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William A. Armstrong and Peter J. Powell

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A POROUS ZINC ELECTRODE FOR USE AT VERY LOW TEMPERATURES

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Primary Power Sources Section
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ABSTRACT

The structure of porous electrodes made from pressed dendritic zinc has been varied to improve the efficiencies of zinc utilization during low temperature discharges. The effects of varying the composition of the plating bath and the rate of deposition of dendritic zinc were investigated as was the use of different binders and current collectors.

When samples of the optimized electrode were discharged in zinc/air bicells at a current density of 16 mA/cm^2, zinc utilization of from 23% at -40° to 91% at 50°C were recorded.

RÉSUMÉ

Nous avons modifié la structure des électrodes poreuses fabriquées de zinc dendritique comprimé afin d'en améliorer le rendement à basses températures. Nous avons étudié les effets de diverses compositions du bain de placage et de différentes vitesses de dépôt du zinc dendritique ainsi que l'emploi de différents agglomérants et collecteurs de courant dans la fabrication des électrodes poreuses.

Le rendement d'électrodes optimisées déchargées dans un module élémentaire zinc air d'une densité de courant de 16 mA/cm^2 a varié de 23% à -40°C jusqu'à 91% à 50°C.

INTRODUCTION

During the evaluation of a prototype reserve-primary zinc/air battery designed to power the AN/TRN-30 beacon (1), it was found that convective air flow through the cell stack was not sufficient to supply the oxygen required by the battery cathodes. This caused a severe reduction in the duration of discharge to the specified cut-off voltage. The cell stack consisted of 44 rectangular bicells in a double bicell design and access of air was restricted by the limited space between adjacent bicells. It is considered unlikely that a cell stack made up of such a large number of units can be designed within the 12 x 4 inch "foot-print" dimensions of the standard family of military batteries with intercell spacing necessary for adequate air circulation.

The original stack design consisted of only 22 bicells, each made up of two air cathodes cemented to a plastic cell frame and enclosing a 44 g porous zinc anode. This arrangement provided much greater intercell spacing. However, the zinc utilizations of 12 to 17% observed when single cells were discharged at a current density of 13 mA/cm^2 and a temperature of -40°C (2) indicated that a battery of this design would not meet the electrical performance specification at very low temperatures. The specification required 2 h of operation at -40° with a current of 3.0A and battery voltage in the range 20 to 30V. This led to the adoption of the "double bicell" stack design comprised of 22 double bicells connected electrically in series, each double bicell being made up of two bicells connected electrically in parallel for a total stack of 44 bicells. As each anode weighed 22 g the total weight of zinc remained the same as that in the original design but the electrode surface area was doubled and this resulted in zinc utilizations of about 25% when individual bicells were discharged at -40° and a current density of about 7 mA/cm^2 (2). This current density enabled a complete battery to provide 3.0A.

The object of the present investigation was to develop a zinc electrode structure capable of meeting the low temperature performance requirements with the original cell stack design of 22 bicells, a design which allows sufficient intercell spacing for adequate access of air to the cathode surfaces. As it has been shown that only high porosity electrodes made from electrolytically deposited zinc can approach the required performance at low temperatures (3), it was decided to start with this basic type of electrode, prepared by the cold pressing of a mixture of dendritic zinc and a binder onto a metal current collector, and to vary the parameters which would affect the pore structure and electrical conductivity of the electrode. Thus the effects of varying the composition of the plating bath and the rate of zinc deposition were investigated as was the use of different types and quantities of binders. Various current collectors and configurations of current collectors were also examined. In addition, the effects of certain additives in the battery electrolyte on zinc utilization at low temperatures were studied.

EVALUATION OF POROUS ZINC ANODES

Zinc electrodes were evaluated by being discharged in bicells under conditions which approximated as closely as possible those which might be encountered in a zinc/air battery capable of meeting the specifications for the AN/TRN-30 beacon (1). In order to minimize the quantities of materials used and the time spent in making air electrodes for the bicells, the weight of zinc used in each anode was 2.7 g rather than 44 g. Electrode areas were reduced proportionately but the width of the bicell cavity was kept at 0.7 cm, the same as that for the full size bicell. Thus the quotient of the volume of electrolyte per weight of zinc (2 ml/g) was the same as would be used in full size battery bicells. The importance of this quotient on the utilization of zinc electrodes discharged at -40° has been demonstrated (2). Highest utilizations are obtained with values of 3 or 4 ml of electrolyte per g of zinc but space and weight limitations restrict the amount of electrolyte that can be used to about 2 ml/g.

The components of the test bicell are shown in Figure 1. The zinc electrode to be tested was housed in a polymethylmethacrylate frame having inside dimensions of 2.86 x 2.86 x 0.6 cm. Two holes in the frame permitted the introduction of electrolyte and the exit of the lead-off tab. A rubber gasket, an air cathode and a polymethylmethacrylate frame with inside dimensions of 2.5 x 2.5 x 0.3 cm were placed on either side of the central frame and the whole was held together with clamps (Figure 2). To complete the bicell, the lead-off tabs of the two air cathodes were connected electrically. The thickness of the central plastic frame plus that of the rubber gaskets formed a cell cavity with a thickness of 0.7 cm.

The air cathodes contained 5 mg/cm^2 silver, 20 mg/cm^2 activated carbon and 2.5 mg/cm^2 polytetrafluoroethylene and were of a type designed for operation at very low temperatures (4). A layer of glass-Vinyon separator material was pressed onto each air cathode on the side which would be adjacent to the electrolyte in the assembled bicell. This material, developed at DREO for its excellent wettability at low temperatures (5), prevented electrical shorting between the anode and cathodes.

To evaluate a zinc anode, the bicell was placed in an environmental chamber at -40° and after 2 hours was activated by being filled with aqueous potassium hydroxide electrolyte (5-6 ml) which had also been equilibrated at that temperature. Five minutes after activation the cell was discharged by

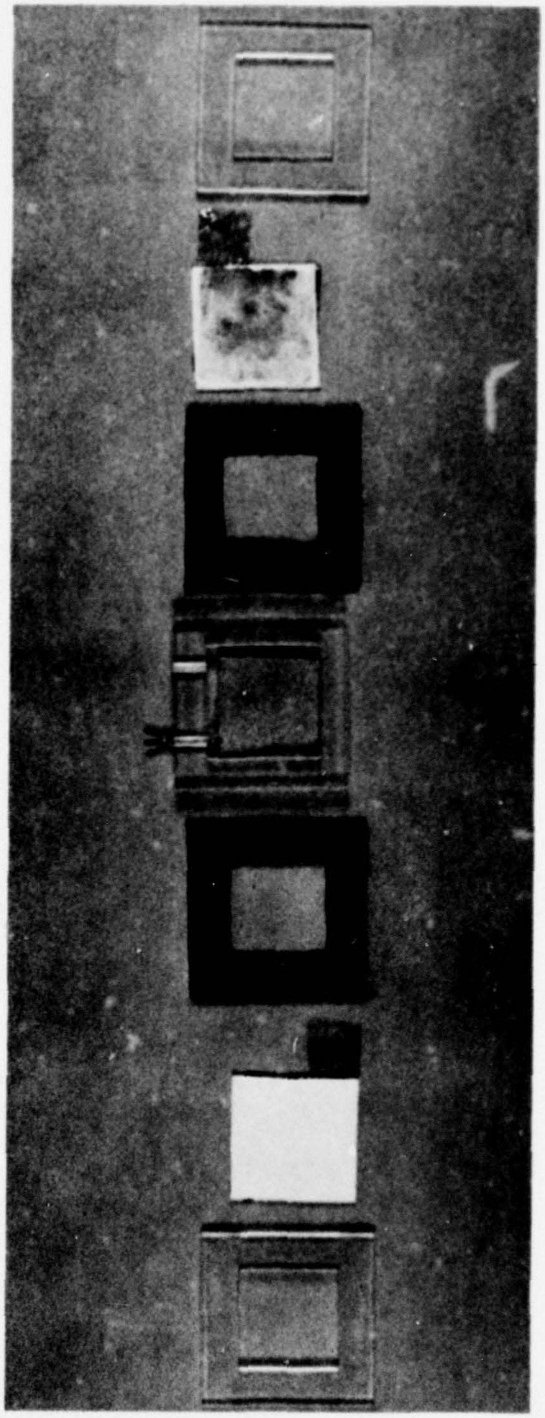

Fig. 1: Components of Test Bicell.

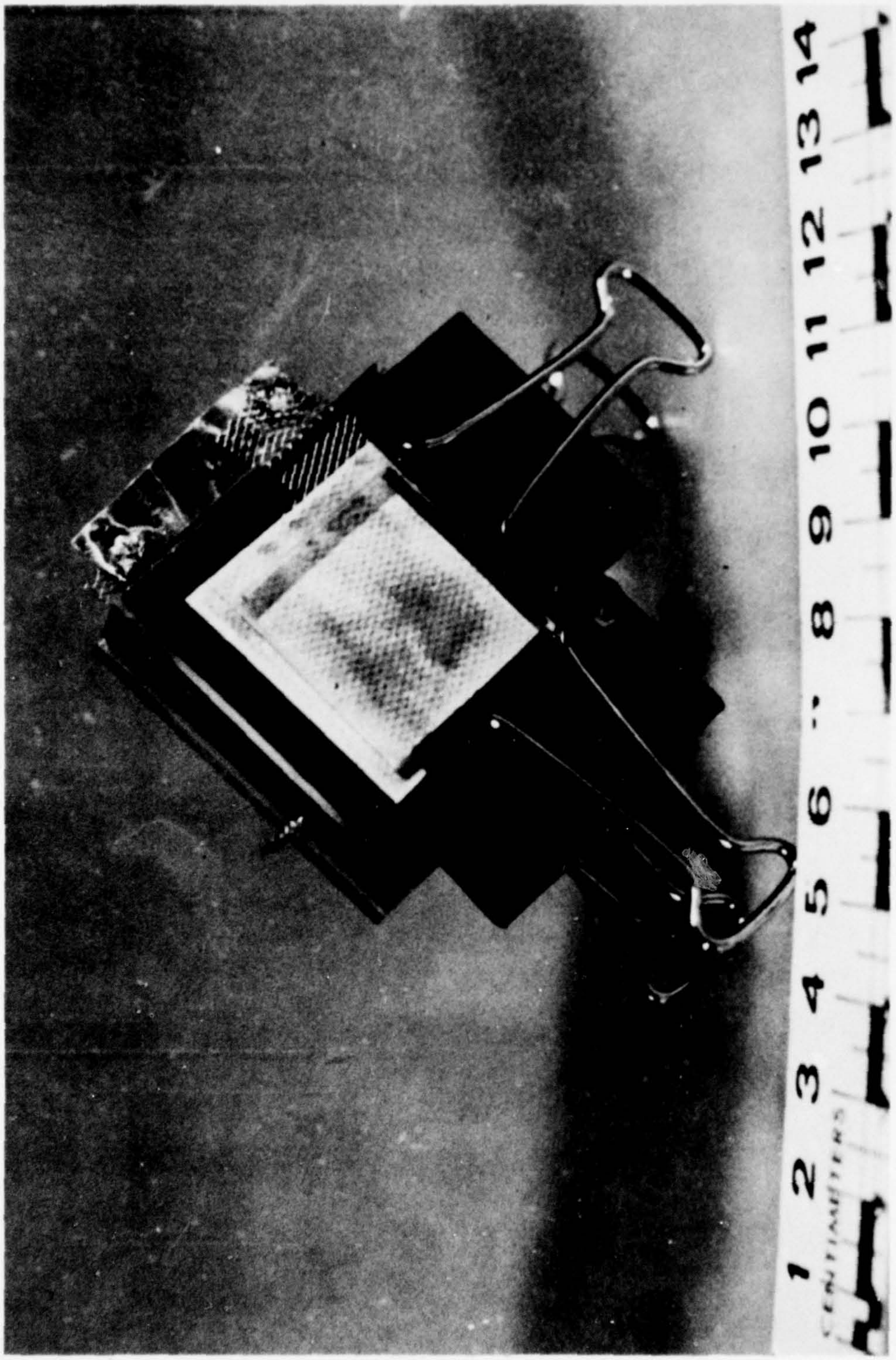

Fig. 2: Assembled Test Bicell.

the impression of a constant current of 200 mA (16 mA/cm^2 on each electrode surface) from a power supply. The circuit was arranged so that upon reaching a cell voltage of 0.90V, the discharge was stopped as was an interval timer used to record the duration of the discharge to the nearest 0.1 minute.

At the start of the investigation new air cathodes were used for each discharge. Experience showed that the cathodes suffered no detectable degradation when operated at -40° and could be used for at least fifteen discharges. The separator material was replaced after every third discharge. Air cathodes operated at room temperature or above were discarded after one discharge.

The possible influence of the performance of the air cathode on the evaluation of zinc electrodes was examined briefly. An air cathode was mounted in a cell along with a nickel screen counter electrode and a mercury/mercuric oxide reference electrode. A current of 100 mA (16 mA/cm^2) was impressed on the cathode and the potential of the cathode with respect to the reference electrode recorded at -40°. As the electrolyte concentration was increased from 5.8 to 8.5 M the polarization of the air cathode increased by 4 mV. Similar experiments were done using battery electrolyte additives discussed later in the report and in no case did the polarization increase by more than 4 mV. Such changes in the potential of the air cathode would not noticeably affect the length of discharge to a 900 mV cell cut-off voltage. Thus passivation of the zinc electrode was, in all cases, the factor limiting the duration of cell discharge.

As the battery to power the AN/TRN-30 must deliver 3.0A, the test cell discharging at 0.2A may be considered as a 1/15 scale model of a battery bicell designed to operate at a current density of 16 mA/cm^2 and having a 40.5 g anode. This means that the minimum operating times for various temperatures given in the battery specification (1) can be used to evaluate the performance of zinc electrodes discharged in the test cell. Thus the minimum acceptable operating period at -40° is 2 hours with a cell voltage in the range 0.90 to 1.36V. This corresponds to about 18% efficiency of utilization of the available zinc.

PREPARATION OF DENDRITIC ZINC

A sheet zinc anode* was situated in a polymethlmethacrylate box half way between two sheet nickel cathodes and sufficient plating solution (described below) added to cover the three electrodes. On impression of a constant current from a power supply, dendritic zinc was deposited on both nickel cathodes. When sufficient zinc had been collected, usually about 15 g, the electroplating was stopped and the dendrites scrapped off the nickel sheets into a shallow tray where they were washed with flowing distilled water for 0.5 hour. The water was then decanted and 0.1N hydrochloric acid

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* The sheet zinc was analyzed spectrographically and found to contain the following impurities: Ag 0.02%, Cu 0.02%, Fe 0.005%, Si 0.001%, Pb 0.03%, Hg 0.003%.

added. After stirring the zinc in this solution for 5 minutes the acid was poured off and washing in distilled water resumed for a further 0.5 hour. The dendritic zinc was next washed several times with absolute methanol and transferred to a filter funnel affixed on an appropriate flask. A sheet of filter paper was placed over the funnel and covered with anhydrous silica gel. The zinc was dried for an hour by attaching the filter flask to the house vacuum and drawing air through, first, the silica gel to remove atmospheric moisture and then the zinc. The dried zinc particles which would pass through a No. 30 screen (600 μm openings) were stored under vacuum in a desiccator.

ZINC FROM SALINE PLATING BATHS

Lithium, sodium, potassium and zinc chlorides were used to prepare plating baths of various compositions from which dendritic zinc was deposited at a number of different current densities. Electrodes for discharge in bicells were prepared by first mixing 2.7 g of dendritic zinc with 0.162 g (6% of the weight of the zinc) Solka-Floc KS1040*. Half of the mixture was poured into a 2.5 x 2.5 cm mold, smoothed and levelled. A piece of expanded copper** 2.4 x 2.4 cm with a 1.2 x 3 cm tab protruding from one corner was next placed in the mold and the rest of the zinc mixture added and levelled. The whole was cold pressed with a 1000 lb force for three minutes.

The porous zinc electrodes prepared in this manner were discharged at -40° and a current of 200 mA in bicells filled with 7.3M KOH electrolyte. The results obtained are recorded in Table I. In most cases only one zinc anode was discharged for each set of conditions. Four electrodes were discharged under the conditions listed for electrode 6. The lengths of discharge recorded were in the range 112 to 115 minutes.

Zinc electrodeposited in lithium chloride electrolyte was contaminated with a fine white precipitate, presumably zinc hydroxide, most of which was removed during the washing process. Electrodes prepared from this material crumbled easily and passivated rapidly when discharged at -40°.

Very hard deposits were obtained with zinc chloride plating baths. The zinc did not mix well with the Solka-Floc and the electrodes lacked mechanical strength. They also passivated rapidly during discharge.

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* Solka-Floc is a highly purified, finely divided cellulose product made by Brown Company, Berlin, N.H., U.S.A. Only material that had passed through a No. 60 screen (250 μm) was used in the preparation of electrodes.

** 3 Cu 6.5 3/0 from Exmet Corporation, Bridgeport, Conn., U.S.A.

TABLE I

The Duration of Discharge at -40°C of Porous Electrodes Made With Dendritic Zinc from Various Saline Plating Baths

Electrode No.	Bath Composition	Plating Current Density (mA/cm^2)	Duration of Discharge* (min)
1	5.8M LiCl	15	3
2	1.5M $ZnCl_2$	15	16
3	1.5M $ZnCl_2$	100	11
4	3.1M KCl - 0.15M $ZnCl_2$	15	92
5	2.7M KCl - 0.30M $ZnCl_2$	15	104
6	2.4M KCl - 0.45M $ZnCl_2$	15	115
7	2.0M KCl - 0.60M $ZnCl_2$	15	110
8	1.4M KCl - 0.90M $ZnCl_2$	15	95
9	3.9M NaCl - 0.15M $ZnCl_2$	15	73
10	5.2M LiCl - 0.15M $ZnCl_2$	15	99
11	4.6M LiCl - 0.30M $ZnCl_2$	15	98
12	3.5M LiCl - 0.60M $ZnCl_2$	15	99
13	5.2M LiCl - 0.15M $ZnCl_2$	100	84
14	2.0M KCl - 0.60M $ZnCl_2$	50	<1
15	2.0M KCl - 0.60M $ZnCl_2$	100	<1

* 2.7g Zn, 7.3M KOH electrolyte, current density 16 mA/cm^2, cell cut-off voltage 0.90V.

Best results were obtained with zinc plated in potassium chloride solutions containing zinc chloride. Of the compositions investigated, 2.4M KCl - 0.45M $ZnCl_2$ gave the zinc deposit best suited for use in a low temperature electrode (electrode 6).

Zinc deposited from lithium chloride solutions containing zinc chloride was slightly less suitable for use in electrodes and the concentrations of $ZnCl_2$ and LiCl had little effect on electrode performance (electrode 10 to 12).

The most suitable plating current density for KCl - $ZnCl_2$ baths was found to be 15 mA/cm^2. Higher current densities gave hard compact deposits which were difficult to press into electrodes and these electrodes passivated very rapidly when discharged at -40° (electrodes 14 and 15). High current densities had less effect on the performance of zinc deposited from LiCl - $ZnCl_2$ baths (electrode 13).

Electrodes similar to No. 6 were prepared with Solka-Floc concentrations of 2% and 8% of the weight of zinc instead of 6%. The duration of discharge at -40° of these electrodes was not significantly different from that of electrode 6.

ZINC FROM ALKALINE PLATING BATHS

As none of the electrodes made from dendritic zinc formed in saline plating baths gave the required two hour discharge at -40°, alkaline plating baths were investigated. Porous electrodes were prepared and discharged at -40° in zinc/air bicells in exactly the same manner as described in the preceding section. The results are listed in Table II.

The concentrations of both potassium hydroxide and zinc oxide in the plating bath affected the properties of the electrodeposited zinc. In preparing the zinc for electrodes 19, 21, 26-28 the concentration of KOH was 3.5M and the plating current density maintained at 50 mA/cm^2 while the concentration of zinc oxide was varied from 0 to 0.3M. The duration of discharge increased from 82 min in the absence of zinc oxide to about 130 min when the concentration of zinc oxide was in the range 0.04 to 0.16M and decreased to 114 min when the concentration of zinc oxide was increased to 0.3M.

With electrodes 21, 24 and 25 the concentration of zinc oxide in the plating bath was 0.16M and the plating current density 50 mA/cm^2 while the concentration of potassium hydroxide was varied from 2.0 to 7.0M. The best result (130 min of discharge) was obtained with a bath 3.5M in KOH.

The plating current densities of 15, 50, 100 and 200 mA/cm^2 were investigated with a bath composition of 3.5M KOH - 0.16M ZnO (electrodes 20-23). Zinc deposited at 50 mA/cm^2 gave the electrode with the longest discharge time.

TABLE II

The Duration of Discharge at -40°C of Porous Electrodes Made from Various Alkaline Plating Baths

Electrode No.	Bath Composition	Plating Current Density (mA/cm^2)	Duration of Discharge* (min)
16	3.5M KOH	5	91
17	3.5M KOH	10	109
18	3.5M KOH	25	95
19	3.5M KOH	50	82
20	3.5M KOH - 0.16M ZnO	15	106
21	3.5M KOH - 0.16M ZnO	50	130
22	3.5M KOH - 0.16M ZnO	100	124
23	3.5M KOH - 0.16M ZnO	200	99
24	7.0M KOH - 0.16M ZnO	50	98
25	2.0M KOH - 0.16M ZnO	50	115
26	3.5M KOH - 0.04M ZnO	50	131
27	3.5M KOH - 0.08M ZnO	50	132
28	3.5M KOH - 0.30M ZnO	50	114
29	3.5M KOH - 0.08M ZnO	15	102
30	3.5M KOH - 0.08M ZnO	100	107

*** 2.7g Zn, 7.3M KOH electrolyte, current density 16 mA/cm^2, cell cut-off voltage 0.90V.**

Three of the electrodes described in Table II (electrodes 21, 26 and 27) discharged for more than two hours at -40° and hence met the requirement at this temperature.

CHANGES IN ELECTRODE STRUCTURE

Attempts were made to increase the electrical conductivity of the porous zinc electrode by changing the mesh size of the expanded copper current collector, by using two current collectors, by using a pleated collector and by substituting expanded zinc for expanded copper as the current collector. Two current collectors or a pleated collector would reduce the number of particle-to-particle junctions in the electron path between the site of electrochemical reaction and the collector while the use of zinc instead of copper would eliminate any possible formation of Cu/Zn corrosion sites. However, none of these changes appreciably affected the duration of discharge at -40°. Some of these arrangements might result in improvements if used in larger zinc electrodes where conductive paths would be longer.

A filler is required to bind the zinc particles while maintaining a high degree of porosity. In the absence of a filler the high pressure required to bind the dendritic zinc particles resulted in electrodes having a porosity too low for efficient discharge at low temperatures. Fillers other than Solka-Floc KS1040 were investigated and details are recorded in Table III. In each case the electrode contained 2.7g of dendritic zinc which had been deposited at a current density of 50 mA/cm^2 from 3.5M KOH - 0.08M ZnO plating bath and the concentration of filler was expressed as a percentage of this weight of zinc. Electrodes were prepared and discharged at -40° as described earlier in this report. All the fillers except Alon wet rapidly in the electrolyte. Water-soluble fillers such as ammonium chloride have been used to increase electrode porosity (6) but must be leached out prior to discharge of the electrode.

Glass fiber was also investigated as a possible filler in pressed zinc electrodes. Attempts to use various samples of Type 475 glass from Johns-Manville having fiber diameters from 0.2 to 1.59 μm were unsuccessful. Mixing the zinc and glass proved difficult and the electrodes fell to pieces easily. No electrode was sufficiently rigid to permit discharge in a bicell.

A study of the effect of changing the porosity of the electrode by varying the pressing load was limited by the cohesiveness of the zinc/Solka-Floc mixture. When forces of less than 1000 lbs were used to form the 2.5 x 2.5 cm electrodes, structural strength was decreased without any increase in the duration of the discharge. Forces greater than 1000 lbs decreased the electrode porosity and the duration of the discharge. Thus the best electrode structure was obtained when 2.7g of dendritic zinc, obtained by electrodeposition at 50 mA/cm^2 from a bath of composition 3.5M KOH - 0.08M ZnO, was mixed with 6% of its weight (1.63g) Solka-Floc KS1040 and pressed with a force of 1000 lbs onto a 3 Cu 6.5 3/0 current collector to form an electrode of dimensions 2.5 x 2.5 x 0.21 cm and having a calculated

TABLE III

The Duration of Discharge at -40° of Porous Electrodes Containing Various Fillers

Type of Filler	Concentration of Filler (%)	Duration of Discharge* (min)
Solka-Floc KS1040	4	103
Solka-Floc KS1040	6	132
Solka-Floc KS1040	8	129
Solka-Floc SW40	6	116
Cab-O-Sil H5**	6	84
Cab-O-Ti†	6	86
Alon††	6	87

* 2.7g Zn, 7.3M KOH electrolyte, current density 16 mA/cm^2, cell cut-off voltage 0.90V.

** Fumed silica.

† Finely divided titanium dioxide, Cabot Corporation, Boston, Mass., U.S.A.

†† Fumed alumina, Cabot Corporation, Boston, Mass., U.S.A.

porosity of about 72%. Porous zinc electrodes prepared in this manner were used in all the following investigations described in this report.

CHANGES IN BATTERY ELECTROLYTE COMPOSITION

In the preceding sections the effect on the electrode performance at -40° of the composition of the plating bath in which the dendritic zinc was electrodeposited was investigated. The composition of the battery electrolyte may also be an important factor in the discharge efficiency of porous zinc electrodes at very low temperatures. For this reason the effect of the concentration of KOH in the electrolyte on the efficiency of utilization of porous zinc electrodes discharged at -40° was studied in the range 5.6 to 7.9M.

Electrodes were discharged as usual in zinc/air bicells at a current of 200 mA (16 mA/cm^2). The results obtained are plotted in Figure 3. It is evident that the greatest utilization of zinc was recorded with the electrode discharged in 6.8M KOH. This corresponds to the concentration at which the maximum limiting current density for planer zinc electrodes has been measured (7). The efficiency of 22.7% corresponds to a discharge of 2.5 hours, well over the 2 hours stipulated in the specifications.

Three different types of battery electrolyte additive: salt, complexing agent and surfactant were also investigated. It was considered possible that salts might promote corrosion and thus break up the passivating layer on the surface of the zinc, that complexing agents might promote the solubility of zinc oxide and reduce the rate of formation of the passivating layer and that a surfactant might alter the conditions at the zinc surface and decrease the rate of passivation. Table IV contains the data collected.

Potassium hydroxide electrolytes to which potassium chloride, potassium cyanide, disodium ethylenediaminetetraacetate or the surfactant Acrysol GS had been added did not produce as good a performance at -40° as the corresponding potassium hydroxide electrolyte with additives. Although the 6.5M KOH - 0.5M LiCl electrolyte gave a longer discharge time than the 6.5M KOH solution, some of the LiCl precipitated in the bicell.

Because of the negative effects observed with the three types of additives and the fact that the required 2 hour run could be obtained without additives, no further studies on electrolyte composition were carried out.

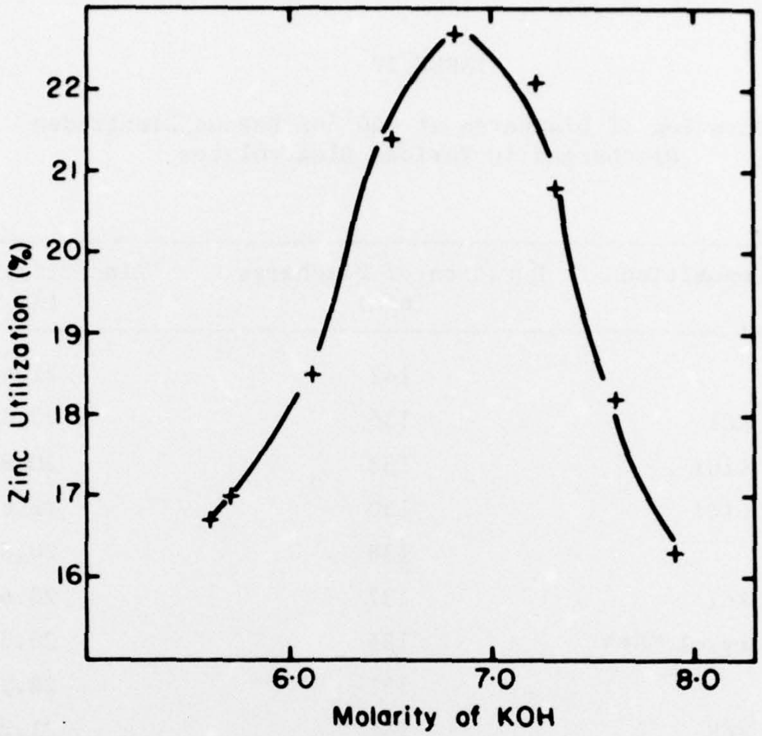

Fig. 3: Dependence of Zinc Utilization on Molarity of the KOH Electrolyte. Bicells discharged at -40°C, 16 mA/cm² to a 0.90V cut-off.

TABLE IV

The Duration of Discharge at -40° of Porous Electrodes Discharged in Various Electrolytes

Electrolyte Composition	Duration of Discharge (min)	Zinc Utilization* (%)
6.5M KOH	142	21.4
6.5M KOH - 0.1M KCl	136	20.4
6.5M KOH - 0.1M LiCl	138	20.8
6.5M KOH - 0.5M LiCl	150	22.6
7.3M KOH	138	20.8
7.3M KOH - 0.1M KCl	137	20.6
7.3M KOH - 1% Acrysol GS**	135	20.3
6.8M KOH	151	22.7
6.8M KOH - 0.1M KCN	141	21.2
6.8M KOH - 0.5M KCN	117	17.6
6.8M KOH - 0.1M Na_2EDTA†	131	19.7
6.8M KOH - 0.3M Na_2EDTA	75	11.3

* 2.7g Zn, current density 16 mA/cm^2, cell cut-off voltage 0.90V.

** Sodium polyacrylate made by Rohm and Haas Co., Philadelphia, Penn., U.S.A.

† Disodium ethylenediaminetetraacetate, Reagent Grade, Fisher Scientific Co., Ltd.

PERFORMANCE OF BEST POROUS ZINC ELECTRODES

The performance of the best porous zinc electrode when discharged in zinc/air bicells with 6.8M KOH electrolyte was investigated over a range of temperatures and current densities.

The changes in cell voltage with time are recorded in Figure 4 for bicells discharged at a current density of 16 mA/cm^2 and temperatures of -40°, -20° and 22°C. The decrease with decreasing temperature of both the cell voltage and the duration of discharge is readily apparent. In Figure 5 the results of similar discharges are recorded as a plot of the available capacity of the electrode in mAh/g of zinc (to a 0.90V cell voltage cut-off) against temperature. Using the theoretical zinc capacity of 820 mAh/g, it can be calculated that the percentage efficiency of zinc utilization ranges from 22.8% at -40° to 90.7% at 50°C. The adverse effect of temperature at values less than 0°C is strikingly evident with a decrease in efficiency from 80% at 0° to 48% at -20° recorded.

Figure 6 illustrates the effect of the magnitude of the current density on the available capacity of zinc during discharge at -40°. Capacity decreases rapidly as the current density is increased beyond 20 mA/cm^2. The value of 16 mA/cm^2 chosen for the battery design is in a region where the efficiency is somewhat less sensitive to small changes in current density.

It has been shown previously (4) that the polarization of an air electrode when operating at a current density of 16 mA/cm^2, increases by about 50 mV as the temperature decreases from 25°C to -40° while an increase of about 20mV occurs as the current density is increased from 10 to 25 mA/cm^2 during a discharge at -40°. As is evident from Figure 4, the cell voltage decreases from 0.95V to the 0.90V cut-off value in a very short time. It is estimated that a change in the cathode potential of 50 mV would change the duration of a cell discharge by not more than 10% if the discharge was carried out at -40° and by a much lower percentage at higher temperatures. Thus the available cell capacity is determined almost entirely by the discharge characteristics of the zinc electrode.

The magnitude of the improvement made to the performance of the zinc electrode at lower temperatures can be appreciated by comparing these results with those obtained by other workers. As mentioned in the Introduction, the highest capacity previously obtained with a pressed dendritic zinc electrode was 17% or 139 mAh/g when discharged at -40° and a current density of 13 mA/cm^2 in a bicell equipped with air cathodes similar to those used in this investigation (2). From Figure 6 it can be seen that the corresponding

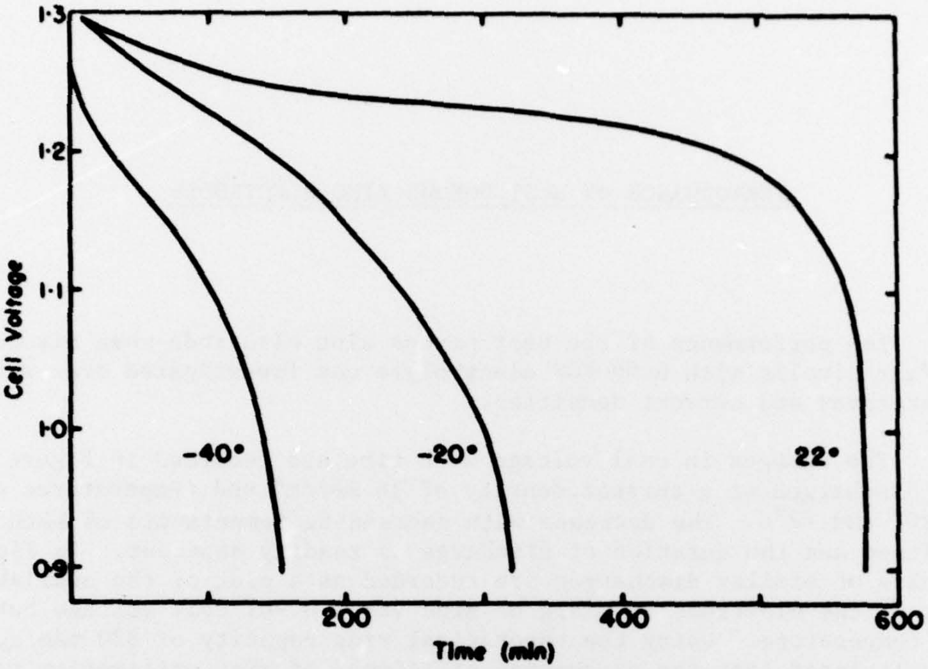

Fig. 4: The Discharge of Bicells at Various Temperatures. Bicells discharged at 16 mA/cm^2 to a 0.90V cut-off.

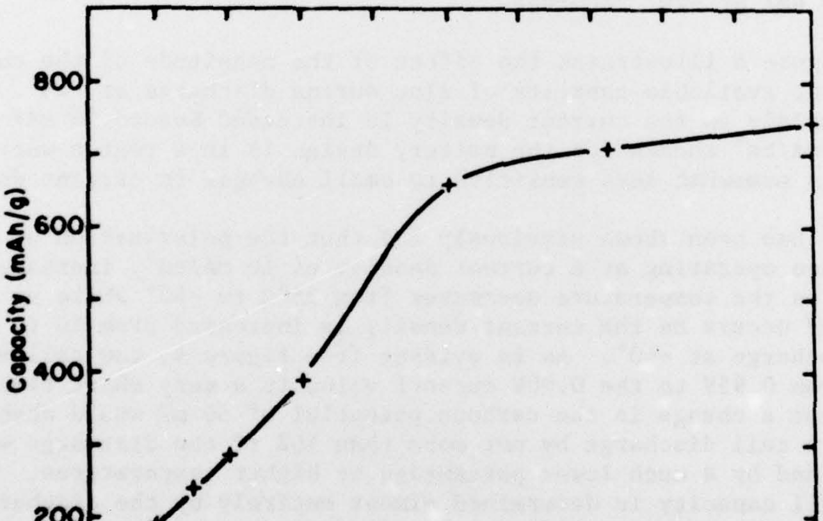

Fig. 5: The Effect of Temperature on the Capacity of Zinc Electrodes. Zinc discharged in bicells at 16 mA/cm^2 to a 0.90V cut-off.

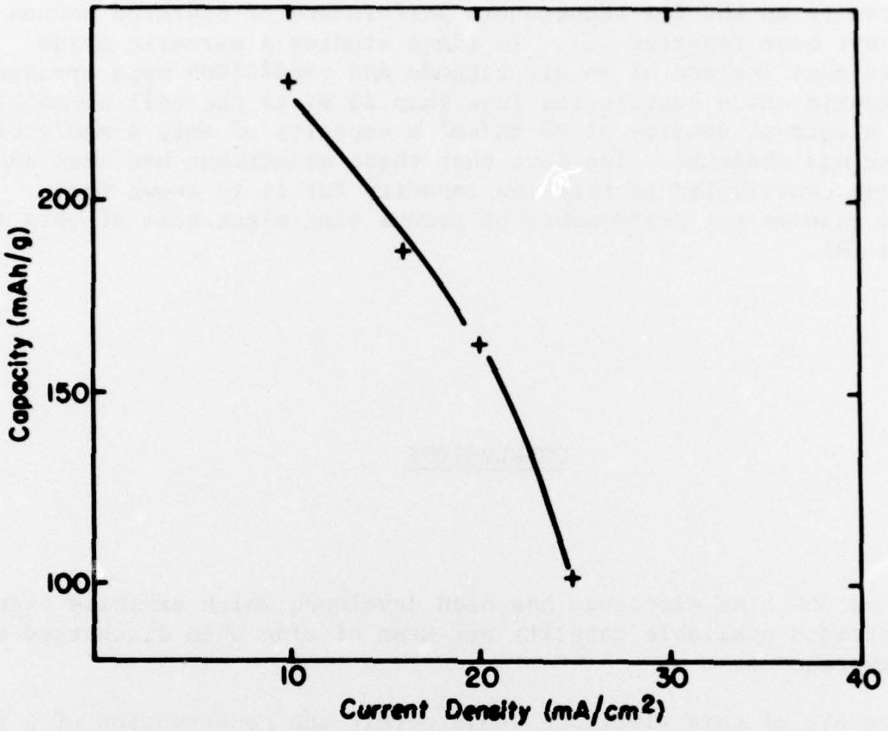

Fig. 6: The Effect of Current Density on the Capacity of Zinc Electrodes. Zinc discharged in bicells at -40°C to a 0.90V cut-off.

value for the DREO electrode is 209 mAh/g.

Results on the low temperature performance of sintered porous zinc electrodes have been reported (8). In these studies a mercuric oxide electrode was used instead of an air cathode and conditions were arranged so that the mercuric oxide contributed less than 20 mV to the cell polarization. At -40° and a current density of 20 mA/cm^2 a capacity of only 4 mAh/g of sintered zinc was observed. The fact that these electrodes had been amalgamated may have contributed to this low capacity for it is known that amalgamation reduces the performance of porous zinc electrodes at very low temperatures (9).

CONCLUSIONS

A porous zinc electrode has been developed which exhibits significantly increased available capacity per gram of zinc when discharged at very low temperatures.

The use of this electrode would permit the construction of a reserve-primary zinc/air battery to power the AN/TRN-30 beacon with a cell stack made up of 22 rather than 44 bicells. It should be possible to design such a stack to meet the dimensions specified for the battery box and with sufficient intercell spacing for adequate convective air flow. The reduction in the number of electrodes required would also result in a significant reduction in the cost of the battery.

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The structure of porous electrodes made from pressed dendritic zinc has been varied to improve the efficiencies of zinc utilization during low temperature discharges. The effects of varying the composition of the plating bath and the rate of deposition of dendritic zinc were investigated as was the use of different binders and current collectors in the electrolyte preparation.

When samples of the optimized electrode were discharged in zinc/air bicells at a current density of 16 mA/cm^2, zinc utilizations of from 23% at -40° to 91% at 50°C were recorded.

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