FINAL REPORT

INVESTIGATION OF SOLID STATE ELECTROLYTE SILVER-ZINC BATTERY

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Contract No.: NAS5-21033

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for

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

FINAL REPORT
for
INVESTIGATION OF SOLID STATE ELECTROLYTE SILVER-ZINC BATTERY

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Goddard Space Flight Center

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ABSTRACT

Study of the solid electrolyte $ZnCl_2 \cdot 2NH_3$ rechargeable silver zinc electrochemical cell by X-ray diffraction analysis of the reaction products led to the following tentative electrode reactions during discharge:

$$11\ Zn + 22\ AgCl + 12\ ZnCl_2 \cdot 2NH_3 + 24\ H_2O$$

$$\underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}}\ 8\ ZnCl_2 \cdot 3NH_4Cl + 3ZnCl_2 \cdot 4Zn(OH)_2 + 22\ Ag$$

This equation leads to the conclusion that some water is consumed when the cell is discharged.

Replacement of $ZnCl_2 \cdot 2NH_3$ by $ZnCl_2 \cdot 4Zn(OH)_2$ gave cells with high internal resistance and limited capacity. The salt formed by exposing a fibrous membrane saturated with $ZnCl_2$ solution to fumes from ammonium carbonate in a dry desiccator comprised $ZnCl_2 \cdot 4Zn(OH)_2$, $ZnCl_2 \cdot 3NH_4Cl$ and a third unidentified component. This electrolyte was used in most of the work prior to this contract.

The temperature coefficient of open circuit EMF was nearly zero over the range from -25°C to 50°C. The internal resistance and polarization increased substantially below -25°C. There is some indication that exposure to 50°C for 29 hours causes some deterioration.

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1. INTRODUCTION

The subject of this investigation is a silver-zinc solid electrolyte electrochemical system discovered by Melpar.* The feasibility of using this cell as a rechargeable energy storage device has been proved in the work performed at Melpar on another NASA contract.[1] In this work it was demonstrated that cells of this type could be operated for more than 30 charge-discharge cycles at temperatures as low as -30°C.

Certain attractive features of this system are:

1. High Energy Density

   The theoretical energy density is about 60 watt hours per pound of active ingredients, which compares favorably with the nickel cadmium cell and other miniature rechargeable batteries.

2. Large Area Structures

   This feature permits very flexible design. Thus, in a balloon battery, the weight aspect density can be controlled by spreading the battery over a large area. In manpack radios the battery can be spread out over the interior of the case.

3. Solid Electrolyte

   There is no liquid to add to the weight, spill or corrode. As far as we are now aware, no gas is liberated on overcharging.

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* Patent Pending

[1] Contract NAS5-11588

The silver-zinc electrochemical system with liquid alkaline electrolyte is not new.[2] In addition to the undesirable liquid electrolyte, disadvantages include failure to realize the theoretical energy density, and problems in obtaining a large number of cycles at a high depth of discharge.

Earlier work on silver-zinc cells included the zinc-silver chloride couple, but with liquid electrolytes, such as calcium chloride solutions. The principal application was in medical equipment and as a reserve battery. Serious deficiencies of the conventional system (having a liquid electrolyte) are silver migration and zinc dendrite formation, ultimately leading to cell failure.[3]

In the solid electrolyte cells reported here those problems are minimized. Instead of migration of silver ions and zinc dendrite formation, the electrolyte undergoes chemical changes during charge-discharge cycling. The primary purpose of the study covered by this report is to determine the cell reaction(s) and identify the reaction products.

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2 "High Energy Batteries," Rammond Jasinkski. Plenum Press N. Y. 1967, pp. 268-70, 277-8.

3 George W. Vinal, "Primary Batteries," p. 279; D. A. Ginger, J. S. Burton, G. C. H. Farmer Paper #32. Proc. 3rd Int. Symposium - R&D in Non-Mechanical Power Sources - Bournemouth pp. 453-64, 1963.

2 EXPERIMENTAL RESULTS

The following steps were taken to determine the cell reaction:

a. X-ray diffraction analysis of the electrolyte before and after discharge.

b. Determination of the effect of moisture content on the cell conductivity.

c. Analysis of moisture isotherms to determine possible existence of hydrates.

d. Effect of variation in electrolyte composition on products formed when cell is discharged.

2.1 PREPARATION AND CHARACTERIZATION OF ELECTROLYTE MATERIALS

In the initial form of the cells, pellets of $ZnCl_2.2NH$, were positioned between AgCl and Zn electrodes. Such cells served for characterization of the reaction products, but due to the thickness required for coherency the pellets and their brittleness, they were unsuitable for practical use.

A later version, more suitable for film structures, had the electrolyte formed by impregnating a fibrous membrane with zinc chloride solution and exposing the wet membrane to fumes omitted by $(NH_4)_2CO_3$ in a closed chamber containing a desiccant.

2.1.1 $ZnCl_2.2NH_3$

The diammine is obtained from a saturated solution of $ZnCl_2$ by adding NH_4OH to complete solution, followed by concentrated HCl to form NH_4Cl and precipitate $ZnCl_2.2NH_3$. Chemical analysis was as follows:

	Preparation 2769-1 Found	$ZnCl_2.2NH_3$ Calculated
Zinc (gravimetric as $Zn_2P_2O_7$)	37.25 37.28 37.34	38.38
Chlorine (gravimetric as AgCl)	42.06 42.06	41.62
Ammonia (by distillation and titration)	20.36 19.93	20.00

X-ray diffraction analysis was made using Cu K_d radiation on Siemens Crystalloflex Equipment. Powder patterns were obtained by diffractometer techniques rather than film techniques. Agreement with ASTM card 1-165 and other published work[4] was sufficient to identify the material, as shown in Table 1.

2.1.2 $ZnCl_2 \cdot 3NH_4Cl$

This compound found in cells which had been repeatedly discharged and charged has been tentatively identified as a component of the electrolyte of partially discharged cells. It was synthesized by crystallization from a solution containing equal weights of $ZnCl_2$ and NH_4Cl. Chemical analysis revealed the following:

	Preparation 149-1 Found		$ZnCl_2$ $3NH_4Cl$
	1st Crop	2nd crop	Calculated
Zinc (gravimetric as $Zn_2P_2O_7$)	21.73 21.84	21.67 21.51	22.03
Chlorine (gravimetric as AgCl)	58.50 58.41	58.03 58.16	59.73
Ammonia (by distillation and titration)	17.06 17.19	16.95 16.92	17.21

The material was subjected to X-ray diffraction analysis as shown in Table 2. There is good agreement with the published results given on ASTM Card 2-584:

2.1.3 $ZnCl_2 \cdot 4Zn(OH)_2$

This basic zinc salt has been identified in some cells containing fibrous separators. It was synthesized by ball milling the calculated formula weight of zinc chloride (136 g) and ainc oxide (325 g) with 600 ml water for three days, collecting the precipitate on a filter and drying at 95°C.

Chemical Analysis was:

	Preparation 115-1 Found	$ZnCl_2$ $4Zn(OH)_2$ Calculated
Zinc (gravimetric as $Zn_2P_2O_7$)	59.56 60.02	61.24
Chlorine (gravimetric as AgCl)	12.45 13.12	13.28

X-ray diffraction analysis as shown in Table 3 is in good agreement with the ASTM Card 7-155.

4 O. Erämetsä and A. Ryhänen - Suomen Kemistilehts, B 39 (12) 277-80 (1966).

2.1.4 Material Obtained by Exposing $ZnCl_2$ Solution to Fumes From $(NH_4)_2 CO_3$.

This was originally believed to be a convenient way of obtaining $ZnCl_2.2NH_3$, but analysis showed that different products were obtained, depending on whether the material was converted in bulk, or after impregnation of paper.

2.1.4.1 Conversion in Bulk: The procedure was to place 3.60 frams of anhydrous $ZnCl_2$ in a small dish and add 2 ml water. When solution was complete the dish was placed in a desiccator containing "Dri-Rite" desiccant and $(NH_4)_2 CO_3$ crystals. After 3 hours, the material was nearly solid, and after 24 hours it reached approximately constant weight. The gain in weight was 20%. This compared with the calculated gain of 25% for the reaction $ZnCl_2 + 2NH_3 \rightarrow ZnCl_2.2NH_3$.

However, X-ray diffraction analysis as presented in Table 4 col.1 shows the presence of $ZnCl_2.2NH_4Cl$, and an unidentified component, possibly a basic zinc salt, or a carbonate, required for stoichiometric balance. Wet chemical analysis gave 40.21%Zn, 41.76%Cl, and 8.67%NH_3, or a mole ratio of 1.00:1.42:0.83. The insufficiency of chlorine also indicates the presence of basic salt.

In a variation of the above, solid NH_4Cl was added to the zinc chloride solution and then exposed to ammonium carbonate fumes in a dry desiccator. In this case, the end product was $ZnCl_2.2NH_4Cl$ with NH_4Cl and some unidentified material, which resembles $ZnCl_2.4Zn(OH)_2$, Table 4, col. 2.

When solid $ZnCl_2.2NH_3$ was mixed with the zinc chloride solution, the product after conversion was nearly all $ZnCl_2.2NH_3$ with possibly a small amount of $ZnCl_2.2NH_4Cl$, Table 5.

2.1.4.2 Conversion of Impregnated Paper: The electrolyte used in the vast majority of the cells made during the contract period comprised filter paper* impregnated with concentrated zinc chloride solution, and then "converted" in a desiccator containing ammonium carbonate and Dri-Rite. The end product was initially assumed to be zinc chloride diammine, $ZnCl_2.2NH_3$, but subsequent analysis by X-ray diffraction indicated the probable composition as $ZnCl_2.3NH_4Cl$, $ZnCl_2.4Zn(OH)_2$ and some unidentified component(s), as shown in Table 5. Impregnating the paper with $ZnCl_2 + ZnCl_2.2NH_3$, followed by conversion yielded $ZnCl_2.2NH_4Cl$, $ZnCl_2.3NH_4Cl$, $ZnCl_2.4Zn(OH)_2$, in addition to the $ZnCl_2.2NH_3$ as shown in Table 5.

2.2 Hydration of Electrolytes

2.2.1 Absorption Isotherm

In earlier work, it had been shown that, after stabilizing the electrolyte in a bone-dry atmosphere, the resistivity was so high

* Whatman #50 is particularly effective

that significant current could not be obtained. On the other hand after stabilizing at very high humidity some liquid phase was produced.

In an attempt to establish the amount of moisture required, and its state of combination, the weight of water absorbed under equilibrium conditions at varying humidities was determined. The relative humidity required was produced in a closed chamber containing a saturated solution of the proper salt. The following series of humidities were used.

Salt	Relative Humidity at 25°C
$NaBrO_3$	92%
$ZnSO_4 \cdot 7H_2O$	90%
KCl	86%
$(NH_4)_2SO_4$	80%
NaCl	75%
$CuCl_2$	67%
NaBr	57%
Dri-Rite Desiccant	9%

About 0.2-g samples were weighed out in small glass beakers and placed in large desiccators containing the above materials. The beaker and sample were weighed periodically and the percent change in weight calculated. The results for $ZnCl_2 \cdot 2NH_3$ are shown in Figure 1. Equilibrium appears to have been reached in humidities up to 86%. The amount of water absorbed increases regularly with increasing R.H. At 86% R.H. and above, the presence of liquid phase was observed. At 92% R.H. the amount of water taken up in 400 hours amounted to over 50% of the original sample weight. The wet sample was placed in a desiccator containing Dri-Rite and it returned to its original dry weight in 48 hours. X-ray diffraction analysis showed the diammine pattern.

The basic salt $ZnCl_2 \cdot 4Zn(OH)_2$ absorbed little moisture even in 92% R.H. The percent moisture absorbed at equilibrium with the indicated humidity was as follows:

R.H.	Percent Absorbed
57%	1.5
67%	1.8
75%	1.9
80%	1.9
86%	2.1
90%	2.3
92%	2.0

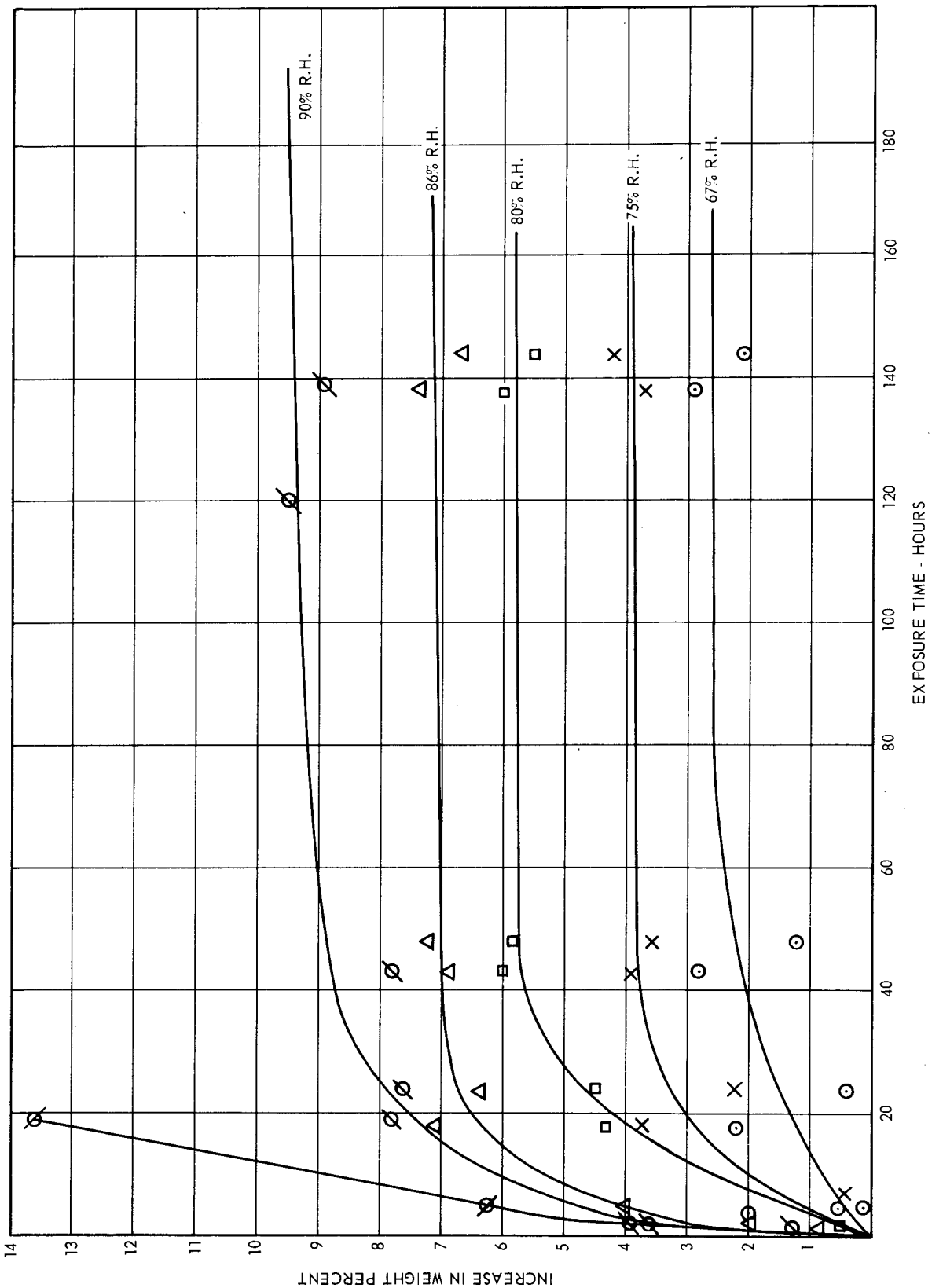

Figure 1. Exposure of $ZnCl_2 \cdot 2NH_3$ to Various Relative Humidities

The double salt $ZnCl_2 \cdot 3NH_4Cl$ was also exposed to the series of controlled humidities. It absorbed moisture rapidly in humidities above 57% and soon liquified completely, similar to the behavior of zinc chloride.

2.2.2 Differential Thermal Analysis*

As another approach to the determination of the state of combination of water in $ZnCl_2 \cdot 2NH_3$, representative samples were subjected to differential thermal analysis (Figures 2 to 4). The following bands, all endorthermic, were identified.

Band No. 1 - This is a broad band, appearing in all samples which had been exposed to high humidity. The upper curves in figures 3 and 4 were ob-ained during the initial cycle which stopped at 225°, after which the samples were cooled to room temperature. The lower curve was obtained by reheating without exposure to moist air. The band designated No. 1 in the figures starts at about 60° to 75°C and has a minimum at about 115°C. It does not appear in Figure 2, which was obtained with dry material, nor in the lower curves of Figures 3 and 4 where the material was reheated. It appears safe to conclude that this band is due to the latent heat of evaporation of water.

Band No. 2 - This band at 150° is obtained only in samples previously reheated to 225° independent of previous exposure to moisture.

Band No. 3 - A small band at about 200°, which does not appear when the material is reheated. This, together with band No. 2 indicates an irreversible change.

Band No. 4 - A large band at 240-250° where the material melts or decomposes.

In summary, the DTA results show that hydrated $ZnCl_2 \cdot 2NH_3$ loses its water over the range 60° to 115°C.; it undergoes an irreversible change at 200°C to another form which undergoes a further change at 150°. The material decomposes or melts at 240-250°.

In order to get some understanding of the changes above 100°, a dry sample of $ZnCl_2 \cdot 2NH_3$ was slowly heated to 220° and held for one hour. The sample melted and lost about 20% of its original weight, and remained a clear glass at room temperature. Reheating to 170° produced no visible change. The material after the heating to 220° showed some of the X-ray diffraction lines of $ZnCl_2 \cdot 2NH_3$, with many lines missing, and with other unidentified lines--Table 6. The reheated sample showed very little resolution as would be expected from a glass. Both samples were very hygroscopic, more like $ZnCl_2$ than $ZnCl_2 \cdot 2NH_3$.

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* Run at GSFC with the assistance of Mr. William Campbell.

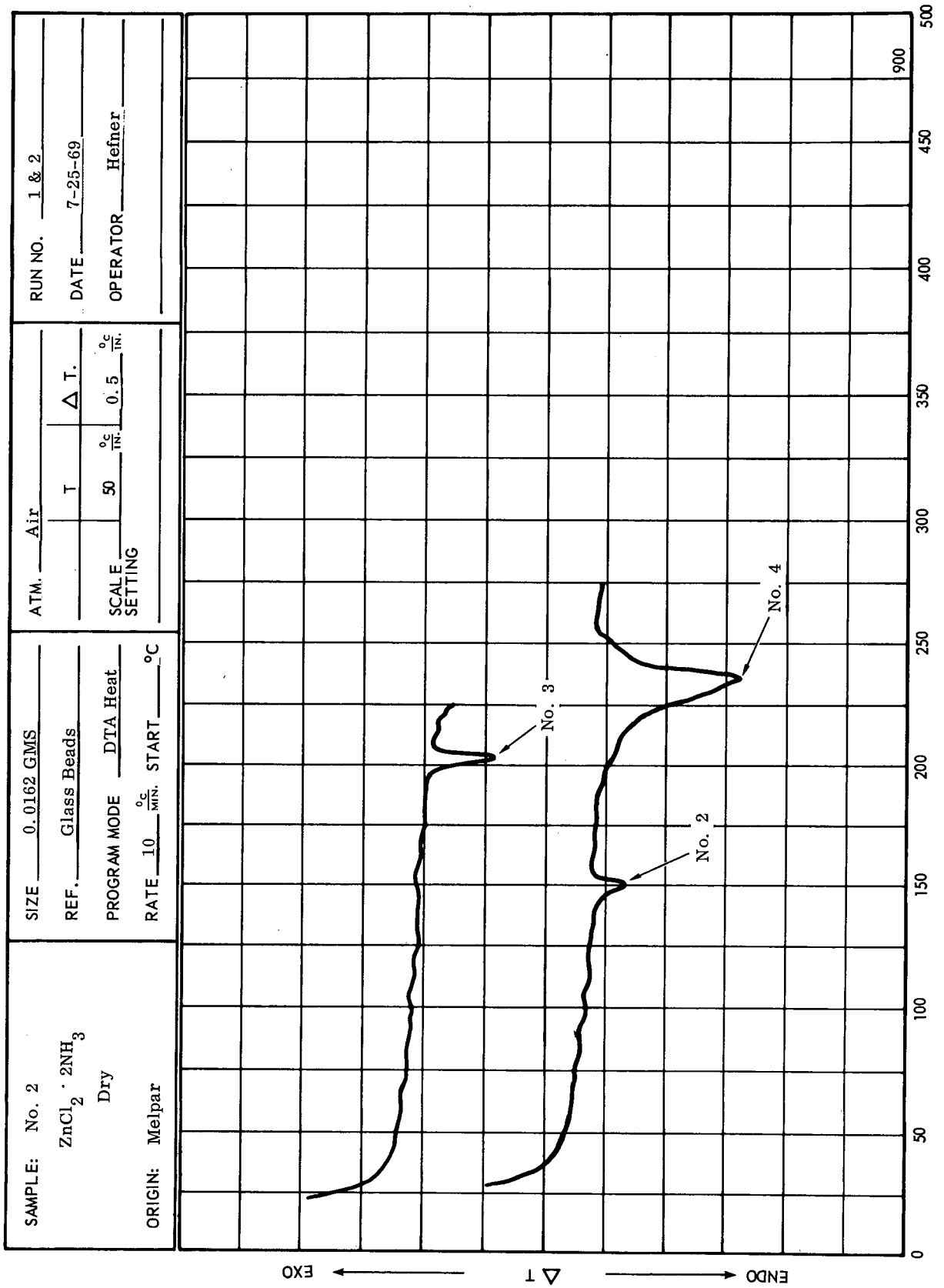

Figure 2. DTA Diagram of Dry $ZnCl_2 \cdot 2NH_3$

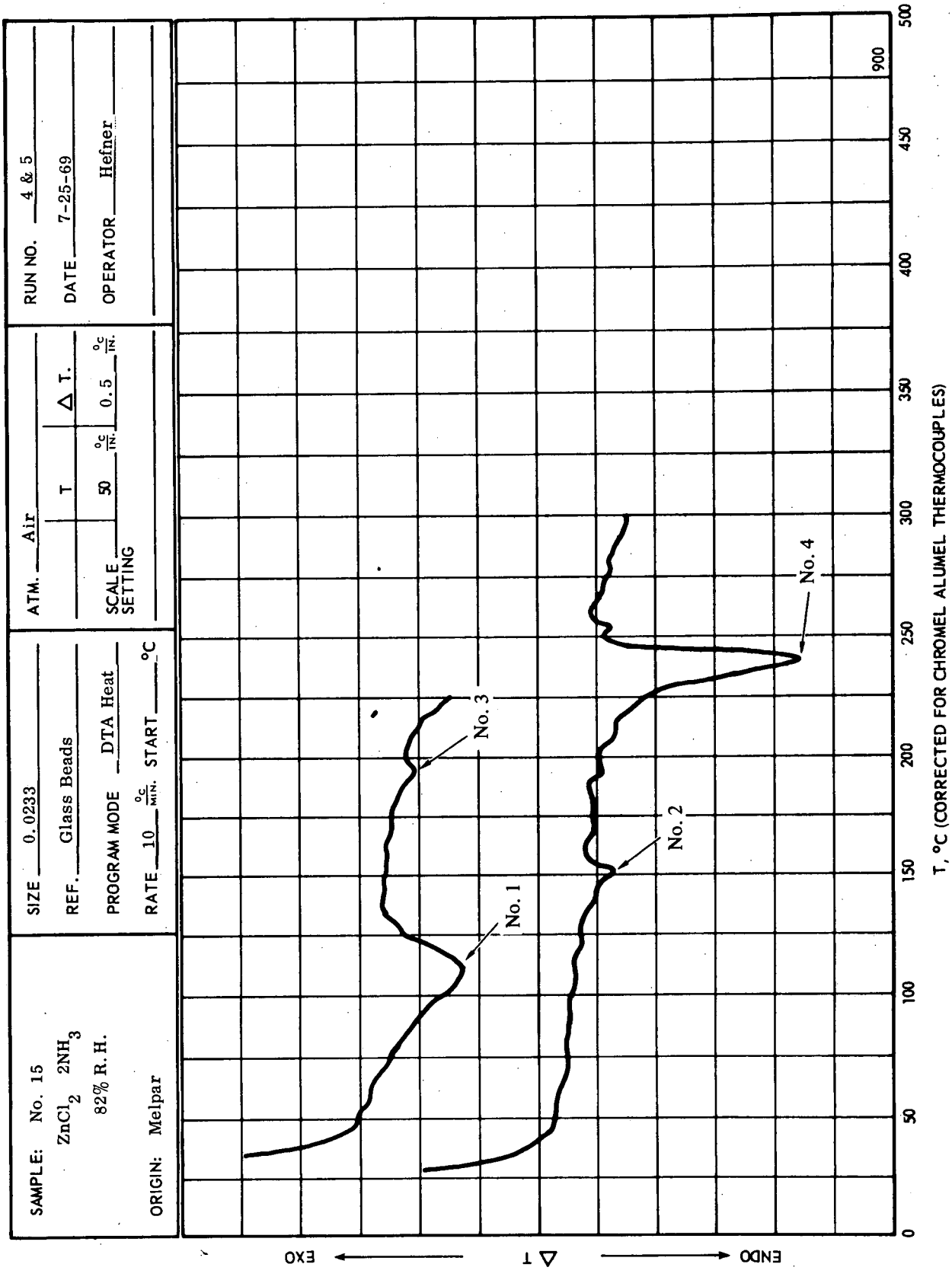

Figure 3. DTA Diagram of $ZnCl_2 \cdot 2NH_3$ Equilibrated at 82% R.H.

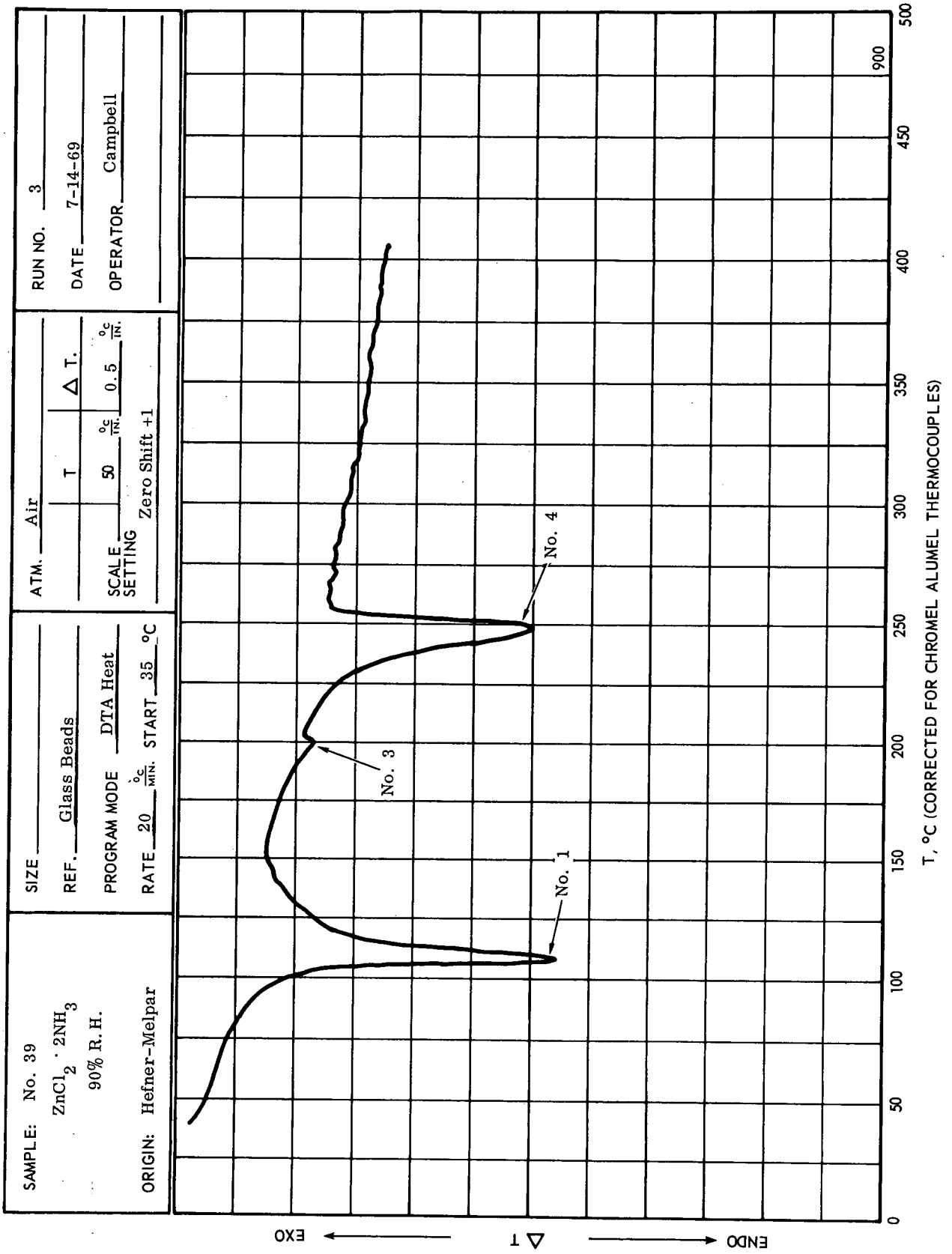

Figure 4. DTA Diagram of $ZnCl_2 \cdot 2NH_3$ Equilibrated at 90% R.H.

The basic salt ($ZnCl_2$ $4Zn(OH)_2$) was also subjected to DTA, both before and after hydration (Figures 5 and 6). Both samples showed virtually identical curves, with two endothermic bands, with minima at 190°-200° and 265°. The former may be the resultant of two bands, very close together.

2.2.3 Relation of Hydration to Conductivity of $ZnCl_2 \cdot 2NH_3$

Pellets were pressed from this material at 15,000 lbs. psi. The weight was 2 g., the diameter 27 mm, thickness 1.7 mm and volume 0.97 cm^3 after pressing. The pellets were conditioned in a series of humidities for two days, after which the resistance was measured on an ac bridge using graphite electrodes.

The results are shown in Table 7, as a function of the moisture content. The latter was interpolated from Figure 1 of this report. It is apparent that the conductivity becomes significant when an appreciable amount of water is taken up - R.H. 67% or 2.2% H_2O and reaches a practical value for cells at about R.H. 80% or 5.8% H_2O.

2.3 Cell Structures

2.3.1 Design Considerations

The structure of all experimental cells is shown in figure 7. The size selected for convenience of fabrication and testing has an active surface of 5cm^2. Obviously this area can be extended or reduced larger or smaller capacity. Several cells can be stacked in series for higher voltage or in parallel for higher current.

The plastic films A, C, and F are chemically resistant adhesive tape. The metal parts are cleaned by standard laboratory methods. The silver electrode B - 0.04mm thick is covered by film C and partly converted to silver chloride by anodization in a chloride bath, to E, 0.05mm thick, is covered by film F and amalgumated. The seal is assembled by placing the electrolyte, film, pellet, etc. between the electrodes, surrounded by the plastic ring C. The structure is then closed by pressing the edges of A and F together and sealing them. Additional sealing or encapsulation may be required, and the cell is usually maintained under pressure applied to A and F during operation.

2.3.2 Fibrous Membrane Electrolyte

Most of the cell performance results were obtained with paper impregnated with $ZnCl_2$ and "converted," as described in

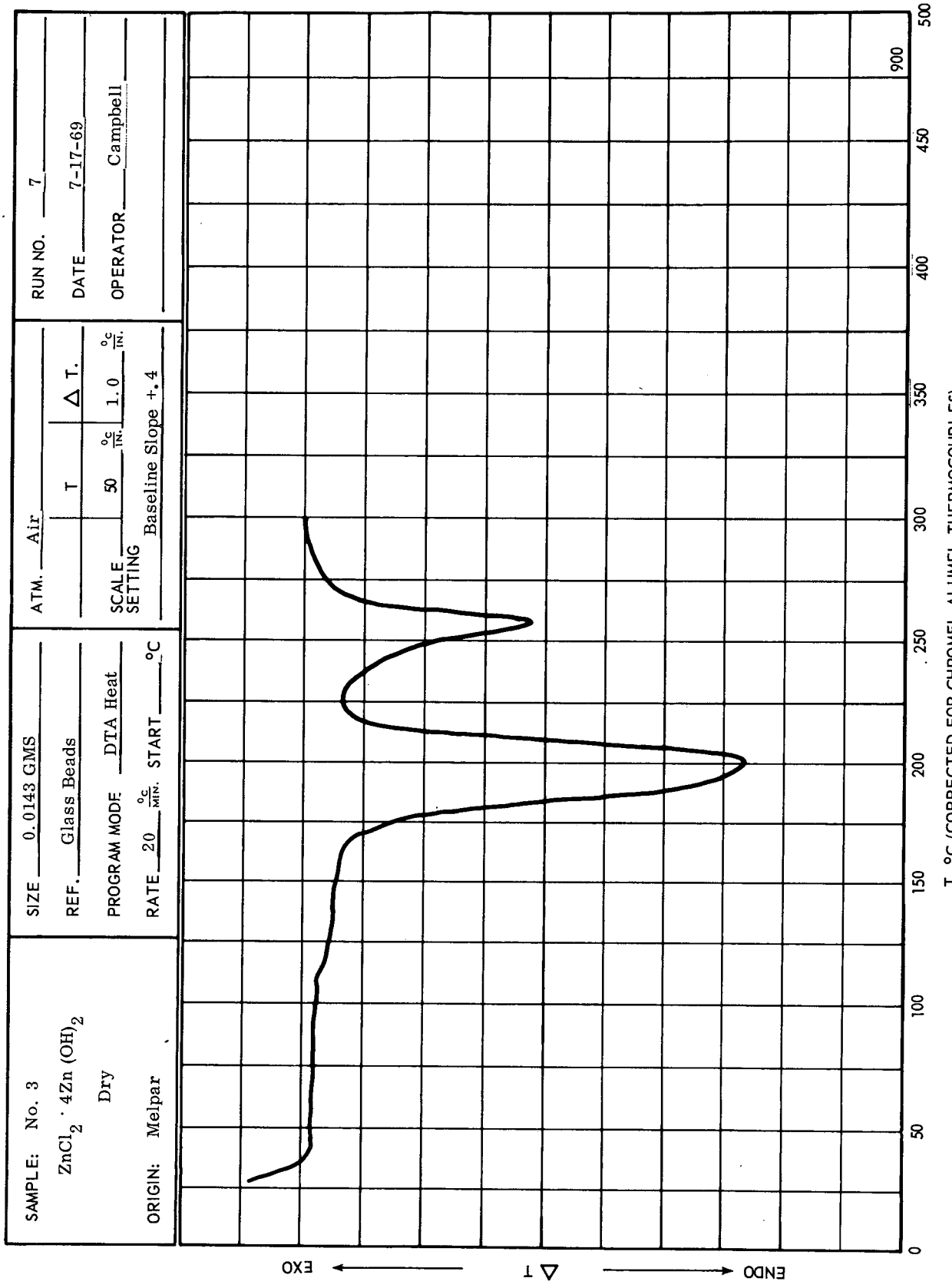

Figure 5. DTA Diagram of Dry $ZnCl_2 \cdot 4Zn(OH)_2$

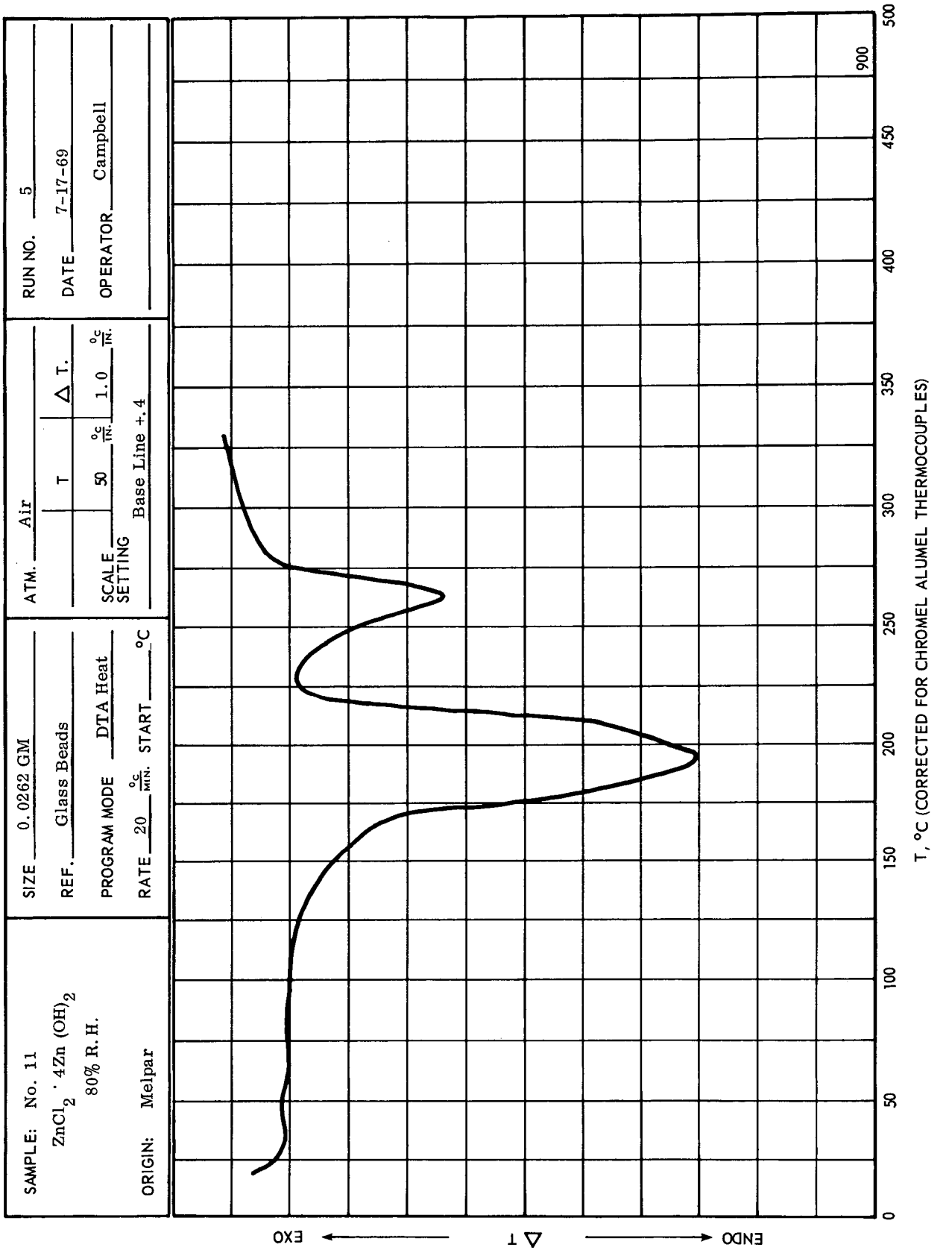

Figure 6. DTA Diagram of $ZnCl_2 \cdot Zn(OH)_2$ Equilibrated at 80% R.H.

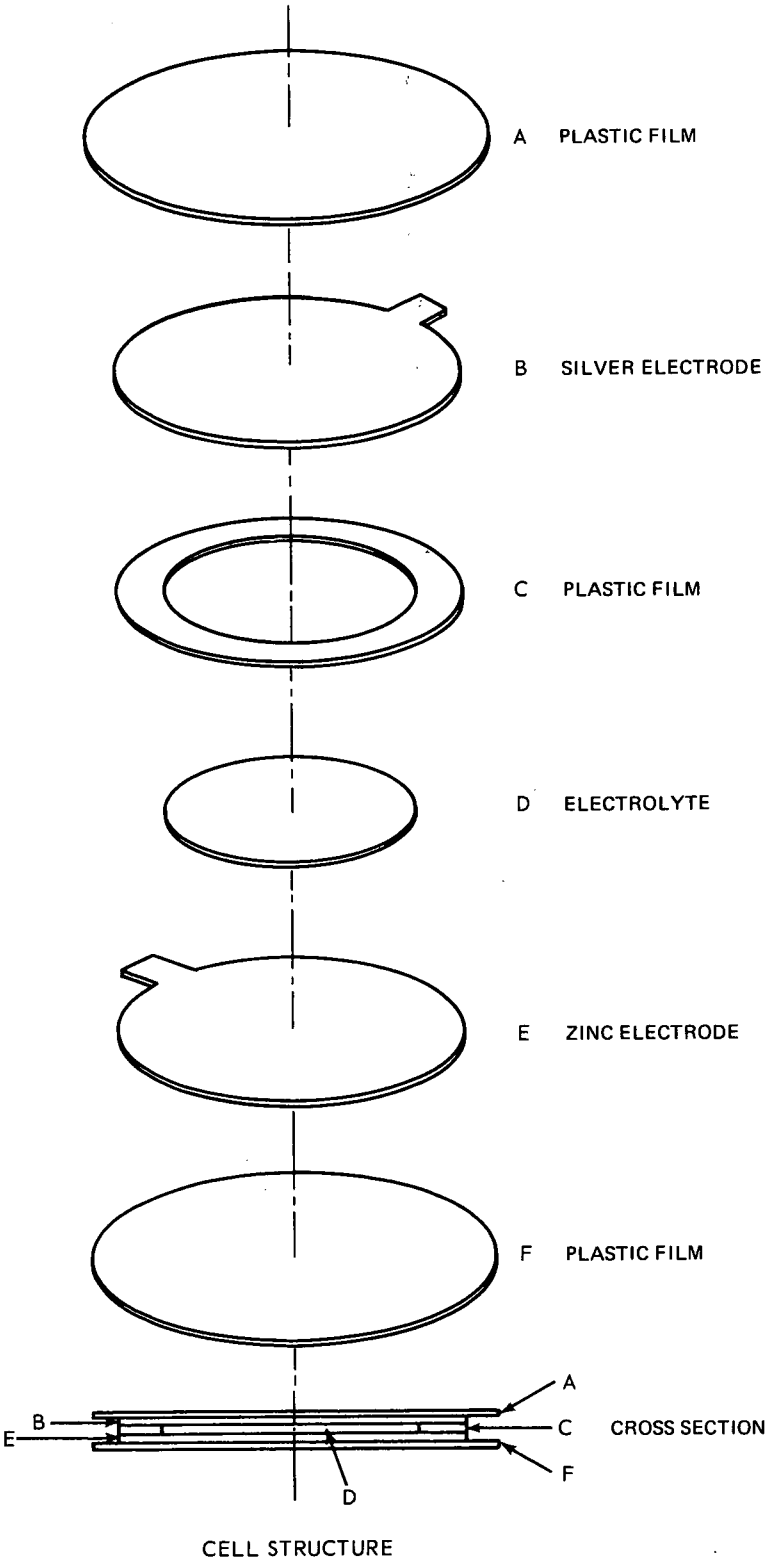

Figure 7. Structure of Experimental Cell

Section 2.1.4.2. In some experiments NH_4Cl or $ZnCl_2 \cdot 2NH_3$ was included in the impregnating solution. After impregnation the electrolyte was "activated" by equilibrating in a moist chamber to reduce the resistance in accord with table 7. The actual amount of hydration is dependent on the particular electrolyte being activated. For a good cell, a resistivity of a few hundred ohm-cm is indicated.

2.3.3 Pellets

In some experiments, the solid electrolyte was compressed into a pellet, at 15000 lbs psi, 27 mm diameter and about 1 mm thick. The pellets, being much thicker than the impregnated fibrous membranes, had a higher resistance which limited the power which could be drawn from the cells. They had the advantages of being composed of materials of known composition, and being easier to dissect for analysis after discharge. In some cases to be described below, the electrolyte material, usually $ZnCl_2 \cdot 2NH_3$, was mixed with very fine particle size pure asbestos before compression.

2.4 Cell Characteristics

Of the large number of parameters which can be employed to characterize cell performance, only those which relate to the mechanism of current flow are emphasized in this investigation. These include polarization, capacity, temperature characteristics and stability. Other operational properties which are less understood are omitted from this phase of the study.

2.4.1 Polarization

The voltage-time relationship at several current densities is shown for a typical cell in figure 8. The curves were obtained on a Sargent Recorder Type MR set for 1.25 V full scale and 60 inches per minute. They are replotted with the curves superimposed at time of application and at removal of the load.

The initial rate of drop in E_L when the load is applied appears to be constant for all loads, and is probably due to lag in the recorder. The slower fall in load voltage is due to slow depletion of carriers at the cathode surface and continues until equilibrium is reached. The process is reversed when the load is removed, with approximately the same time constants. The blips at the 90 mA curves are probably due to insufficient damping of the recorder. The rise in E_L for the 25 and 50 mA curves after the initial drop is most probably due to heating effect of the high current density.

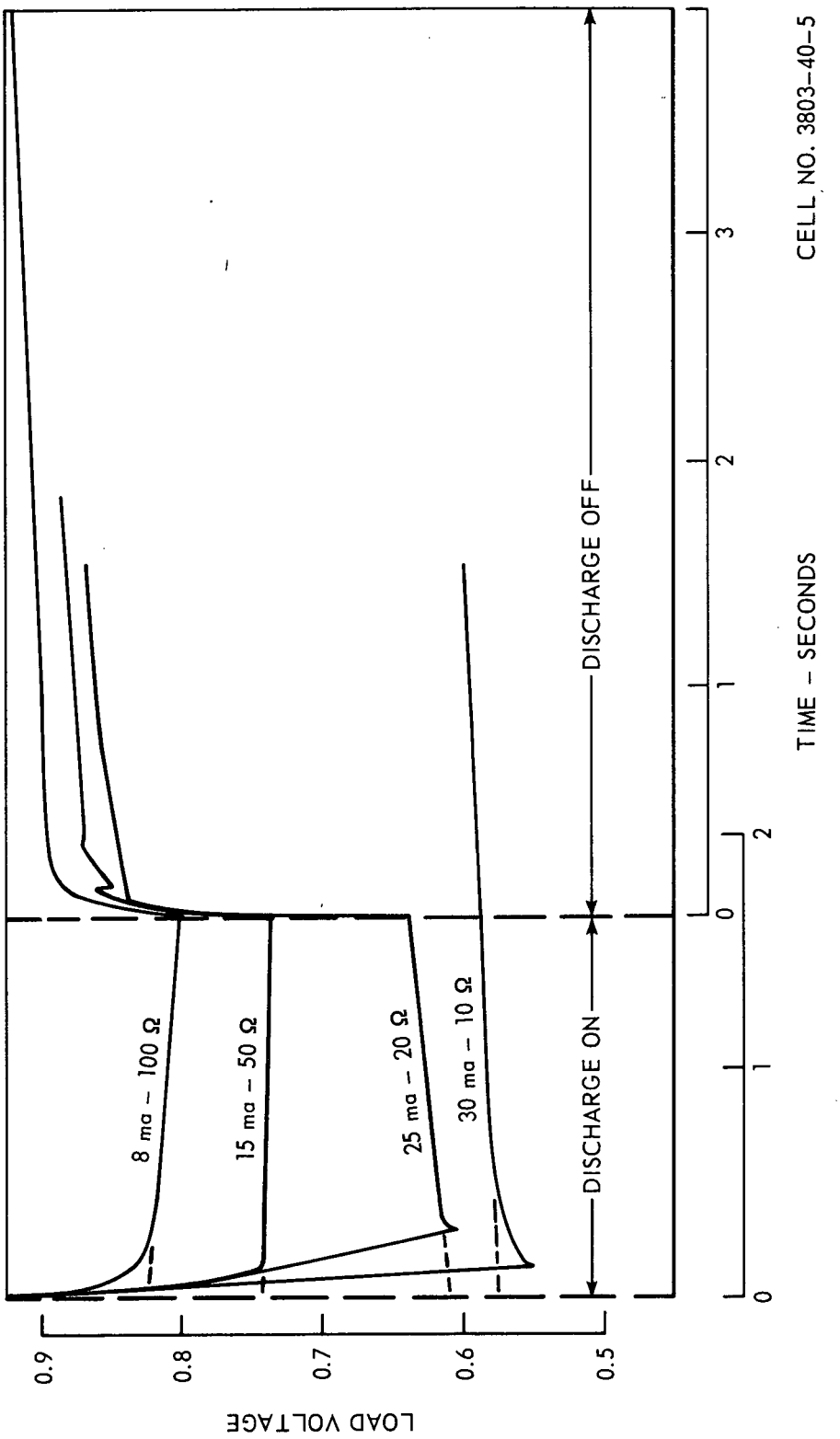

Figure 8. Polarization of Cell 3803-40-5

The initial drop in E_L is due to ohmic resistance of the cell, before significant polarization occurs. This can be shown by extrapolating the resistance from the relation $R=\frac{E_o-E_L}{I}$:

E_o Volts	E_L Volts	E_o-E_L Volts	I Amps	$\frac{E_o-E_L}{I}$ ohms
0.92	0.83	0.09	0.008	11
0.92	0.74	0.18	0.015	12
0.92	0.62	0.30	0.025	12
0.92	0.57	0.35	0.030	12

2.4.2 Capacity

The capacity of several types of cells were determined by discharging at constant current and observing the load voltage. In order to maintain the current constant, the external load was adjusted as the discharge proceeded. The capacities when the load voltages dropped to 80% of the initial value, and to zero, are shown in Table 8. In all cells, the limiting capacity is the silver chloride, which was formed by anodization of silver in HCl, at the rate of 25 ma for 1 hr.

Cell 3803.53-1 was charged and completely discharged three times after the initial discharge. The results are shown in Figure 9. The results indicate a loss in capacity with repeated cycling. However, where the depth of discharge is much less, repeated cycling has little effect on cell performance. Figure 10 shows some results of repeated cycling where the depth of discharge is only 10%.

Additional evidence of rechargeability is obtained from an experiment in which the cell was assembled in the simplest form in the completely discharged state. The electrolyte was $ZnCl_2.2NH_3$, dispersed in Polyox WSRN resin and conditioned at 90% R.H. A film of this dispersion was placed between silver and platinum electrodes. If the electrode reactions during charge are as predicted, silver should be converted to silver chloride and an equivalent amount of zinc deposited on the platinum.

Before charge the initial potential was about 0.12V with the platinum positive. The cell was then placed on charge at 1ma rate with the silver as the positive electrode. After a few minutes the charging was interrupted and the open circuit voltage became 0.98 V with the silver positive. The charging was resumed with E_L = 1.03 V and continued for 2-1/2 hours during which time the load was reduced periodically to maintain the charge current at 1mA. At the conclusion the charging potential was 1.19 V, and the cell had received an estimated charge of about 2-1/2 mAhours.

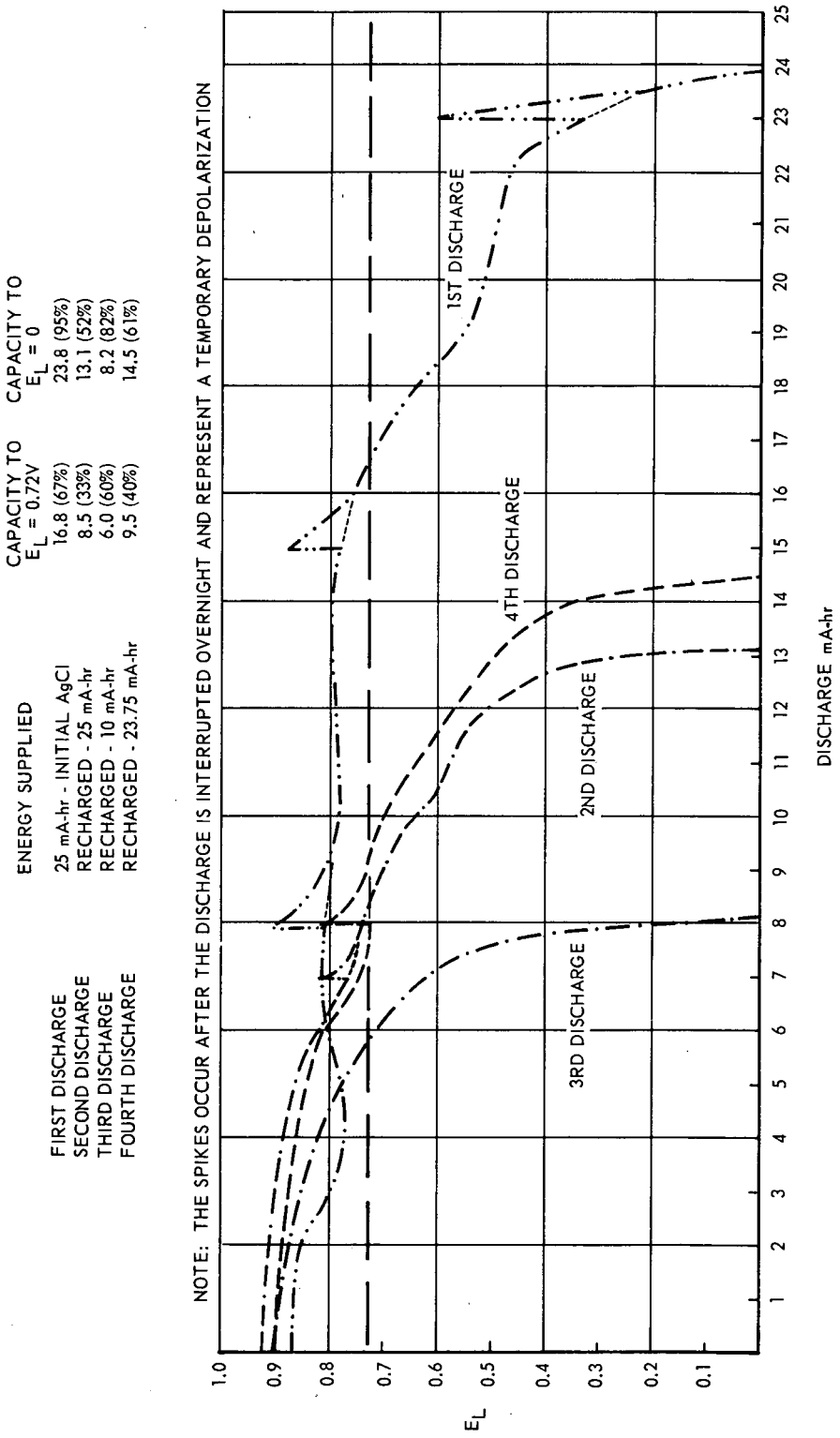

Figure 9. Recharge Characteristics of Cell 3803-53-1 — Complete Discharge

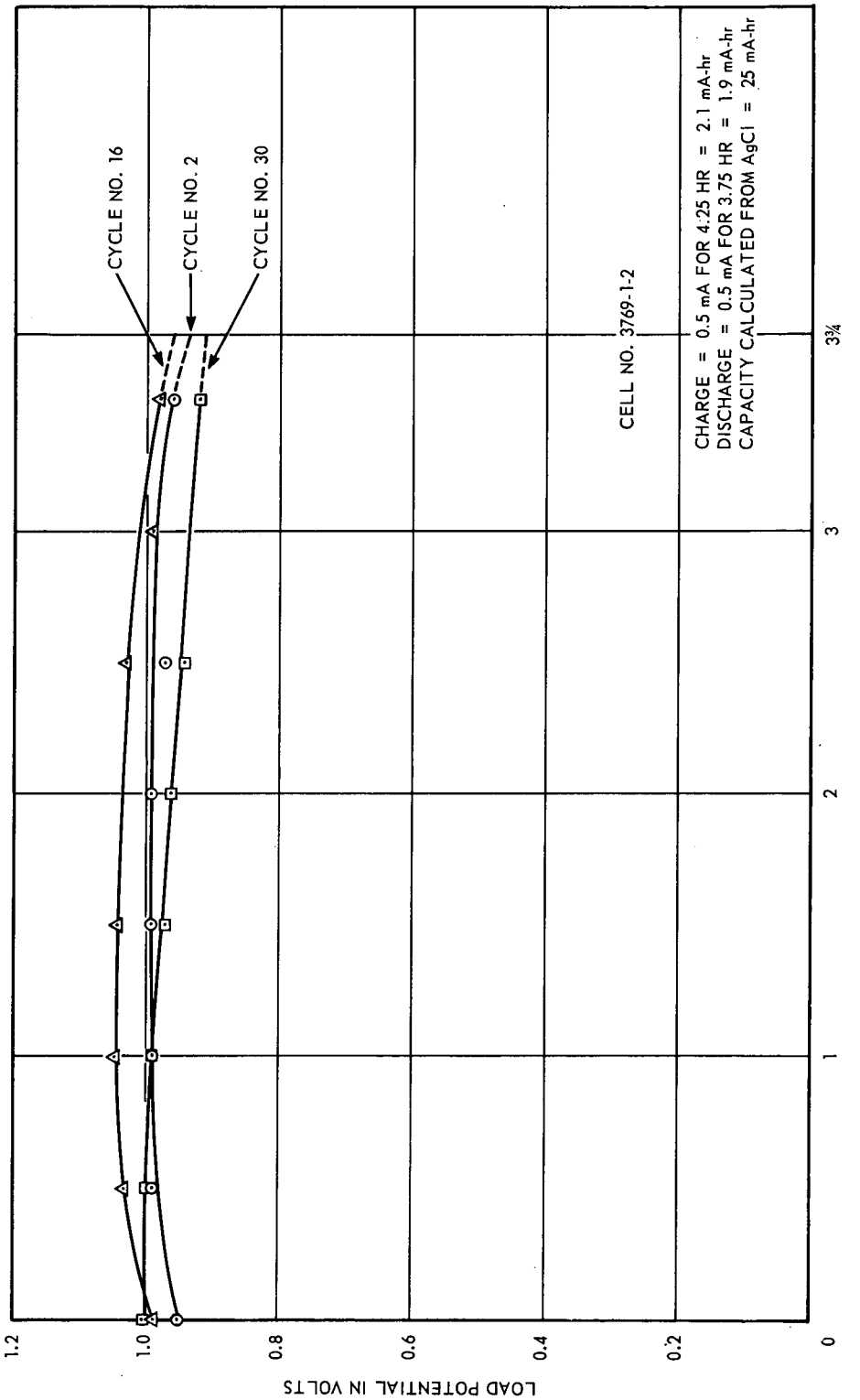

Figure 10. Discharge Characteristics of Cell 3769-1-2
Shallow Discharge

The cell was then taken apart and the layers separated. The electrolyte remained white. The silver had a dark coating which was removed with ammonium hydroxide with a weight loss of 0.01055 g. Acidification of the extract with HNO_3 produced a precipitate of AgCl. The platinum had a dark coating, which dissolved in HCl with gas evolution and a loss in weight of 0.0025 g. The extract remained clear when neutralized with ammonia. Addition of solium sulfide formed a white precipitate of ZnS.

Based on Faraday's Law, charge consumed in the formation of 0.01055 g. of AgCl is:

$$\frac{0.01055}{0.0053} \text{ or } 2.0 \text{ mA hr.}$$

Similarly, the formation of 0.0025 g of Zn requires:

$$\frac{0.0025}{0.0012} \text{ or } 2.1 \text{ mA hr.}$$

These values are in approximate agreement with the 2.5 mA hr. supplied, and the following electrode reactions appear to be established:

$$\text{Anode - } Ag^{\circ} + Cl^{-} \rightleftarrows AgCl + e$$

$$\text{Cathode - } Zn^{\circ} \rightleftarrows Zn^{++} + 2e$$

2.4.3 Temperature Characteristics

The open circuit potentials of three cells, having $ZnCl_2 \cdot 2NH_3$ electrolyte was measured at a series of temperatures. The cells were placed in an environmental test chamber, and maintained at each temperature for at least 24 hours before readings were taken. Open circuit potentials were measured on a Leeds and Northrup Volt Potentiometer. The results are shown in figure 11. The readings were taken in the following sequence of temperatures: 22.5°, 7°, -25°, -43°, 26°. The results show that the effect of temperature on open circuit potential is very small.

After measuring E° at each temperature a series of loads was applied to the cells, from which the I-V Curves shown in Figures 12, 13, 14 were plotted. It appears that useful current can be drawn from the cells even at -25°C.

2.4.4 Shelf Life Failure Modes

In addition to loss of capacity with deep charge-discharge cycles, described in section 2.5.2 above, several types of failure occur during storage with no load applied (Shelf Life).

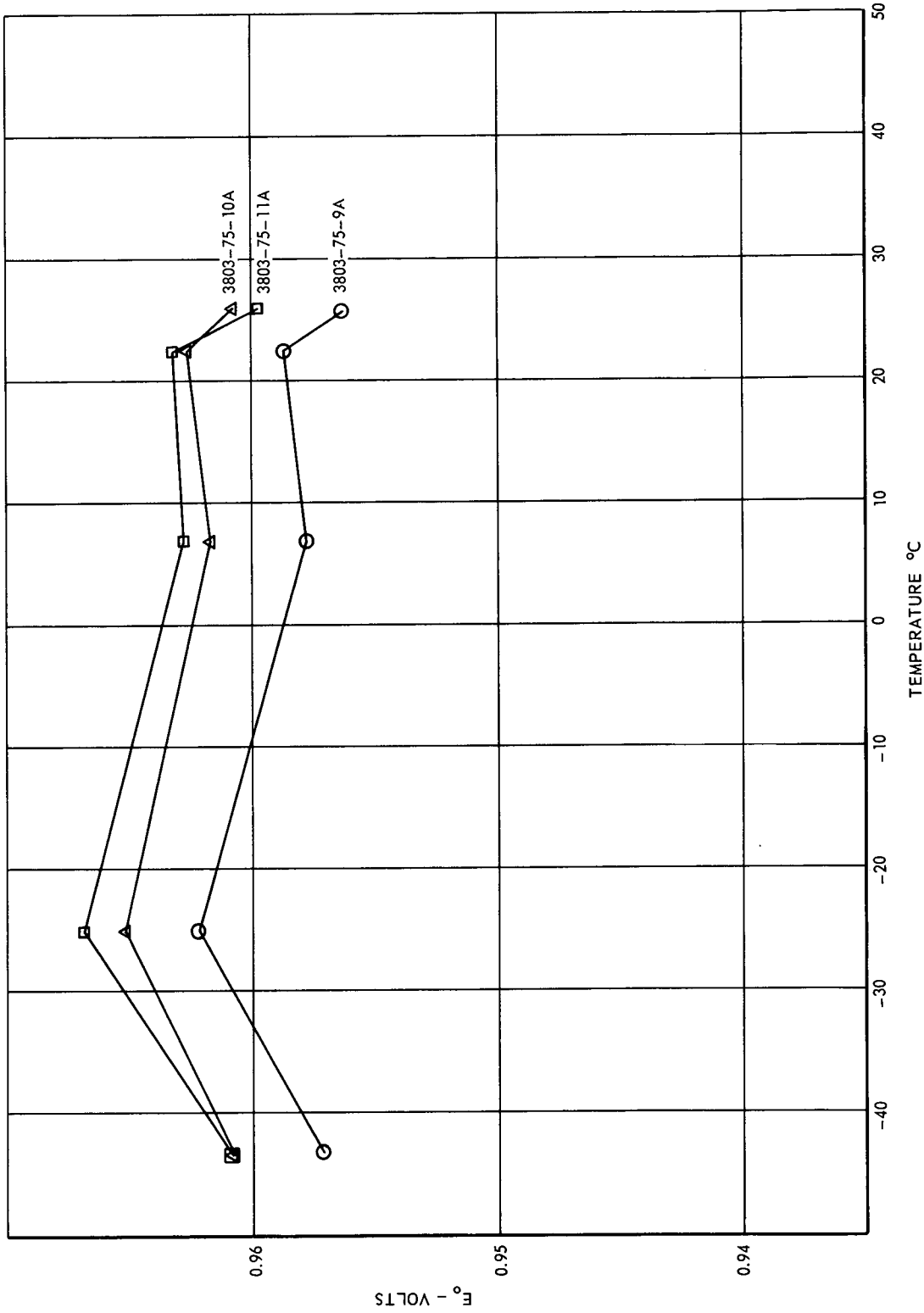

Figure 11. Open Circuit Potential at Various Temperatures

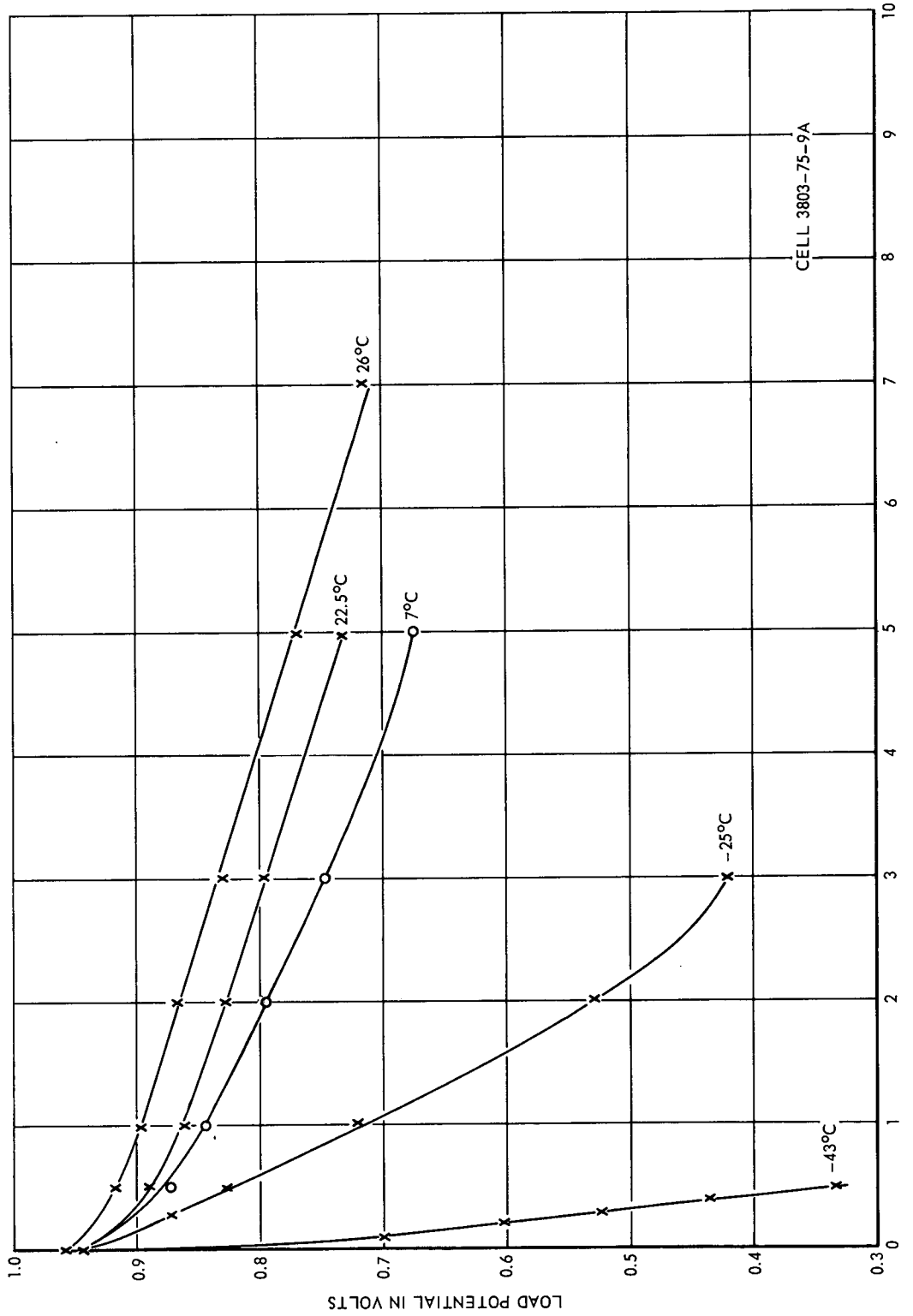

Figure 12. Load Potential of Cell 3803-75-9A at Various Temperatures

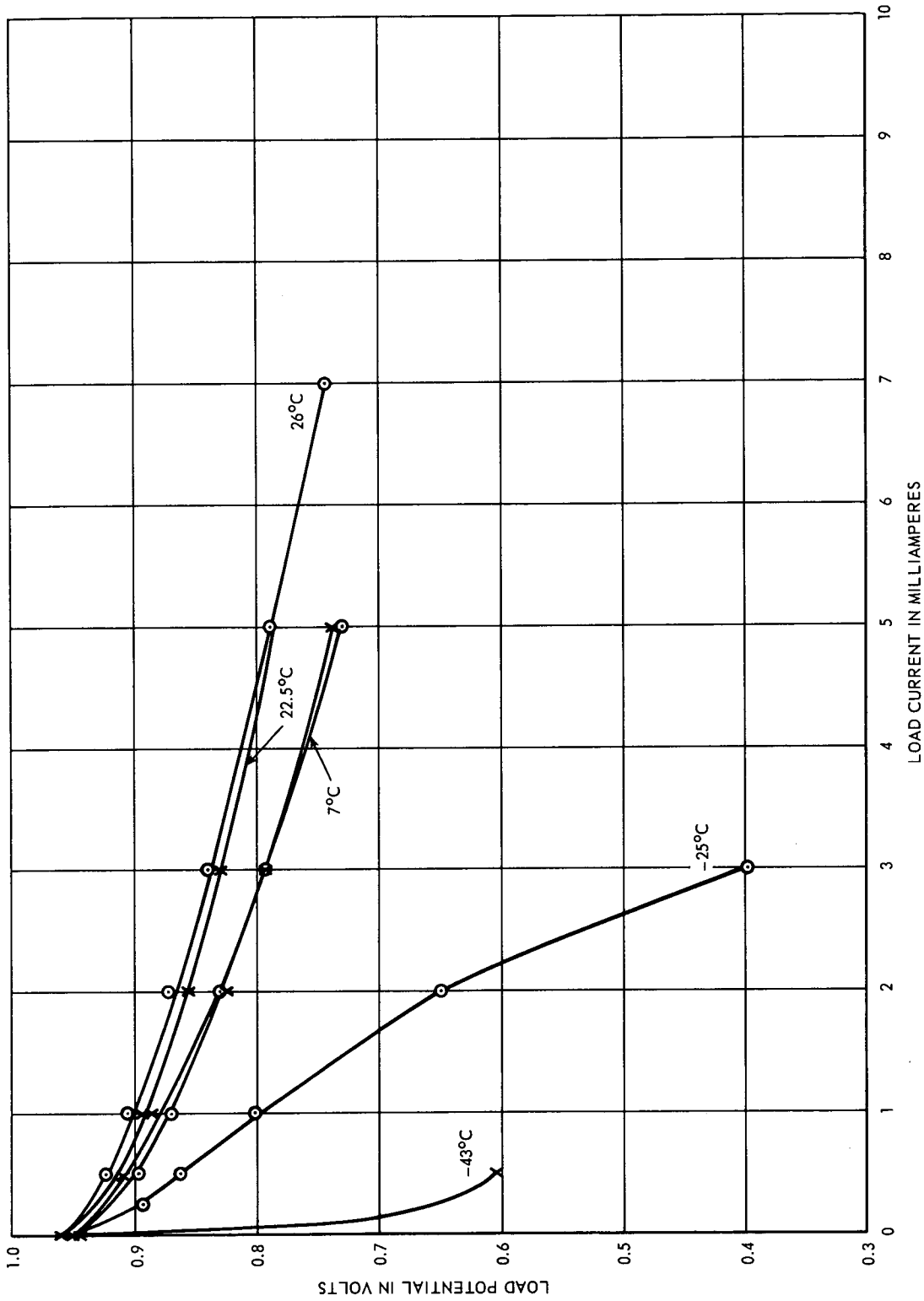

Figure 13. Load Potential of Cell 3803-75-10A at Various Temperatures

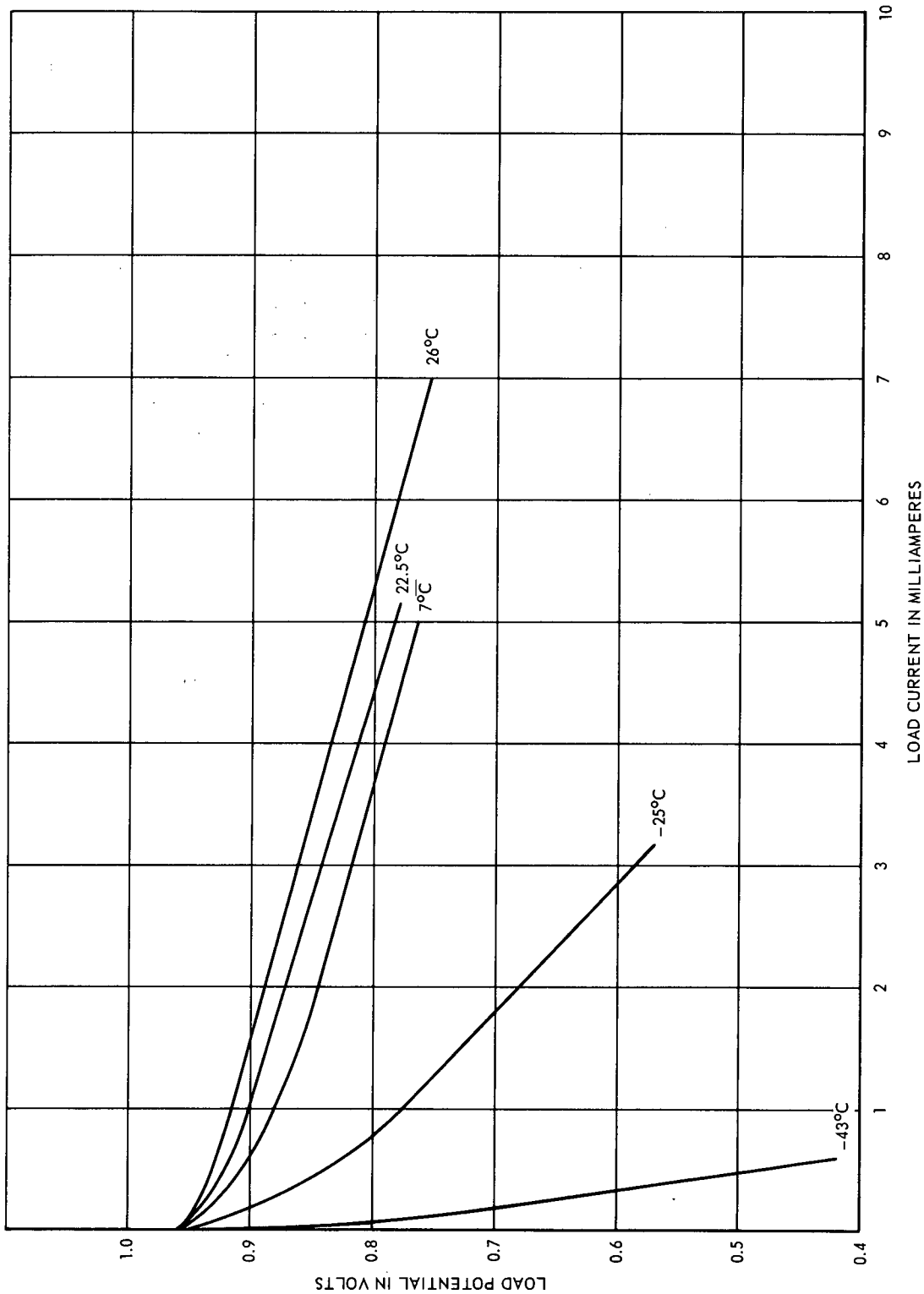

Figure 14. Load Potential of Cell 3803-75-11A at Various Temperatures

One mode of failure contributing to short shelf life of cells containing polyethylene oxide* is the progressive hardening of the binder probably caused by zinc ions. The result is embrittlement of the film with loss of solubility and increase in internal resistance. This type of failure during shelf storage is uncommon with cellulose fiber separators. Initial experiments with asbestos fiber separators as described above appear promising.

Another type of failure occurring during shelf life tests is a sudden drop in the open circuit voltage to nearly zero. This takes place after the cell has been stored without apparent change in its electrical characteristics for a long period; in some cases this is several months. This self discharge is due to an internal short, which appears to be localized at one or more spots at the edge of the cell. When the cell is separated at such areas, the open circuit voltage is largely restored, but the cell has completely lost capacity.

A third type of failure observed in shelf life is progressive increase in internal resistance, which limits the current density obtainable. In many cases this can be attributed to loss of water, of hydration through imperfect sealing of the package. A useful test for leakage is by using dye penetration when the cell is immersed in a dye solution under partial vacuum. When the vacuum is released the dye enters the package through imperfections in the seal.

2.5 Cell Reaction

2.5.1 $ZnCl_2.2NH_3$ Electrolyte

A cell was fabricated using a pellet of this material, and zinc and silver electrodes, the latter being anodized to AgCl with 25 mA hr theoretical capacity. The cell was conditioned by applying a series of short pulses of heavy load, and then discharged at 1 mA rate until the load voltage dropped to zero. The discharge was completed through a direct short over night. A low open circuit voltage was detected, but no current could be drawn.

The cell was then carefully taken apart and the electrolyte-electrode interfaces subjected to X-ray diffraction analysis.

On the silver side of the electrolyte $ZnCl_2.2NH_3$ was the sole constituent. Silver chloride was not identified (Table 9). The zinc side showed, in addition to the $ZnCl_2.2NH_3$ originally present, $ZnCl_2.4Zn(OH)_2$ and $ZnCl_2.3NH_4Cl$ (Table 10).

The cathode reaction during discharge appears to be:

$$AgCl + e \rightarrow Ag^{\circ} + Cl^{-}$$

---

* Polyox WSRN-8000, manufactured by Union Carbide.

Based on the above analysis, it would appear that some of the $ZnCl_2.2NH_3$ is hydrolyzed at the anode, forming the basic salt, $ZnCl_2.4Zn(OH)_2$. Water is required for this reaction, and the HCl formed combines with NH_3 liberated to form NH_4Cl, which in turn combines with $ZnCl_2$ to form $ZnCl_2.3NH_4Cl$. We therefore postulate the following anode reactions:

$$Zn \rightarrow Zn^{++} + 2e$$
$$Zn^{++} + 2Cl^{-} \rightarrow ZnCl_2$$
$$5ZnCl_2 + 8H_2O \rightarrow ZnCl_2.4Zn(OH)_2 + 8HCl$$
$$ZnCl_2.2NH_3 + 2HCl \rightarrow ZnCl_2 + 2NH_4Cl$$
$$ZnCl_2 + 3NH_4Cl \rightarrow ZnCl_2.3NH_4Cl.$$

When the reactions at the two electrodes are combined, and allowance made for stoichiometric balance, we obtain the following for the overall cell reaction:

$$11\ Zn + 22\ AgCl + 12\ ZnCl_2.2NH_3 + 24\ H_2O$$
$$\underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}}\ 8\ ZnCl_2.3NH_4Cl + 3ZnCl_2.4Zn(OH)_2 + 22\ Ag$$

2.5.2 Other Electrolytes

Cells were also fabricated from the materials described in Section 2.2.4 and completely discharged. Clear cut identification of the electrolyte before and after discharge was not obtained. Table 11 shows the X-ray diffraction results obtained from a discharged cell having a pellet of electrolyte as described in Section 2.2.4.1-- the product obtained by reacting zinc chloride with fumes from ammonium carbonate. The original electrolyte appears to have undergone changes at both surfaces, but identification of the reaction products is not clear.

Similar results were obtained with the fibrous membrane electrolyte. The diffraction patterns obtained are given in Table 12. The products were not identified.

3. NEW TECHNOLOGY

No items of new technology were developed during the period of the contract.

4. CONCLUSIONS AND RECOMMENDATIONS

The objective of determining the mechanism of current transport has been attained in electrochemical cells employing zinc chloride diammine as electrolyte. Moisture is necessary for hydration to provide ionic conductivity and as a component in the cell reaction. Similar results were observed for another solid zinc chloride complex electrolyte, but the components and reaction products were not identified. Rechargeability and operation at -25°C was confirmed.

It is suggested that the program be continued emphasizing useful zinc complex electrolytes and characterizating the reaction products. Further work should also include identification of the factors which affect capacity and stability. Improved materials and designs should be sought, and the overall structure be optimized for maximum power and energy density. Structural modifications should include larger area and multicell units.

In addition to the sheet-like, flexible structure which is unique, the rechargeability and operation at -25°C shown in this report indicate possible areas of application. For example, in a portable radio, the battery package would be a thin packet of cells in the form of sheets to be positioned on the inside walls of the radio case. Another example would be in the power supply system for weather balloons. A battery of the cells would be spaced so as to avoid damage to high speed aeroplanes on impact, and would be charged periodically. Other applications would be for miniature instruments, watches, hearing aids, etc. Future work will include adaptation to these and other applications.

APPENDIX I

TABLE 1

X-RAY DIFFRACTION PATTERN OF $ZnCl_2 \cdot 2NH_3$

Preparation 3769-1		ASTM Card 1-165		Ref 4	
dA	I/I_o	dA	I/I_o	dA	I/I_o
		5.80	100	5.85	85
5.71	85			5.74	100
5.57	90				
		5.19	5		
		4.93	5		
4.19	10			4.24	11
4.00	3	4.00	8		
3.85	65	3.88	88	3.88	73
3.31	80			3.38	71
3.27	70	3.28	20	3.29	50
3.21	60			3.24	51
		3.13	10		
2.90	100	2.92	62	2.93	72
2.84	80			2.87	78
2.77	9				
2.72	8	2.73	10		
2.65	10	2.64	5		
2.46	2	2.46	15		
2.32	10	2.33	10	2.33	10
2.21	15			2.22	12
2.18	20	2.18	15	2.20	20
2.17	15			2.18	14
2.13	30	2.11	10	2.13	18
2.01	10	2.01	15	2.02	10
1.94	15	1.94	15	1.95	17
1.87	20	1.88	10	1.88	13
1.84	2				
1.79	9	1.78	10		
1.74	10	1.73	5	1.74	7
1.72	8				
1.71	9			1.71	6
1.69	35	1.68	12	1.69	25

4. O. Erämetsä and A. Ryhänen -
Suomen Kemistilehts B39(12) 277-80 (1966).

TABLE 1

X-RAY DIFFRACTION PATTERN OF $ZnCl_2 \cdot 2NH_3$ (Continued)

Preparation 3769-1		ASTM Card 1-165		Ref 4	
dA	I/I_o	dA	I/I_o	dA	I/I_o
1.65	8				
1.62	5	1.61	5		
1.57	1	1.57	8		
1.56	1				
1.54	1				
1.48	1				
1.47	2				
1.42	5	1.42	5		
1.40	2				
1.37	2				
1.35	2				
1.28	2				

TABLE 2

X-RAY DIFFRACTION PATTERN OF $ZnCl_2 \cdot 3NH_4Cl$

Preparation 149-1		ASTM Card 2-584	
dA	I/I_o	dA	I/I_o
7.56	30	7.7	25
7.08	8	7.1	10
6.32	10		
5.68	75	5.8	80
5.04	65	5.10	25
4.87	55	4.95	25
4.48	10		
4.29	15	4.32	5
4.02	25	4.05	5
3.95	5		
3.85	35	3.85	35
3.75	10		
3.52	15	3.52	5
3.13	100	3.15	100
2.97	45	2.95	5
2.94	75		
2.87	60	2.88	15
2.81	15		
2.74	25	2.76	5
2.71	20	2.72	5
2.61	20		
2.45	65	2.46	60
2.41	12		
2.38	5		
2.34	30	2.34	2
2.25	15		
2.19	10		
2.17	5		
2.13	10		
2.10	10		
2.06	20	2.05	40
2.01	10		
1.96	5	1.96	60
1.94	10		

TABLE 2

X-RAY DIFFRACTION ANALYSIS OF $ZnCl_2 \cdot 3NH_4Cl$ (Continued)

Preparation 149-1		ASTM Card 2-584	
dA	I/I_o	dA	I/I_o
1.86	3		
1.81	10	1.81	10
1.78	10		
1.77	30	1.77	10
1.76	15		
1.74	10		
1.67	5		
1.65	15		
1.63	5		
1.61	10		
1.57	10		
1.55	10		
1.53	10		
1.51	15		

TABLE 3

X-RAY DIFFRACTION PATTERN OF $ZnCl_2 \cdot 4Zn(OH)_2$

Preparation 115-1		ASTM Card 7-155	
dA	I/I_o	dA	I/I_o
7.76	100	7.89	100
5.25	5	5.35	21
		4.02	21
3.93	10	3.93	8
3.89	10		
3.53	15	3.53	23
3.15	10	3.17	37
2.90	10	2.94	31
2.85	15	2.88	25
2.70	20	2.73	53
2.66	40	2.67	67
2.59	15	2.60	21
2.44	5	2.47	10
2.35	20	2.37	37
2.16	3	2.17	5
2.05	5	2.06	7
2.01	10	2.02	22
1.95	10	1.97	4
1.84	3	1.86	8
1.82	3	1.83	4
1.76	5	1.79	13
1.68	10	1.69	13
1.57	15		
1.55	10		
1.51	10		
1.43	5		
1.36	5		

TABLE 4

X-RAY DIFFRACTION PATTERN OF "CONVERTED" $ZnCl_2$ - BULK

Converted $ZnCl_2$				$ZnCl_2 \cdot 2NH_4Cl$ 12-304		NH_4Cl 7-7		$ZnCl_2 \cdot 4Zn(OH)_2$ 7-135	
Bulk		Bulk + NH_4Cl							
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
								7.87	100
6.19	10	6.28	10	6.32	11				
				6.27	11				
5.72	12	5.83	8						
5.61	20	5.68	8						
				5.22	11			5.25	21
5.13	100	5.13	100	5.19	100				
4.57	80	4.60	30	4.64	25				
4.17	20	4.19	10	4.23	11				
								4.02	21
								3.94	8
3.85	20	3.87	15			3.87	23	3.89	10
		3.82	5	3.84	1				
		3.71	5	3.73	5				
3.58	95	3.60	55	3.64	30			3.58	23
				3.61	25				
3.45	25	3.45	15						
3.36	10	3.39	15	3.38	1				
		3.28	15						
3.22	15	3.22	25	3.25	20				
3.12	15	3.14	40	3.16	20			3.17	37
3.08	5			3.13	25				
				3.00	25				
2.98	10	2.98	25	2.97	11				
		2.95	8					2.94	31
2.91	10	2.90	10						
2.85	10	2.87	10					2.88	25
				2.78	60				
2.75	25	2.76	25	2.76	30	2.74	100		
2.70	10	2.70	10					2.72	53
2.67	8	2.67	5					2.67	67
		2.62	3	2.63	5				

TABLE 4

X-RAY DIFFRACTION PATTERN OF "CONVERTED" $ZnCl_2$ - BULK (Continued)

Converted $ZnCl_2$				$ZnCl_2 \cdot 2NH_4Cl$ 12-304		NH_4Cl 7-7		$ZnCl_2 \cdot 4Zn(OH)_2$ 7-135	
Bulk		Bulk NH_4Cl							
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
2.59	25	2.59	10	2.60	15			2.60	21
2.50	5	2.51	5	2.49	11				
2.47	10	2.47	10					2.49	3
								2.47	10
2.37	8	2.37	8	2.38	9			2.37	37
2.35	25	2.35	8	2.36	13				
2.29	10	2.30	15	2.31	11				
				2.30	15				
				2.29	11				
2.24	10	2.25	10			2.24	4		
				2.22	3				
				2.21	3				
		2.20	10	2.20	3				
2.16	10			2.18	3			2.17	5
		2.13	3	2.11	5				
2.09	15	2.08	5	2.09	9			2.07	7
				2.05	3				
2.02	5	2.02	5	2.03	5			2.02	22
								2.01	9
				1.96	7			1.97	4
				1.95	5			1.96	9
1.94	10	1.94	10	1.93	7				
		1.92	5	1.90	3			1.90	8
				1.89	3				
1.87	20	1.88	10	1.88	9				

TABLE 5

X-RAY DIFFRACTION PATTERN OF "CONVERTED" $ZnCl_2$ - FIBROUS MEMBRANE

Converted $ZnCl_2$				$ZnCl_2 \cdot 2NH_3$ Table 1		$ZnCl_2 \cdot 2NH_4Cl$ 12-304		$ZnCl_2 \cdot 3NH_4Cl$ Table 2		$ZnCl_2 \cdot 4Z(OH)_2$ Table 3	
Alone		+ $ZnCl_2 \cdot 2NH_3$									
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
9.93	100										
		7.69	45			7.48	1	7.56	30	7.89	100
								7.08	8		
6.11	10	6.33	20			6.32	11	6.32	10		
						6.27	11				
5.68	15	5.98	10	5.80	100			5.68	75		
		5.89	30								
		5.79	25								
5.54	15	5.62	35							5.35	21
5.19	15			5.19	5	5.22	11				
5.06	15					5.19	100	5.04	65		
				4.93	5			4.87	55		
						4.64	35				
								4.48	10		
						4.23	11				
				4.00	8					4.02	21
		3.92	100	3.88	88					3.93	8
3.82	25							3.85	25		
3.56	10	3.63	20			3.64	30	3.52	15	3.52	23
						3.61	25				
3.48	5	3.49	5								
3.41	3	3.40	15	3.37	20						
3.39	3										
3.31	5	3.30	30	3.28	20						
3.25	10	3.24	25			3.25	20				
3.19	10	3.15	75	3.13	10	3.16	20	3.13	100	3.17	37
						3.13	25				
3.10	30										
						3.00	25				
3.05	5					2.97	11	2.97	45		
		2.94	30	2.92	62			2.94	75	2.94	31
2.88	10	2.88	20					2.87	60	2.88	25

TABLE 5

X-RAY DIFFRACTION PATTERN OF "CONVERTED" $ZnCl_2$ - FIBROUS MEMBRANE (Continued)

Converted $ZnCl_2$				$ZnCl_2 \cdot 2NH_3$ Table 1		$ZnCl_2 \cdot 2NH_4Cl$ 12-304		$ZnCl_2 \cdot 3NH_4Cl$ Table 2		$ZnCl_2 \cdot 4Zn(OH)_2$ Table 3	
Alone		+ $ZnCl_2 \cdot 2NH_3$									
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
2.82	10	2.82	3					2.81	15		
		2.76	10			2.78	60				
2.73	10	2.73	10	2.73	10	2.76	30	2.74	25	2.73	53
2.67	15	2.67	10	2.64	5			2.71	20	2.67	67
2.64	10	2.59	7			2.60	15	2.61	20	2.60	21
2.54	5										
2.48	5			2.46	15	2.49	11	2.45	65	2.47	10
2.35	5	2.38	15	2.33	10	2.36	13	2.41	10	2.37	37
		2.35	7					2.34	30		
2.31	5	2.31	10			2.31	11				
2.28	8					2.30	15	2.25	15		
						2.29	11				
2.22	10	2.19	5	2.18	15					2.17	5
2.17	5	2.14	7					2.19	10		
		2.10	15	2.11	10	2.10	5	2.13	10		
								2.10	10		
2.07	10					2.07	9	2.06	20	2.06	7
		2.03	10	2.01	15	2.03	5	2.01	10	2.02	22
1.93	5	1.94	10	1.94	15	1.96	7	1.96	5	1.97	4
						1.95	5	1.94	10		
1.87	5	1.88	5	1.88	10	1.93	7	1.86	3		
		1.86	7			1.88	9			1.83	4
1.80	10	1.80	5	1.78	10	1.82	9	1.81	10	1.80	8
		1.75	3			1.80	7	1.78	10	1.79	13
		1.73	3	1.73	5	1.77	5	1.77	30		
								1.76	15		
1.71	8	1.72	7					1.74	10		
1.68	5	1.69	7	1.68	12			1.65	15	1.69	13
1.58	5	1.59	3					1.61	10		
1.57	8	1.57	3	1.57	8			1.57	10		

TABLE 6

X-RAY DIFFRACTION PATTERN OF $ZnCl_2 \cdot 2NH_3$
AFTER HEATING TO 220°

Before Heating-Table 1		After Heating	
dA	I/I_o	dA	I/I_o
5.71	90	5.94	50
5.57	90		
		5.04	100
		4.53	10
4.19	10	4.13	5
3.85	65	3.82	50
		3.53	50
3.31	80		
3.27	70		
3.21	60	3.22	50
		3.10	40
2.90	100	2.88	60
2.84	80		
2.77	9		
2.72	8	2.72	90
2.65	10		
2.46	2		
2.32	10	2.33	10
		2.30	10
2.21	15		
2.18	20	2.17	10
2.17	15		
2.13	30	2.13	5
2.01	10	2.00	25
1.94	15	1.94	40
1.87	20	1.86	10
1.84	2		
1.79	8	1.80	10
1.74	10		
1.72	8		
1.71	9		
1.69	35	1.69	20
1.65	8	1.65	5
1.62	5		
1.57	1		
1.56	1	1.56	30

TABLE 7

EFFECT OF HYDRATION OF $ZnCl_2 \cdot 2NH_3$ ON CONDUCTIVITY

RH	Resistance Ohms	Resistivity Ohm-cm	Conductivity Ohm^{-1}-cm^{-1}	Moisture Content*
0	1500000	50000000		
	80000	2700000		
	450000	15200000		
	210000	7080000		
	Avg=	21245000	3×10^{-8}	0
1.2%	820000	2760000		
	830000	2800000		
	Avg=	2780000	4×10^{-7}	0
33%	180000	605000		
	180000	605000		
	Avg=	605000	2×10^{-6}	0
67%	85	2760		
	130	4380		
	160	5390		
	Avg=	4140	2×10^{-4}	2.2%
75%	60	2020		
	50	1680		
	70	2360		
	Avg=	2090	5×10^{-4}	3.8%
80%	9.0	303		
	9.0	303		
	8.3	270		
	Avg=	292	3×10^{-3}	5.8%
85%	10.5	353		
	9.0	303		
	9.0	303		
	Avg=	320	3×10^{-3}	7.0%

* Interpolated from figure 1.

TABLE 8

TYPICAL CELL CAPACITIES

Cell No.	Electrolyte	Capacity	
		To E_L = 80% of E_0	To E_L = 0
		ma hr	ma hr
3803-50-96	$ZnCl_2$ converted on paper	12.5	19.5
3803-40-7	$ZnCl_2$ + $ZnCl_2 \cdot 2NH_3$ converted on paper	8.	16.
3798-40-5	$ZnCl_2$ + NH_4Cl converted bulk pellet	--	22.
3803-51-3	$ZnCl_2$ + NH_4Cl converted on paper	9.5	12.5
3803-53-1	$ZnCl_2$ + NH_4Cl converted on asbestos	16.8	23.8

TABLE 9

X-RAY DIFFRACTION PATTERN OF ELECTROLYTE FROM DISCHARGED CELL AT SILVER-ELECTROLYTE INTERFACE ELECTROLYTE INITIALLY $ZnCl_2 \cdot 2NH_3$

Material from Interface		$ZnCl_2 \cdot 2NH_3$ Table 1	
dA	I/I_o	dA	I/I_o
5.72	20	5.71	85
5.54	77	5.57	90
3.82	60	3.85	65
3.33	10	3.31	80
3.27	7	3.27	70
3.20	7	3.21	60
3.16	11		
2.89	53	2.90	100
2.84	100	2.84	80
2.75	6	2.77	9
2.71	4	2.72	8
		2.65	10
		2.46	2
2.33	12	2.33	10
2.21	3	2.21	15
2.19	5	2.18	20
		2.17	15
2.12	2	2.13	30
2.02	6	2.01	10
1.97	17	1.94	15
1.93	10		

TABLE 10

X-RAY DIFFRACTION PATTERN OF ELECTROLYTE FROM DISCHARGED CELL AT ZINC - ELECTROLYTE INTERFACE ELECTROLYTE INITIALLY $ZnCl_2 \cdot 2NH_3$

Material from Interface		$ZnCl_2 \cdot 2NH_3$ Table 1		$ZnCl_2 \cdot 4Zn(OH)_2$ Table 3		$ZnCl_2 \cdot 3NH_4Cl$ Table 2	
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
7.56	83		30	7.76	100	7.56	30
6.15	4					6.32	10
5.75	31	5.71	85				
5.64	30	5.57	90			5.68	25
5.25	1						
5.16	3						
4.						5.04	65
4.21	3	4.19	10			4.48	10
						4.87	55
4.00	2	4.00	2				
3.88	10			3.93	10		
3.85	20	3.85	65	3.89	10	3.85	35
3.53	10			3.53	15	3.52	15
3.35	30	3.31	80				
3.28	45	3.27	70				
3.21	24	3.21	60				
3.13	20			3.15	10	3.13	100
						2.97	45
2.90	100	2.90	100	2.90	10	2.94	75
2.84	50	2.84	80	2.85	15	2.87	60
						2.81	15
2.78	7	2.77	9				
2.71	24	2.72	8	2.70	20	2.74	25
						2.71	20
2.64	29	2.65	10	2.66	40		
2.57	10			2.59	15	2.61	20
2.45	3	2.46	2			2.45	65
2.36	11			2.35	20		
2.32	13	2.33	10			2.34	30
2.21	14					2.25	15
2.19	60					2.19	10
2.18	5					2.17	5
2.13	14	2.13	30			2.13	10
2.11	4					2.10	10
						2.06	20
2.01	11	2.01	10	2.01	10	2.01	10

TABLE 11

X-RAY DIFFRACTION PATTERN OF ELECTROLYTE FROM DISCHARGED CELL - CONVERTED $ZnCl_2$ BULK ELECTROLYTE

Electrolyte Table 4		Discharged Cell				Ag ASTM 4-9783		$ZnCl_2 \cdot 2NH_4Cl$ 12-304		NH_4Cl 7-7	
		Ag Side		Zn Side							
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
		7.56	8					7.48	1		
				7.03	100						
6.19	10	6.07	5					6.32	11		
								6.27	11		
5.72	12			5.75	10						
5.61	20										
				5.40	20			5.22	11		
5.13	100			5.28	30			5.19	100		
		5.04	8								
				4.93	10						
				4.74	25						
4.57	80							4.64	35		
				4.29	5						
4.17	20	4.18	5					4.23	11		
3.85	20	3.79	5	3.80	10					3.87	23
3.58	95	3.55	3	3.69	15			3.64	30		
		3.52	5	3.45	10			3.61	25		
3.45	25			3.40	12						
3.36	10										
3.29	10										
3.22	15	3.19	3	3.23	10			3.25	20		
3.12	15			3.16	5			3.16	20		
3.08	5	3.09	15	3.10	15			3.13	25		
2.98	10	2.96	3	3.01	20			3.12	9		
								3.00	25		
2.91	10	2.88	3	2.86	5			2.97	11		
2.85	10	2.84	6	2.82	55						
2.75	25	2.73	10	2.76	60			2.78	60	2.74	100
2.70	10	2.70	20					2.74	30		
2.67	8			2.66	12						
2.59	25	2.63	8	2.62	20			2.63	5		
		2.56	8	2.56	20			2.59	15		
2.50	5			2.50	15			2.49	11		
2.47	10										
				2.40	5						

TABLE 11

X-RAY DIFFRACTION PATTERN OF ELECTROLYTE FROM DISCHARGED CELL - CONVERTED $ZnCl_2$ BULK ELECTROLYTE (Continued)

Electrolyte Table 4		Discharged Cell				Ag ASTM 4-9783		$ZnCl_2 \cdot 2NH_4Cl$ 12-304		NH_4Cl 7-7	
		Ag Side		Zn Side							
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
2.37	5			2.38	8			2.38	9		
2.35	25							2.36	13		
		2.32	100			2.36	100	2.31	11		
2.29	10			2.30	15			2.30	13		
								2.29	11		
2.24	10			2.23	5					2.24	4
2.16	10			2.16	3						
				2.14	5						
				2.13	3						
				2.11	5						
2.09	15	2.08	5	2.08	3						
				2.05	3						
2.02	5	2.02	50			2.04	40				
				2.00	3						
				1.97	15						
1.94	10										
1.87	20										

TABLE 12

X-RAY DIFFRACTION PATTERN OF ELECTROLYTE FROM DISCHARGED CELL - CONVERTED $ZnCl_2$ FIBROUS MEMBRANE

Electrolyte Before Discharge		Discharged Cell				$ZnCl_2 \cdot 3NH_4Cl$ Table 2		$ZnCl_2 \cdot 4Zn(OH)_2$ Table 3	
		Ag Side		Zn Side					
dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
9.93	100			8.92	100	7.56	30	7.76	100
		6.55	100	6.71	10				
6.11	10					6.32	10		
		5.90	2						
5.68	15			5.61	11				
5.54	15			5.47	8	5.68	25		
5.19	15								
5.06	25					5.04	65		
				4.19	19	4.87	55		
				4.08	20			3.93	10
3.82	25					3.85	35	3.89	10
3.56	10	3.53	4			3.52	15	3.53	15
3.25	10			3.25	30				
3.19	10								
3.10	30	3.14	100			3.13	100	3.15	10
3.05	5			3.02	17				
				2.96	28	2.97	45		
						2.94	75		
2.88	10					2.87	60	2.90	10
2.82	10			2.80	20	2.81	15	2.85	15
2.73	10			2.70	27	2.74	25		
2.67	15			2.65	25	2.71	20	2.70	20
						2.61	20	2.66	40
2.54	5			2.51	5			2.59	15
2.48	5					2.45	65		
2.35	5	2.37	42	2.41	20	2.34	30	2.35	20
2.31	5								
2.28	8					2.25	15		
2.22	10								
2.17	5	2.17	2	2.19	5	2.19	10		
						2.17	5		
		2.11	30	2.12	5	2.13	10		
2.07	10	2.01	18	2.09	18	2.10	10		
		1.97	29	1.99	6	2.01	10	2.01	10
1.80	10			1.80	5				
1.71	8			1.71	6				
1.68	5			1.70	8				
1.58	5	1.59	1	1.59	10				