(NASA-CR-135144) THE DEVELOPMENT OF A POTASSIUM-SULFIDE GLASS FIBER CELL AND STUDIES ON IMPURITIES IN ALKALI METAL-SULFUR CELLS (Dow Chemical Co.) 35 p HC A03/MF A01 CSCL 10A G3/44

N77-23602

Unclas

26118

DOW CHEMICAL U.S.A.

An Operating Unit of The Dow Chemical Company

WALNUT CREEK, CALIFORNIA

NASA CR-135144

THE DEVELOPMENT OF A POTASSIUM-SULFIDE GLASS FIBER CELL AND STUDIES ON IMPURITIES IN ALKALI METAL-SULFUR CELLS

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Prepared for

National Aeronautics and Space Administration
Lewis Research Center
Contract NAS 3-18525

1. Report No. NASA-CR-135144	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

DEVELOPMENT OF A POTASSIUM-SULFUR GLASS FIBER CELL AND EFFECTS OF IMPURITIES IN ALKALI METAL-SULFUR CELLS

5. Report Date

6. Performing Organization Code

7. Author(s)

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8. Performing Organization Repo

9. Performing Organization Name and Address

Dow Chemical Company
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10. Work Unit No.

11. Contract or Grant No.

NAS3-18525

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

13. Type of Report and Period C

Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes

Program Officer: J. Stuart Fordyce, NASA-Lewis Research Center, Cleveland, Ohio

16. Abstract

Potassium sulfur rechargeable cells, having as the electrolyte the thin walls of hollow glass fibers made from K^+ permeable glass, were developed. The cells had short lives, probably due to the materials of construction and the impurities in the potassium.

A study of the effect of the impurities was made in the analogous Na-S system. Calcium, potassium and NaOH/oxide impurities caused increased resistance or corrosion of the glass fibers. For long lived cell operation, the Na must contain less than 1 ppm Ca and less than "a few" ppm of hydroxide/oxide. Up to 150 ppm K can be tolerated.

After purification of the Na anolyte, cell lifetimes in excess of 1000 deep charge-discharge cycles or over 8 months on continuous cycling at 10-30% depth of discharge are obtained.

17. Key Words (Suggested by Author(s))

Alkali Metal - Sulfur Cell
Potassium - Sulfur Cell
Rechargeable Cell
Sodium Purification
Potassium Glasses

18. Distribution Statement

Unclassified - Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

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SUMMARY

Technical Goals

This research program is the extension of work begun under Contract No. NAS3-16806. The program had as its objective the development and demonstration of a potassium sulfur secondary battery using hollow glass fibers as the membrane separator. The first part of the program involved additional glass fiber research, tubesheet development, making and testing of small working modules, and fabrication and evaluation of 5 A-hr. K/S cells.

After sufficient understanding of problems involved to achieve the final goal, it was decided that there should be a second part to this research program involving basic research into analyzing the modes of failure of such cells. The sodium sulfur system was used as a study model, since the knowledge and techniques of the sodium system were further advanced. Under this contract the effects of various impurities and contaminants in the sodium anolyte were studied and the corrective measures for each harmful entity were defined.

General Methodology

At the onset of this contract much knowledge had been gained on the potassium glass system developed under Contract NAS3-16806 in addition to a very extensively developed parallel Na/S system. The initial program called for an attempted development of laboratory test cells of 0.5 to 5 A-hrs. (1000-5000 fibers) sizes. The general test cell assembly of Na/S cells was used in fabricating such K/S cells, with slight modifications of compositions and processing incorporated when deemed necessary to achieve what was believed to give the best chance of success.

The second part of this contract was started after it was found that the lifetimes of K/S cells thus assembled were very limited. Single fiber test modules were devised that enabled the study of effects of anolyte impurities separately. The Na/S system was used as the study model since there was available much more background knowledge as well as material. Various observations were studied and interpreted, and in cases where a possible failure cause was determined or implied, corrective measures were proposed and successfully applied. These results were then applied to the 1000 fiber (0.5 A-hr. Na/S) test cells to verify that the improvement of lifetime was actually realized.

Technical Results

The glass (fiber membrane) composition was modified from T305 ($K_2O \cdot 2B_2O_3 \cdot 0.2\ SiO_2 \cdot 1/12\ KBr$) to T330 ($K_2O \cdot 2B_2O_3 \cdot 0.3\ SiO_2 \cdot 1/12\ KBr$) and was successfully spun into fibers of desired size (70μ O.D. x 50μ I.D.) and of reasonably high quality. These fibers were successfully used to fabricate a number of 1000 fiber cells. The lifetimes of the K/S cells were very short, ranging from several hours to a few days under "normal" operating conditions, to a longest of 23 days when left at open circuit. These results suggested similar, but faster acting failure modes compared with those of the Na/S counterpart. This prompted a change in scope from designing, building, and running test modules to analyzing failure modes resulting from anolyte (and/or anolyte impurity) effects. The sodium system was chosen for this study because of the more extensive background knowledge and material supply.

The failure mode study used a single fiber anode assembly, and a "dianode" assembly where accurate measurements of fiber resistance made it possible to control amounts of various impurities and to study their effect. Specifically Ca°, K° in large amounts and Na_2O/NaOH in the sodium were determined to be harmful. It was determined that Ca° and Na_2O/NaOH must be removed. A purification procedure was devised that enabled the preparation of sodium the use of which should give much improved cell lifetimes. This study was then extended to the use of this purified sodium in 1000 fiber Na/S test cells. The wetting property of this sodium was so different that the test cells had to be modified slightly, but at the end cells were built that exceeded the initial goal of 1000 deep (>90%) charge/discharge cycles. Over 2500 charge-discharge cycles at 80% depth and over 8 months of continuous operation on shallow cycling (10-30%) was attained.

INTRODUCTION

The need for a battery as an efficient, compact and reliable energy storage system with minimal ecological impact is ever increasing. Stationary power storage (load leveling) and vehicular propulsion are among the commercial applications for systems with good energy density and power density performances. Such performances can be expected from both the sodium-sulfur and potassium-sulfur hollow glass fiber cells. Future space requirements require similar technology advances.

Work began at Dow on the sodium-sulfur glass fiber cell concept in 1965. This design of a secondary battery uses the walls of fine hollow glass fibers as the electrolyte/separator. Thousands of hollow glass fibers, bundled together in parallel and filled with sodium as the anolyte, are immersed in a catholyte consisting of a mixture of sodium polysulfide and sulfur. The resulting cell has a very high energy per unit weight at a high power per weight.

In 1973, work was started on NASA Contract NAS3-16806. The work covered initial exploration of the potassium sulfur system analagous to the sodium-sulfur system. In particular, it called for investigating candidate materials for use as the glass membrane (electrolyte/separator) as well as compatible auxiliary components, such as the tubesheet and catholyte materials. This was prompted in part by the fact that a limited total life was being obtained in the sodium system (<300 deep charge/discharge cycle). The causes of failure were not understood and it was hoped that such causes did not exist in the analogous potassium system.

The membrane composition and other auxiliary components having been roughly defined, the present effort was undertaken as an extension of NAS3-16806. Objectives were to: (1) further define compositions; (2) make the necessary components, such as hollow glass fibers of desired sizes; (3) make actual modules similar to the sodium system; (4) test and evaluate these modules for performance.

Most of the components needed for assembly of a 0.5 A-hr. size K/S glass fiber test cell were developed and/or tested under contract NAS3-16806 (ref. 1). These components included glass membrane material, tubesheet (header) material and cathode material.

The components had to meet the following requirements:

(1) Glass for fibers (electrolyte-separator)

- (a) Must be chemically inert to all ingredients concerned - K, S, K_2S_x
- (b) Must possess reasonable potassium ion conductance - preferably a resistivity of $\leq 5 \times 10^4$ Ω -cm at operating temperature, although several times that is still usable based on electrical requirements of the cell.

(c) Must not be electronically conductive, $S^=$ ion conductive, or K° permeable

(d) Must be processable by existing technology into hollow fibers of desirable dimensions and of acceptable quality.

(2) Tubesheet material

(a) Must be chemically inert.

(b) Must be physically compatible with the glass fibers.

(c) Can be applied and formed into desired physical form -- this calls for compatibility with all other assembly components with respect to treatment conditions.

(3) Cathode material

(a) Must be chemically inert.

(b) Must have low electronic and resistance in $S_x^=$.

Under contract NAS3-16806, a glass, coded T305 ($K_2O\cdot 2B_2O_3\cdot .2\ SiO_2\cdot$ 1/12 KBr) was developed. It satisfied the first three requirements for electrolyte/separator, but was later shown to give poor quality fibers with existing fiber spinning technology.

Under the same contract, marginally usable tubesheet materials were also developed. Cathode materials developed earlier in our laboratory were shown to be adequate.

The analogous Na/S system and its components were further along in development. High quality fibers from T406 glass ($Na_2O\cdot 2B_2O_3\cdot 0.2\ SiO_2\cdot 0.16$ NaCl) could be spun routinely. This glass was satisfactory both in chemical inertness and electrical resistivity ($\sim 2 \times 10^4\ \Omega$-cm @ 300°C). Size control during spinning was good over a wide range. A substantial quantity of compatible tubesheet material was available. At the beginning of this contract, Na/S multi-fiber test cells containing about 1000 (70μ OD x 50μ ID) fibers with a theoretical capacity of 0.3 to 0.4 A-hrs. could be fabricated. These cells operated with predictable electrical characteristics and could be operated up to 250 deep charge/discharge cycles over a life span of 7-30 days.

The present effort is divided into two parts:

(1) Improvement in the potassium-sulfur cell components
(2) Finding and mitigating causes of alkali-metal-sulfur cell failure.

EXPERIMENTAL AND RESULTS

I. Improvement in Potassium-Sulfur Cell Components

(A) Hollow Glass Fiber Fabrication

In the final report for Contract NAS3-16806 (ref. 1) two marginally successful spin runs of T305 glass ($K_2O \cdot 2B_2O_3 \cdot 0.2\ SiO_2 .\ 1/12\ KBr$) using a boron nitride spinnerette were reported. Boron nitride was subsequently found to be responsible for poor quality fibers (containing bubbles, or seeds). A platinum spinnerette of the same physical form as the BN spinnerette was made.

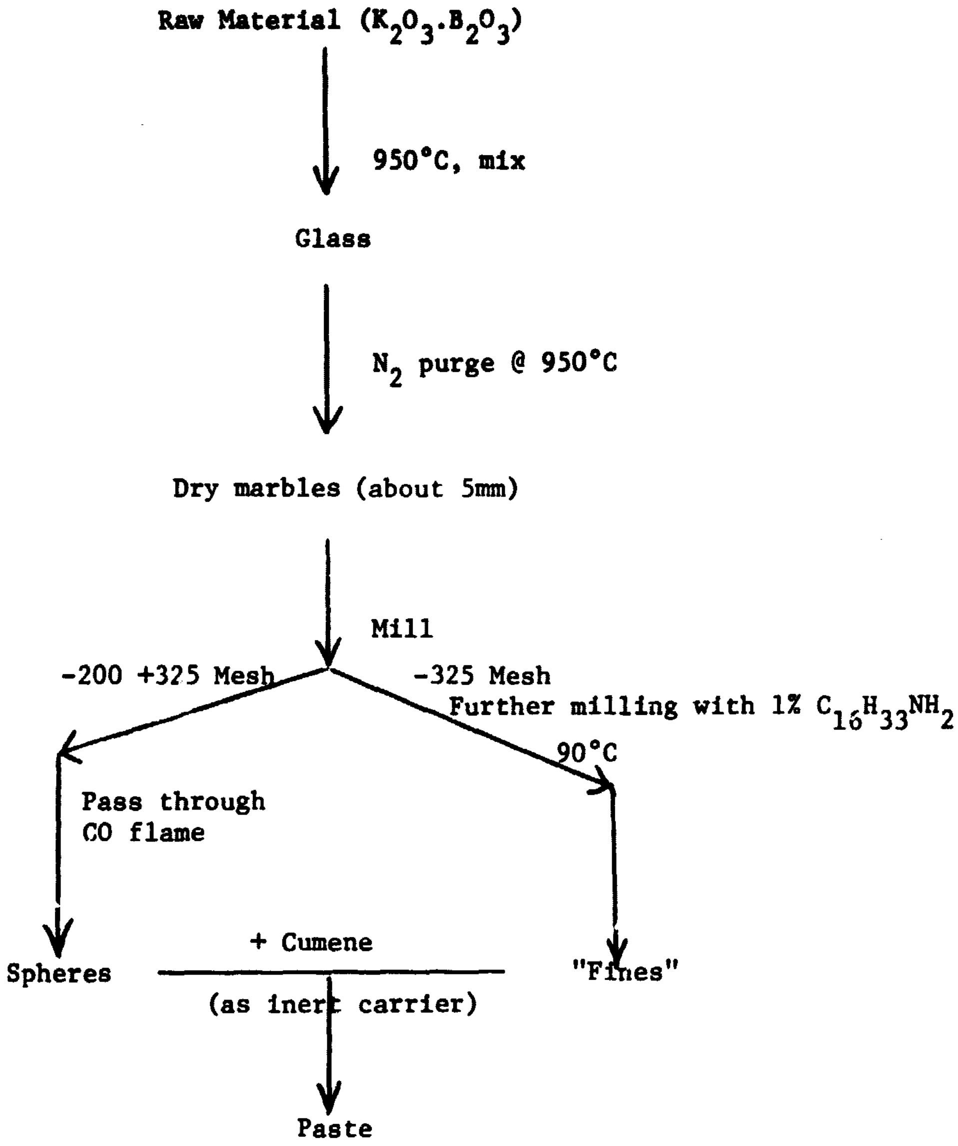
Since the wetting property and easy devitrification of this borate glass on platinum would make T305 very difficult to spin, a slight compositional change was made to T330 ($K_2O \cdot 2B_2O_3 \cdot 0.3\ SiO_2 \cdot 1/12\ KBr$). The added SiO_2 makes the glass much less prone to crystallization at high temperature(∿600°C) and only a small penalty on conductivity (∿12%) results.

Two spin runs using T330 glass were made using the new platinum spinnerette. Some equipment problems during the first spin run were experienced. The second trial gave a continuous spin run of 212 minutes without a break (@ 338 rpm; 22"/rev.)

This translates to a single 70μ OD, 50μ ID fiber of 40 kilometer length! The fiber was collected in a usable form -- cut and stored as parallel array of fibers 5 1/2" long, spaced @ ∿50/cm and sealed on one end.

(B) Tubesheet Material

The T330 glass used for fibers has a thermal expansion coefficient of 137 x 10^{-7}/°C. Thus it seemed that T314 (97% B_2O_3, 3% K_2O) with thermal expansion coefficient of 135 x 10^{-7}/°C would be a likely candidate for a corresponding tubesheet. This glass is difficult to grind to a proper "fineness" even with the high temperature grinding process developed under Contract NAS3-16806 (ref. 1). That fineness was a necessity in achieving the extruding property needed for the material to be applied as a high density extrudable paste to form the tubesheet. T321, (94.5% B_2O_3· 5.5% K_2O) with an expansion coefficient of 124 x 10^{-7}/°C was more readily ground to a fine powder and was used as a compromise material. The mismatch of thermal expansion coefficients is probably not responsible for the very short lifetime of cells made (see Cell Testing Section). This material was made and processed into the tubesheet paste as shown in the following diagram.



PREPARATION OF TUBESHEET PASTE

(C) 1000 Fiber Test Cell Assembly

These test cells were made similarly to the anologous sodium cells (ref. 2). Schematically, Figure 1 shows the procedure employed.

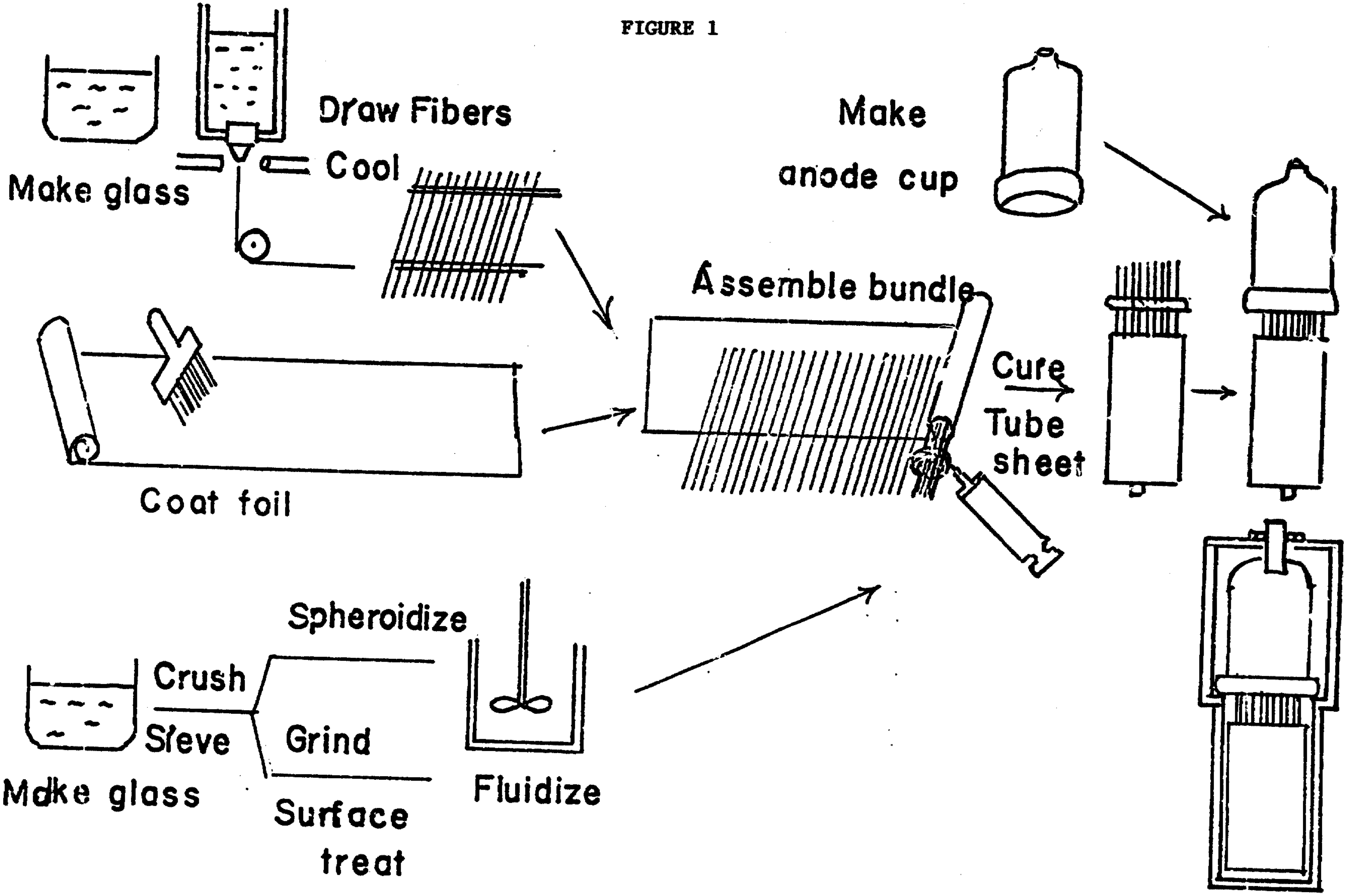
The fibers, assembled in a parallel array, are placed on top of the graphite coated aluminum foil used as the cathode pick-up. The assembly is "jelly-rolled" together while the tubesheet paste is applied to form the header for the assembly. Solvent is removed from the paste by vacuum evaporation. The resulting tubesheet header is a powder compact of the tubesheet glass. The powder compact is fused under vacuum at 380-383°C for 105 minutes. The anode (K) container is attached. After an electrical lead is attached to the foil, the assembly is placed in a pyrex casing, K is added to the anode container, and sulfur added to the fiber bundle.

(D) Testing of 1000-Fiber Cells

The finished cell is heated to 300°C for testing. Normally, in the Na/S system, the cells are discharged to make Na_2S_x in situ, thereby bringing the catholyte composition into the "operating range". When this was done for the K-S cells, failure occurred within hours. All of the 25 cells made for this study (there were five more made with a different tubesheet material and lower quality fibers, which all failed very shortly after start) failed within 1-2 days of the initial discharge cycle. The only cell that lasted longer than four days was one that was never discharged. It lasted (on open circuit) for 23 days. Of the rest of the cells, most of them lasted as long as they were left at open circuit (usually for 0-3 days), but as stated before, as soon as they were discharged to the "operating region", failure followed within hours of current passage. The longest lasted for only 31 cycles at 1/2 hour charge/1/2 hour discharge @ 0.075 A, which corresponds to only about 6% capacity discharge per cycle.

The fact that the time to cell failure depended so strongly on total current implied that the mode was not due to a static mechanical stress or pre-existing leak or crack. It was more likely associated with the effects of anodic or cathodic impurities that are cumulative with current. Because of the short lifetimes, attempts to scale-up these cells to the 5 A-hr. size as originally planned were abandoned. Instead, attention was given to analyzing the failure mode. In the analogous sodium system, a current dependent failure mode (($\sim$250 deep cycle limit) was also happening. This suggested that this failure mode was likely to be associated with the anolyte, and led to the second part of this research effort.

FIGURE 1


Make glass
Draw Fibers
Cool
Coat foil
Make
anode cup
Assemble bundle
Cure
Tube
sheet
Spheroidize
Crush
Sieve
Grind
Surface
treat
Fluidize
Make glass

II. Finding and Mitigating Causes of Cell Failures in Alkali Metal-Sulfur Cells

Anolyte Impurity Study

(A) Study Models

The logical basic component for this study was a single hollow glass fiber anode. This consisted of a Na reservoir attached hermetically to and communicating without restriction with a single uniform fiber of known dimension. The requirements were:

(1) Anode reservoir and "tubesheet" (hermetic seal) must be chemically resistant and inert to Na.

(2) Hollow glass fiber material must be chemically inert, ionically conductive enough to Na^+ to furnish usable data, invariant with Na^+ passage, and must be formable into fibers of uniform and desired size.

(3) Final structure must be rugged enough to withstand necessary experimental handling.

For fibers, uniform 70μ OD, 50μ ID T406 ($Na_2O \cdot 2B_2O_3 \cdot 0.16 NaCl \cdot 0.20 SiO_2$) fibers were used. This glass has an electrical resistivity of ca 2×10^4 Ω-cm @ 300°C. The anode reservoir was made of 94/6 glass ($0.06 Na_2O \cdot 0.94 B_2O_3$) and the tubesheet consisted of 95.5/4.5 glass ($0.045 Na_2O \cdot 0.955 B_2O_3$). The tubesheet was formed and sintered. The resulting unit is schematically represented in Figure 2.

Sodium was introduced into the reservoir and fiber (filling it to ∿1 mm from end) under vacuum. Typically, 1-2 ml of Na was used to fill the assembly in order to provide an essentially infinite reservoir (∿10^4 fiber volumes) of uniform initial composition.

These basic units were used in several different study models. These included single fiber Na/glass/Na_2S_x cells, Na/glass/Na "cells" and Na/glass/Na_2S_x/glass/Na "dianode cells". The most versatile, easily interpretable, and useful model that gave almost all the desired data turned out to be the "dianode cell" with reference probe shown in Figure 3. Following is a description of its functional components.

Two single fiber anodes and a sodium filled T406 glass tube (∿1 mm diameter, 200μ wall) were placed in a common pool of molten Na_2S_4 at 300°C. This is not a true cell in that no voltage is ever produced. When current is passed from the

Figure 2
SINGLE FIBER ANODE ASSEMBLY

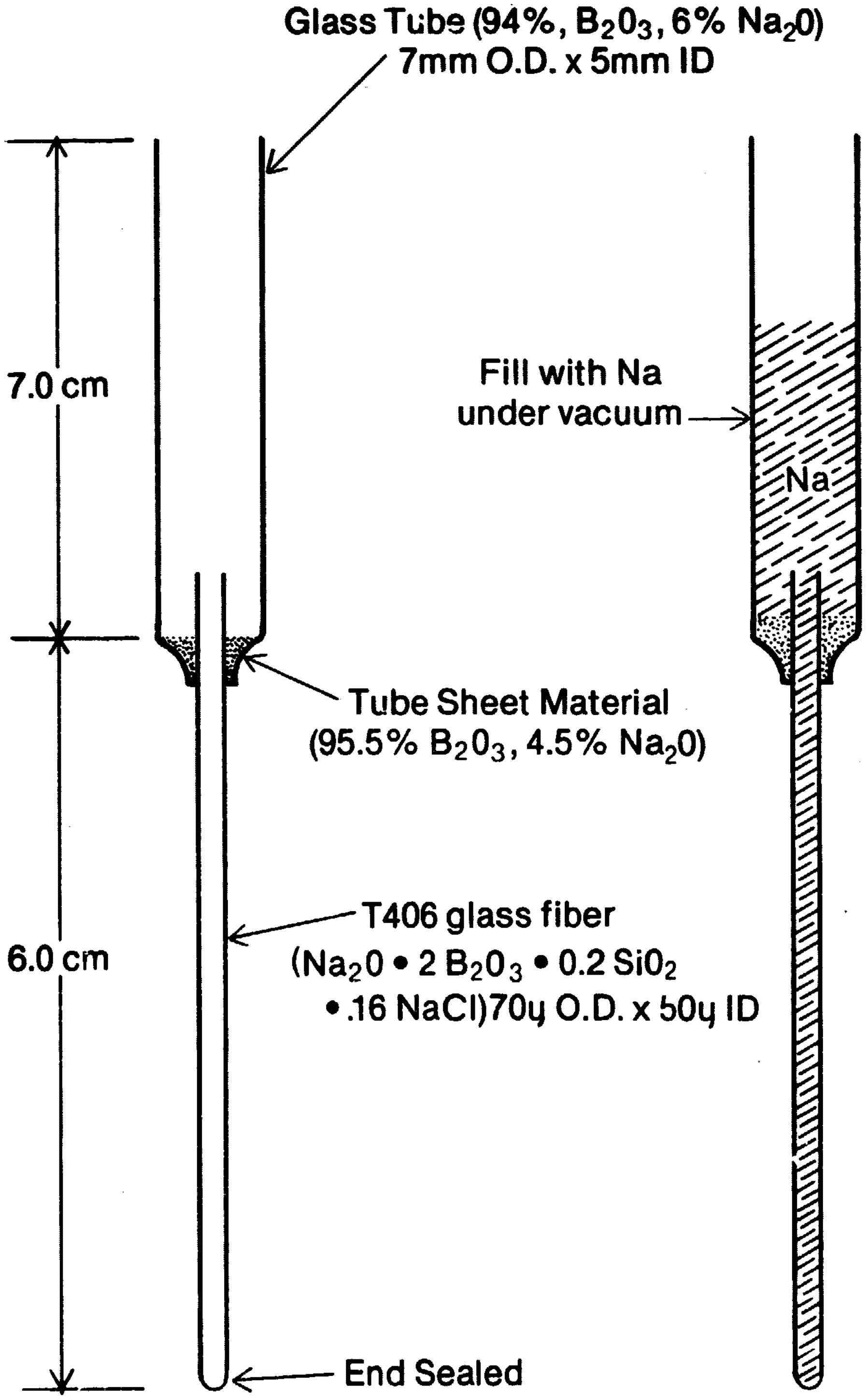
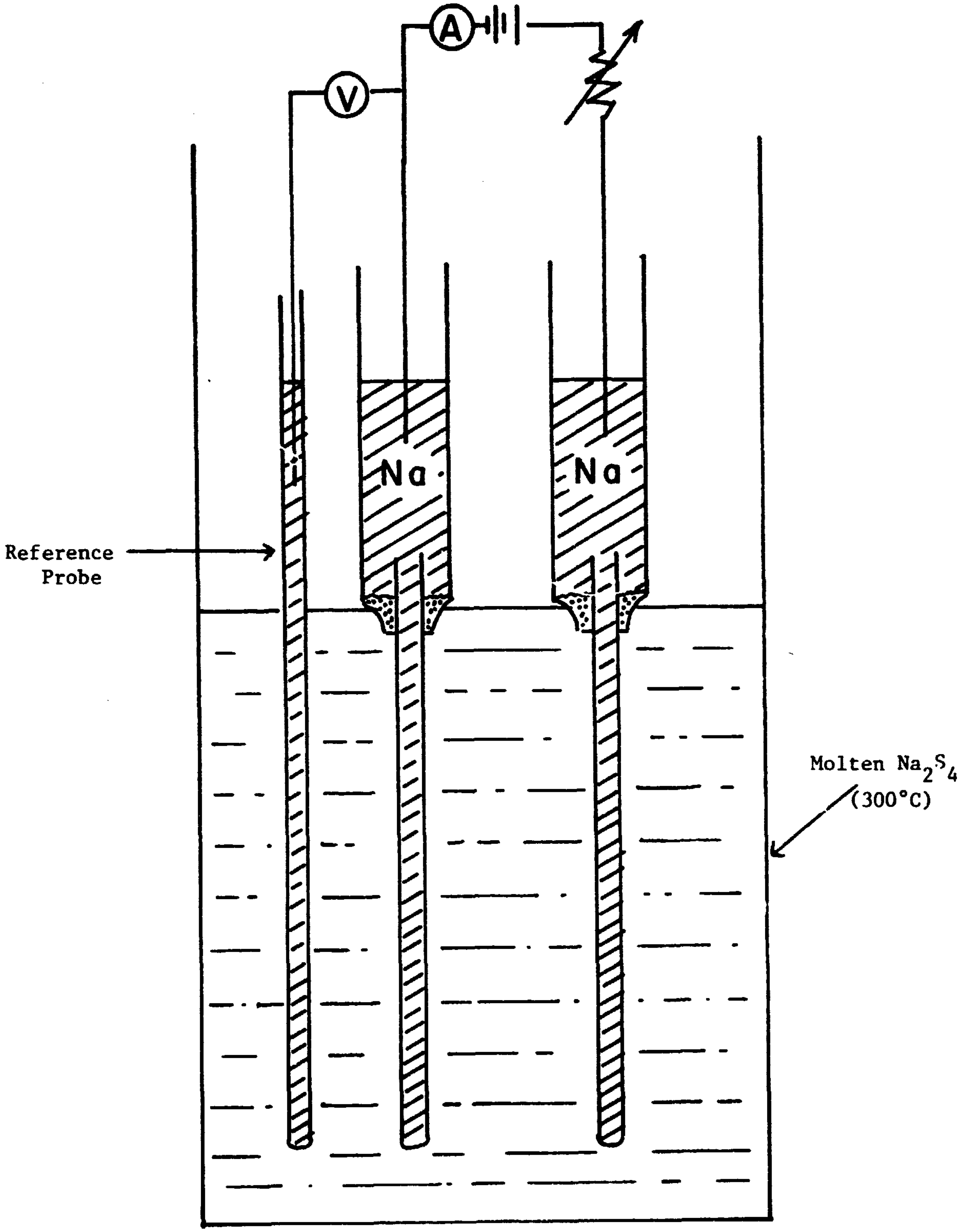


FIGURE 3

DIANODE ASSEMBLY



lead of one Na reservoir to the other, the net result is a Na transfer from one reservoir to the other with no change of the catholyte composition. Furthermore, since the reference probe is essentially identical to each electrode, there never is any "open circuit potential" across the two electrodes or from the probe to either electrode. This makes the resistance measurement of either electrode both simple and accurate. It is simply the ratio of the voltage drop between the pertinent electrode and the probe to the impressed current between the two electrodes (catholyte resistance is negligible). Since the glass membrane should be invariant under pure Na^+ flow, changes of resistance of the "discharging" electrode with time are a measure of the effects of anolyte impurities on the discharging fiber.

(B) Results from "Dianode Cells"

(1) Calcium

A batch of sodium was prepared by filtering commercial (Baker Analyzed) Reagent Grade Sodium at 150°C through an "M" Pyrex frit. At the time when the anolyte study was begun, this had been the "standard" sodium used to make the larger multi-fiber cells. When sodium thus treated was used in a dianode cell, a resistance increase of the discharging glass electrode was seen which increased with total current passed. This is shown in Figure 4 where R/Ro, the resistance relative to the initial value, increases as sodium is passed through the cell. The resistance rise is due to the calcium impurity in the sodium. Calcium, being an easily ionized divalent metal, co-enters into the glass fiber wall with Na^+ during discharge, displacing two sodium ions. Since calcium ion is a divalent ion, it has very low mobility in the glass, and gives a very high resistance site. During further discharge, more and more Ca^{++} will enter the fiber surface and the result is the formation of a rather uniform high resistance "skin" on the interior wall of the fiber. When current is reversed, conductive "holes" in the skin tend to be formed, and the resistance drops. On a very prolonged discharge, the resistance increase is dramatic. In the operation of typical 1000 fiber cells, this degree of resistance increase before failure is not seen. Although correlation of the calcium effect with any observed failure mode could not be made, the calcium was eliminated because its presence tended to obscure the effects of other impurities. The removal of calcium metal from Na via oxidation by Na_2O, followed by filtration to remove CaO and excess Na_2O is well known (ref. 3). In our laboratory, this operation was performed in a N_2 dry box to produce sodium containing ∿1 ppm total Ca. Using this "Ca-free" Na, the resistance is invariant with coulombs passed as in dianode assembly DA 15 (Figure 5).

Figure 4
CHANGE OF RESISTANCE OF GLASS ELECTRODE DUE TO CALCIUM IN SODIUM

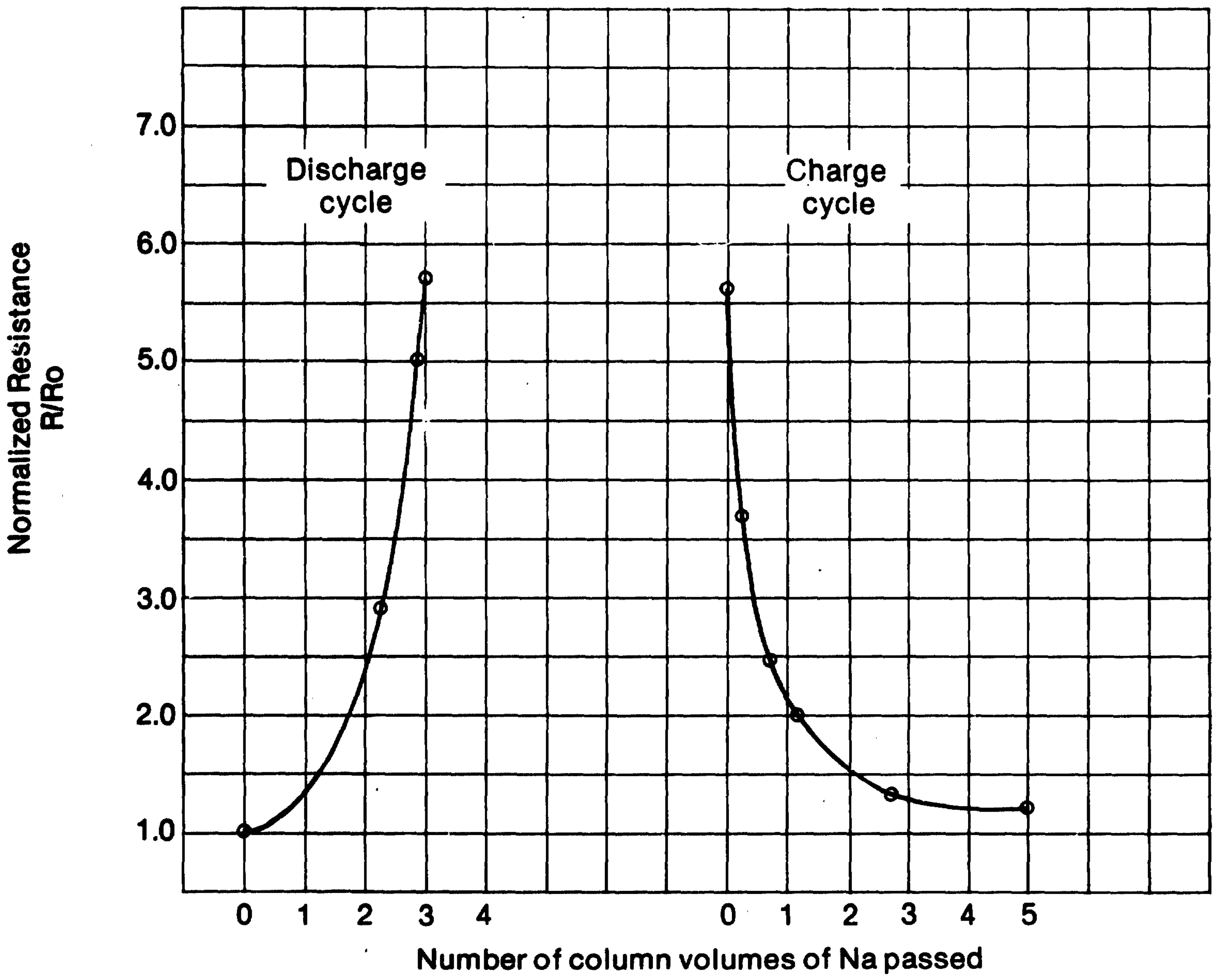
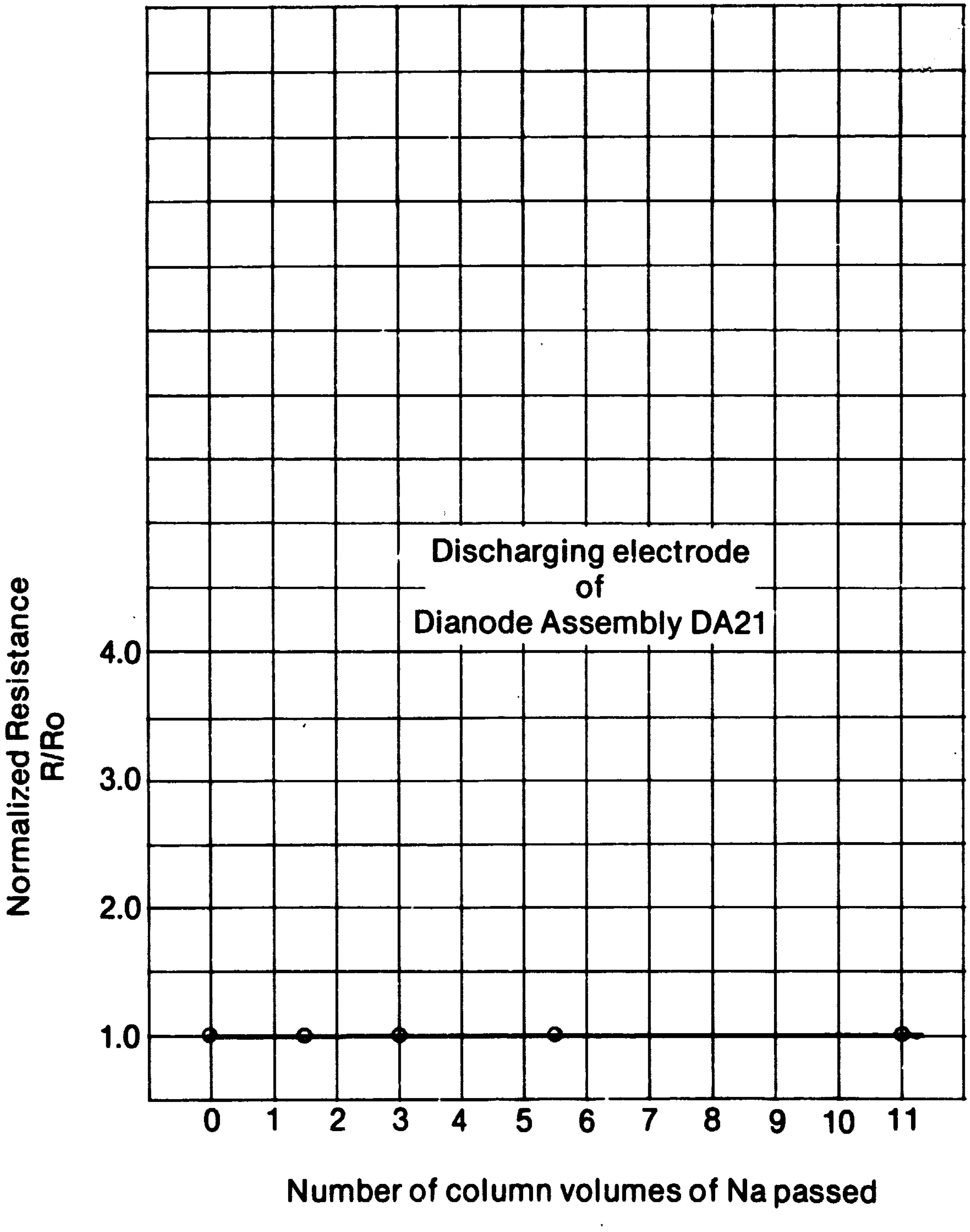


Figure 5
RESISTANCE CHANGE OF A DISCHARGING ELECTRODE WITH Ca-FREE SODIUM



(2) Potassium

When an electrode in a dianode assembly such as DA 21, using "Ca free" sodium was given prolonged discharge, a resistance rise was again seen, except this time it leveled off after some 200 fiber volumes of Na had passed through the glass fiber wall. This was interpreted as the effect of potassium. From the literature on diffusion coefficients in silicate glasses (ref. 4), potassium ions can be expected to behave like "labeled sodium ions" of lower mobility than normal Na ions. They will enter the glass network with the Na ions during discharge, but unlike the Ca^{++}, they are able to move through the glass network (at slower rate than the Na^+) and eventually exit on the other side of the membrane. This establishes a quasi-steady state of concentration inside the glass membrane; with a higher K^+/Na^+ ratio than in the starting Na by a factor which is approximately equal to the ratio of ionic diffusion coefficients. A rise of resistance occurs which is roughly proportional to the original K concentration.

As an experimental check, dianode assemblies DA 21, 22, 23, and 59 with potassium levels of 130, 650, 220 and <10 ppm respectively were made. Figure 6 shows the resistance increases for the assemblies. The results agree with the hypothesis strikingly well. Since the starting potassium in the sodium is normally 150 ppm, and in an actual cell there is a limited total allotment of starting sodium per fiber (∿4 to ∿20 column volumes, depends on design) a resulting resistance increase of 1-5% can be expected. This should not be a primary source of stress or failure.

(3) Sodium Oxide/Hydroxide

When an electrode in a dianode assembly such as DA 39 is continuously discharged for many hundreds of fiber volumes, another resistance increase is seen in the resistance vs. time curve, as seen in Figure 7. This increase is significant, for, while a similar dianode can normally take many hundreds of current reversals, one which has shown this second increase fails within seconds of current reversal, predictably and without exception. Furthermore, the current reversal corresponds to the time of the cycle (Discharge ⟶ Charge trip point) where the majority of multi-fiber cells fail. The causes for failure may be the same.

Figure 6
EFFECT OF POTASSIUM ON RESISTANCE OF GLASS ON PROLONGED DISCHARGE

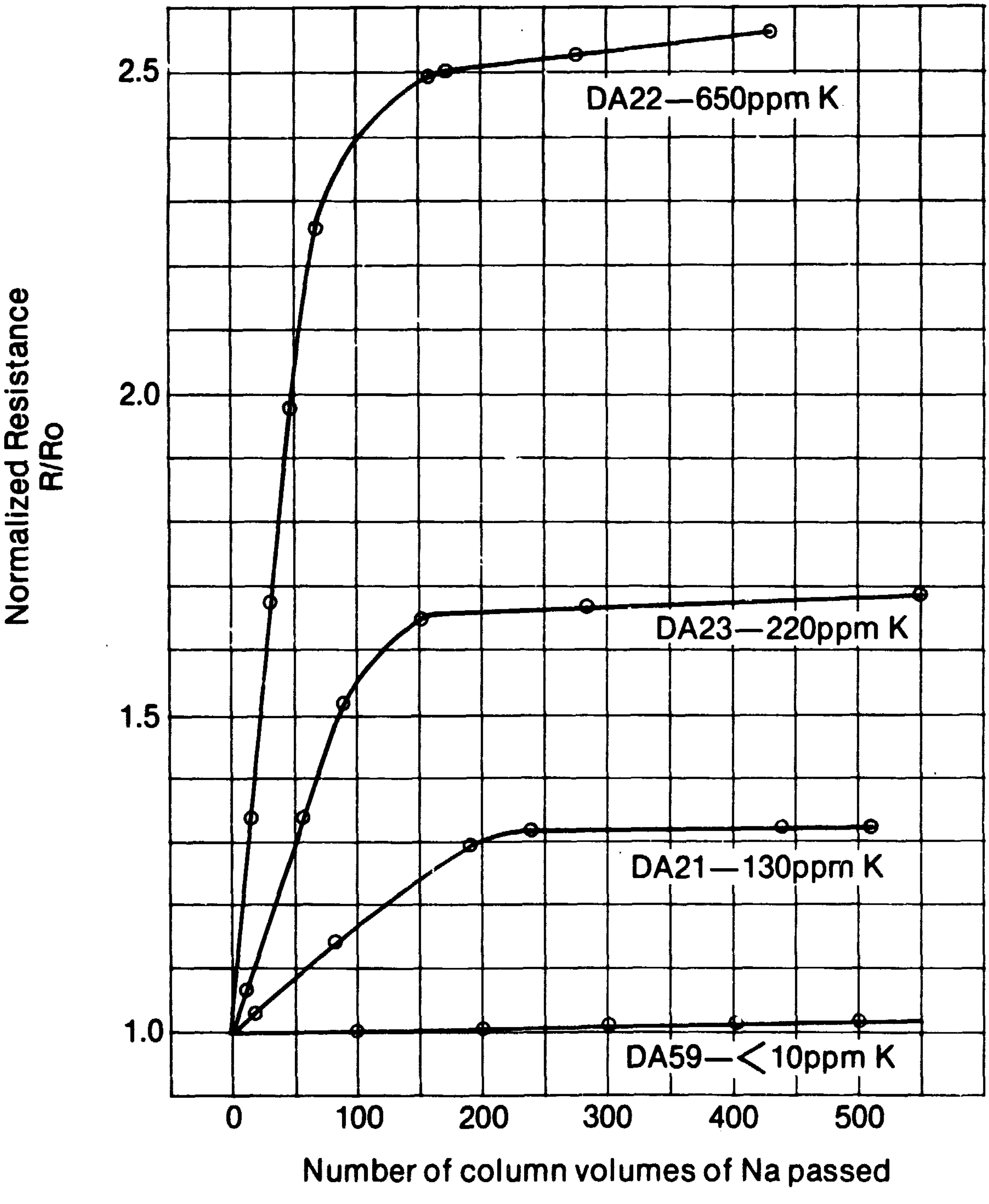
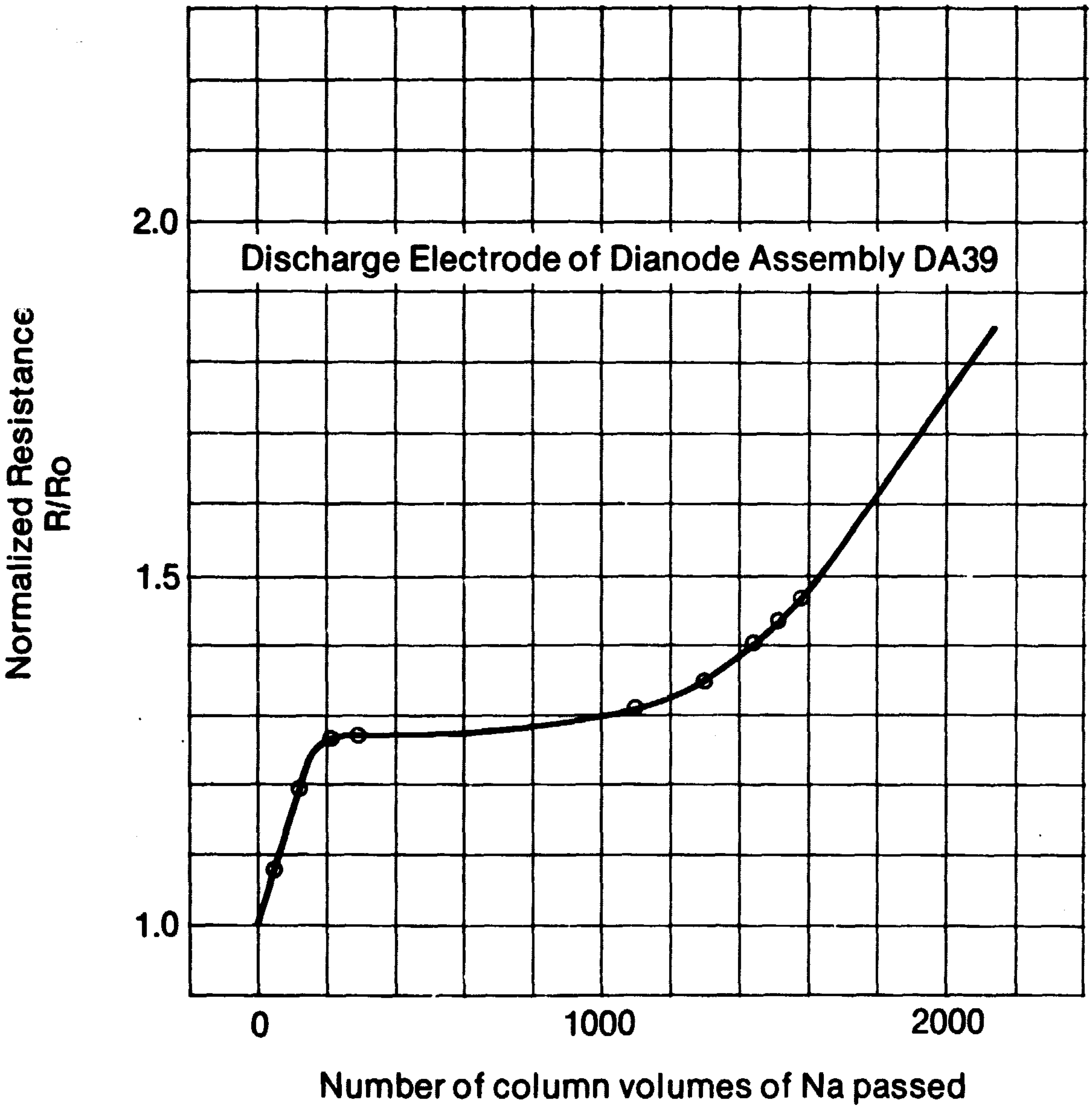


Figure 7
EFFECT OF Na_2O/NaOH ON RESISTANCE OF GLASS ON PROLONGED DISCHARGE



When a failed fiber is recovered and its interior surface examined under an optical microscope, the glass surface shows an increasingly rough character as the fiber is scanned toward the originally sealed end, which is now broken off. As the surface is roughened, it is also dewetted by sodium. The interior fiber surface near the reservoir end still appears shiny and wetted by Na. The roughening of the surface seems to have been caused by some impurity that:

(1) is soluble in the Na, originally at a concentration not high enough to react with the fiber wall,

(2) cannot go through the fiber wall, hence concentrates (see Appendix B) toward the sealed end of the fiber as the electrode is discharged, and

(3) reacts with the fiber wall when the concentration does get over the threshold (separate phase?) and causes the rough look and dewetting,

(4) effects the fiber in such a way that the fiber can break almost immediately on current reversal,

(5) is variant in concentration in various Na preparations. This second resistance increase shown up at different volumes of discharge depending on the "batch" of Na used. The batch that gives a later increase also gives the longer life current cycling dianode cells. The lifetime tests on cycling dianode assemblies were current cycled at about 10 fiber volumes of sodium/cycle.

A solution of sodium hydroxide in metallic sodium does not seem reasonable, and a colloidal suspension seems easier to accept. However, in this case it seems that the only way to fit sodium oxide/hydroxide into the role of the culprit is to regard them as true solutes. They are the logical candidates, and reducing the amount of oxide/hydroxide does indeed minimize this effect.

(C) Oxide Removal

Na_2O in sodium can be reduced with a more active metal, such as Zr, at high temperatures through a "hot loop" (ref. 3). Rather than a hot loop, a batch process was used as follows:

Into a cylindrical Ni crucible about 10 cm^2 cross section, is placed 40 ml of Ca-free sodium and ∿2 gm of -200 mesh Zr/Ti (50/50 mole %) alloy (Ventron #88410). A Ni cover is placed on the crucible to minimize Na volatilization and the crucible is heated to 500 ± 10°C for 16 hours. The crucible is then cooled to 150°C, and the Na is sucked up into pyrex ampoules and stored for later use. The whole operation is carried out in a N_2 dry box.

The sodium, thus prepared, has distinctly different wetting properties and a more shiny surface than before treatment. When used in a dianode assembly, as typified by DA 50 (Figure 8), the electrode discharged over 2500 fiber volumes before a second resistance increase developed. Reversal of current caused an immediate failure of this glass fiber also, the damage on the glass fiber was primarily localized at the very end of the fiber (∿1 mm broken) and over 3/4 of the fiber length remained pristine without any visible signs of attack.

Since zero concentration of oxide and hydroxide is an unattainable goal, and since in actual operating cells the exchange volume of sodium, depending on design, is only 4x to 20x the column volume, the above mentioned method was used as the standardized Na purification process -- calling the sodium obtained "gettered Na". This sodium was used in actual operating 1000-fiber cells to see whether cell lifetimes could reach desirable levels.

(D) Cell Operation (1000-Fiber) with Gettered Na

(1) Change of Assembly Process

Reproducible and dependable techniques for assembling and testing small 1000 fiber test cells of the following specifications have been developed:

Fibers: 1000 spaced at 42/cm, 5 cm working length

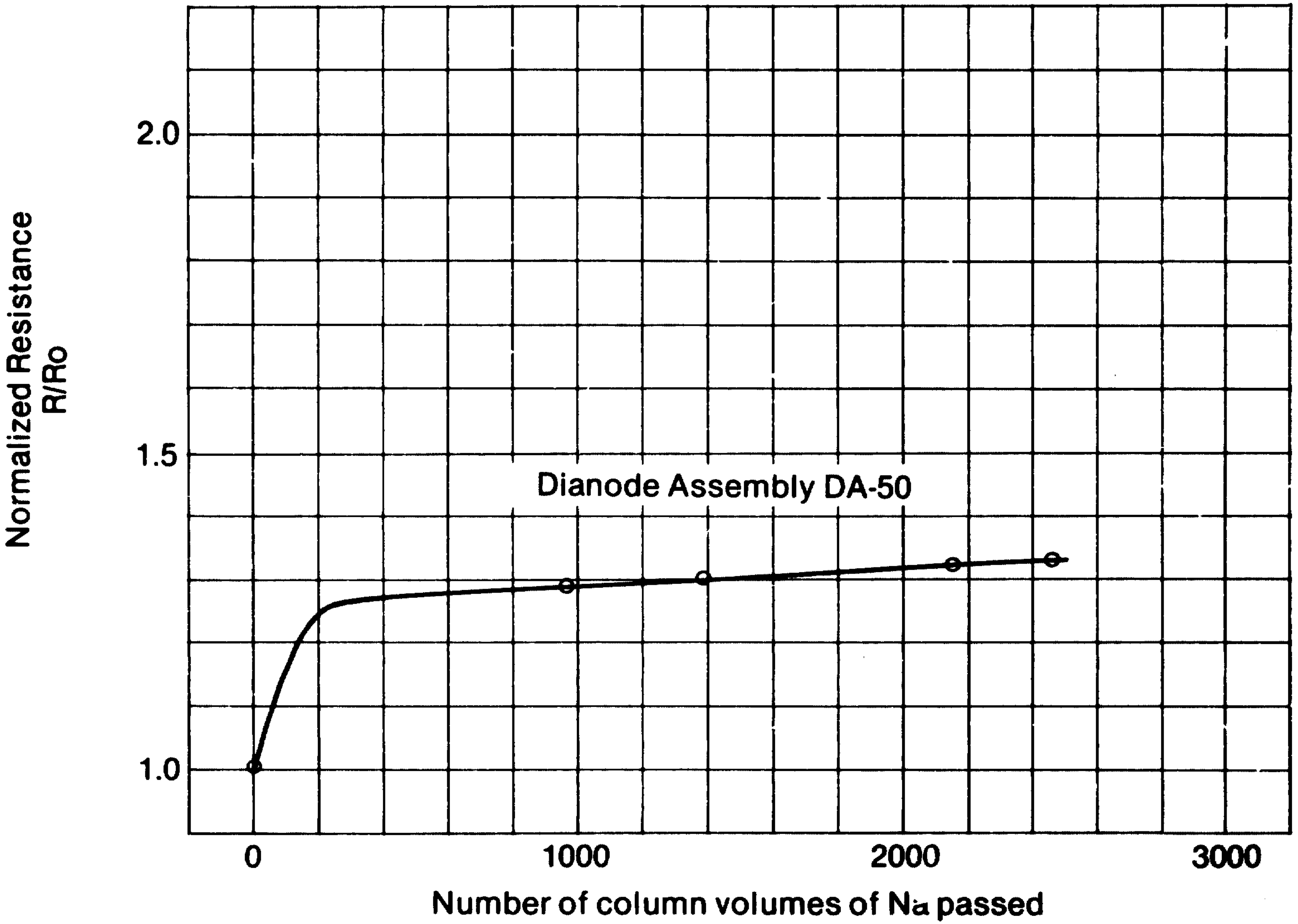
Cathode: Molybdenum (∿1000 Å) coated on 1100 alloy Al foil

Spacer: 4.0 - 5.0 mil 1100 alloy Al

Capacity: 0.5 A-hr. (using 4 mil spacer thickness)

Fibers used for this study, unless otherwise specified, are 70μ OD; 50μ ID; T406 ($Na_2O\cdot 2B_2O_3\cdot 0.2\ SiO_2\cdot 0.16\ NaCl$) glass.

Figure 8
RESISTANCE CHANGE OF A DISCHARGING ELECTRODE WITH GETTERED, Ca-FREE SODIUM (POTASSIUM CONTENT ≈ 130PPM)



Tubesheet Material: 94/6 glass ($0.06\ Na_2O \cdot 0.94\ B_2O_3$)

The assembly process includes the following steps:

(1) Rolling of bundle and applying tubesheet material paste.

(2) Initial drying of the tubesheet material paste to remove the liquid carrier.

(3) Fusion of the tubesheet material at 383°C for 1.75 hours under diffusion pump vacuum.

(4) Sealing of anode container on top of the tubesheet by induction heating (anode cup has a 94/6 glass "lip" that is applied by hot dipping).

(5) "Checking of Assembly" for gross leaks (broken fiber, etc.) with N_2 pressure applied to inside of anode cup.

(6) Assembling into cell configuration, ready for sodium and sulfur loading. (This is the last step where mechanical damage from handling can result.)

(7) Applying BCl_3 gas treatment (surface treatment of fibers to insure sodium filling and wetting).

(8) Filling with reagents -- Na introduced into fibers under vacuum and then S added in inert atmosphere.

(9) Sealing top joint and wire leads and heating to operating temperature.

(10) Starting cell by controlled discharge. Internal resistance drops to theoretical or essentially theoretical level when enough Na_2S_x is formed to bring all the fiber surfaces to operation.

(11) Cycling the cell in the desired mode, either time controlled or voltage controlled.

When the gettered Na was first used in the standard test cells (PS 1-4) rapid failures, seemingly unrelated to fibers (as seen in the voltage recordings) occurred. These failures are attributed to the greatly increased wetting ability of the gettered sodium, and hence its seeping through the thought-to-be-impervious tubesheet. Leakage through the tubesheet was $<10^{-2}$ ml/sec @ 5 psig N_2. Raising the fusion temperature (step 3) would be an obvious solution since the tubesheet residual porosity depends largely on the fusion schedule. However, any higher temperature fusion makes the fibers too prone to mechanical damage during steps 4 through 6 since fibers at the fiber-tubesheet junction get more fragile as curing temperature is increased. A two stage heating method for fusion was finally adopted with the second heating step to a higher temperature carried out after step 6. This second heating step was done under N_2 pressure rather than under vacuum to prevent a "puffing" behavior of the tubesheet at higher temperatures.

The second heating temperature was initially set at 397°C, but even this was insufficient for making an impervious tubesheet. After several trials at different temperatures, a schedule of 1 3/4 hours at 405°C under N_2 pressure (2/3 atm) was developed as a standard second heating step.

(2) Improved Lifetime

The results summarized in Table I demonstrate the improved performance and can be regarded as a major breakthrough for this technology.

The system can sustain, essentially without change of characteristics, (1) over 1000 deep (∿90%) charge/discharge cycles. (2) over 2500 charge-discharge cycles of ∿80% depth or (3) over 8 months of operation on shallow cycling (10-30%) with total currents equivalent to 5000 deep cycles.

(D) Indication of Need for Further Improvement of Na Quality During Operation

So far, this anolyte study had led to an order of magnitude improvement in cell lifetimes. However, some of the variations in lifetimes suggest that further improvements and/or more adequate quality controls are needed. The observed lifetime variations include:

(1) Maximum lifetime decreases as depth of cycling increases.

(2) In the 70-100% depth of cycling region, lifetime varies over a wide range at a given depth level.

(3) A disproportionately large number of cells fail at the discharge to charge trip point, for all "age" brackets. This suggests that the oxide/hydroxide mode of failure is still present.

TABLE I

PERFORMANCE DATA OF 1000-FIBER Na/S TEST CELLS

Cell Number	Operational Mode			Life		
	Cycle Time Charge + Discharge	Current (Nominal)	Depth/Cycle	Cycles	Amp.-Hrs.	Days
PS 25	1/2 hr. + 1/2 hr.	1A	>95%	1030	1030	47
PS 34	1/2 hr. + 1/2 hr.	0.8A	80%	940	750	41
PS 35	1/2 hr. + 1/2 hr.	0.8A	80%	1180	950	49
PS 36	1/2 hr. + 1/2 hr.	1A	>95%	650	650	27
PS 37	1/2 hr. + 1/2 hr.	1A	>95%	480	480	20
PS 40	1/2 hr. + 1/2 hr.	1A	>95%	1800	1800	75
PS 44	1/2 hr. + 1/2 hr.	1A	>95%	480	480	23
PS 47	1/2 hr. + 1/2 hr.	0.6A	60%	770	460	34
PS 49	1/2 hr. + 1/2 hr.	0.55A	55%	2040	1120	87
PS 51	1/2 hr. + 1/2 hr.	0.8A	80%	1760	1420	45
PS 52	1/2 hr. + 1/2 hr.	0.8A	80%	3160	2540	103
PS 53	1/2 hr. + 1/2 hr.	0.3A	30%	5500+	1660+	232+
PS 54	2 min. + 2 min.	0.8A	5%	83000+	4430+	231+
PS 55	1/2 hr. + 1/2 hr.	0.85A	85%	2890**	2450**	121**
PS 57	1/2 hr. + 1/2 hr.	1A	>95%	1350	1350	57
PS 58	1/2 hr. + 1/2 hr.	0.8A	80%	1900	1520	80
PS 59	++	0.85A	100%	330	285	15
PS 60	++	1A	100%	1920	1920	80

Old record before Na purification was <250 Amp-hrs.

Cells are all 1000 70μ O.D. 50μ ID T406 fiber cells with 0.5 amp-hr. capacity.

+ Still in operation at this writing.
** Failed via equipment failure.
++ On limiting voltage control.

Late in this program it was realized that a latent oxide source in the system exists. The tubesheet and anode cup lip sealing glass contain some H_2O and are slow water vapor emitters. Also, the gettered Na when suction-filled into pyrex ampoules contains varying amounts of excess Zr/Ti getter and this excess getter may have been responsible for the variation of longevity observed. The logical implication is that the gettered Na is satisfactory for the initial cell filling, but a residual amount of getter, is needed to keep the oxide/hydroxide concentration down to an acceptable level. According to calculations in Appendix B, this depends largely on depth of cycling and design of the cell -- or more specifically, to the number of column volumes of Na exchanged/cycle.

CONCLUSION

Hollow glass fibers suitable for use in a potassium sulfur hollow glass fiber cell have been made. Compatible auxiliary components have also been developed and 1000 fiber, 0.5 A-hr. size K/S cells were assembled and tested. These cells had short lives. Results indicated that a similar mode exists in K/S system similar to that in the Na/S system, except that it occurs at a much higher rate.

The second phase of the program -- to analyze effects of anolyte impurity, using the Na/S system as the model -- was more successful. Effects of various impurities were characterized and processes for the removal of the harmful impurities were refined. The purified anolyte, in conjunction with some necessary accompanying cell assembly processes, made it possible to produce Na/S hollow glass fiber cells, each containing 1000 fibers, with 0.5 A-hr. capacity, which withstood over 1000 charge/discharge cycles at over 90% depth and very high rates (complete charge and discharge cycle of 1 hr.) or over 8 months of continuous charge/discharge service at 10-30% of capacity.

For this type of performance, the calcium level in the sodium must be less than about 1 ppm and the NaOH/oxide content must be no more than "a few" ppm. Potassium is acceptable as an impurity up to about 150 ppm or so.

Difficulties in making a long lived K-S glass fiber cell include making strong, stable glass fibers containing potassium cations which have low ionic resistance.

APPENDIX A

GENERAL PREPARATIVE METHODS

1. Glass

Reagents and pretreatments include the following:

B_2O_3	Purified Boric Anhydride powder (J. T. Baker) was surface dried in a vacuum oven over a period of seven days, with temperature raised slowly to 105°C, this gradual raising of temperature is necessary so it does not "cake". It is stored in a polypropylene bottle in a dry box.
K_2CO_3	Potassium Carbonate, Anhydrous (J. T. Baker) was used as commercially available.
KF	Potassium Fluoride, Anhydrous granular (J. T. Baker) was used without further purification.
SiO_2	"Supercil", (-325 mesh) was passed through a -80 mesh sieve to remove large agglomerates.
KCl + KBr:	Reagent grade crystals were dissolved in hot water, then precipitated as a fine powder by adding this solution into large amounts of acetone under stirring. The powder is collected by filtration and dried up to 300°C in air.

Typically individual reagents are weighed out and combined in a tightly closed glass jar and mixed by tumbling for several minutes. The mixture is then poured into a Pt dish and placed in a 900°C preheated muffle furnace. After melting (10 minutes) the contents are stirred with a Pt tipped rod, then reheated to 900°C. This stirring and reheating process is repeated three or four times. The glass is then poured into either a cold graphite or chromium plated copper mold.

2. S

Commercial Reagent Grade "flowers of sulfur" is melted and then distilled over a two-foot Vycor bed maintained at >900°C in order to react any organic impurity to CS_2 and H_2S. The distilled sulfur is then purged with nitrogen at 145°C for 4-5 days.

3. K_2S_x

Potassium Carbonate (anhydrous granula from J. T. Baker) is dried by baking in a weighed round bottom flask for 24 hours. It is then cooled and the actual weight determined by difference. Sufficient sulfur for the reaction is added and the

$$4K_2CO_3 + 13S \longrightarrow 4CO_2 + K_2SO_4 + 3K_2S_4 \qquad \text{(A-1)}$$

mixture is warmed to 400°C under N_2 and maintained at 400°C for 24 hours. The mixture is filtered hot in a nitrogen glove box. The filtrate will be of composition near $K_2S_{3.5}$ due to the side reaction.

$$3K_2CO_3 + S \longrightarrow K_2S_2O_3 + 3CO_2 + 2K_2S_4 \qquad \text{(A-2)}$$

It is cooled and crushed and stored in a N_2 glove box.

APPENDIX B

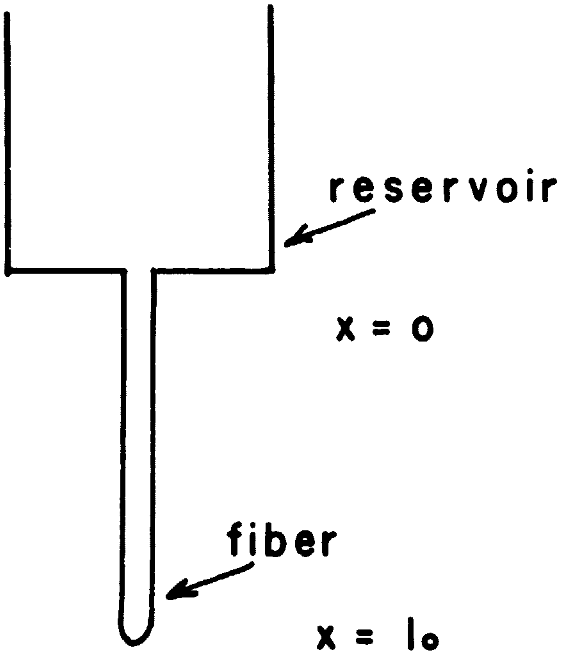
ON THE CONCENTRATION PROFILE OF A SOLUBLE IMPURITY, NON-PERMEABLE THROUGH THE GLASS, DURING DISCHARGE

There is an impurity concentration effect, similar to a chromatographic effect, that occurs with hollow fibers, but not with macroscopic tubular β-alumina cells. In a conventional tubular approach with the β-Al_2O_3 tube large enough to allow convective mixing, impurities that cannot permeate the membrane will be essentially uniformly distributed in the reservoir and hence during discharge will build up to a uniform concentration of $\frac{CoVo}{V}$, where Co = initial concentration of solute
Vo = volume of solvent
V = volume of tube interior

With small diameter hollow fibers, this is not the case. Most of the sodium is stored in a separate reservoir which only communicates with the fibers from one end. During a typical discharge cycle, the volume of sodium in the fiber is replaced many times over. Furthermore, the very large l/d ratio, where l = fiber length and d = fiber internal diameter, and smallness of cross section make plug flow a reasonable approximation.

Therefore, it is desirable to make a model calculation to have some idea of this chromatographic effect on the possible behavior of impurities originally present at very low concentrations. This calculation is aimed at resolving some effects low initial concentrations of corrosive agents such as Na_2O/NaOH have at different depths of discharge or with different cell designs.

Let us set up a simple model as follows:



let the total fiber length be l_o, cross section area A

let the fiber be initially filled with the solvent (sodium) containing an impurity (NaOH/oxide) at initial concentration, Co

let the reservoir be filled with the same solvent with the same impurity but at initial concentration, $C_o^{'}$, with the volume being very large comparing to that of the fiber

let both C_o and $C_o^{'}$ be small enough to be regarded as infinitely dilute

let the solvent flow be plug flow with no diffusion along the length of the fiber, and maintained at uniform concentration across any fiber cross section.

Now let us examine what happens to the impurity concentration as the solvent starts to permeate through the fiber wall. Since diffusion is disallowed, time and permeation rate can be absorbed into one independent variable, and we shall express it in units t_o. Each t_o represents, in a modified time scale (which takes into consideration any change of permeation rate), "time" for one fiber volume, of solvent to permeate through the fiber wall.

Initial analytical solutions, obtained by solving integral equations via differentiation under the,integral sign, failed to give meaningful answers, even when $C_o = C_o$. The trouble in such solutions lies in the fact that there is a "moving singular point" -- boundary originally existed at x = o where x is the distance from the entrance of the fiber. Since the concentration is dependent only on the residence time in the active part of the fiber, and the concentration profile of the region of fiber filled by Na from the reservoir is really time independent, one can easily write down the following solution for a time t, corresponding to the passage of n column volumes of solvent (sodium).

at $t = nt_o$

$$C(x) = \begin{cases} e^{n}C_o & \text{for } l_o\,(1-e^{-n}) \leq x \leq l_o \\ \dfrac{C_o^{'}}{1 - x/l_o} & \text{for } 0 \leq x \leq l_o\,(1-e^{-n}) \end{cases} \qquad \text{(B1)}$$

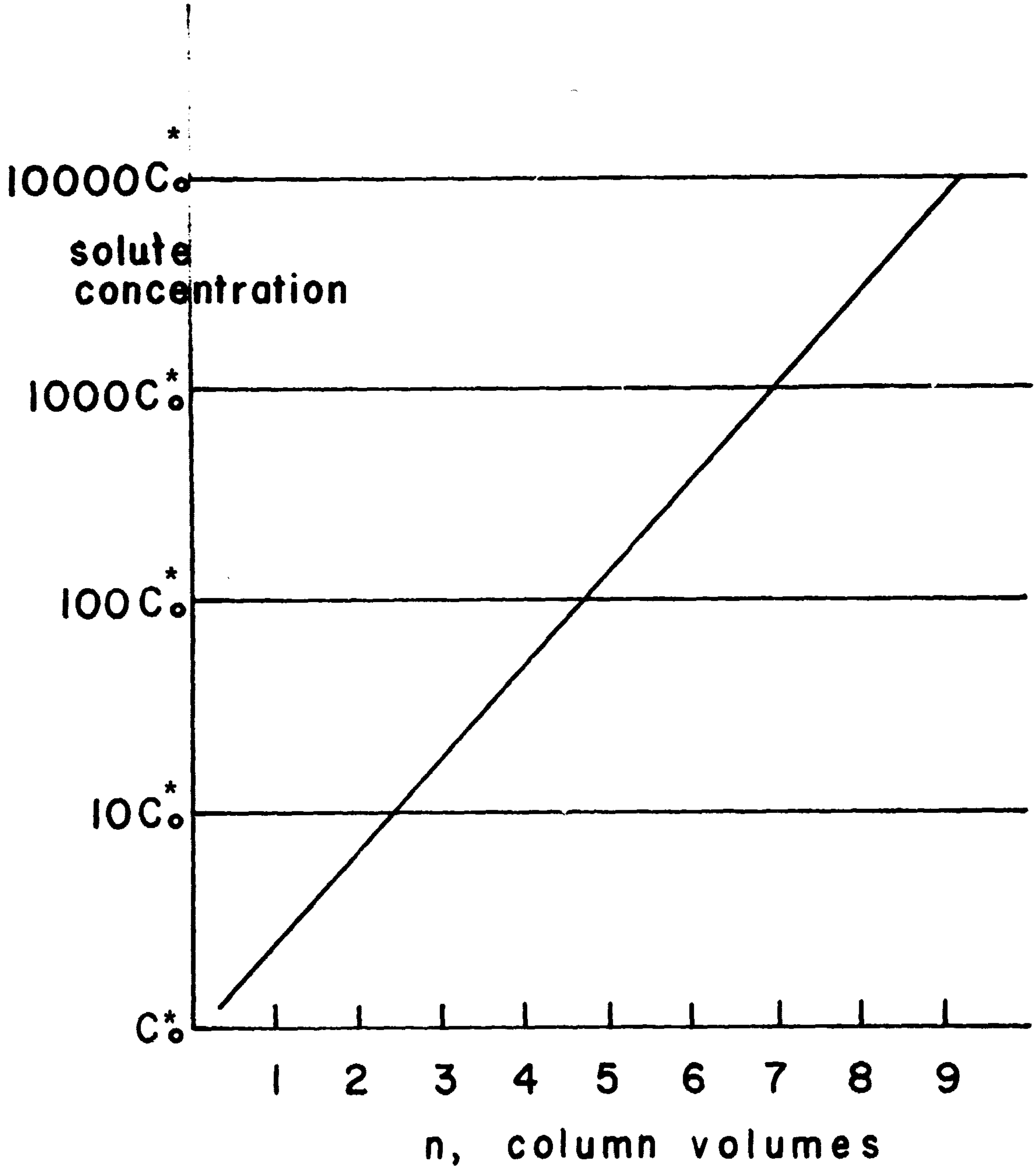
Where Cx = concentration of solute (NaOH/oxide) at distance x, from the entrance of the fiber,

l_o = length of fiber.

For large n, this is a very steep increase toward the sealed end of the fiber In reality, diffusion would occur and the actual increase would be much less. Nevertheless, this gives an approximate idea on how this exchange volume nV can be an important design parameter. Figure 9 shows the maximum solute concentration as a,function of the column volume, where Co* is the larger of C_o and C_o.

FIGURE 9

INCREASE IN SOLUTE CONCENTRATION AT BOTTOM END OF FIBER



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