5

24 HOUR GRIND ●—●

48 HOUR GRIND ○—○

$\frac{3}{4}\%$ + $\frac{3}{4}\%$ Amine

Corning 7123 Glass

S.E.M.

24 hr. - 1143 part'l., 1000X

48 hr. - 1482 part'l., 3000X

..... 24 hr. grind with % mass reduced by factor of three

⊗ → Number of large grains averaged into these data points.

B.H. Bieler
4/19/76

A big problem in handling dry glass powders in a low humidity atmosphere is caused by the static pick-up. The powders are very hard to sieve and transfer. A great help came in the discovery that the powders could be ground and sieved in a relatively dry room (instead of a controlled atmosphere box) and then dried sufficiently by heating for eight hours or more at 275°C at 10^{-4} mm. Using this technique, rough grinding and sieving can be done relatively fast, and the glass then dried before the final Vibra-Mill grind.

The -200 + 325 mesh glass spheres used in the paste of tube sheet material are made by dropping proper sized glass particles through a CO + O₂ flame. A hydrocarbon or hydrogen flame would impart water to the spheres. A number of attempts were made to replace this expensive and CO-using technique by dropping the glass particles down a hot tube. The attempts were unsuccessful. When using a vacuum in the hot tube, the glass particles had poor heat pick-up. When an inert atmosphere was introduced into the hot tube, many glass particles hit and stuck on the hot wall. A graphite liner was inserted into the hot tube. This temporarily decreased the amount of glass sticking to the wall, but after a short period of time, the glass began to stick to the graphite. So far, the CO + O₂ flame is still used to make the spheres. The use of hydrocarbon flames followed by attempts to remove the water imparted to the glass will be tried next.

Unsuccessful attempts were made to spherodize the glass particles in an Argon Plasma.

Cumene (isopropyl benzene) is used as the vehicle to suspend the tube sheet glass powders when making a paste. The cumene works better if it contains about 1% (by weight) each of hexadecyl amine and dodecyl amine. The use of 2% hexadecylamine by itself works OK, but some precipitates out on standing.

Fusion of the Tube Sheet

The tube sheet which holds the fibers together and separates the sodium chamber from the sulfur chamber is made by fusing together the glass particles of the tube sheet material at a high temperature. The definition of "high temperature" has gone through several stages. Fusion must be complete so that sodium does not penetrate into the sulfur chamber.

When the sodium had some oxide and calcium present, the fusion conditions used were 1 1/2 hours under 10^{-3} - 10^{-4} mm vacuum, and 383°C for the 95 1/2 B₂O₃ - 4 1/2 Na₂O glass or 394°C for the 94 B₂O₃ - 6 Na₂O glass.

On removal of the oxide from the sodium by scavenging with Zr-Ti alloy, the wettability and the spreadability of the molten Na increased to the point that the Na penetrated previously undetected pores. In order to prevent penetration, the fusion temperatures had to be raised to:

<u>Glass</u>	<u>Temperature</u>
95-1/2 B ₂ O ₃ - 4-1/2 Na ₂ O	393°C
94 B ₂ O ₃ - 6 Na ₂ O	405°C

The quality control test used to measure whether a tube sheet is fully fused consists of watching for bubbles when 5 psig of N₂ gas is pressurized against the tube sheet. This is quite insensitive. It² indicates complete fusion for the 95-1/2/4-1/2 glass at 383°C. A more sensitive test is measuring gas flow on the vacuum side as a vacuum is applied across the tube sheet. It is more sensitive by a factor of ten and correlates with the 393°C fusion temperature.

Thermal Cycling of the Cell

One of the Tasks of the effort included trying to determine what construction details are necessary to allow thermal cycling of the cell. In the past it had been determined that one of the necessary features was to control the solidification and remelting of the sodium. When sodium melts, it expands about 10%. If sodium in the fibers melts before the Na in the reservoir, it expands and breaks the fibers. Therefore, if the cell is to be reheated through the melting of sodium, the sodium in the anode cup reservoir must be melted first -- followed by melting the sodium in the fibers.

The first trials of cooling the cell during this period were cooling from 300°C to a temperature where the reactants were still liquid and reheating to 300°C. Two 0.5 ampere hour 1000 fiber cells, in the fully charged condition, were cooled from 300°C to 120°C. At this temperature the sulfur catholyte and the sodium anolyte are both still liquid. The cells were reheated to 300°C, and then the temperature cycling was repeated several times, leaving the cells at 120°C for as long as several hours. When the cells were reheated to 300°C, they discharged and charged normally.

One of the cells was cooled to room temperature and reheated without the special precautions concerning the sodium remelting. No output voltage was obtained when the cell was reheated.

In addition to the Na remelting, there is probably a problem with the solidification of the sulfur-sulfide catholyte. From its solidification temperature down to room temperature, the cell bundle consists of adjacent thin layers of aluminum foil and solid sulfur-sulfide, with fine hollow fibers embedded in it. All three elements have different expansion coefficients and the strains may break the fibers. A special design has been suggested that may allow cooling of the catholyte. This design would provide extra space between the anode cup and the cell case so that if the cell were inverted while the catholyte is still molten, the catholyte would flow into the extra space reservoir and solidify there.

C. Metal Alloys Suitable for Containers

One Task is to develop metal alloys suitable for containers and low cost electrical feed-throughs. No work has been done on development of low cost electrical feed-throughs. The anode feed-through being used in the metal cased cells is a commercial Cermaseal Company feed-through, available at a cost of approximately \$1.00 in large quantities. The development of a lower cost electrical feed-through has received lower priorities in the development effort. This low priority is based on the need to first define the material to be used as the cell case.

At the beginning of this period, aluminum was the preferred material for the cell. Corrosion of sulfur and sulfide on aluminum is minimal as shown by the lack of attack on the 0.5 mil thick aluminum cathode foils. Some of these foils had been immersed in sulfur-sulfide for over a year.

Tests had shown that an evacuated sealed aluminum can could maintain its structural integrity at 300°C for at least three weeks if the diameter:wall ratio were 40:1 or less.

A study of cell failures, however, indicated that if the cell failed by certain modes, such as drastic disintegration of the tube sheet, localized temperatures could rise above 700-800°C. Because of this, stainless steel is being considered as the case. Temporarily, the metal cases are being built of very thick material until the temperatures and pressures reached when failure occurs are determined.

Experience at the Ford Motor Company and General Electric with the Na-S system indicated that the use of stainless steel as a cathode-connected case led to non-uniform current densities. This was due to blocking the $\beta\text{-Al}_2\text{O}_3$ electrolyte with corrosion products of the sulfur-sulfide on the stainless steel. A test was made to see if this phenomenon happened with the hollow glass fiber Na-S cell.

A 1000 fiber, 0.5 ampere-hour cell (PS-40) was assembled with a sheath of 316 stainless steel around the fiber-foil bundle. This cell was operated at 1 ampere (10 ma per cm^2), completely charging and discharging in 1 hour cycles. This deep charge-discharge cycling is at about five times the design current density, so the voltage drop across the cell is several times the 0.1 volts of design. The cell has operated over 75 days with no change in cell characteristics or capacity. Coulombs passed are equivalent to over a year of continuous operation at normal current density, and the cell has deep cycled over 1400 times. It appears that the 316 stainless does not adversely affect the cell operation. The different results of this test from the experience with the $\beta\text{-Al}_2\text{O}_3$ cells may be due to the different current densities involved.

D. Evaluate Characteristics of Operating Cells

In the design of the hollow fiber Na-S cell, the spacing between fibers and between cathode foils controls the amount of sulfur catholyte that surrounds each fiber. For a slower rate cell, the spacings can be further apart. Prior to this effort, the fibers were generally spaced from 0.28 mm to 0.128 mm apart. Foil to foil spacing was usually about 0.1 mm. These spacings gave cells of high current but lower ampere-hour capacity. For a 6-10 hour capacity larger spacings would be preferable. Thus, fiber-fiber spacings of 0.33 mm and foil-foil spacings of 0.125 mm give sufficient volume to retain enough catholyte around each fiber for about eight hours at the 2 ma/cm² current density. Cells utilizing these spacings have been built and operated.

Figure 14 shows polarization data on such a cell. For this data, the cell was operated at about 2 amperes, twice the design current. Cell resistance stays pretty constant and low for about 5/8 of the charge cycle. The resistance is mostly that of the glass membrane. The resistance begins to climb for the final 3/8 of the charge as the resistance of the sulfur phase in the catholyte becomes important. On discharge, the resistance decreases rapidly during the first 5% of discharge and then is fairly constant for the rest of the discharge. The reason for the slight increase in resistance at the end of the discharge on this cell is unknown. Figure 13 is for a 5 ampere-hour cell with a cathode foil of carbon on 5005 alloy aluminum.

It was mentioned earlier that when the cathode foil consists of molybdenum evaporated on 1145 alloy aluminum, a different polarization curve is obtained (Figure 10). The resistance rises continually and almost linearly during charge almost 30%. It is low and constant on discharge. The amount and character of the resistance rise varies with the foil used. In Figure 10, the Mo is 1000 Å thick. When the Mo is much thinner, the resistance rise is not so pronounced. Figure 15 shows the characteristics of a larger 40 ampere-hour cell having 15000 fibers. The quantitative aspects are being determined.

On consecutive cycles, cell characteristics remain reproducible. Figure 16 is a graph showing the output and charging voltages of many consecutive cycles of a 1000 fiber 0.5 ampere-hour cell deep cycling at a very high, 20 minute, rate. This continues with no apparent change for over 1000 cycles. Failure of the cell is abrupt rather than losing capacity. On the cell having over 1400 deep cycles to date (PS 40), cell resistance and capacity has changed less than 10%.

FIGURE 14 - POLARIZATION DATA

3000 Fibers, 5 A-hour Cells
Cathode: C on 5005 Al

FIGURE 15

POLARIZATION DATA

15,000 Fiber, 40 A-hour Cell

Cathode: Mo on 1145 Al

Chg/Dschg at 4.4 A

Data taken after 6 days and 60 cycles

----- Charge Voltage
 - - - - - Open Circuit Voltage
 - · - · - Discharge Voltage
 _____ Cell Resistance

Cell Voltage, Volts

7

2.4
2.3
2.2
2.1
2.0
1.9
1.8

Charge Cycle

Discharge Cycle

Time, Minutes

Cell Resistance, Ohms

0.034
0.032
0.030
0.028

0 20 40 60 0 20 40 60

Fig. 16 High rate
Charge-Discharge

These characteristics are different from the characteristics noted early in the program, where the Ca impurity in the sodium caused the cell resistance to increase with increasing coulombs passed.

E. Evaluation of Other Factors Affecting Cell Life

Some of the factors affecting cell life already discussed include the impurities in sulfur, the Mg content of the cathode foil, and the quality of the glass fibers.

The impurities in the sodium had a strong effect of shortening cell life. The most important impurity was calcium. The calcium impurity enters the glass structure and causes strains which result in fiber breakage. This investigation was done using the dianode assembly shown in Figure 4. The normal filtered sodium had about 400 ppm Ca. As one "anode" in the assembly was continuously "discharged" and the other "anode" charged, the resistance of the glass on the discharging anode rose until the fibers broke (Figure 17). The resistance of the "charging" fibers rose very little. When the Ca content was lowered to 15 ppm, a similar study showed no resistance increase over the same time period of discharging about 5 column volumes of Na (Figure 18). The Ca is easily removed from the sodium by digesting the Na with Na_2O at 300°C and filtering:

When the dianode assembly is cycled continuously for two weeks on two hour cycles at 5 column volumes per discharge, no resistance increase is seen (Figure 19).

The potassium present in the sodium also enters the glass structure and causes the glass resistance to increase. Its action is different from the Ca, however, since it equilibrates with the sodium ion content of the glass and the catholyte and the glass resistance does not continue to build up when the cell is cycled. Even on extended discharge, a limit is reached at a given K content. Figure 20 shows the effect on the discharging electrode of a dianode assembly using Na with a K content of 130 ppm. The resistance rose 30% during the first 325 ma-hr/cm. The slow rise in resistance following this (14% in 2665 ma hr/cm²) is due to something else. Normally a cell is reversed after about 16-20 ma-hr per cm².

The rise in resistance due to K in the Na is directly proportional to the amount of K present. Figure 20 shows how the glass resistance increases with time for K levels of 130, 220, and 650 ppm in the sodium. In an actual operating cell, this amount of resistance increase is much less due to the limited amount of Na and K present. Some low K sodium was made by distilling off K along with about 50% of the original Na. The K content of the remaining Na was about 20 ppm. Figure 21 also shows how the resistance increase due to the K was lowered. It appears that at the normal content of about 130 ppm, there does not seem to be enough strain in the glass to cause fiber weakening and breakage.

FIGURE 17

EFFECT OF CALCIUM IN SODIUM ON GLASS RESISTANCE - DIANODE ASSEMBLY

Na has 0.04 percent Ca

FIGURE 18

EFFECT OF CALCIUM-FREE SODIUM ON GLASS RESISTANCE - DIANODE ASSEMBLY

Na has less than 0.0015% Ca

FIGURE 19

EFFECT OF CALCIUM-FREE SODIUM ON GLASS RESISTANCE - DIANODE ASSEMBLY DURING A
CHARGE-DISCHARGE CYCLE

One Hour Charge - One Hour Discharge

FIGURE 20

EFFECT OF POTASium IN SODIUM ON GLASS RESISTANCE - DIANODE ASSEMBLY

Na has 0.5 ppm Ca and 130 ppm K
Current density = 13 ma/cm²

FIGURE 21

EFFECT OF POTASSIUM IN SODIUM ON GLASS RESISTANCE - DIANODE ASSEMBLY

All curves discharging electrode

Another life limiting impurity in the sodium is the oxide content. On prolonged discharge to cell failure using the Ca-free Na, it was noted that fiber failure was usually near the bottom sealed end of the fiber. Examination of the broken fiber ends revealed badly pitted internal surfaces of the fibers. Further up from the end, the interior surface of the fiber looked pristine. Apparently, as the sodium passed down and through the fiber during discharge, a material concentrated at the lower end of the fiber that pitted the glass. It is assumed that the material is "oxides of sodium".

Some of the Ca-free sodium was treated at 500°C with a powdered Zr-Ti alloy to scavenge out oxide. The oxide content was lowered from 10-20 ppm to "less than a few" ppm. When this sodium is used in the dianode assembly, the resulting lifetime was greatly improved. Table IV shows the results. Over 25,000 ma hr/cm² of Na was passed through the glass without any evidence of cell failure. At the design current of 2 ma/cm², this corresponds to an active life of over 500 days. The failure mode changed from fiber failure to "failures in the tube sheet region". As was previously pointed out, this was also noted on actual operating cells in both the 0.5 and 6 ampere-hour size. Higher temperature fusion of the tube sheet helped to rectify this problem.

There are a number of construction details which affect cell life. The conditions of fusion of the tube sheet are extremely important. A good vacuum is needed during the fusion otherwise the fibers are weakened. The higher the temperature of the fusion, the weaker and more brittle are the fibers at the tube sheet juncture. The fibers can be stored for at least three months in a dry sealed can without weakening.

Thicker walled fibers reduce chance of physical damage during cell assembly. There is a greater "yield" of good 6 amp. hr. cells from 20 μ walled or 15 μ walled fibers than from 10 μ walled fibers. However, once a cell is successfully assembled, the lifetime of the cell due to "operating degradation" is no less with thin walled fibers than with thick walled fibers. In fact, the longest lived cell to date, 75 days of deep charge-discharge, has fibers with 6 μ walls.

As was pointed out previously, the rate of charge-discharge at least up to 15 times the design rate has no apparent effect on fiber life. The depth of discharge apparently does have an effect. A comparison of cells in Tables I and II shows that cells undergoing shallow cycling last longer than deep cycled cells.

F. Cost Estimate for the Cell (September 1976)

- 1) Basis of Estimate. This estimate is based on the production of 1,250,000 cells per year, each cell being 0.8 kw hour. This is equivalent to storage capacity of 10^6 Kwhr per year. Acceptance rates are 90% on the fibers and 95% on the fabrication with no allowance for salvage materials.

The raw material and parts costs, other than those made in-house, are based on quotations from bonafide suppliers. Labor is taken as \$7.00 per hour, excluding fringes and supervision. Overhead is taken as 160% on labor (includes fringes, supervision, G&A, selling expense) and 10% on raw materials (to cover quality control, utilities, and various indirect costs). Depreciation is straight line over 10 years. An after-tax return of 15% on the initial investment is assumed with the investment being the sum of depreciated values of the equipment and working capital. Working capital is taken as 30% of the value of annual production at factory cost. Income taxes are assumed equal to the after-tax profit. Installed cost of equipment is 2 1/2 times base capital cost. Use 4 shift operation.

- 2) Cell Design

Size: 400 ampere hour; 8 hours, 50 amperes

Turn-around efficiency: 90%

Discharge depth: $\text{Na}_2\text{S}_{3.5}$

Fibers: 50 x 70 μ , active length = 11.6 cm

Total length = 12.5 cm

Total per cell = 112,700

Fiber lay down tapes: 3, 0.635 cm wide x .00127 cm thick

Foil and spacer tape: Cathode foil; 11.5 cm high, .00127 cm thick
38.25 cm per cell

Spacer tape; .0204 cm thick
.635 cm high
3825 cm per cell

Tube sheet: Thickness = 0.95 cm
Diameter = 10.86 cm

Mandrel: .635 x .153 cm tube; 12.7 cm total length
3.81 cm outside bundle

Anode lead: .635 x .153 cm tube; 10.60 cm length
3.845 cm outside body

Bundle size: 10.29 cm diameter, 20.04 cm high

Gap between top of foil and tubesheet; 1.1 cm.

3) Summary of Costs, (1,250,000 good cells/year)

	<u>\$/year</u>	<u>\$/cell</u> (95% acceptance)
Raw Materials	8,087,500	6.47
Labor	4,898,544	3.919
Overhead (1) 160% labor	7,837,670	6.270
(2) 10% of Materials	808,750	.65
Depreciation (10% on Capital)	564,000	.451
Income Tax (15% on Capital)	<u>564,000</u>	<u>.451</u>
Total	\$23,136,464	\$18.51
		or \$23.14/kwhr.

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		or \$23.14/kwhr.

Al Anode Lead: 10.60 cm long, 0.635 x .153 cm tube

$$\text{anode lead} = \frac{(10.6)(\pi)}{4} [(.635)^2 - (.153)^2] (2.7 \text{ gm/cc}) = 8.837 \text{ gm/cell}$$

$$\text{require: } \frac{8.837}{(.95)(453.6)} = \underline{0.0205 \text{ lbs.}}$$

Upper Body (S.S.) 13.741 cm high, 11.085 cm x 11.013 cm tube

$$\text{Upper body} = \frac{(13.741)(\pi)}{4} [(11.085)^2 - (11.013)^2] (7.86 \text{ gm/cc}) = 122.88 \text{ gm}$$

$$\text{require: } \frac{122.88}{(.95)(453.6)} = \underline{0.2852 \text{ lbs.}}$$

Lower Body (S.S.): 13.177 cm high, 10.604 cm x 10.533 cm tube.

$$\text{lower body: } \frac{13.177}{(.95)(453.6)} = \underline{0.2388 \text{ lbs/cell}}$$

Top Cap (S.S.): 0.353 cm thick, 11.085 cm diameter

$$\text{Upper cap: } \frac{\pi}{4} (11.085)^2 (.353) (7.80 \text{ gm/cc}) = 265.48 \text{ gm}$$

$$\text{require: } \frac{265.48}{(.95)(453.6)} = \underline{0.6161 \text{ lbs/cell}}$$

Bottom Cap (S.S) .338 cm thick, 10.604 cm diameter

$$\text{bottom cap: } \frac{\pi}{4} (10.604)^2 (.338) (7.80 \text{ gm/cc}) = 238.18 \text{ gm}$$

$$\text{require: } \frac{238.18}{(.95)(453.6)} = \underline{0.5527 \text{ lb/cell}}$$

Ceramic Seal: Use 1.0526 units per cell (95% yield) at \$1.00 each

Glass Sleeve: Use 1.0526 units per cell (95% yield) at 0.10 each

5) Labor and Capital Cost Summary (1,250,000 cells/year)

<u>Operation</u>	<u>Labor \$/Year</u>	<u>\$/Cell</u>	<u>Capital, \$</u>
Spinning	1,003,800	0.803	722,980
Bundle making	669,200	.535	20,000
Add tube sheet glass	153,916	.123	118,000
Grind tube sheet glass			
Fuse tube sheet			
Weld	869,960	.696	3,000
Weld	347,984	.278	2,000
Weld	347,984	.278	2,000
Weld	695,968	.557	3,000
Cure	80,304	.064	110,000
Weld	347,984	.278	2,000
Test Station	113,764	.091	10,000
Load Na & S	200,760	.161	500,000
Rating Test	66,920	.054	5,000
Total	\$4,898,544	3.919	\$1,502,880

X2.5 for hook-up and
buildings

= \$3,757,200

NOTE: 53% of labor cost is in welding
20% of labor cost and 48% of capital cost is in fiber spinning

6) Labor and Capital Cost Development

Flowsheet:

① Fiber Spinning: 63.17 gms per cell

Spin at 1.25 grams/minute/hole: 10 holes = 12.5 gm/min/machine

machines required: $\frac{(63.17)(1.25)(10^6)}{(12.5)(5.256)(10^5)\text{min}(.96)} \left(\frac{1}{.9}\right) \left(\frac{1}{.95}\right) = 14.6$ or 15 machines

Take-up spools required: $\left(8 \frac{\text{spools}}{\text{hole}}\right) \left(10 \frac{\text{holes}}{\text{machine}}\right) (15 \text{ machines}) = 1200$ on-line spools

need approximately 3,000 spools at \$1.00 each = \$3,000

Take-up units required: (1 per hole) $\left(10 \frac{\text{holes}}{\text{machine}}\right) (15) = 150$ units

need 150 units at \$4,000 each = \$600,000

15 melt tanks required:

cost of each tank:	Liner	= \$1316
	Screens	= 1259
	Body	= 90
	Core	= 64
	3 Controllers	= 1500
	Labor	= <u>100</u>
	Total	= \$4,329

need 15 tanks = (15)(4329) = \$64,935

1 spinnerette per hole + 10% spares: cost = \$333

need (10)(15)(1.1) spinnerettes = \$54,945

Total Capital for Spinning = \$722,980

Labor for spinning at 1 man/machine/shift

= (1)(4)(15)(7.00)(2390) = \$1,003,800/year
or \$0.803/cell

②

Bundle Winding:

$$\text{Wind } 1,250,000 / .95 = 1,315,789 \text{ cells/year} = \underline{2.61 \text{ cells/minute}}$$

$$\begin{aligned} \text{Each machine winds at } 10 \text{ meters/min.}; \quad & \frac{38.25 \text{ meters/cell}}{10 \text{ meters/min}} = 3.825 \text{ min/cell} \\ & = .26144 \text{ cells/min} \end{aligned}$$

$$\text{No. of machines required} = \frac{2.61}{.26144} = 10 \text{ machines}$$

$$\text{Capital for bundle winding} = (\$2,000/\text{machine})(10) = \underline{\$20,000}$$

$$\begin{aligned} \text{Labor at } 1 \text{ man/machine/shift} &= (10)(4)(7.00)(2390) = \underline{\$669,200/\text{year}} \\ &= \$0.535/\text{cell} \end{aligned}$$

④⑤⑥

Prepare Tube Sheet-Weld Cathode:

Use jig holding 20 cells:

Load cells in jig at 10 per minute	= 2.0 min per jig
Machine tube sheet at 1 min. total	= 1.0 min. per jig
Cure tube sheets, 3 hour cycle	
27 jigs/load	= 6.7 min per jig
Weld cathode, 3 cells/minute	= 6.7 min per jig
Transfer to cell body	= <u>4.0 min per jig</u>
Total Time	= 20.4 min/20 cells

Capital: 4000 cell/day curing oven	= \$100,000
Grinding Unit	= 5,000
Welding Unit	= 2,000
50 jigs at \$220	= <u>11,000</u>
Total	= \$118,000

Labor: Use 0.5 man/shift for curing unit in addition to grinding and welding

$$(20.4 - 6.7) = 13.7 \text{ man-minutes/20 cells} = 87.6 \text{ cells/1 man-hour}$$

$$\text{require: } \frac{(2.61 \text{ cells/min})(60)}{87.6 \text{ cells/man-hour}} = 1.8 \text{ man/shift}$$

$$\text{Cost} = [(1.8 + .5) \text{ man/shift}](4)(7.00)(2390) = \$153,916/\text{year} \\ = \underline{\$0.123/\text{cell}}$$

⑦ Welding Lower Body to Upper Body and Bottom Plate:

Time required:	Machine CVT, punch bottom plate,	2 min.
	Weld lower to upper body	1 min.
	Weld bottom plate to body	1 min.
	Assemble	<u>1 min.</u>
	Total	5 min.

$$= 12 \text{ cells/man-hour}$$

$$\text{Labor} = \frac{(2.61)(60)}{(12)} = 13.05, \text{ or } 13 \text{ men per shift}$$

$$\text{cost} = (13)(4)(7.00)(2390) = \$869,960/\text{year} = \underline{\$0.696/\text{cell}}$$

$$\text{Capital} = \text{saw and welder} = \underline{\$3,000}$$

⑧ Weld Cathode to Body

Time required: 2 min. each or 30 per man hour

$$\text{Labor} = \frac{(2.61)(60)}{(30)} = 5.2 \text{ man per shift}$$

$$\text{Cost} = (5.2)(4)(7.00)(2390) = 347,984/\text{year} = \underline{\$0.278/\text{cell}}$$

$$\text{Capital: welder} = \underline{\$2,000}$$

⑨ Weld Anode Cup to Anode Lead:

Time required: 2 minutes each or 30 per man hour

$$\text{Labor} = \frac{(2.61)(60)}{30} = 5.2 \text{ man per shift}$$

$$\text{Cost} = (5.2)(4)(7.00)(2390) = \$347,984/\text{year} = \underline{\$0.278/\text{cell}}$$

$$\text{Capital: welder} = \underline{\$2,000}$$

⑩ Weld Ceramic Feed Through to Anode Lead and Top Cover:

Time required: 2 minutes each step or 30 per man hour each step.

$$\text{Labor: } \frac{(2.61)(60)(2)}{30} = 10.4 \text{ man per shift}$$

$$\begin{aligned} \text{Cost} &= (10.4)(4)(7.00)(2390) = \$695,968/\text{year} \\ &= \underline{\$0.557/\text{cell}} \end{aligned}$$

Capital - welding machine = \$3,000

⑪ Seal Anode Cup to Tube Sheet:

Time required: use jig to hold 60 units

$$\begin{aligned} \text{set body on jig at 10/min} &= 6 \text{ min.} \\ \text{set glass sleeve, anode on tube} &= 10 \text{ min.} \\ \text{sheet} &= 20 \text{ min.} \\ \text{cure in 3 hours, as in } \textcircled{4} &= \underline{20 \text{ min.}} \end{aligned}$$

Total 36 min. per jig

Use 1/2 man/shift for cure in addition to assembler

Assemble time for 60 cells = 36-20 = 16 min/jig = 225 cells/hour.

$$\text{Labor: } \frac{(2.61)(60)}{225} = 0.7 \text{ man hour/shift}$$

$$\text{Cost} = (0.7 + 0.5)(4)(7.00)(2390) = \$80,304/\text{year} = \underline{\$0.064/\text{cell}}$$

$$\begin{aligned} \text{Capital: Curing unit} &= \$100,000 \\ 20 \text{ jigs at } \$500 &= \underline{10,000} \\ &= \$110,000 \end{aligned}$$

⑫ Weld Top on Body:

Time required: 2 minutes or 30 per man hour

$$\text{Labor} = \frac{(2.61)(60)}{30} = 5.2 \text{ man per shift}$$

$$\text{Cost} = (5.2)(4)(7.00)(2390) = \$347,984/\text{year} = \underline{\$0.278/\text{cell}}$$

$$\text{Capital: Welder} = \underline{\$2,000}$$

⑬ Testing for Pressure and Electrical Shorts: (keep in jig)

Time required: 90 cells per man-hour for both tests.

Labor: $\frac{(2.61)(60)}{90} = 1.7 \text{ man hour/shift}$

Cost: $(1.7)(4)(7.00)(2390) = \$113,764/\text{year} = \underline{\$0.091/\text{cell}}$

Capital: Testing Unit = \$10,000

⑭ Load Sodium and Sulfur:

Time required: Allow 10 minutes in machine to fill cell

Labor: Assume 3 men/shift to fill 3758 cells per day.

Cost: $(3)(4)(7.00)(2390) = \$200,760/\text{year} = \underline{\$0.161/\text{cell}}$

Capital: Similar to bottle filling unit = \$500,000

⑮ Electrical Test:

Labor: Use 1 man per shift

Cost = $(1)(4)(7.00)(2390) = \underline{\$66,920/\text{year}} = \underline{\$0.054/\text{cell}}$

Capital: Assume simple discharge apparatus = \$5,000