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DEVELOPMENT OF A HIGH TEMPERATURE BATTERY

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W. J. Subcasky, T. M. Place, H. A. Parker-Jones, and W. G. Anderson

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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AERONUTRONIC
DIVISION OF PHILCO CORPORATION
A SUBSIDIARY OF Ford Motor Company,
FORD ROAD/NEWPORT BEACH, CALIFORNIA

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ABSTRACT

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A number of experimental cells with sodium anodes and CuCl cathodes were discharged. The membranes used to separate the anode and cathode compartments were fabricated from a NaX zeolite or a high sodium porcelain. Cell lifes were erratic and varied from 6 to 22 hours. The results of these tests and compatibility tests indicated an attack of the membrane by molten alkali metals. Substitution of a magnesium or magnesium alloy anode with a LiCl-KCl anolyte for the sodium eliminated the attack on the membrane. Cell life was still erratic but in two cases cell lives approaching 70 hours under drain were achieved. Cracking of the zeolite membranes was noted and ascribed to a volume change which occurred when the sodium ions in the zeolite were replaced with lithium ions from the anolyte. Cells constructed with other porous separators and molten CuCl cathodes had lives of the order of 15 hours compared to cells with porous separators and solid CuO cathodes which had lives in excess of 72 hours.

Resistivities in fused salts were determined for membranes prepared from NaA, NaX, and LiX by vacuum hot pressing; from NaX and LiX by silicate bonding, from NaX and LiX by phosphoric acid bonding, and from clays of a high sodium content. The LiX was prepared from NaX by ion exchange.

Methods of bonding NaX and LiX zeolites by silicate or phosphate bonding and vacuum hot pressing were investigated. The effect of various fabrication techniques upon the structure of the zeolite was followed by x-ray diffraction studies. The thermal coefficients for the various bonded zeolites were determined and methods of forming high temperature seals were investigated.

Compatibility tests showed extensive reaction of sodium with a high sodium porcelain, a sodium-alumino-phosphate composition, and a wide variety of zeolite compositions. This reaction necessitated a change from molten sodium to solid magnesium or magnesium alloy anodes. Compatibility tests were also run for the various materials in the proposed cell design and molten LiCl-KCl and CuCl.

Author

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SECTION 1

INTRODUCTION

1.1 OBJECTIVE

The objective of this program is the development of a high energy density battery capable of operation for 72 hours under ambient conditions as are believed to exist on the planet Venus. For purposes of the program, such conditions were specified to include a temperature of $800^{\circ}F$ and an atmospheric pressure of 10 bars.

1.2 PROGRAM REVIEW

A battery system utilizing a salt electrolyte fusible below $800^{\circ}F$ (i.e. a "thermal battery") was chosen as most suitable to the Venus environment. The specified duration of 72 hours imposed much more stringent limitations on the self-discharge rate than is the case with conventional thermal batteries. It was anticipated that the self-discharge process most likely to limit battery life would be that resulting from the diffusion of electrode materials through the separator. Two methods of controlling this process exist: (1) use of insoluble or only slightly soluble electrodes, or (2) development of a separator having selective permeability to ions and dissolved species. In the latter case the separator would be required to have a high permeability to ions of the electrolyte, but very low permeability to the dissolved electrode materials. An additional factor of importance in this connection was that insoluble electrodes generally produce lower potentials and greater polarization problems than do soluble electrodes. This consideration and the importance of high energy density for the intended mission decreed that a battery system involving soluble electrodes and the second of the above two methods for controlling self discharge, be adopted.

Two types of materials exist potentially capable of meeting the separator requirements. These are the synthetic zeolites, and certain porcelains or glasses. The latter had been subjected to considerable investigation and were known to have good ion selectivity but unacceptably high resistance at $800^{\circ}F$. The zeolites had been extensively studied in aqueous electrolytes at temperatures up to $200^{\circ}C$. In such electrolytes they have good conductivity and appreciable if not well documented ion selectivity. No information was available on their conductivity in fused salts. However, some data existed on their intrinsic ion conductivity at $800^{\circ}F$ and above, and this together with the results of theoretical reasoning indicated that a zeolite could be found having the right combination of ion conductivity and specific ion permeability required for the purposes of this program. There appeared to be good reasons for believing that the synthetic zeolites were most promising.

In accordance with the foregoing, the program was initiated with the working hypothesis that a suitable semi-permeable separator would be obtainable, and initial work on cathode materials stressed soluble electrodes. For reasons as discussed in previous reports, CuCl and $BiCl_3$ were selected as the most promising, and ultimately, attention was centered on CuCl. A not unimportant reason for its selection was that it could be conceived as intermediate to the development of $CuCl_2$ as a depolarizer. This latter material develops about the highest cathode potential possible in fused chloride melts.

Anodes of interest were exclusively those of the alkali metal or alkaline earth groups, all of which exhibit satisfactory polarization behavior and which develop about the same potential, with the exception of Mg and Be. The only point to be decided was whether a solid or a liquid anode would be most suitable. This decision was dependent upon details of final cell design. Selection of a liquid anode was tentatively made based upon ease of maintaining contact with the current collector and also with the separator without the need for a reservoir of electrolyte in the anode compartment.

Research and development work on the separator problem has by far occupied a major part of the program. It has been directed primarily to the various zeolite materials, with a small amount of work on the porcelains. In some cases porcelains formed from zeolites were fabricated by fusing to destroy the zeolite structure. Results are presented in this and previous reports. In general it has been found that the type X zeolite has lower resistance than types A or Y, and further that resistance is lowest for the sodium zeolite form. In spite of this effort, a satisfactory membrane has not yet been demonstrated. Aside from the general problem of devising a material having all of the desired properties, the difficulties which have been encountered may be summed up as falling into three different categories: (1) attack on the zeolite by the anode material, (2) sealing problems, and (3) disruption of the membrane structure by exchange with foreign ions from the electrode materials or the electrolyte. Because of these difficulties, it has not been possible to demonstrate unequivocally that the materials studied have the desired selective permeability or electrical conductivity.

Some data on the attack of separator materials by molten alkali metals has been presented in previous reports, and additional work is presented in the following sections of this report. It has been concluded that the problem cannot be solved within the scope of the present program. Consequently the concept of a liquid anode has been abandoned and replaced by the alternative of a solid anode, i.e. Ca, Mg or Mg·Li alloy. In this case physical contact between the anode and the separator will be avoided, electrical contact being maintained by means of a film of electrolyte.

The sealing problem has provided a major impediment to the program, and is particularly annoying because it is one which manifests itself much more importantly in the membrane development than it is expected so to do in the actual construction of a practical cell. The screening of separator compositions requires that each membrane specimen be sealed to the appropriate part of the test cell structure. If a rigid seal be used, the wide thermal range to which the cell is exposed requires a close match (probably within 1%) in coefficient of expansion between the membrane, support, and sealant, if cracking of the membrane is not to occur. Since different membrane materials have different coefficients of expansion, meeting this requirement for each material is very laborious. Use of a flexible sealing material would materially alleviate the problem. Extensive use has been made of the only flexible sealant available, namely an RTV silicone rubber, which can withstand the cell operating temperature. However, the evidence obtained to date strongly indicates that due to the ubiquitous antiwetting character of silicones, conductivities obtained from measurements on membranes sealed in place with such material are subject to serious question.

Finally, in those cases where satisfactory seals have been obtained, there is strong evidence that cracking of the membrane occurs due to changes in material volume consequent upon the exchange of ions with the surroundings. Most of the work carried out to date has been with sodium zeolites, and ceramics in the sodium form. In the cell, the membrane is in contact with the KCl·LiCl eutectic and with CuCl. Exchange of the Na with either K, Li or Cu, or any combination thereof can occur. Such exchange would lead to the observed effect.

This report presents the effort carried out during the last quarter in attempting to solve these problems. It includes work on the fabrication of separator membranes from a number of different materials, both zeolite and nonzeolite, and their test in different research cells. Certain other tests such as their stability under extended contact with electrolyte and their resistance as a function of such contact are also reported. Toward the end of the report period conferences with NASA program monitors led to the decision to concentrate on zeolite materials, and this decision was implemented. Most recent work has been concerned exclusively with the synthesis of lithium zeolites and their fabrication into membranes. Preliminary results have indicated some promise in terms of conductivity and ion selectivity. However difficulties associated with cracking of the membranes have not yet been eliminated.

Also presented in this report is data on two cell tests carried out using insoluble electrodes and fritted glass porous separators. The electrodes were Mg·Li alloy and CuO. Durations of over 72 hours were obtained with little difficulty. No measurement was made of electrode utilization, but qualitative observations indicated a very low rate of self discharge. These results suggest that the quickest path to a 72 hour thermal cell would be through use of insoluble electrodes and porous separators. The approach presently in effect is of longer range but if successful should provide for the maximum attainable energy density.

SECTION 2

EXPERIMENTAL

2.1 EQUIPMENT

During this reporting period new circuits and electrolytic cells were constructed to permit studies of various solid membranes in experimental cells.

2.1.1 DISCHARGE CIRCUIT

Test cells were discharged with a sine wave transistorized commutator (1). This instrument is a modification of the well-known Kordesch-Marko bridge (2). A circuit diagram of the instrument as constructed for use in our Laboratories is given in Figure 1. This particular circuit permits direct measurements of either the IR drop in the cell or the cell voltage corrected for IR drop depending on the position of switch S_4. In actual operation this switch was a single pole double throw relay activated periodically by a commercial timer. (Industrial Timer Corp., Timer Assembly CM-8, Gear Assembly A-12).

A block diagram of the experimental arrangement used to automatically record cell performance is given in Figure 2. In operation the timer at fixed intervals actuated the relay R_1. The contacts of this relay are actually switch S_4. This switches the output of the commutator between the two measured quantities; the iR free cell voltage and the iR drop. These two quantities are measured on a potentiometric recorder (Sargent, Model MR) which has a range of up to 2.5 volts. The cell current flows through the switch S_7 which in turn is controlled by the latching relay R_2. In series with the coil of this latching relay are three switches; S_5 which is one set of relay contacts and S_7 and S_8 which are controlled by the position of the recorder pen. These latter two switches are adjusted so that S_7 is open

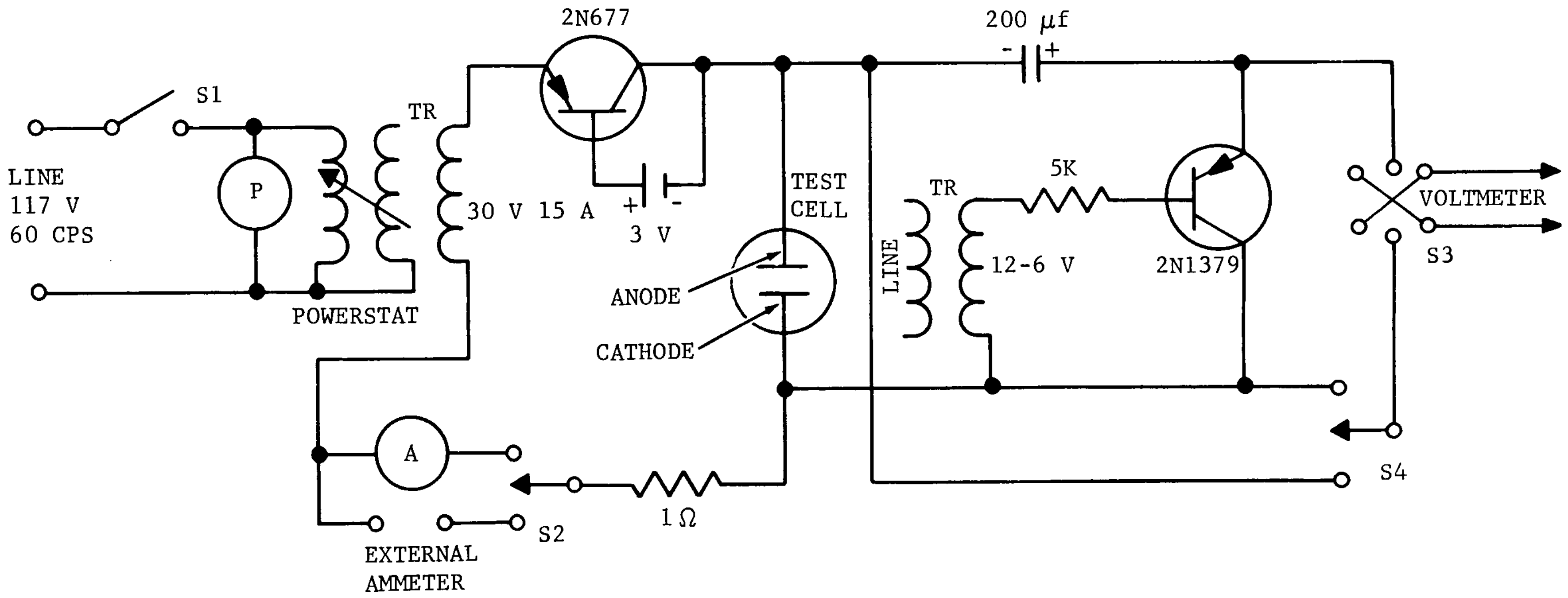

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FIGURE 1. COMMUTATOR DISCHARGE CIRCUIT

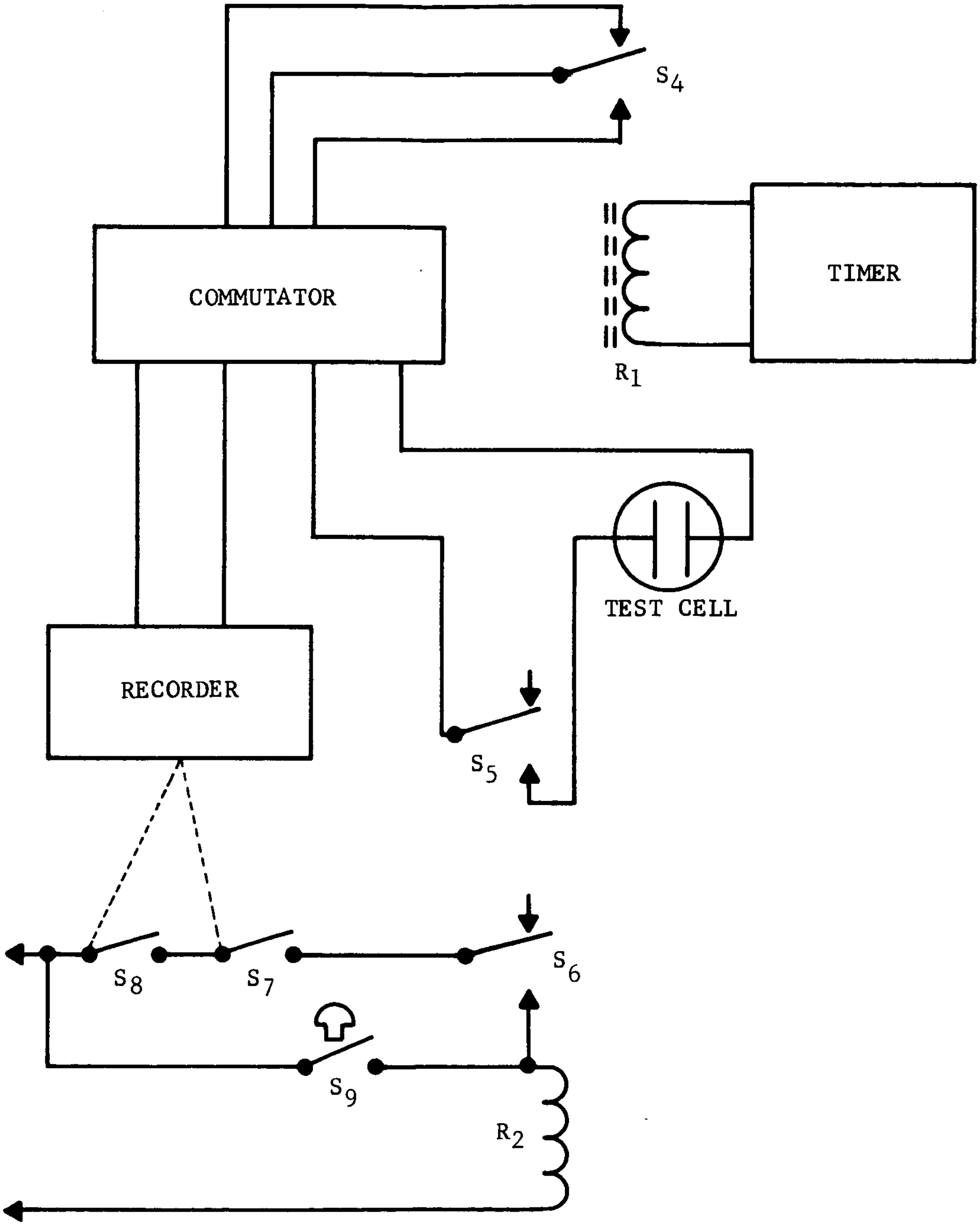

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FIGURE 2. EXPERIMENTAL ARRANGEMENT FOR RECORDING CELL PERFORMANCE

when the pen is above a certain point on the scale and S_8 is open when the pen is below a certain point on the scale. At the intermediate positions both switches are closed. Switch S_9 is of the momentary close, push button type. It will effectively by-pass all the other switches in the circuit of the relay coil.

In operation, S_9 is closed for a short period of time. This closes the circuit for the cell current through S_5 as well as the contacts of the latching switch S_6. In the meantime the pen of the recorder shifts to some place between the two previously set extremes and closes both S_6 and S_7. This provides an alternate path for power to the coil of R_2. This alternate path keeps R_2 actuated even when S_9 is released. R_2 will remain actuated until either S_6 or S_7 are opened by the recorder pen. This type of operation was adopted to permit automatic recording of data over long time periods without possible damage to the equipment if the cell voltage should drop to zero (S_8 opens) or the IR drop reaches a high value (S_7 opens).

2.1.2 ELECTROLYTIC CELLS

A schematic diagram of a typical cell used for the majority of the discharge and resistivity tests is shown in Figure 3. The outer container was 30x240 mm Pyrex or Vycor test tube. The anode compartment was a Pyrex or alumina tube about 95 mm in length and 10 mm inside diameter supporting various types of membranes as shown in Figure 4. Either molten sodium with a tungsten lead or a strip or slug of a Li-Mg alloy along with an Ag-AgCl reference electrode of the type described in detail in the Section 2 of the First Quarterly Report (3) was used in the anode compartment.

The main body of the cell contained the cathode material, either a molten mixture of CuCl and KCl or solid CuO (not represented on Figure 3) in molten LiCl-KCl eutectic mixture, along with an Ag-AgCl reference electrode and a chromel-alumel thermocouple.

Tungsten rods were generally used as current collectors in the anode and the cathode compartments of the cells.

Current drains used throughout these tests were in general based on a current density of 6.7 mamps/cm^2 of the membrane area exposed to the electrolytes. The cells were discharged using the commutator described in Section 2.1.1. Both the IR drop and the IR free voltage of the cell during discharge were recorded.

The first measurements of the resistivity of a type A sodium zeolite formed by vacuum, hot pressing and containing no binder, were measured in the experimental cell shown in Figure 5a. Molten bismuth metal and the LiCl-KCl eutectic were used in both compartments of the cell. The liquid metal ensured a uniform metallic contact on both sides of the zeolite membrane. The membrane was allowed to soak in the eutectic melt for about one hour

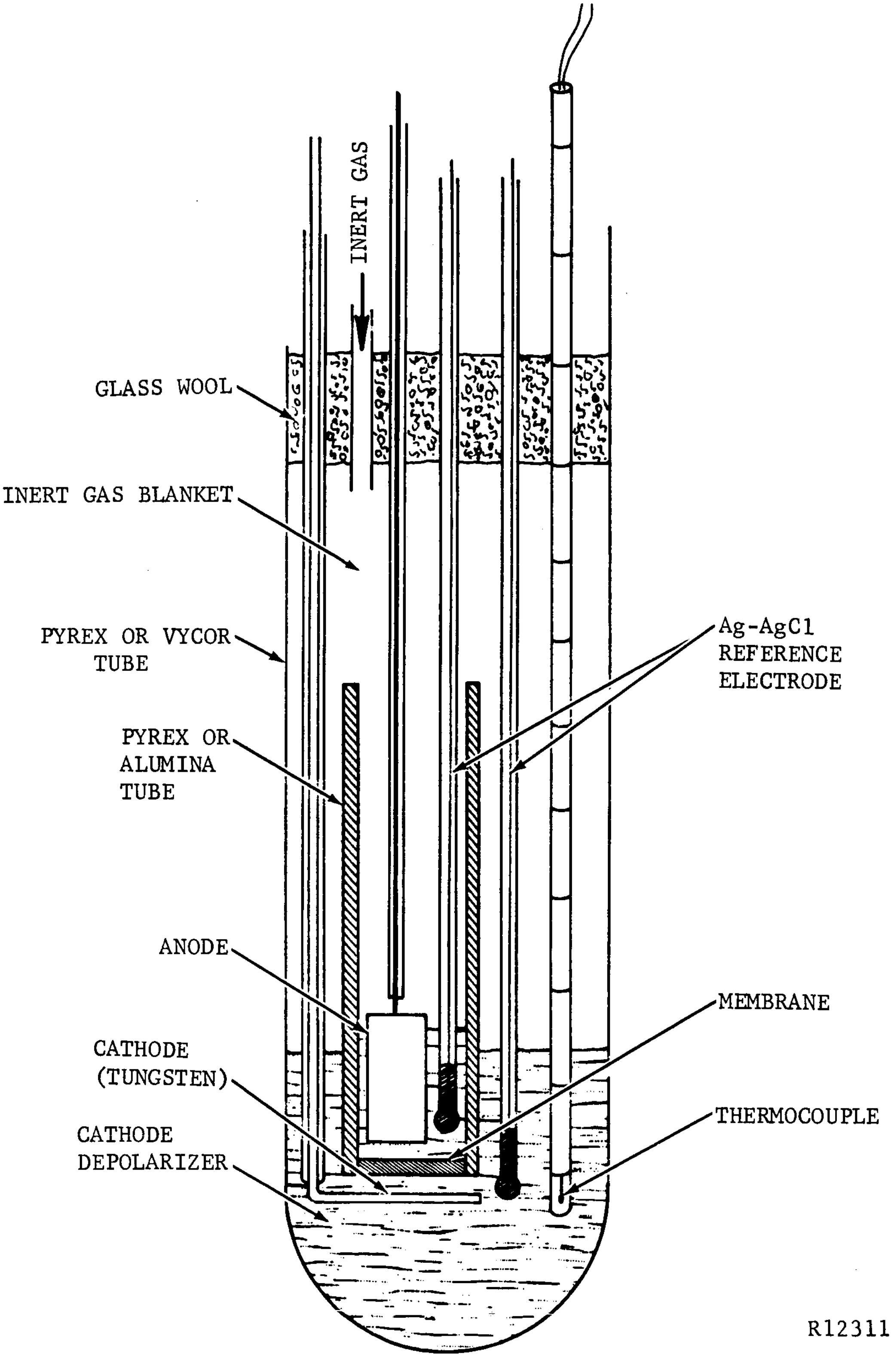

FIGURE 3. EXPERIMENTAL CELL

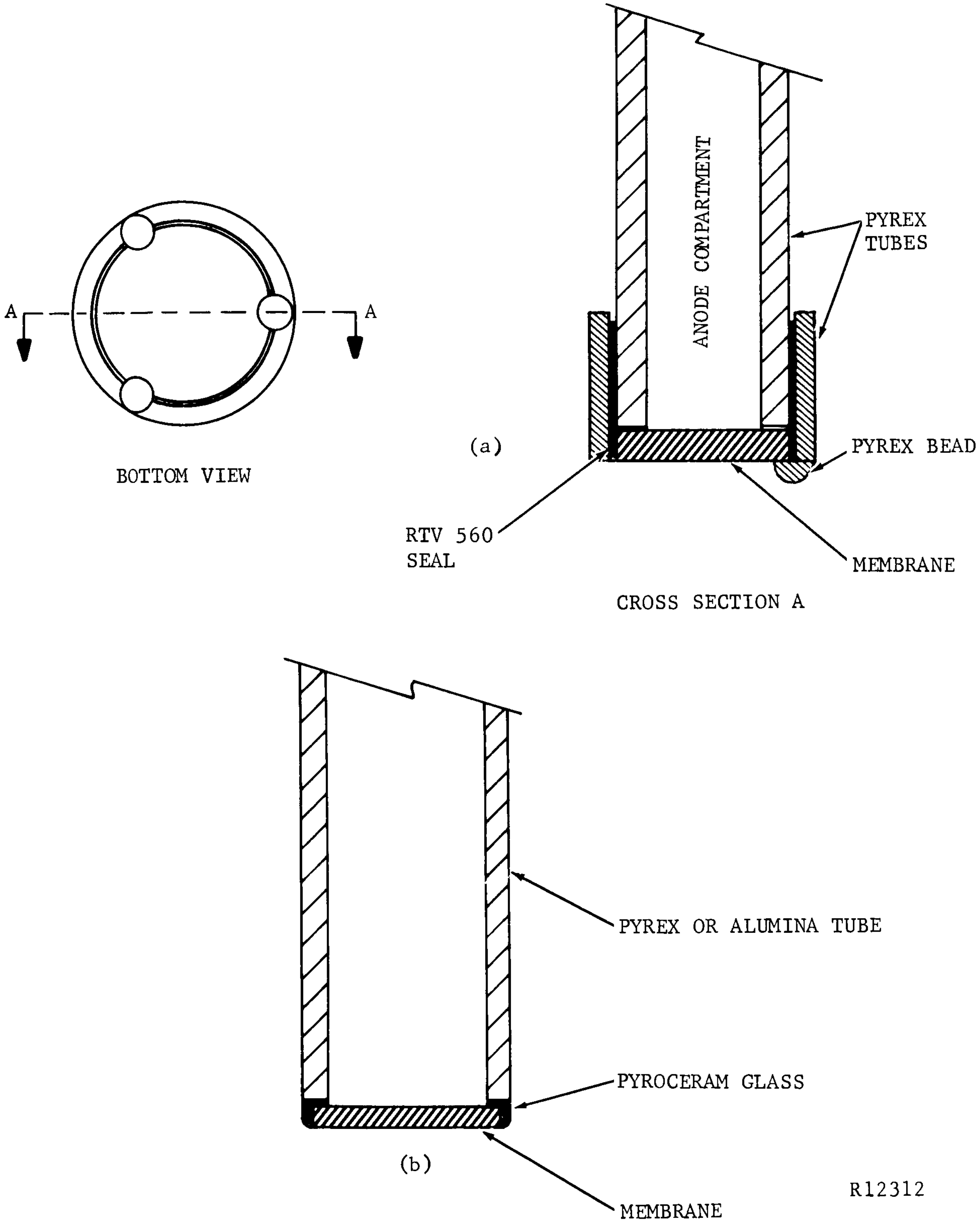

FIGURE 4. ANODE COMPARTMENTS

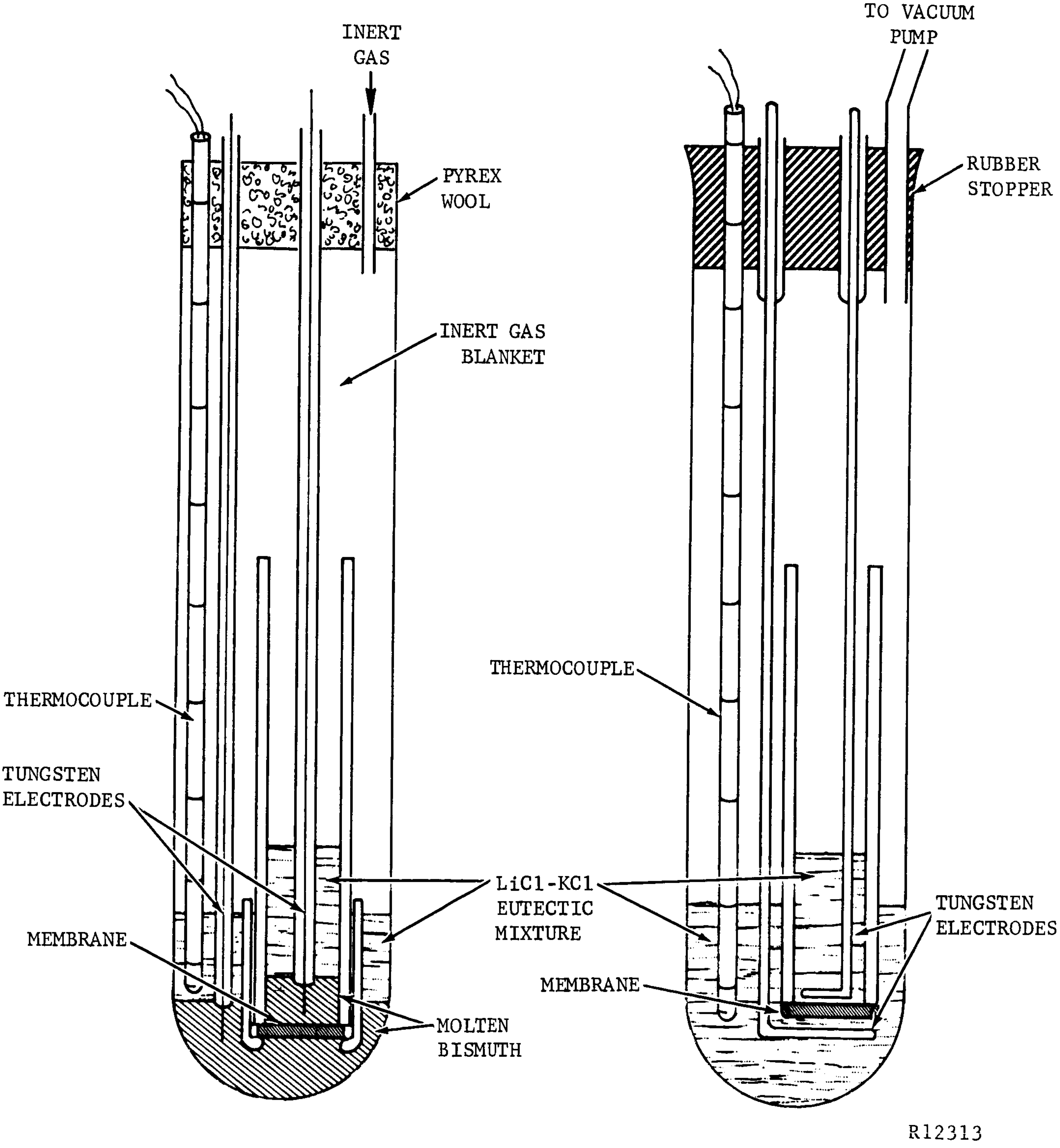

FIGURE 5. EXPERIMENTAL CELLS

and then was lowered into the bismuth pool. Tungsten electrodes were placed in contact with the molten bismuth in both compartments. The resistance of the cell was measured with an AC Conductivity Bridge (1000 cps).

In later tests where only the resistivity of the membranes was desired or where the progress of salt penetration was to be followed from resistance measurement the cell shown in Figure 5b was used. This cell consisted of a Vycor test tube containing Pyrex or alumina tubes supporting pellets of the membrane materials under test. The membrane pellets were usually 0.5 inches in diameter and ranged from 0.015 to 0.040 inches thick. Some bonding procedures caused shrinkage in the pellets, and in these cases the pellet diameter was less than 0.5 inches. The tubes were filled with the eutectic melt and immersed in more of the melt at 415°C. By means of tungsten electrodes immersed in the electrolytes, inside and outside the tubes, the resistances across the pellets were measured with an AC Conductivity Bridge (1000 cps). The impregnation was performed under vacuum. Resistance measurements were made at atmospheric pressure.

2.2 ANODES

During the Third Quarter sodium metal was first selected as the anode material for testing in experimental cells. Because of the corrosive nature of molten sodium on membranes demonstrated in the experimental results given in Section 3.1 and in the results of compatibility tests given in Section 3.5, it was dropped from further consideration.

To eliminate degradation of cell membranes by direct contact with molten alkali or alkaline earth metals, a solid Mg-Li-Al alloy (Brooks & Perkins LA 141) immersed in LiCl-KCl eutectic mixture was employed in the anode compartments of experimental cells as shown in Figure 4. The alloy contains 13-15% by weight lithium and 1.0-1.5% aluminum; it melts at about 580°C and has a specific gravity of 1.35 (4). It was used in the form of strips or pellets fabricated with chips milled from sheet stock. The milling was performed under kerosene and the chips were washed and dried with methyl ethyl ketone. Pellets 0.5 inch long were pressed in a 0.5 inch diameter die utilizing an upper punch with a .020 inch hole through the center of its longitudinal axis. This hole permitted integral pressing of a 10 mil iron wire lead spot-welded to a 180 mesh stainless steel collector screen. The collector screen and wire lead assembly were inserted into the die cavity during filling. Minimum pellet density (74% of bulk density) with sufficient strength was obtained at pressing pressures of 8000 psi.

The relatively high initial anodic potential observed in most tests using the Mg-Li-Al alloy appears to be that of the lithium component in the alloy. The depletion of lithium was indicated by a shift of the potential to that of the remaining magnesium. The time required for this shift to occur was a function of the size, the shape, and the porosity of the anode, other factors, such as temperature and current density, being kept constant.

2.3 CATHODE STUDIES

The selection of cuprous chloride as cathode depolarizer in most cells tested during this report period was based on the following points:

a. There is essentially no polarization in the cathodic deposition of solid copper from pure molten cuprous chloride at current densities up to 0.5 A/cm^2 (5).

b. Oxidation products of anode materials such as lithium, sodium, and potassium can be added coulometrically (ionic transfer across the separator) to CuCl in relatively large quantities before freezing of the catholyte occurs. Thus, CuCl remains molten at 425°C with up to approximately 38 mole per cent of LiCl, 35 mole per cent of NaCl and 55 mole per cent of KCl (6).

c. The omission of an electrolyte in the cathode compartment increases the energy density of test cells.

d. Practical materials such as nickel or Armco iron can be used to contain molten CuCl and act as a current collector without being deteriorated by the salt.

e. A solid reduction product, metallic copper, forms in the cathode compartment of the cells. This was the ultimate reason for the disqualification of $BiCl_3$ as a cathode depolarizer. The final reduction product of this salt is bismuth metal which is molten at the operating temperature of the cell. Depending on the orientation of the cells in space, the molten inert metal can partially or completely obstruct the ionic path between anode and cathode compartments.

The melting point of CuCl was depressed for lower temperature operation by dilution with 10 mole per cent of KCl. This binary mixture melts at about 360°C. This temperature limitation was imposed by the silicone rubber compound (General Electric RTV 560) used to seal the membranes to the cell compartments. With the development of a sealant for operation at higher temperatures, the KCl can be eliminated with a corresponding increase in the cell energy density.

The performance of cells using cupric oxide in KCl-LiCl eutectic mixture was briefly investigated. It was anticipated that using an insoluble cathode depolarizer will decrease, to some extent, the energy and power densities of a thermal cell. Cupric oxide was attractive as a depolarizer because it is only slightly soluble in molten LiCl-KCl electrolyte thus permitting satisfactory cell operation for extended period of time with porous separator having a relatively low resistivity.

It was found experimentally that the voltage of cells using CuO with a LiCl-KCl eutectic mixture at 425°C was about 0.5 volt lower than the corresponding cell using CuCl-KCl (10 mole %) as cathode material. No further study is planned with cell having a CuO cathode.

2.4 MEMBRANES

Early in this reporting period, as noted, emphasis was centered on the use of NaX zeolite in place of NaA zeolite. The high conductivity and lower melting point of the Type X zeolites were considered advantageous from the standpoint of cell performance and sinterability. The NaX material was sintered with the retained zeolite structure and also as a completely fused ceramic material. The fused material was amorphous and very translucent with no crystal phase detected by x-ray diffraction. The theoretical glass composition was considered to be that reported for the crystalline zeolite, namely $Na_2O \cdot Al_2O_3 \cdot 2.8\ SiO_2$. Fabrication and sintering procedures were the same as those reported in the 2nd Quarterly Technical Report (8). The principal criteria for an acceptable membrane were (1) a retained zeolite structure as shown by x-ray diffraction, and (2) a structurally strong, scratch resistant material suitable for a 10-15 mil thick membrane.

With the introduction of the Mg-Li-Al alloy anode and LiCl-KCl anolyte in the single cells, the development of lithium exchanged zeolites was initiated. The desire to use LiX for the formation of membranes was prompted by the observations that NaX membranes after immersion in molten LiCl-KCl eutectic usually cracked. X-ray diffraction patterns of Type X zeolites (see Table II, Second Quarterly Report) showed a decrease in the d spacings when sodium ions are replaced by lithium ions. On a volume basis this shrinkage amounts to 1.5%.(See Appendix for calculation of volume change.) This volume change in a rigidly bonded membrane could possibly cause cracking.

Similar procedures were used for bonding and studying of the lithium zeolites as had been previously used with the sodium zeolites.

The following membrane bonding techniques were investigated during this quarter: hot pressing with no binder and bonding with sodium silicate, phosphoric acid, and a Pyroceram sealing glass #45.

During the course of the cell research incorporating sodium anodes the compatibility of the zeolites in molten sodium was found to be poor. In general, silicates are not highly resistant to sodium. However, in the case of a limited time and temperature requirement, (a three day battery) it seemed feasible that some degradation could be accommodated. In conjunction with this, an investigation of sodium-aluminate composition was undertaken which contained no silica. The concept was based on the development of a sintering aid (P_2O_5) for sodium aluminate; a refractory (m.p. 1700°C), hygroscopic compound. Compositions for sintering evaluation were selected on the basis of a K_2O, Al_2O_3, P_2O_5 phase diagram describing stable crystalline and noncrystalline areas (10). These compositions and some of their properties are described in Section 3.4.

SECTION 3

RESULTS

3.1 CELL TESTS

During the Third Quarter cells of the following types were tested:

$$\mathrm{Na} \;//\; \text{Separator} \;//\; \begin{matrix}\mathrm{CuCl,}\\ \mathrm{KCl}\end{matrix} \;/\; \mathrm{W}$$

$$\begin{matrix}\text{Mg-Li-Al}\\ \text{alloy}\end{matrix} \;/\; \begin{matrix}\mathrm{LiCl,}\\ \mathrm{KCl}\end{matrix} \;//\; \text{Separator} \;//\; \begin{matrix}\mathrm{CuCl,}\\ \mathrm{KCl}\end{matrix} \;/\; \mathrm{W}$$

$$\begin{matrix}\text{Mg-Li-Al}\\ \text{alloy}\end{matrix} \;/\; \begin{matrix}\mathrm{LiCl,}\\ \mathrm{KCl}\end{matrix} \;//\; \text{Glass frit} \;//\; \begin{matrix}\mathrm{LiCl,}\\ \mathrm{KCl}\end{matrix} \;/\; \mathrm{CuO} \;/\; \mathrm{W}$$

All cells using CuCl as the cathode were discharged at temperatures below 415°C to avoid degradation of the silicone rubber sometimes used to seal the membrane to its support tube. Cells with CuO cathodes did not use the silicone rubber sealant and therefore were discharged in the range of 420-430°C.

3.1.1 CELL TYPE: $\mathrm{Na} \;//\; \text{separator} \;//\; \mathrm{CuCl,KCl} \;/\; \mathrm{W}$

Two types of separators were used in cells of this type. In one case a type X zeolite in the sodium ion form, designated NaX, was used as the starting material. The various techniques used to prepare these membranes are described in Section 3.4. The other type of separator was prepared from a porcelain composition (7) first reported by investigators at the National Bureau of Standards.

Performances of cells of this type in terms of IR free cell voltage and electrode potentials could be averaged to the values given in Table I.

TABLE I

AVERAGE PERFORMANCE FOR CELLS OF THE
TYPE Na // separator // CuCl, KCl / W

IR free cell voltage	
(a) at start of test	3.38 volts
(b) after depletion of Cu^{++}	2.53 volts
(c) at end of test	2.36 volts
Anode potential vs Ag-1m AgCl reference electrode	- 2.36 volts
Cathode potential vs Ag-1m AgCl reference electrode	
(a) at start of test	+ 1.02 volts
(b) after depletion of Cu^{++}	+ 0.17 volts

Since the resistance of the separator was far greater than the combined resistances of all other parts of the cell, the resistivity of the membrane was computed directly from the total resistance of the cell.

The test conditions and the performance of individual cells of this type are summarized in Table III. The cell voltage and resistivity of Cell No. 54 are also shown in Figure 6. The effect of temperature on the resistivity of the membrane of this cell is given in Table II.

TABLE II

RESISTIVITY OF Z-16 (700°C/30 min.) MEMBRANE

Temperature (°C)	Resistivity (ohm-cm)
410	3010
422	2170
430	1921
440	1643

3.1.2 CELL TYPE: Mg-Li-Al alloy / LiCl, KCl // separator // CuCl,KCl / W

The membranes tested in this type of cell were fabricated from samples of NaX zeolite Z-16 sintered at 700°C for 30 minutes and from alumina (AL 300). Some of the zeolite membranes were bonded to porous zirconia to increase their strength. The membranes were sealed to Pyrex or alumina tubes using a silicone rubber compound (General Electric RTV 560), a pyroceram seal (Pyroceram 45) or a glass seal (80/20). A number of these membranes were impregnated with the fused salts in the cells by applying vacuum for various periods of time before operating the cells.

Table IV gives the results of a series of tests using cells with CuCl cathodes with Z-16 membranes sealed to a Pyrex tube with the silicone

TABLE III

PERFORMANCE OF CELLS

Na // Separator // CuCl,KCl / W

Cell No.	54	57	55	56	58	59	60	61
Membrane								
Type	Z-16	Z-16	Z-16	Z-17	Z-17	Z-19	NBS	NBS
Sintering temperature °C	700	700	780	940	960	1280	1150	1150
IR free voltage, volts								
a. At start of test	3.43	3.22	3.35	3.36	3.45	3.43	3.56	3.50
b. After depletion of Ca^{++}	2.62	--	2.53	2.79	2.34	2.66	--	2.67
c. At end of test	2.58	1.45	2.22	2.44	1.30	2.60	2.63	2.30
Anode potential vs. Ag-1m AgCl reference electrode, volts	--	--	-2.33	-2.44	--	--	--	--
Cathode potential vs. Ag-1m AgCl reference electrode, volts								
a. Start of test	--	--	+1.02	+0.92	--	--	--	--
Resistivity, ohm-cm								
a. Start of test	6,240	13,900	4,150	16,700	16,700	3,800	12,900	14,000
b. End of test	3,010	2,030	797	3,880	2,490	3,000	6,755	5,200
Duration of test, hours	6	22	6	12	21½	13	23	28
Nature of failure								
Membrane cracked	X	X	X	X	X			
Seal failure			X					
Metallic Copper shorts				X				X
Membrane disinitegrated						X	X	
Support	Pyrex		Pyrex	Pyrex	Pyrex	Pyrex		Pyrex
Sealant	RTV 560		RTV 560	RTV 560	RTV 560	RTV 560	-	RTV 560
Wt. of anode material(Na),gms	1.13	0.83	1.1	0.94	--	0.9	1.02	0.80
Wt. of cathode material,gms	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0

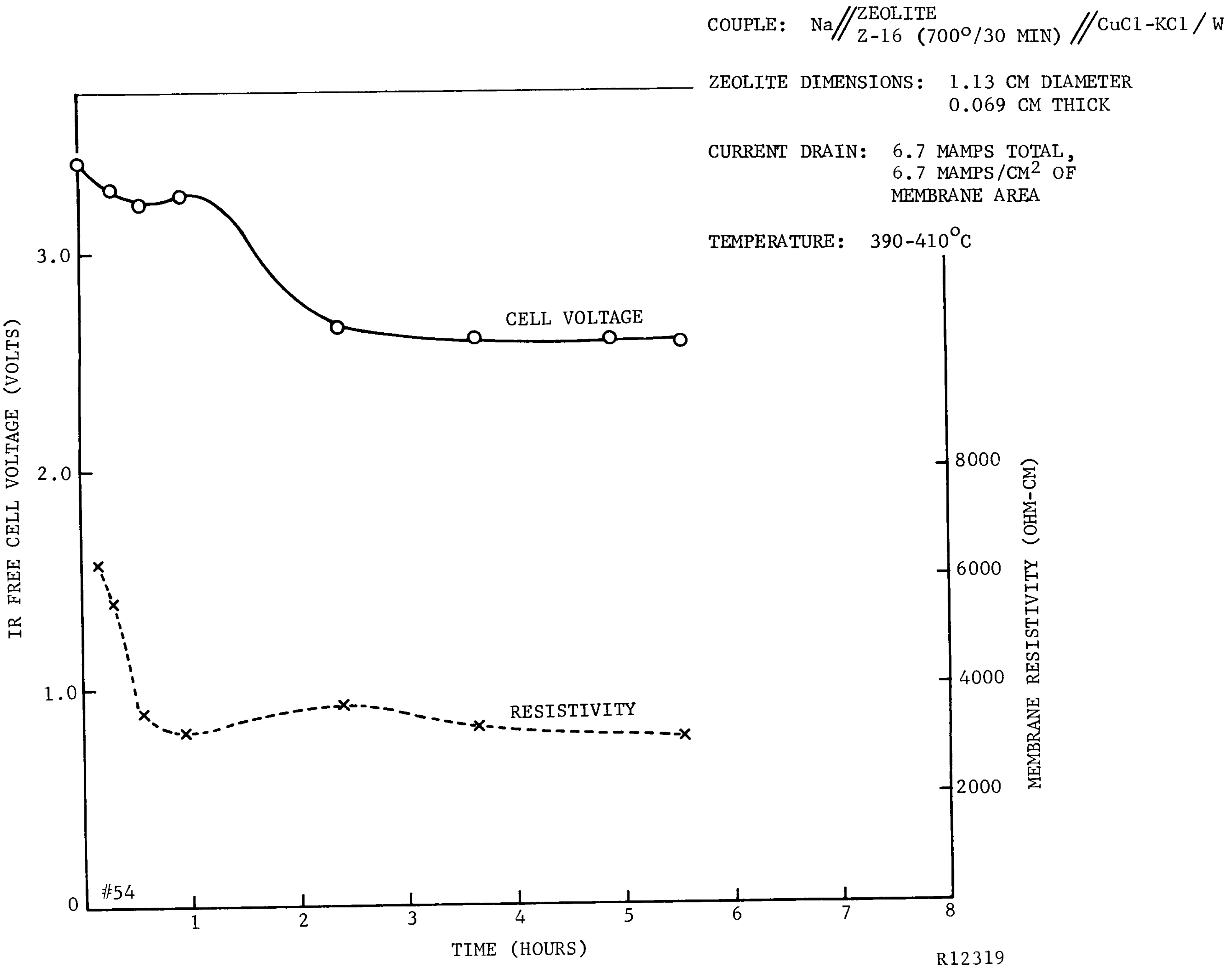

FIGURE 6. PERFORMANCE OF CELL NO. 54

TABLE IV

PERFORMANCE OF CELLS

$$\frac{\text{Mg-Li-Al}}{\text{alloy}} \Big/ \frac{\text{LiCl,}}{\text{KCl}} \Big/\!\!\Big/ \text{Z-16} \Big/\!\!\Big/ \frac{\text{CuCl,}}{\text{KCl}} \Big/ \text{W}$$

Cell No.	62	63	64	67	72	73*
IR free voltage, volts						
a. At start of test	3.29	3.50	3.49	3.24	3.40	3.40
b. After depletion of Cu^{++}	2.50	--	2.52	2.39	2.58	--
c. At end of test	1.93	--	0.94	1.02	1.47	2.51
Anode potential vs. Ag-1$\underline{m}$ AgCl reference electrode, volts	-2.56	-2.53	--	-2.39	-2.55	--
Cathode potential vs. Ag-1$\underline{m}$ AgCl reference electrode, volts						
a. Start of test	+0.75	+0.98	--	+0.84	+0.87	--
Resistivity, ohm-cm						
a. Start of test	5030	6700	5140	4140	3960	3670
b. End of test	314	6700	785	596	short	548
Duration of test, hours	72	1	47	69	8½	22½
Weight of LiCl-KCl, gms.	2	2	2.5	--	2	2
Weight of CuCl-KCl, gms	5	3.5	3.5	--	3	3
Weight of Mg-Li-Al, gm		Not Determined				
Nature of failure						
Cracked membrane		X	X			X
Cracking of tube supporting membrane				X	X	
Cell shorted by metallic copper at edge of membrane where seal failed					X	

* Cell 73 was left on open circuit throughout its operation.

rubber compound. The IR free cell voltages and membrane resistivities for Cells #62 and 67 are shown in Figures 7 and 8, respectively. Membrane cracking occurred repeatedly to various extents in these tests. In some cases, it appeared that the cells operated under acceptable conditions for long periods of time with slightly cracked membranes. Cell failures occurred usually as a result of a short or a self-discharge reaction within the cells.

Two cells using zeolite membranes bonded to porous zirconia were discontinued shortly after start because of the exceedingly high resistivity (5x10^5 ohm-cm) of the membranes even though these were impregnated before their operation.

Three cells using Z-16 zeolite membranes sealed with Pyroceram 45 on an alumina tube (AV30) failed within three hours because of substantial cracks in the membranes. The membrane in the first cell fell off the alumina tube within a few minutes following the start of the test. The two other cells gave the following results:

Cell Number	70	71
Initial Open Circuit Voltage, Volts	2.98	2.95
Initial Anode Potential vs. Ag-1$\underline{m}$ AgCl, volts	-2.60	-2.53
Initial Cathode Potential vs. Ag-1$\underline{m}$ AgCl, volts	+0.40	+0.45
IR Free Voltage at End of Test, volts	2.37	2.35
Initial Resistivity of Membrane, ohm-cm	114	4647
Final Resistivity of Membrane, ohm-cm	--	1954
Duration of Test, hours	2¼	3

Results obtained with two cells using porous alumina as membrane were as follows:

Cell Number	74	77
Initial Open Circuit Voltage, volts	3.08	3.14
Final Open Circuit Voltage, volts	1.1	1.3
Initial Resistivity, ohm-cm	98	<50
Final Resistivity, ohm-cm	535	407
Duration of Test, hours	16½	15

The membranes were found intact when dismantling the cells. The decrease in cell performance was attributed to diffusion of cuprous ions into the anode compartment of the cells and direct chemical reaction with sodium.

3.1.3 CELL TYPE: Mg-Li-Al alloy / LiCl, KCl // Glass frit // LiCl, KCl / CuO / W

These cells utilized as a separator a 0.178 cm. thick, fine glass frit (nominal maximum pore diameter 4-5.5 microns) fused to the bottom of the Pyrex tube serving as the anode compartment. The tube contained the alloy immersed in about 3 grams of the LiCl-KCl eutectic mixture. The glass frit rested

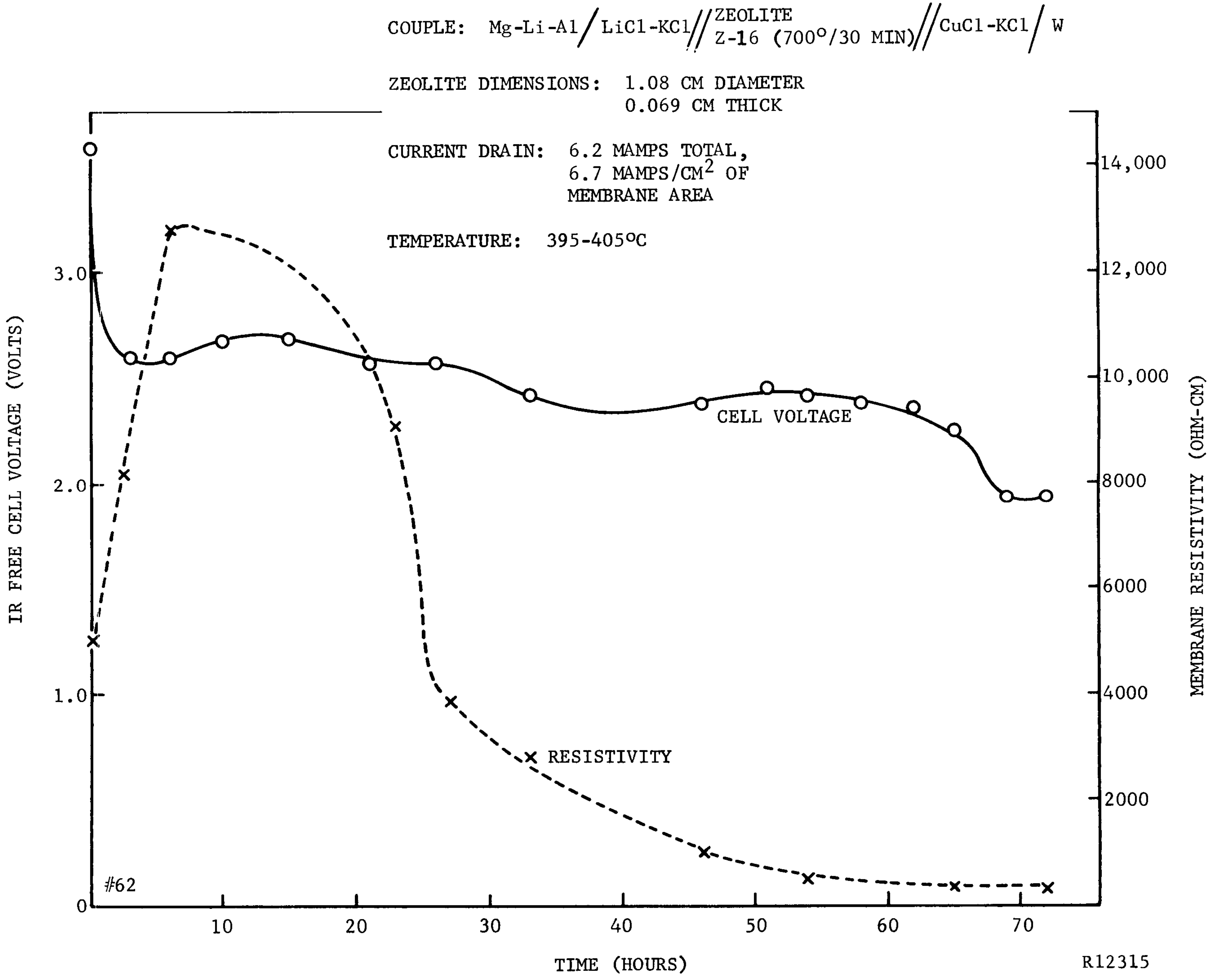

FIGURE 7. PERFORMANCE OF CELL NO. 62

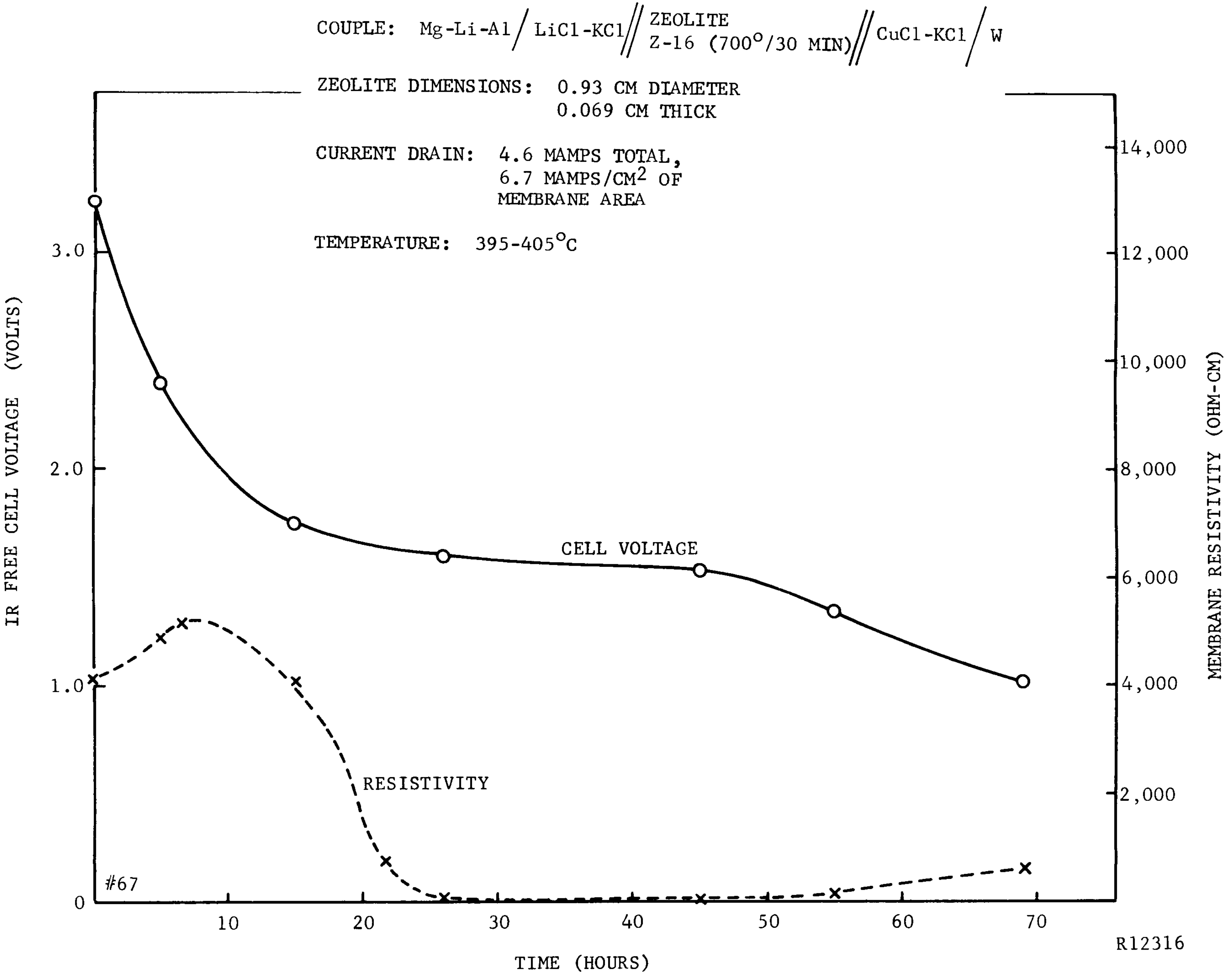

FIGURE 8. PERFORMANCE OF CELL NO. 67

on top of approximately 10 grams of CuO in wire form placed in the bottom of a Vycor tube with 6-17 grams of the eutectic mixture and a W or Cu wire collector. These cells were operated at 420°-430°C. Results are given in Tables V and VI. Potential-time and resistivity-time curves for cell #75 at a current density of 6.7 mamps/sq.cm. of glass frit are shown in Figure 9. Deterioration of the alloy section above the anolyte rather than the coulometric dissolution of the immersed section compelled the replacement of the anodes during cell discharges. This deterioration was ascribed to chemical attack by trace amount of oxygen present in the argon atmosphere maintained above the electrolytes. The transformation in the cell voltage as the lithium on the surface of the alloy anode was consumed is readily apparent. Before this transformation the anode acted essentially as though it were a solid lithium electrode; after the transformation it acted essentially as a magnesium electrode.

With cell #75 the anode compartment was removed after 48 hours of operation. Chemical analysis of this compartment showed a total of 46.2×10^{-6} moles of Cu(II) present. A new anode and anode compartment was added and the test continued. No analysis could be made of the cells after the tests because failure of the glass tube forming the anode compartment permitted mixing of the catholyte and anolyte. With cell #76 the high resistance was probably due to a deficiency of electrolyte in the anode compartment.

The results of cells of this type should be compared with cell using a similar porous separator but a molten cathode (previous section). Within a relatively short period of time the molten CuCl diffused through the porous alumina separator and caused shorting. With the solid cathode with a relatively low solubility at the operating temperature of the cell, the diffusion of cupric ions through the separator was relatively slow and no difficulties with shorting occurred.

It is significant to note that cells of this type function satisfactorily, with the exception of anode replacement as previously noted, for discharge times in excess of the required 72 hours. As a matter of fact, cell #75 performed for a total of 156 hours at cell voltages in excess of 1.35 volts. This cell ran 107 hours after the replacement of the anode compartment. During the final 73 hours of discharge, no changes or additions were made to this cell. At the request of the NASA Technical Monitor, no further work was done with porous separators and solid cathodes.

3.2 RESISTIVITIES

Resistivities of membranes and separators used in complete cells assembled for discharge studies are given in Section 3.1. Those studies in which only resistivity of the membrane was measured are described in this section. These cells contained no electroactive materials.

A NaA membrane was formed by vacuum, hot pressing according to the procedure

TABLE V

PERFORMANCE OF THE CELL

Mg-Li-Al Alloy / LiCl, KCl // Glass frit // LiCl, KCl / CuO / Cu

Cell No. 75
Electrolyte weight 20.0 gms
CuO weight 9.75 gms

Current Drain: 5.0 mamps, 6.7 mamps/cm^2 of glass frit

Time Hours	Cell Voltage	iR Drop	Remarks
0	2.07	0.025	Start of test
6	1.53	--	Now operating as Mg anode
24	1.38	0.090	
30	1.88	0.090	Replaced anode
45	1.38	0.075	
49	2.11	--	Replaced anode & anode compartment.
53	1.95	0.075	
57	1.50	--	Now operating as an Mg anode
73	1.48	0.010	
83	--	--	Replaced anode
117	1.43	0.020	
141	1.41	0.020	
156	1.36	--	End of test, total time after replacement of anode compartment - 107 hrs. Total time after last replacement of anode - 73 hrs.

Cell testing stopped - tube forming anode compartment broke.

TABLE VI

PERFORMANCE OF THE CELL

Mg-Li-Al Alloy / LiCl, KCl // Glass frit // LiCl, KCl / CuO / W

Cell No. 76

Electrolyte weight 9.2 gms
Cathode weight 10.0 gms

Current Drain: 5.0 mamps, 6.7 mamps/cm^2 of glass frit

Time Hours	Cell Voltage	iR Drop	Remarks
0	2.01	0.014	Start of test
2	2.02	--	
7	1.56	--	Now operating as Mg anode
10	1.52	0.015	
16	1.46	0.065	
20	1.35	0.68	Replace anode, previous anode air oxidized due to lack of inert gas
25	1.05	0.60	
51	1.27	0.15	
69	1.70	0.10	Replace anode, add additional anolyte
75	1.36	0.10	Now operating as Mg anode
96	1.28	0.11	End of test

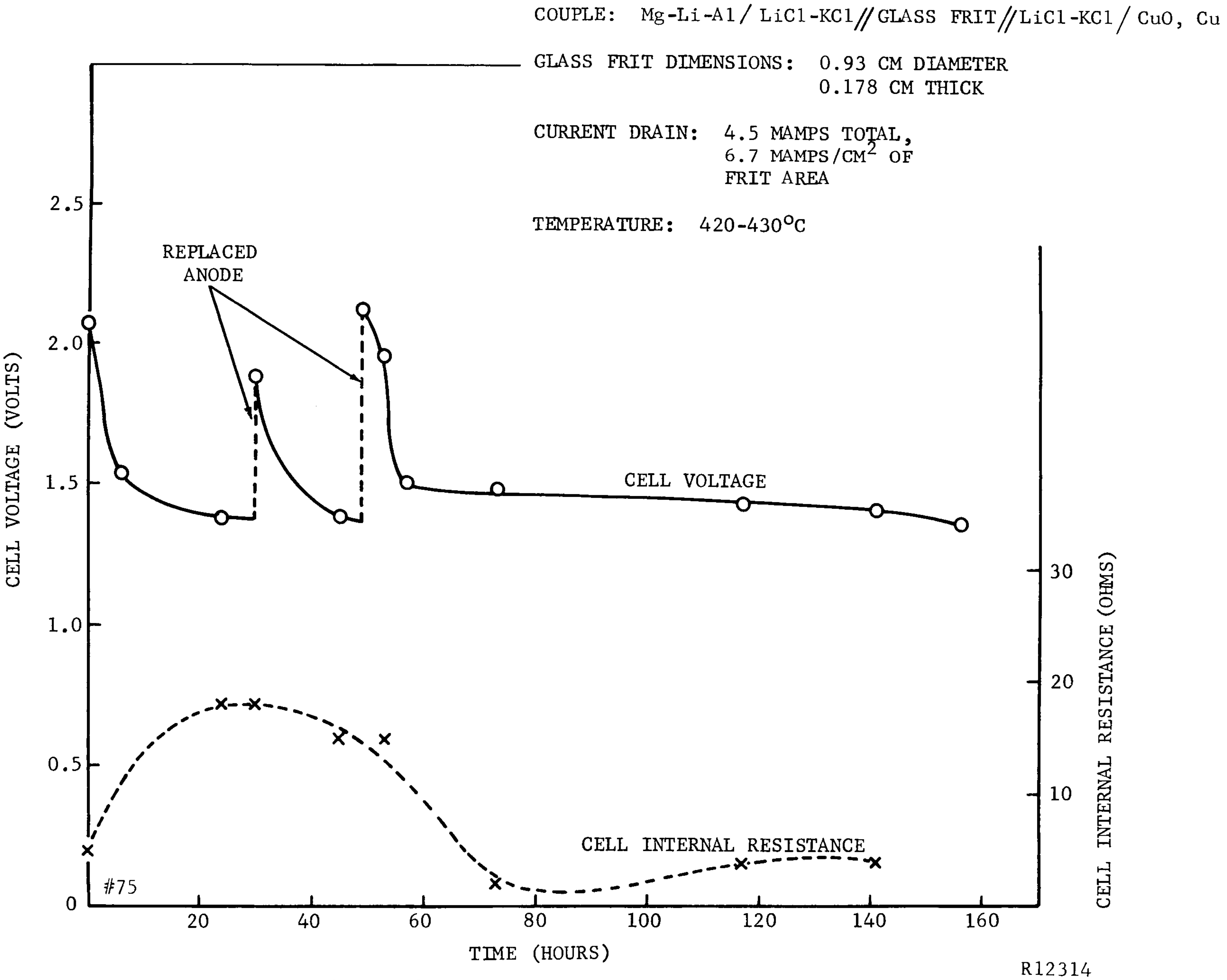

FIGURE 9. PERFORMANCE OF CELL NO. 75

given in Section 2.2.2 of the First Quarterly Report (3). Resistivites were measured as a function of time and temperature with an A.C. Conductivity Bridge using the cell shown in Figure 5a. The resistivities are shown in Table VII.

TABLE VII

RESISTIVITY OF NaA MEMBRANE

Time	Temperature (°C)	Resistivity (ohm-cm)
0	408	20,700
30 min.	441	4,680
60 min.	445	4,080
15 hrs. 55 min.	445	208

The membrane was found slightly crazed after the test but was otherwise intact. The bonding of RTV 560 to the membrane and the Pyrex tube appeared unaffected by the treatment. When breaking the zeolite membrane, glassy material could be observed in contrast with the initial porous aspect of the material.

Experiments were initiated to determine the effect of intercrystalline and intracrystalline inclusion of salts in membranes immersed in ionic melts on the resistivities of these membranes. These results were obtained in a cell of the type shown in Figure 5b. The membrane attached to its support tube was subjected to vacuum for various periods of time. Resistance value obtained while the membranes were under vacuum were very erratic. Therefore, all reported measurements were taken when the cell was at atmospheric pressure. The results of these resistivity measurements and the condition of the membrane are given in Table VIII.

Resistivities of a porcelain of high sodium content which had been subjected to ion exchange in molten $LiNO_3$ are given in Section 3.3 and Table IX.

3.3 ZEOLITE AND PORCELAIN ION EXCHANGE

The NaX zeolite was exchanged for lithium by repeated immersion in aqueous LiCl solutions and vacuum filtration as described in the Section 1.1.2 of the Second Quarterly Report (8). The exchanged zeolite was carefully washed by repeated suspension in distilled water and vacuum filtration until no chloride ion was detected in the filtrate using the silver nitrate test. At this point a sample of the washed zeolite was dissolved in nitric acid and again tested with silver nitrate. Only a trace of chloride ion was found. These tests indicate that both the external and internal surfaces of the zeolite crystallites were essentially free of exchanging salts. This point is important because it has been found that the resistivity results given for LiX in the Second Quarterly Report, Section 1.3.1 were actually for a sample which contained appreciable amounts of LiCl. To distinguish

TABLE VIII

RESISTIVITIES OF ZEOLITE MEMBRANES

Membrane Material	Tube Supporting Membrane	Sealant	Initial Resistivity (ohm-cm)	Final Resistivity (ohm-cm)	Duration of Impregnation	Remarks
Z-16 *	Pyrex	RTV 560	--	242	3 hours	Part of membrane separated off when retrieving tube from melt
Z-16 *	Pyrex	RTV 560	168K	248	12 hours	Membrane cracked
Z-16 *	Pyrex	RTV 560	6050	5300	5½ hours	Tiny cracks visible with magnifying instrument
Z-22	AV30	80-20 glass	845	365	40 minutes	Partial surface deterioration, no cracks
Z-22B	AV30	80-20 glass	154	154	30 minutes	Vacuum not used, membrane cracked
Z-22B	Corning 7052	80-20 glass	945	945	25 minutes	Failure of sealant
Z-22	AV30	80-20 glass	129	92	15-3/4 hours	Small cracks visible with microscope
Z-25	Pyrex	RTV 560	380K	3.79K	21½ hours	Sealed membrane heated to 400°C for ½ hr. before immersion in fused salt, wetting of membrane prevented by strong hydrophobic action induced by RTV 560.
Z-25	Corning 7052	80-20 glass	84	84	25 minutes	Membrane cracked
Z-25	Corning 7052	80-20 glass	108	108	25 minutes	Membrane cracked
NaX**	Pyrex	RTV 560	11.4K	13.9K	65 hours	Small cracks mostly near edge of membrane
NaX**	Pyrex	RTV 560	22K	228	65 hours	Small cracks, failure of sealant
LiX**	Pyrex	RTV 560	8.9K	2240	65 hours	Membrane cracked throughout; failure of sealant

* Sintered at 700°C for 30 min.

** Vacuum hot pressed.

these samples, the zeolite containing no LiCl was designated LiX-PJ.

The extent of exchange which was obtained will be determined by analyzing the zeolites for their lithium and sodium content using flame photometry.

Solutions of LiX were prepared for the determination of lithium by flame photometry using the following method. A 0.500 gram sample of finely ground LiX was placed in a platinum dish, moistened with water, and treated with three separate 5-ml portions of 48 per cent hydrofluoric acid, evaporating to near dryness after each addition. 10 ml. of 18 M sulfuric acid was added and the mixture was heated just to strong fumes of SO_3. The residue was taken up in 10 to 15 ml water and transferred to a Vycor test tube. The solution was evaporated to fumes and heated while delivering a slow stream of air above the solution from a quartz tube until all the sulfuric acid was removed. The residue was dissolved in 0.7 N sulfuric acid solution. Standard solutions were prepared with appropriate additions to compensate for the interfering effects of acidity and aluminum concentration as suggested by Brumbaugh and Fanus (9). The results of the flame photometry work with LiX and other exchanged zeolites were not completed during this reporting period.

Replacement of sodium ions with lithium ions in membranes made of special porcelain of high sodium content (NBS porcelain) was performed as follows. A pellet of this porcelain was sealed on AV30 tube (alumina) with a Pyroceram #45 glass seal. The alumina tube was partially filled with lithium nitrate melt and immersed in more of the melt at 290 ± 2°C. A second but unsealed pellet of the same material was also immersed in $LiNO_3$ melt.

After 24 hours of impregnation, tungsten electrodes were placed in the melts, inside and outside the alumina tube, and the resistance of the sealed membrane at 290° was evaluated as a function of time with an AC Conductivity Bridge at 1000 cps. The results aregiven in Table IX.

TABLE IX

RESISTIVITY OF LITHIUM EXCHANGED PORCELAIN

Time	Resistance (ohms)	Resistivity (ohm-cm)
24 hours	40.5	729
32 hours	30.5	549
46 hours	27.4	493
78 hours	26.0	468
118 hours	25.6	461

The membranes were found slightly crazed but strong and uncracked. The bonding of the membrane to the alumina tube appeared unaffected by the treatment. However, as previously reported (8), when the lithium nitrate is replaced with the LiCl-KCl eutectic, current flow through the porcelain caused extensive crazing.

3.4 MEMBRANE DEVELOPMENT

The primary objective of this portion of the program was the development of compatible zeolite membranes and seals. The secondary objective dealt with porous membrane substrates and nonzeolite membrane materials.

3.4.1 ZEOLITE MEMBRANE DEVELOPMENT

Membranes fabricated during this reporting period from the Type X zeolite are given in Table X. In this table, Z-14 and Z-16 were the best compositions evaluated containing the NaX zeolite. The sintering limits were determined by the results of the x-ray diffraction, i.e. 740°C/30 minutes for composition No. Z-14 containing 18 wt. % H_3PO_4 and 700°C/30 minutes for composition No. Z-16 containing 21 wt. % of sodium silicate.

With the introduction of the Mg-Li-Al alloy anode and LiCl-KCl electrolyte in the cell research, the development of lithium exchanged zeolite membranes was initiated. Composition numbers Z-21 through Z-27 in Table X describe preliminary experiments with the LiX prepared as described in the Second Quarterly Report (8). In these compositions it was clearly evident that the sintering temperature was very critical near 700°C and that exchanged zeolites, must be carefully washed. Residues of the exchanging chlorides were found to be very detrimental to good sintering behavior.

A new lot of lithium exchanged zeolite LiX-PJ, (described in Section 3.3 of this report) caused no sintering difficulty due to impurities. This zeolite was characterized as described in Table XI. The low melting and transformation point of the lithium exchanged zeolite LiX was very sharp at approximately 700°C. In the absence of a binder, an amorphous transformation appeared to be rapidly nucleated after 1 to 2 hours at 700°C. The unique properties of the exchanged zeolite offered the possibility of fabricating a binder free membrane. The main problem, of course, was to arrest the amorphous reaction sufficiently to develop bonding without loss of the zeolite structure. As shown in Table XI, LiX-PJ with no binder sintered at 700°C for 30 and 90 minutes retained good structure, but was soft to medium in hardness. Suitable structural integrity for the goals of this program require a "medium-hard" or "hard" scratch resistance.

The use of 18% H_3PO_4 as a binder provided satisfactory strength, however there was a compromise in the apparent crystal structure with the loss of peak intensities and "amorphous" swelling of the diffractagram. Reduction of the binder phase may decrease this effect. The most satisfactory sintering condition for Z-28 was 700°C/15 min.

As indicated in Table X, a limited amount of work was done using a #45

TABLE X

MEMBRANE FABRICATION DATA

Number	Material	Binder, Wt%	Sinter, °C/Min.	Structure and Remarks
Z-14	NaX	H_3PO_4, 18	740/30	Zeolite
Z-14	NaX	H_3PO_4, 18	850/30	Distort. Zeolite & Glassy Phase
Z-15	NaX	H_3PO_4, 10	780/30	Zeolite
Z-16	NaX	$Na_2Si_2O_5$, 21	700/30	Zeolite
Z-16	NaX	$Na_2Si_2O_5$, 21	780/30	Distorted Zeolite & Glassy Phase
Z-17	NaX	None	940/30	Unidentified Crystals & Glass
Z-19	NaX	None	Calcine 950/30 Sinter 1280/2hrs.	Glass
NBS	Clays	None	1150/2 hrs.	Mullite & Glass
Z-21	LiX	$Na_2Si_2O_5$,16	700/30	Blisters 4 pits during sintering - contains soluble salts
Z-22	LiX	H_3PO_4, 18	740/30	Same as Z-21
Z-22B	LiX(W)	H_3PO_4, 18	680/30	Washed LiX, Sealed to AV-30 Al_2O_3 tubes with #45 glass & 80/20(45/95)
Z-23	CaX_2	H_3PO_4, 18		
Z-24	NaX	#45 glass, 5	740/30	Insufficient strength
Z-25	LiX(W)	$Na_2Si_2O_5$, 16	680/30	Washed LiX Sealed to AV-30 tubes same as Z-22B
Z-26	NaX	#45 glass, 10	740/30	Insufficient strength
Z-27	NaX	#45 glass, 15	750/20	Good strength -"Amorphous"x-ray
Z-28	LiX-PJ	H_3PO_4, 18		See Table XI
Z-29	LiX-PJ	$Na_2Si_2O_5$, 16		Evaluation to be initiated.

TABLE XI

MEMBRANE FABRICATION DATA

Number	Material	Binder, Wt%	Sinter, °C/Min.	Dia., In.	Structure & Remarks
	LiX-PJ	None	700/30	.498	Diffraction Pks. Essentially same as raw material, soft
	LiX-PJ	None	800/30	.339	Amorphous x-ray, hard
	LiX-PJ	None	750/30	.368	Amorphous x-ray, hard
	LiX-PJ	None	690/overnite	.387	Amorphous x-ray, hard
	LiX-PJ	None	700/90	.474	Similar to 700/30, slight swell in background, medium
	LiX-PJ	None	690/180	.481	Soft
	LiX-PJ	None	700/120	.413	Sharp reduction in pk. intensity compared to 700/90, medium
	LiX-PJ	None	700/120	--	Amorphous x-ray, hard
Z-28	LiX-PJ	H_3PO_4, 18	Unfired		Weak diffraction, slight swell in background.
	LiX-PJ	H_3PO_4, 18	680/30	.470	Weaker than unfired, higher swell, medium
	LiX-PJ	H_3PO_4, 18	690/30	.461	Similar to 680/30, hard
	LiX-PJ	H_3PO_4, 18	700/30	.453	Similar to 680/30, hard
	LiX-PJ	H_3PO_4, 18	700/15	.462	Hard
	LiX-PJ	H_3PO_4, 18	680/120	.455	Hard
	LiX-PJ	H_3PO_4, 18	680/90	.460	Similar to 690/30, hard

Number	Material	Pressure, psi	Sinter, °C/Min.	Tot. Compress, mils	Remarks
HP-1	LiX-PJ	2450	600/55	2	Poor structural integrity, Alignment Prob., Soft
HP-2	LiX-PJ	2450	600/60	5	Poor structural integrity, Reduced fill, soft
HP-3	LiX-PJ	2450	650/30	20	Poor structural integrity, soft.
HP-4	LiX-PJ	4900	650/120	27	Sticking in die, sample fractured, medium.
HP-5	LiX-PJ	4900	700/45	49	First good pellet, good x-ray diffraction, medium hard.
HP-6	LiX-PJ	4900	700/120	20	Good pellet, medium hard.
HP-7	LiX-PJ	4900	720/90	66	Glass, excessive shrinkage & cracking, medium hard.

TABLE XI (Contd)

Number	Material	Pressure, psi	Sinter, °C/Min.	Tot. Compress, mils	Remarks
HP-8	LiX-PJ	7350	700/45	43	Good pellet, x-ray poor, mixed phases & amorph. swell
HP-9	LiX-PJ	7350	680/60	58	Similar to HP-8.
HP-10	LiX-PJ	7350	650/5½ hrs.	22	Good pellet, x-ray diffraction peak intensities and angles similar to raw material

glass as the binder. This glass is a Pyroceram material obtained from Corning Glass. Its composition is proprietary.

Hot pressing of the lithium exchanged zeolite was initiated in order to derive a "pure" zeolite for cell research free from the unknown perturbations of the binder materials. Also, hot pressing appeared to be the obvious approach for attaining high strength with a maximum of retained zeolite crystal structure, particularly with the temperature sensitive lithium exchanged zeolite.

Zeolite pellets 0.5 inches in diameter by 0.062 inches thick were hot pressed in alumina dies mounted in a small tube furnace contained between the platens of a small manual hydraulic press. A wash of -325 mesh Al_2O_3 was applied to the alumina punch faces to facilitate ejection of the pellet. The pressed pellets were subsequently lapped to remove traces of the wash before x-ray analysis.

Table XI, Membrane Fabrication Data, shows the work accomplished to date with hot pressed samples HP-1 through HP-10. As noted in Table XI the transformation of LiX-PJ was also critical when hot pressed near 700°C. The relatively high compression, 49 mils, of HP-5 was partially due to the compression of a Garlock 900 pad at the punch-platen interface. This has been replaced with a 10 mil thick platinum pad. Excellent x-ray diffraction comparisons were obtained in samples HP-5, 6, and 10. In particular, it was difficult to differentiate the x-ray diffraction patterns of HP-10 and the starting materials. Suitable strength and crystal structures were attained at 4900 psi at 700°C/2 hours and at 7350 psi, 650°C/5½ hours. Work is in progress at both pressure ranges to press and lap LiX-PJ membranes for evaluation and cell research.

3.4.2 NONZEOLITE MEMBRANE INVESTIGATION

During the course of this program, the compatibility of the zeolites with molten metals was found to be poor. This is generally attributed to an attack on the silicate. In an attempt to retain sodium as an anode material, an investigation of sodium aluminates containing P_2O_5 as a sintering aid was initiated. It was hoped that these compositions, having no silica, might withstand attack by molten sodium.

Table XII indicates the compositions selected for sintering evaluations. These compositions were selected on the basis of a K_2O, Al_2O_3, P_2O_5 phase diagram describing stable crystalline and noncrystalline areas by Z. N. Syritskaya (10). Composition C-9, made with 67 $NaPO_3$ and 33 Al_2O_3 (wt %) to yield a theoretical composition of 33.3 Na_2O, 33.3 Al_2O_3, and 33.3 P_2O_5 (mole %) was polycrystalline, nonhydroscopic, and structurally sound after sintering at 700°C for 16 hours. Subsequent liquid sodium compatibility tests were negative (Section 3.6). Further development was discontinued when the cell research was focused on the use of Mg-Li-Al anode materials in preference to sodium.

TABLE XII

SODIUM ALUMINUM-PHOSPHATE COMPOSITIONS

No.	Mole % Na_2O	Mole % Al_2O_3	Mole % P_2O_5
C-5	50.0	46.2	3.8
C-7	50.0	43.4	6.6
C-8	40.0	40.0	20.0
C-9	33.3	33.3	33.3
C-10	10.0	22.5	67.5
C-11	20.0	20.0	60.0

3.4.3 POROUS MEMBRANE SUPPORTS

Porous membrane supports were fabricated by dry pressing and sintering. The objective of this work was to develop a porous material thermally compatible with the zeolite membranes. This approach would allow the fabrication of 2 inch diameter 10 mil membranes with the thicker porous substrate providing the structural strength.

Table XIII Porous Membrane Substrate Materials, describes the materials fabricated. The ZrO_2 materials were selected to provide a match for the high expansion zeolites, approximately $10 \times 10^{-6}/^{\circ}C$. All materials fabricated contained open pore structures as shown by their relatively high porosities determined from water absorption measurements. A 2 inch disc, 1/16 inch thick of composition S-4, Table XIII, containing 90% Al_2O_3, 7% H_3PO_4, and 3% ball clay was sintered and lapped. A similar 2 inch disc of zeolite composition Z-14 was sintered and lapped for mating to the S-4 substrate. An edge seal of the 80/20 Pyroceram blend was successfully achieved between the S-4 substrate and the Z-14 zeolite. The Z-14 disc was approximately 15 mils thick.

The material AL-300, shown in Table XIII is a raw alumina material in block form supplied by Western Gold and Platinum Co., Belmont, California. Discs machined from AL-300 were sintered at 1400°C/16 hrs. and 1500°C/2½ hours. Their respective porosities of 39 and 15 % show the latitude one may have for the development of porous substrates. High temperatures will completely vitrify the material. AL-300 also exhibits excellent strength at 10-15 mils. In addition to substrate applications this material may also be useful as a membrane. The use of these materials as porous separators is given in Section 3.1.2.

3.5 SEALING AND CELL FABRICATION METHODS

The elasticity displayed by silicone rubber compounds such as General

TABLE XIII

POROUS MEMBRANE SUBSTRATE MATERIALS

Number	Material, Wt %	Sinter °C/Hrs.	% Porosity	Remarks
S-1	100 RMB-4F Ramming Mix (Zircoa)	1200/15	--	Strong, porous, ZrO_2 plate
S-2	88 RMB-4F, 17 No.36F Grain (Zircoa)	1400/4	27	Strong, porous, ZrO_2 plate
S-3	70 Al_2O_3* (-100 m.), 18 Al_2O_3* (-325m) 12 H_3PO_4	1400/4	14	Strong, porous Al_2O_3 plate, poor green strength
S-4	60 Al_2O_3* (-100 m.), 30 Al_2O_3* (-325 m.) 7 H_3PO_4, 3 OM48 clay	1400/4	25	Better green strength
S-5	91 Al_2O_3 (-325 m.), 9 QS-13 Pemco Frit	1000/10	34	Good strength
Al-300	Wesgo Product, 96% Al_2O_3	1400/16	39	Excellent strength @ 12-15 mil thick
Al-300	Wesgo Product, 96% Al_2O_3	1500/2½	15	Excellent strength @ 12-15 mil thick

* Alcoa Tabular Alumina T-61

Electric RTV 560 at temperatures up to 400°C is a specifically desirable attribute in the bonding of zeolite type membranes to supporting tubes because of the apparent shrinkage observed in these membranes when immersed in fused salts. RTV 560 has been extensively used as a sealant for these membranes in our studies in spite of the lyophobic action apparently created by a silicone film spreading from the sealant or vapor deposited on all surfaces in the vicinity of the bonded sites. Since the silicone film was destroyed by sodium and cuprous chloride melts in initial cell experiments, the effect of the lyophobic film on the apparent resistivity of membranes was not truly evaluated until the active ingredients in the cells were separated from the membranes by the inert LiCl-KCl eutectic melt. In recent instances membranes bonded to supporting tubes with RTV 560 were found to be "nonwetted" by the molten LiCl-KCl even after 24 hour immersion at 400°C.

Other sealing techniques were attempted using glass resins (Owens-Illinois Type 100) mixed with about 20% by weight of powdered mica. The mixture gave a satisfactory bond with metals such as nickel but not with glass or alumina in our experimental cells.

The eventual battery configuration, as described in the Second Quarterly Report, was designed to utilize an alumina ring for membrane support and to provide sealing surfaces for Kovar bellows on each side for the anode and cathode compartments. Suitable sealing glasses were required to mount the membrane and its support on a step in the I.D. of the alumina ring. The feasibility of this approach was applied to the development of glass seals between membranes and ½" diameter 96% alumina tubes (McDanel AV-30).

Dilatometry experiments and data were accumulated for the materials of interest in order to determine their thermal limitations. Table XIV indicates that in general, the zeolite materials exhibited thermal expansions similar to Al_2O_3. However, the development of a glass phase in these materials causes a significant change in their thermal coefficients, i.e. Z-14 sintered 850°C/30 min.

Sealing techniques were devised using Pyroceram glasses 45 and 95. Thermal coefficients of the sealing glass were modified by blending glasses 45 and 95. Z-16 membranes were readily bonded to ½" diameter McDanel AV-30 alumina tubes with an 80/20 ratio of glass 45 to glass 95. The lower fusion point of glass 95 also improved the wetting of the intersurfaces during sealing. Sealing was performed in a small tube furnace between 670°C and 700°C for 5 to 7 minutes. The time and temperature being governed by the transformation temperature of the particular zeolite composition. Z-16 membranes were readily bonded to ½" diameter McDanel AV-30 alumina tubes with an 80/20 ratio of glass 45 to glass 95. The lower fusion point of glass 95 also improved the wetting of the intersurfaces during sealing. These glasses have exhibited excellent resistance to attack by the LiCl-KCl electrolyte and molten CuCl. In some cases, successful glass seals with the 80/20 glass were made between phosphate and sodium silicate bonded lithium zeolites and AV-30 alumina or kovar glass. More effort is needed, though, to improve the reliability of the sealing technique.

TABLE XIV

COMPARISON OF THERMAL COEFFICIENTS OF EXPANSION

Material	αin/in/°C x 10^{-6}	Temp. Range °C	Remarks
Z-14	6.62	25-600	Sintered 740°C/30 Min.
Z-14	9.38	25-600	Sintered 850°C/30 Min.
Z-16	7.61	25-600	Sintered 700°C/30 Min.
Z-19	14.02	25-600	
NBS	5.00	25-600	
Al_2O_3	6.89	25-600	ΔRR Morganite
Pyrex (7740)	3.25	25-500	
Na-Ca Glass (0800)	9.2	0-300	Literature
Kovar Glass (7056)	5.1	0-300	Literature
ZrO_2	10.0	0-1000	Literature CaO Stabilized
Rodar or Kovar	5.7	30-500	Mfrs. Data

Initial sealing experiments with the LiX zeolites indicated that these materials had a relatively low thermal coefficient of expansion. Dilatometry is planned to determine the extent of this variation.

3.6 COMPATIBILITY TESTS

Preliminary cell tests indicated a possible reaction between the sodium anode and the zeolite separator. Therefore early in the Third Quarter, a series of experiments were run to better define the compatibilities of these materials. In these tests the proposed separator in the form of a thin pellet and an excess of the alkali metal were sealed in Pyrex ampules under vacuum. The alkali metal was chosen to match the cation of the separator. The ampules were then placed in a muffle furnace at 425°C (800°F) for 72 hours. After this time period, the ampules were opened and the excess alkali metal removed by reaction with methanol or ethanol. The following separator compositions were tested during this past quarter: Z-14 sintered at 740°, Z-14 fired at 850°, Z-16 sintered at 700°, Z-16 fired at 780°, Z-17 fired at 940°, NBS porcelain, and pellets of NaX, NaY, KA and LiX formed by vacuum, hot pressing. (See Table X for a further description of the sample fabrication data.) Subsequent experiments have shown that this sample of LiX also contained LiCl. Similar results were found with the porcelain and with all zeolite samples -- disintegration of the pellet and formation of a dark powder.

As part of the final effort to use a sodium anode, the compatibility of the following materials with metallic sodium for 72 hours at 425°C was determined in the usual manner: a sodium-alumino-phosphate material designated C-9, a laminate of the NBS porcelain on porous ZrO_2, and a vacuum, hot pressed cylinder of NaX vacuum impregnated with molten LiCl-KCl. After exposure, the alumino-phosphate material was completely disintegrated leaving a dark sludge. Although the ceramic on zirconia appeared to be in one piece it was completely blackened and could not be handled without breakage. Impregnation of the zeolite with LiCl-KCl did not improve the compatibility with molten sodium--the results were the same as before--darkening and disintegration of the zeolite in contact with the sodium. As a result of these compatibility tests, the use of molten alkali metals as anodes with separators of this type was dropped from consideration. Further studies involving anodes will probably be made with solid magnesium or magnesium alloys.

In anticipation of fabrication of prototype cells, the compatibilities of some of the proposed components were determined. Samples of 9.5 mil pellets of NaX bonded with $Na_2Si_2O_5$, Kovar A (composition 29% Ni, 17% Co, 0.3% Mn, bal. Fe) and an Au-Cu brazing alloy (Incoro 60) were sealed in ampoules containing either the LiCl-KCl eutectic or a mixture of CuCl containing 10 mole per cent KCl. After 72 hours at 425°C, the samples were examined. The zeolite pellets were fragile; even before treatment one of the samples cracked. The zeolite in contact with the LiCl-KCl remained in one piece while in the molten salt but cracked after washing and drying. The sample of Kovar in contact with LiCl-KCl showed no apparent reaction with about a 1% total weight loss. The Kovar sample in contact with CuCl-KCl showed a weight gain of 14% due to a grainy but apparently protective deposit of Cu. The sample of brazing alloy in contact with LiCl-KCl showed a 0.25% weight loss and a slight green color in the fused salt. No measurements were made upon the sample in contact with CuCl-KCl since it broke into several small pieces, all of which could not be recovered. No further experiments on the alloy could be completed because of the small amount of sample available.

SECTION 4

FUTURE WORK

During the next Quarter, efforts will be concentrated in the following areas:

1. Ion exchange studies and analysis to determine the extent of exchange which occurs between NaX and

   a. Aqueous LiCl
   b. Aqueous LiCl-KCl of the eutectic composition
   c. Molten LiCl-KCl eutectic
   d. Molten CuCl

2. Bonding techniques with particular emphasis on hot pressing LiX to determine the conditions for maximum strength without the loss of the zeolite structure.

3. Effect of immersion in molten salts on the strength and composition of zeolite membranes.

4. Development of suitable composition for sealing zeolite membranes to inert supports.

5. Upon development of suitable sealing techniques determination of the resistivity of LiX membranes in fused salts.

6. For membranes which perform satisfactorily in the molten salt and resistivity tests, determination of performance in experimental cells with a Mg anode and a CuCl cathode.

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APPENDIX

VOLUME CHANGE IN TYPE X ZEOLITE

The Type X zeolites have a face-centered, cubic structure. The length of the unit cell, a_o, can be determined from the equation

$$a_o = d_{hkl} (h^2 + k^2 + l^2)^{1/2}$$

where d_{hkl} is the spacing for the crystal plane having the indices h, k, and l.

The data for NaX and LiX given in the following table is taken from Table II of reference 8.

CRYSTAL PARAMETERS OF NaX and LiX

	LiX(59% exchanged)		NaX	
$h^2+k^2+l^2$	d_{hkl}	a_o	d_{hkl}	a_o
3	14.37	24.889	14.47	25.062
8	8.79	24.858	8.85	25.028
11	7.49	24.844	7.54	25.010
19	5.70	24.846	5.73	24.977
27	4.79	24.889	4.81	24.993
32	4.40	24.891	4.42	25.004
35	4.21	24.906	4.23	25.025
40	3.931	24.864	3.946	24.958
43	3.794	24.877	3.808	24.969
44	3.749	24.867	3.765	24.973
Averages		24.873 ± 0.021		25.000 ± 0.032

Since these zeolites have a cubic structure, the volume of the unit cell is

$$V_o = a_o^3$$

For LiX $V_o = 1.5388 \times 10^4$

NaX $V_o = 1.5625 \times 10^4$

Volume Change 1.52%

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