

- [54] **ALKALINE CELLS WITH ANODES MADE FROM ZINC FIBERS AND NEEDLES**
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[73] Assignee: **Union Carbide Corporation**, New York, N.Y.
[22] Filed: **Mar. 13, 1972**
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Related U.S. Application Data

- [62] Division of Ser. No. 25,490, April 3, 1970, abandoned.
[52] **U.S. Cl.** **136/30**
[51] **Int. Cl.** **H01m 41/00**
[58] **Field of Search** 136/30, 31, 125, 126, 76; 204/10, 14, 55 R

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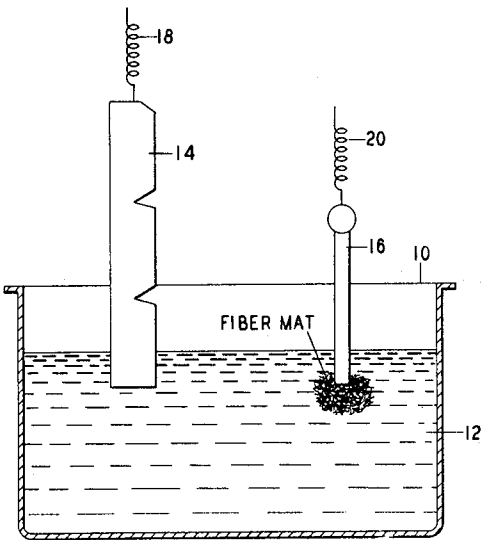
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Assistant Examiner—C. F. Lefevour
Attorney, Agent, or Firm—John R. Doherty

[57] **ABSTRACT**

Stable, high surface area, virtually pure zinc filaments and in particular zinc fibers and needles having a unique crystal structure consisting essentially of one or more single crystals preferentially orientated with an *a* axis parallel to the axis of the filament. The zinc fibers and needles are prepared by the electrolysis of a soluble zinc salt-containing electrolyte solution under conditions of extremely high cathode current density. Galvanic cell anodes are fabricated using the zinc fibers or needles by compression molding techniques.

9 Claims, 14 Drawing Figures



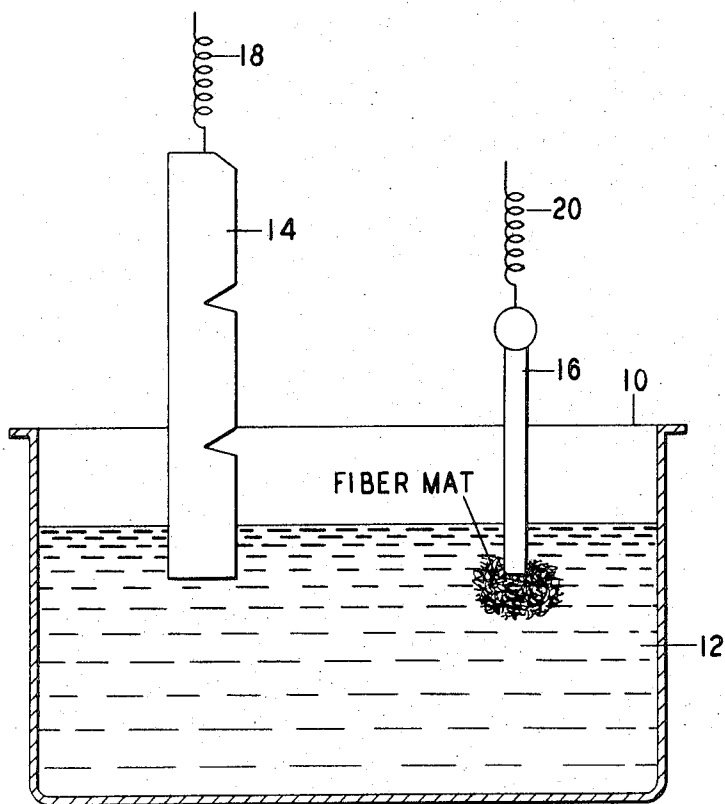


FIG. 1

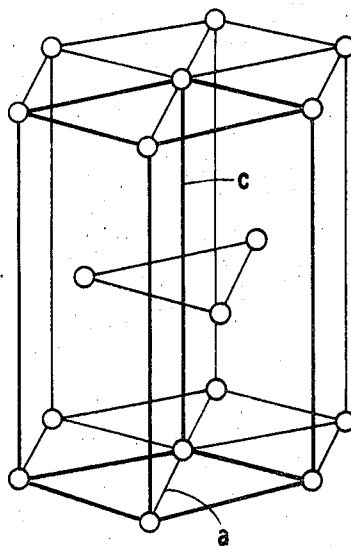


FIG. 2.

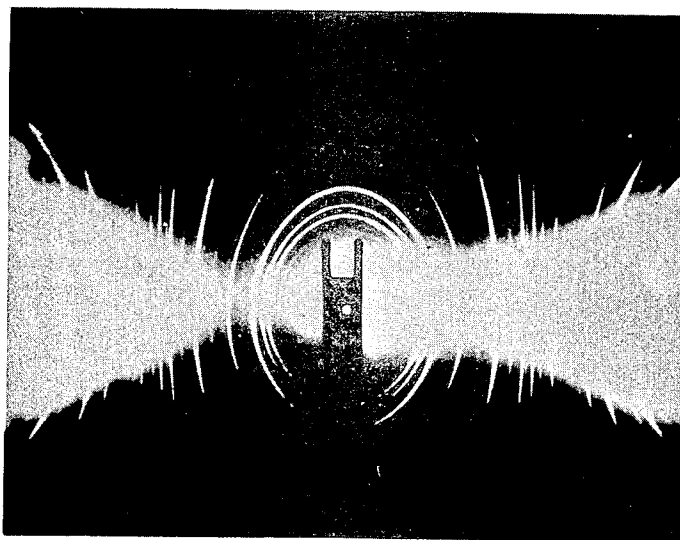


FIG. 3.

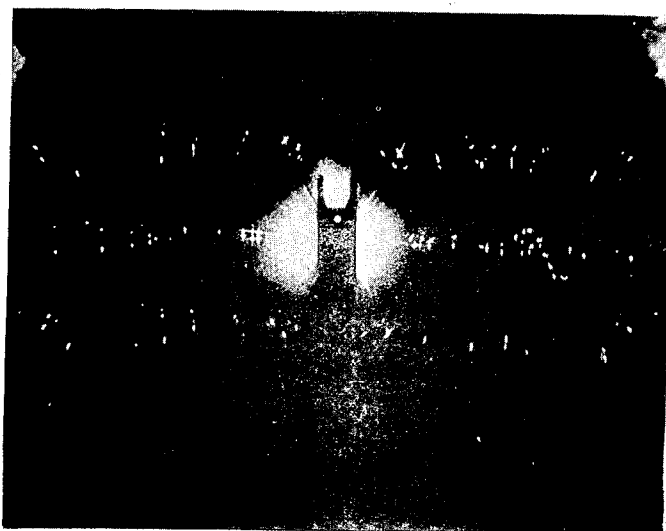


FIG. 4.

ANODIC POLARIZATION CURVES AT 25°C

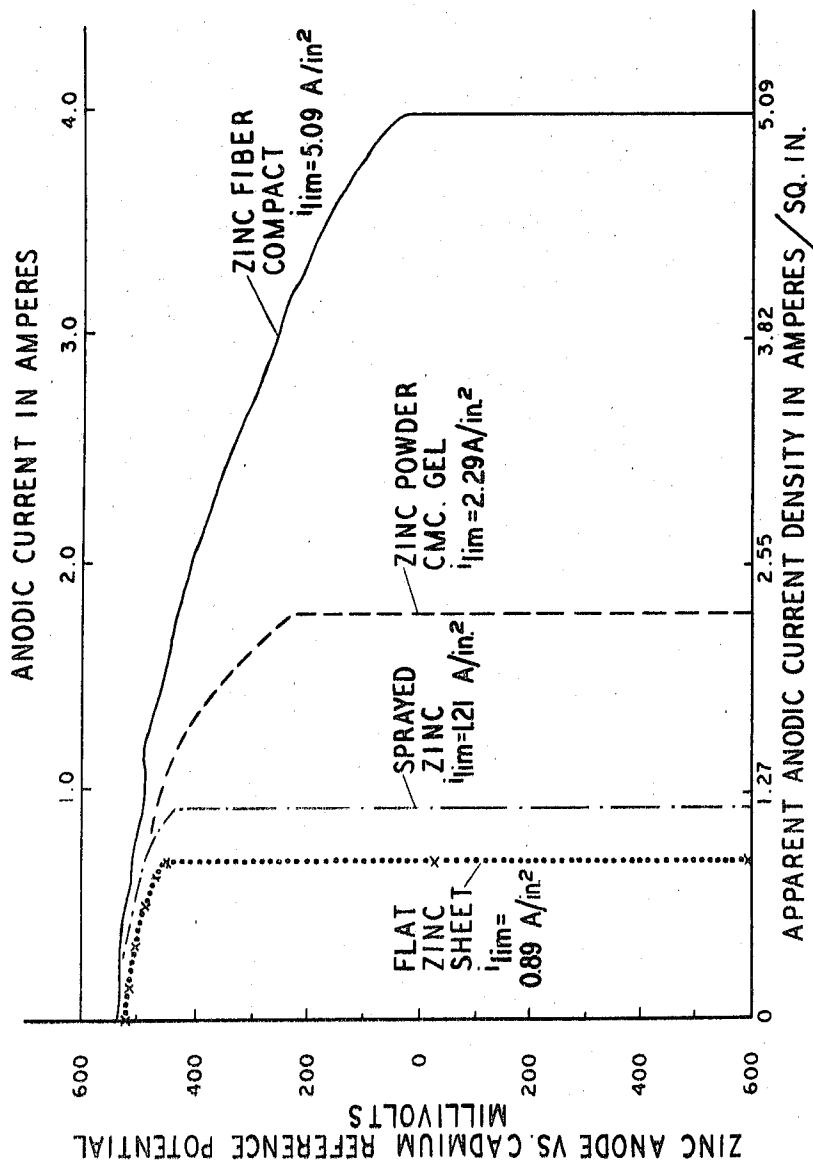


FIG. 5.

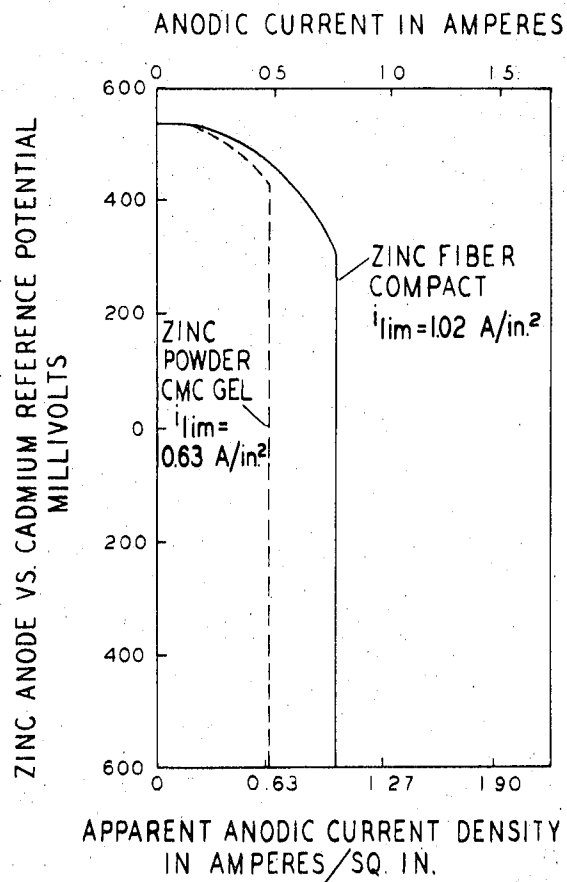
ANODIC POLARIZATION CURVES AT -20°C 

FIG. 6.

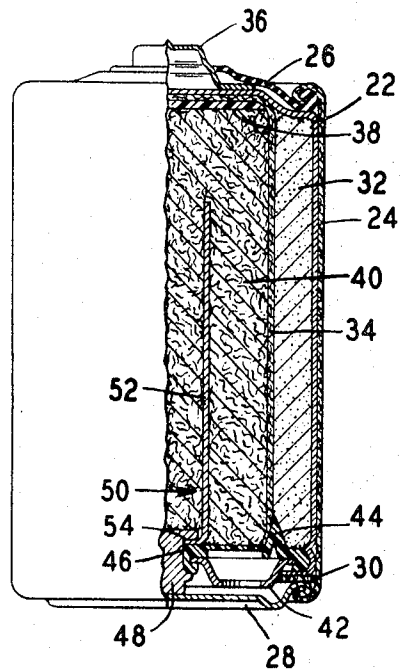


FIG. 7.

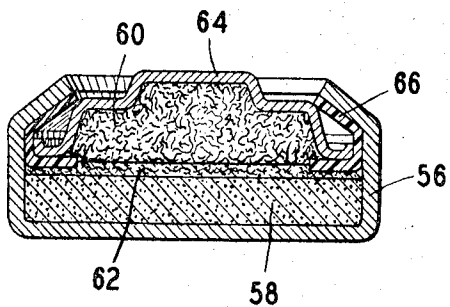


FIG. 9.

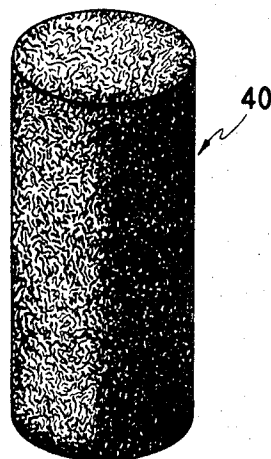


FIG. 8.

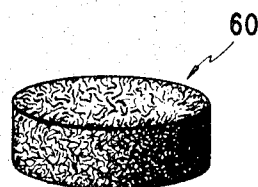


FIG. 10

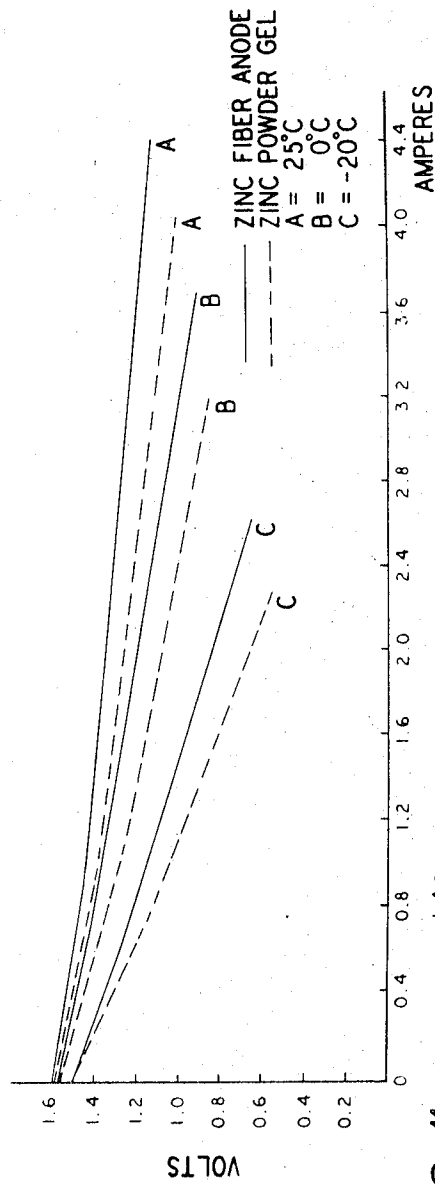


FIG. 11

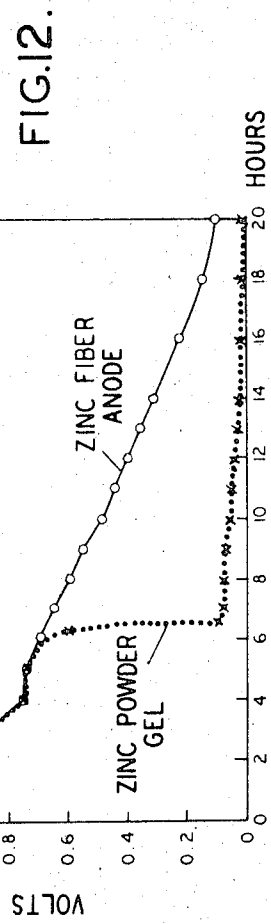


FIG. 12.

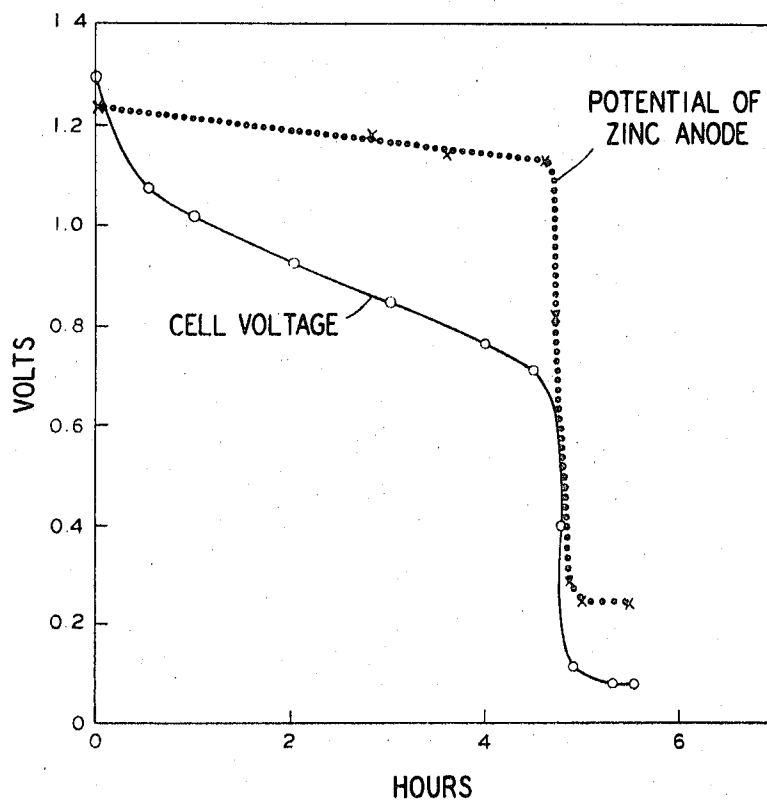


FIG. 13.

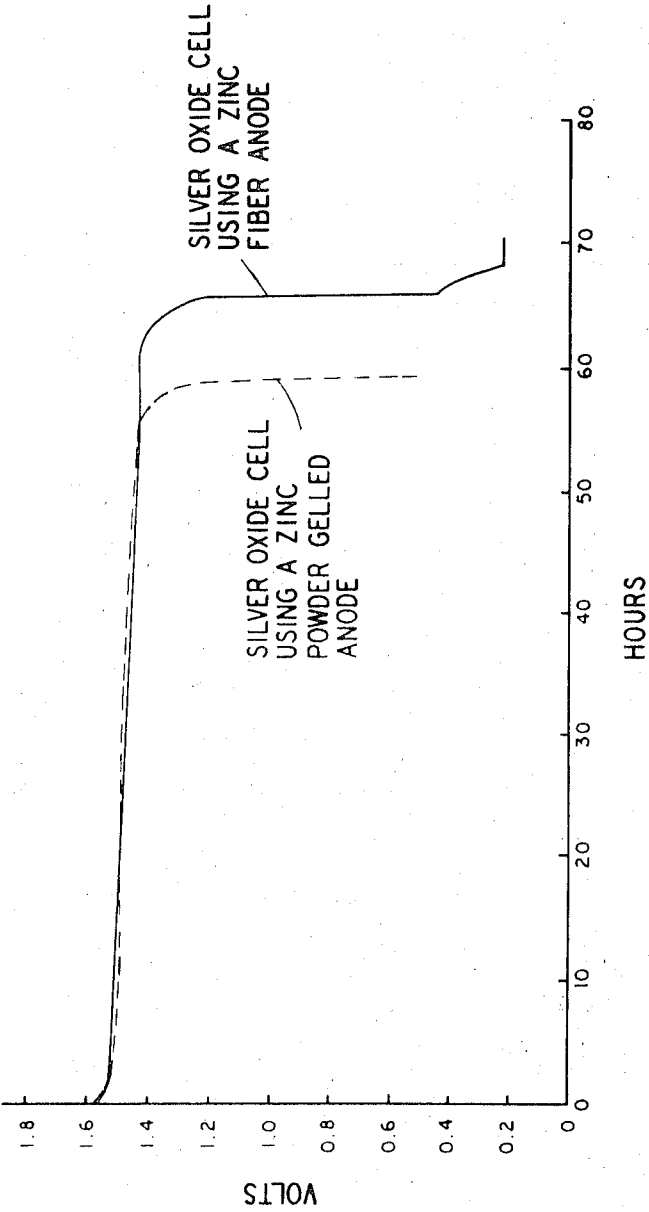


FIG. 14

ALKALINE CELLS WITH ANODES MADE FROM ZINC FIBERS AND NEEDLES

This is a division, of application Ser. No. 25,490 filed Apr. 3, 1970, now abandoned.

This invention relates to zinc filaments in general and more particularly to novel zinc fibers and needles and to a process for their preparation. In one aspect, the invention relates to galvanic cell anodes fabricated from the novel zinc fibers and needles and to both primary and secondary galvanic cells using such anodes especially, though not exclusively, in conjunction with an alkaline electrolyte.

BACKGROUND OF THE INVENTION

Galvanic cells of the type employing a zinc anode and an alkaline electrolyte generally require that the anode possess a high surface area. This requirement is essential for reducing the tendency of zinc to passivate in the alkaline environment and furthermore to obtain satisfactory high rate discharge, particularly at low temperatures, by a more efficient utilization of the active zinc material.

Prior art high surface area zinc anodes for use in alkaline galvanic cells have been made using conventional zinc powder. In one form of anode, the zinc powder is suspended within a suitable gelling agent such as carboxymethyl cellulose containing the alkaline electrolyte, these particular anodes being often referred to as "gelled powder anodes."

The difficulty with anodes of this type is that the gelling agent, which is electrochemically inactive and thus capable of performing no useful purpose other than to support the zinc powder, takes up considerable space which might otherwise be occupied by the active material and consequently its use necessarily reduces the volumetric efficiency of the cell. Another serious problem is that the zinc powder from which these anodes are made usually contains substantial amounts of metallic impurities. These metallic impurities are capable of forming local cell couples with zinc which can give rise to wasteful corrosion of the anode and to the generation of gas during storage of the cell. These problems can be effectively overcome by amalgamating the zinc powder prior to fabricating the anode but this is an expensive procedure and increases the cost of manufacturing the cell.

In sealed secondary or rechargeable alkaline galvanic cells using a gelled powder anode, it has been furthermore found that the gelling agent is readily oxidized and tends to break down upon repeated cycling, that is, charge and discharge, and thus destroys the mechanical integrity of the anode body. Another serious problem encountered with these gelled powder anodes is that under conditions of overcharge the gel network tends to prohibit rapid oxygen recombination with the active anode material and consequently dangerous internal gas pressures may develop in the sealed cells.

High surface area anodes have also been fabricated from a dendritic zinc sponge produced by electrolytic methods such as disclosed in U.S. Pat. No. 3,071,638 issued to M. B. Clark et al on Jan. 1, 1963. While this dendritic zinc sponge is advantageous in that it can be produced substantially free of impurities, it possesses an extremely high surface area and is pyrophoric and susceptible to spontaneous combustion if proper care is not taken in handling the material during the fabrication of the anode.

SUMMARY OF THE INVENTION

The invention contemplates the provision of novel zinc filaments and in particular novel zinc fibers and needles possessing certain properties which make them ideal for use in fabricating galvanic cell anodes. The zinc fibers and needles of the invention are quite readily distinguishable in physical appearance from other forms of zinc material heretofore known in the art. The zinc fibers of the invention may best be described as filaments having a thin elongated central spine portion with a number of poly-directional side growths or branches. The zinc needles of the invention may best be described as filaments having a fairly smooth central spine portion with only a few or a minimum of poly-directional side growths or branches. The term "filament" as used herein refers in the broadest sense to any thin elongated body whose length may be hundreds or thousands of times greater than its width, and possessing considerable tensile strength, toughness and pliability. The term "poly-directional" as used herein refers to the physical arrangement of the side growths or branches which, during formation, tend to grow in many different directions or along many planes and is used specifically to denote the three dimensional character of the fibers and needles as distinguished from the flat fern-like structure of dendritic particles.

The novel zinc fibers and needles of the invention are primarily characterized by their stability, unique crystal structure, exceptional purity and high surface area. The zinc fibers and needles are stable in that they do not rapidly oxidize upon exposure to the atmosphere. The crystal structure of the zinc fibers and needles is unique and readily distinguishable from any other form of zinc material. Broadly, the zinc fibers and needles may be defined as being composed of one or more single crystals having a preferred orientation. More precisely, the zinc fibers and needles may be defined as filaments the major part of which is composed of a thin elongated crystal spine portion consisting essentially of one or more single crystals preferentially orientated with an *a* axis ([100] or [010] direction) parallel to the axis of the filament, i.e., an *a* axis coincides with the primary direction of growth. The poly-directional side growths or branches are essentially polycrystalline and may be either granular, dendritic or platelet in form. The crystals are generally of irregular shape in cross-section and have a fairly large grain size as compared to conventional forms of zinc such as zinc powder. The zinc fibers and needles are substantially free of metallic impurities, containing only trace amounts of such impurities as aluminum, copper, lead and tin. The zinc fibers and needles possess a specific surface area which is intermediate that of conventional zinc powder and pyrophoric zinc sponge. The specific surface area of the zinc fibers and needles is between about 0.4 and 0.6 square meter per gram. The length of the zinc fibers and needles may vary from relatively short fibers of about 1/8 inch to long fibers of about 2 inches while the needles may vary from short needles of about 1/8 inch to long needles of up to about 4 inches in length. The average diameter of width of the fibers and needles is about six thousandths of an inch.

In the practice of the invention, the novel zinc fibers and needles are prepared by the electrolysis of a soluble zinc salt-containing electrolyte under conditions of

extremely high cathode current density. Generally, the cathode current density should be at least about 500 amperes per square foot.

The novel zinc fibers as defined hereinabove are prepared when the electrolysis is carried out at a temperature of about 25°C. The novel zinc needles are prepared when the electrolysis is carried out at an elevated temperature. The temperature at which the zinc needles can be formed will vary depending upon the particular electrolyte employed.

The process for preparing the novel zinc fibers and needles of the invention may be carried out in a typical electrolysis cell using a conventional zinc pig anode and a thin cathode suspended in the electrolyte bath. The fibers or needles electroform at the cathode and may be broken off and collected at the bottom of the bath or if the fibers or needles are not removed and the electrolysis is allowed to proceed, the fibers or needles tend to electrodeposit in the form of an interconnected skeletal zinc fibrous mat. This interconnected skeletal zinc fibrous mat consists basically of multiple fibers or needles joined to one or more neighboring fibers or needles throughout the mat. By the term "electroform" or "electroformation" as used herein is meant the production of zinc fibers and needles by electrodeposition.

Galvanic cell anodes can be readily fabricated from the novel zinc fibers and needles using conventional compression molding techniques. The novel zinc fibers or needles prepared as described above are placed within the mold and then compression molded to form an anode compact of the desired size and configuration. In forming the anode compact, the interconnected skeletal zinc fibrous mats are preferably used. If the individual zinc fibers or needles are used, it is essential that they should be thoroughly intermingled when placed within the mold. When compression is applied, the fibers or needles readily interlock or interknit with one another producing a highly cohesive anode body which is capable of supporting its own weight and retaining the shape in which it is molded.

Anode compacts fabricated as described above may be advantageously used in a variety of both primary and secondary galvanic cell systems. Primary LeClanche type dry cells employing a manganese dioxide cathode may be made using an anode compact of the invention. One advantage of the anode compact in this dry cell system is that of improved resistance to leakage. The liquid cell reaction products can readily be absorbed by the zinc fibers or needles and thus become effectively immobilized within the cell.

More particularly, anode compacts fabricated in accordance with the invention are most advantageously used in both primary and secondary alkaline zinc galvanic dry cell systems. One of the principal advantages of anode compacts in such cell systems is that they afford a very high active surface area for a more efficient utilization of the anode material.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be more particularly understood by reference to the detailed description of the preferred embodiments thereof taken in conjunction with the accompanying drawing, wherein:

FIG. 1 is a schematic view of a typical electrolysis cell used for preparing the zinc fibers and needles in accordance with the invention;

FIG. 2 is an isometric view showing the hexagonal crystal lattice of zinc;

FIG. 3 is an X-ray diffraction pattern of conventional zinc powder;

FIG. 4 is an X-ray diffraction pattern of zinc fibers prepared in accordance with the invention;

FIGS. 5 and 6 are polarization curves showing the performance of high surface area galvanic cell anodes made from zinc fibers as compared with conventional types of anodes known in the art;

FIG. 7 is an elevational sectional view of a typical alkaline zinc galvanic dry cell employing an anode compact in accordance with the invention;

FIG. 8 is a perspective view of the anode compact used in the cell of FIG. 7;

FIG. 9 is an elevational sectional view of a typical miniature button type alkaline zinc galvanic dry cell employing an anode pellet in accordance with the invention;

FIG. 10 is a perspective view of the anode pellet used in the cell of FIG. 9;

FIG. 11 is a graph showing the relationship between cell voltage and current of typical primary alkaline zinc manganese dioxide galvanic dry cells employing the anode compact as compared with similar cells using a gelled powder anode at various temperatures;

FIG. 12 is a graph showing the discharge voltage of a typical primary alkaline zinc-manganese dioxide galvanic dry cell employing the anode compact as compared with a similar cell using a gelled powder anode of the conventional type;

FIG. 13 is a graph showing the discharge voltage of a typical primary alkaline zinc-manganese dioxide galvanic dry cell employing a gelled powder anode as compared with the potential of the gelled powder anode versus a reference electrode; and

FIG. 14 is a graph showing the discharge voltage of a typical primary alkaline zinc-silver oxide galvanic dry cell employing the anode compact as compared with a similar cell using a gelled powder anode of the prior art.

FIG. 1 shows schematically a typical electrolysis cell for preparing zinc fibers and needles in accordance with the invention. The cell consists of an open tank 10 which is approximately three-quarters filled with a soluble zinc salt-containing electrolyte bath 12. Suspended in the electrolyte bath 12 is a high purity zinc pig anode 14 such as is conventionally used in the electroplating art. A wire cathode 16, for example of zinc, is dipped just below the surface of the electrolyte bath 12. In a practical cell, an array of multiple cathodes suspended within the electrolyte bath from a common bus bar may be used, there being only one cathode shown here for the purposes of illustration. The anode 14 and cathode 16 are connected respectively through means of wires 18, 20 into an external circuit (not shown). The circuit includes a source of direct electrical current and means such as rheostat for controlling the flow of electrical current through the cell.

To carry out the electroformation process of the invention, the external circuit is closed suitably by means of a switch and electrical current is allowed to flow through the cell. The anode is consumed during the electrolysis forming zinc ions in the electrolyte and depositing zinc at the cathode in accordance with the following reactions:

Anode: $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^{-}$

Cathode: $\text{Zn}^{++} + 2\text{e}^{-} \rightarrow \text{Zn}$

Essentially all of the electrical current flowing through the cell is utilized in forming the zinc deposit. The cell electrolyte is invariant in that the anode is continuously replenishing zinc ions into the electrolyte as zinc ions are removed at the cathode.

It has been unexpectedly found in accordance with the invention that if the electrolysis is carried out using a soluble zinc salt-containing electrolyte of high ionic conductivity with the operating conditions of the cell being so adjusted as to provide an extremely high cathode current density, zinc fibers or needles can be electroformed at the cathode. The electroformation process is also dependent on the temperature of the electrolyte bath. It has been found that when the electroformation process is carried out at a temperature of about 25°C., zinc fibers will be deposited. At higher temperatures above about 25°C., zinc needles are electroformed. The temperature at which the zinc needles begin to electroform will vary depending on the electrolyte composition and the concentration of the zinc salt used in the electrolyte bath.

From the earliest experimental work leading to the invention, it was recognized that one of the essential requirements for carrying out the electroformation process is the maintenance of extremely high cathode current densities. It has been found in accordance with the invention that the cathode current density should be maintained at about at least 500 amperes per square foot. In the preferred practice of the invention, the cathode current density should be maintained at above about 1,000 amperes per square foot. This is considerably higher than that used in the conventional electroplating art for depositing smooth coatings of zinc from an alkaline zinc cyanide bath wherein cathode current densities of from about 10 to 50 amperes per square foot have been reported (Electroplating Engineering Handbook by A. K. Graham, page 214, Reinhold Publishing Company). In the production by electrolytic methods of dendritic zinc sponge according to the Clark et al patent, supra, cathode current densities of only about 140 amperes per square foot are required. Since the current density is inversely proportional to the cathode surface area for a given current, it is advantageous to employ a cathode of the smallest practical surface area exposed to the electrolyte and preferably a very thin wire cathode is used. During the electroformation process, the zinc first deposits at the cathode in the form of individual fibers of needles which may be easily broken off and then collected at the bottom of the electrolyte bath. If the process is allowed to proceed without removing the individual fibers or needles, the electroformation will continue with more and more fibers or needles being deposited from the initial growth at the cathode surfaces. The growth of more and more fibers or needles will continue in this manner so long as sufficient electrical current is flowing through the cell to promote the electrodeposition of the fibers or needles and eventually an interconnected skeletal zinc fibrous mat will be formed. This skeletal fibrous mat consists basically of multiple fibers or needles joined to one or more neighboring fibers or needles in the mat.

Once the electroformation process has been started and the formation of the interconnected skeletal fi-

brous mat has begun, it may be necessary to periodically increase the flow of electrical current through the cell, such as by means of the rheostat, in order to meet the increased current requirements due to the increasingly greater number of fibers or needles being deposited. It is virtually impossible during this period of the process to determine the cathode current density with any degree of accuracy due to the rapidly changing surface area of the zinc deposits. However, the electroformation process may be expediently carried out by properly controlling the amount of electrical current flowing through the cell to provide an estimated cathode current density which is above the minimum requirement to promote the electroformation of the fibers or needles. The proper range of cathode current density can be estimated simply by visual observation of the type of deposit or reaction occurring at the cathode. If the cathode current density is too low, no fiber or needle deposits can be observed. The deposit in this instance will be of the level, adherent type or the powdery type. If the cathode current density is too high, gas evolution (hydrogen) will be readily observed.

In the practice of the invention, the electrolyte may contain any zinc salt whose principal requirement is that it be soluble in a solvent of high dielectric constant resulting in a solution of sufficient ionic conductivity to permit the maintenance of at least the minimum cathode current density necessary for electroforming the zinc fibers and needles of the invention.

Suitable soluble zinc salts include the acetate, bromide, chlorate, chloride, formate, iodide, 1-phenol-4-sulphonate, sulphate, thiocyanate, borate, bromate, fluogallate, fluoborate, fluosilicate, glycerophosphate, nitrate, phosphate, and sulphonate. Suitable solvents for the zinc salt include water, alcohols such as methanol, ethanol, and *n*-propanol, nitromethane, propylene carbonate and dimethylformamide. Cost and conductivity considerations are the two most important factors upon which the choice of the zinc salt and solvent should be based. Zinc chloride and zinc sulphate are the two preferred choices for the zinc salt from the standpoint of cost and conductivity. An aqueous solution of zinc chloride is the most preferred electrolyte solution. Water is the preferred solvent because of its low cost and freedom from fire hazard and toxicity. An additional salt such as ammonium sulphate may be used to increase the conductivity of the electrolyte bath.

The concentration of the soluble zinc salt in the electrolyte solution is not too narrowly critical so long as enough zinc ions are present in the electrolyte to promote the electroformation of the zinc fibers and needles and further provided that a sufficiently high conductivity is maintained. Generally, the electrolyte solution should contain at least above about 30 per cent by weight of the soluble zinc salt in solution.

As indicated above, it has been found that while the zinc fibers of the invention may be electroformed at a temperature of about 25°C. under the conditions of extremely high cathode current density, elevated temperatures of above about 25°C. are required to form the zinc needles and that the specific temperature at which the zinc needles will begin to deposit will vary depending on the electrolyte composition and the concentration of the soluble zinc salt used. To illustrate, it has been found that whereas zinc fibers will be electroformed at a temperature of about 25°C. using a 47 per

cent by weight solution of zinc chloride in water, the temperature of the electrolyte must be elevated to about 80°C. before zinc needles will be deposited. With basically the same electrolyte solution but using methanol as the solvent, zinc needles will be deposited at a temperature of about 40°C. It will be appreciated that determination of the temperature at which the zinc needles will be electroformed in accordance with the invention for any given electrolyte composition and concentration of the zinc salt is a simple matter of routine experimentation and that such experimentation is well within the ability of one skilled in the art.

An important feature of the electroformation process of the invention is that the individual zinc fibers and needles may be advantageously varied in length by properly controlling the cathode current density, that is, by adjusting the amount of electrical current flowing through the cell. It has been found that in addition to the temperature of the electrolyte bath, the current density maintained at the cathode has a profound influence on the nature of the zinc deposit and specifically the maximum length to which the respective individual fibers or needles may grow. By varying the electrical current flowing through the cell and consequently the cathode current density, the length of the fibers or needles may be varied from relatively short to long fibers or needles. The length of the fibers or needles will vary in inverse proportion to the cathode current so that by increasing the cathode current the length of the fibers of needles will be decreased and conversely by decreasing the cathode current the length of the fibers or needles will be increased. It will thus be seen that long, medium and short fibers or needles may be readily prepared. The zinc fibers may be prepared in lengths ranging from relatively short fibers of about 1/8 inch to long fibers of about 2 inches in length while the zinc needles may be prepared in lengths ranging from relatively short needles of about 1/8 inch to long needles of up to 4 inches in length.

Table 1 below illustrates the effects of both temperature and cathode current upon the nature of the zinc deposit. The electrolyte solution used to obtain the data shown in the table was a 47 per cent by weight solution of zinc chloride in water. Zinc needles electroformed at a temperature of about 80°C. using this electrolyte.

TABLE I

EFFECT OF TEMPERATURE AND CATHODE CURRENT UPON THE NATURE OF ELECTROFORMED ZINC			
Form of Electroformed Zinc	Approx. Length inches	Temperature °C.	Cathode Current Amperes
Short Fibers	1/8 - 1/4	25 - 65	300
Long Fibers	1	25	80
Very Long Fibers	1 - 2	25	15
Short Needles	1/8 - 1/4	90	100
Long Needles	1	90	50
Very Long Needles	2 - 4	90	15

These data dramatically show the effects of varying both the temperature and the electrical current flowing through the cell. As shown in the table, the temperature of the electrolyte was varied from about 25° to 90°C. producing both zinc fiber and needle deposits. The effect of varying the electrical current on the zinc deposit is also demonstrated. At high current values, short fibers and needles were electroformed. Conversely at low current values, long fibers and needles

were deposited. Values of current density could not be measured because of the rapidly changing surface area of the zinc deposits but the current density was estimated to be well above about 500 amperes per square foot.

To illustrate the practice of the invention, zinc fibers have been prepared using an electrolysis cell similar to that shown in FIG. 1 except that two arrays of seven thin zinc wire cathodes of about 0.312 inch in diameter dipping approximately 0.2 inch into the electrolyte solution were used, one array on each side of a zinc pig anode. The electrolyte was a 47 per cent by weight solution of zinc chloride in water and the anode-to-cathode distance was about 5 inches. The temperature of the electrolyte was maintained at about 25°C. Upon closing the electrical circuit, a current of about 180 amperes flowed through the cell and zinc was observed to electrodeposit at the cathode surfaces in the form of individual fibers. The fibers formed initially at the higher current density edges of each cathode and could be easily broken off immediately as they were formed by scraping the surfaces of each cathode, the fibers then falling to the bottom of the electrolyte bath. When the electrolysis was allowed to proceed without removing the fibers, more and more fibers were observed to electrodeposit from the surfaces of the fibers initially formed at each cathode and this process continued with each of the fibers joining to one or more neighboring fibers until an interconnected skeletal zinc fiber mat was produced. Eventually the weight of the fiber mat so produced caused it to be broken off from the cathode surfaces and the mat then fell to the bottom of the electrolyte bath. The process was continued to produce more and more fiber mat.

Zinc needles have also been prepared using the same electrolyte composition as disclosed in the above example. The process was carried out under essentially the same conditions except that the electrolyte was maintained at a temperature of about 90°C.

Crystallographic studies have been made in order to determine the crystal structure of the zinc fibers and needles of the invention. It is known from the literature that the zinc crystal is a hexagonal lattice composed of three unit cells. FIG. 2 shows diagrammatically this hexagonal lattice for zinc with one of the unit cells being shown in darkened outline for purposes of illustration. It will be seen from the drawing that there are two zinc

atoms to the unit cell. The unit cell is composed of one-eighth of a zinc atom on each of the corners and one zinc atom at a location within the cell. Each corner atom is shared by eight unit cells of adjacent crystals. The two axes of the zinc lattice are identified as the *a* and *c* axes in the literature and are shown in the diagram of FIG. 2.

An X-ray diffraction pattern for conventional zinc powder is shown in FIG. 3. The zinc powder shows con-

tinuous lines representing the randomness of crystal orientation and polycrystalline nature in the zinc powder.

X-ray diffraction data have also been obtained for the zinc fibers and needles of the invention. These data were obtained by the rotating crystal method. The fibers and needles were mounted with their growth direction, i.e., direction along their length, perpendicular to the impinging X-ray beam.

FIG. 4 shows the X-ray diffraction pattern for zinc fibers prepared in accordance with the invention. The X-ray diffraction pattern for the fibers shows the characteristic spots arranged on layer lines when the crystal is aligned with its growth axis perpendicular to the X-ray beam.

The identity or repeat distance along this crystal growth axis can be calculated from the distance between the layer lines on the film and was found for both the fibers and needles to be 2.665 Å. This is the same value published in the literature for the distance between zinc atoms along the *a* axis of the crystal. It will be seen that the zinc fibers and needles of the invention are composed of one or more zinc crystals preferentially orientated with an *a* axis ([110] or [010] direction) parallel to the axis of the filament which is coincident with the primary direction of growth.

Table II below gives the X-ray diffraction data for the zinc fibers of the invention. The table lists the *d* values in Å for the observed line and the Miller indices (*hkl*) for a unit cell corresponding to the observed line in the X-ray diffraction pattern. In a separate column are listed the observed locations of reflection on the zinc fiber orientated with its long direction perpendicular to the impinging X-ray beam.

TABLE II

X-RAY DIFFRACTION DATA FOR ELECTROFORMED ZINC FIBER			
<i>d</i>	Intensity (Powder Data)	<i>hkl</i>	Observed location of reflection on Zn fiber direction perpendicular to impinging X-ray beam
2.473	53	002	0 layer line only
2.30	40	100	0 and 1st layer lines
2.091	100	101	do.
1.687	28	102	do.
1.342	25	103	do.
1.332	21	110	1st layer line only
1.237	2	004	0 do.
1.1729	23	112	1st do.
1.1538	5	200	0 and second layer lines
1.1236	17	201	do.
1.0901	3	104	0 and 1st layer lines
1.0456	5	202	0 and second layer lines

Theoretically, if the fibers are composed of more than one crystal and they have preferred orientation along the *a* axis ([100] or [010] direction), *h* and/or *k*=0 on the zero layer line and *h* and/or *k*=1 on the first layer line. It will be readily seen from the table that the observed data agree with the theoretical.

Crystal grain studies have also been made on the zinc fibers and needles of the invention. The data obtained were compared with results of similar studies conducted on conventional zinc powder. All of the specimens studied were mounted, sectioned, polished and etched to bring out the grain structure. In the case of the zinc fibers and needles, the specimens were all sectioned through a plane taken in a direction perpendicular to the central spine portion of the fibers and needles.

Crystal grain size measurements were taken on the zinc fibers in a direction essentially perpendicular to the growth axis and the crystals were found to range in size from the largest grain diameter of about 0.01 inch to the smallest grain diameter of about 0.0002 inch (2×10^{-4}). The average grain diameter of the crystals was determined to be about 0.005 inch.

Crystal grain size measurements were taken on the zinc needles and the crystals were found to range from the largest grain diameter of about 0.002 to the smallest grain diameter of about 0.0001 inch. The average grain diameter of the crystals was found to be about 0.0008 inch.

Crystal grain size measurements were taken on the zinc powder and the grain diameter was found to range from about 0.000004 to 0.001 inch. The average grain diameter of the zinc powder was found to be about 0.0002 inch.

Zinc fibers and needles prepared in accordance with the invention have been found to be an excellent material for use in fabricating anodes for galvanic cells and especially those of the type employing an alkaline electrolyte. The fibers and needles possess a high surface area which is far in excess of that of conventional zinc powder but which at the same time is not so highly developed as to be pyrophoric and susceptible to rapid oxidation upon exposure to the atmosphere. Moreover, the fibers and needles contain only trace amounts of impurities and consequently they are less prone to the formation of local corrosion coupled resulting in wasteful corrosion of the anode and gassing during storage of the cells.

Surface area measurements of the zinc fibers and needles have been taken using the krypton absorption BET method.* The fibers and needles were found to possess a specific surface area of between about 0.4 and 0.6 square meter per gram. Conventional zinc powder using the same method was found to possess a specific surface area of only about 0.016 square meter per gram. It will thus be seen that the zinc fibers and needles have more than 30 times more surface area per unit weight than does the powder. Zinc sponge has a specific surface area many times that of the zinc fibers and needles (approximately 4 to 7 square meters per gram) but is highly pyrophoric. The advantage of the zinc fibers and needles is that they possess a considerably higher specific surface area than does the zinc powder without the disadvantage of rapid atmospheric oxidation observed with the higher surface area zinc sponge.

*BET method — Journal of American Chemical Society, Vol. 60, pg. 309, 1938, S. Brunauer, P. H. Emmett and E. Teller.

Qualitative spectrographic and colorimetric analyses have also been conducted on the zinc fibers and needles of the invention. These studies have demonstrated that the fibers and needles are one of the purest forms of zinc obtainable within a reasonable economic framework. The electroformation process is accompanied by electropurification and it has been found that the zinc fibers and needles so produced contain only trace amounts of impurities such as aluminum, copper, lead and iron. Table III below shows the results of the spectrographic analysis for impurities in zinc fibers as compared with conventional zinc powder. It will be readily seen from the table that the zinc powder contains minor amounts of both lead and iron while the zinc fibers contain only trace amounts of these impurities.

TABLE III

QUALITATIVE SPECTROGRAPHIC ANALYSIS					
Zinc Fibers Electroformed from Pig*			Zinc Powder		
Major	+Minor—	+Trace—	Major	+Minor—	+Trace—
Zn		Cu	Zn	Pb→	Cu
		Ni		Fe	Cd
		Al			Ag
		Si			Mg→
		Fe→			
		Mg→			
		←Pb			
		Sn→			
		Ca			

*Zinc Pig purity — 99.990% zinc, 0.003% lead (max), 0.001% iron (max), 0.003% cadmium (max).

Arrows indicate that impurities are present at upper or lower range shown by plus and minus signs
Major — above 1,000 ppm
Minor (+) — 1,000 ppm
Minor (—) — 100 ppm
Trace (+) — 10 ppm
Trace (—) — 1 ppm

Table IV below shows the results of the colorimetric analysis for iron in the zinc fibers and needles. The table also includes an analysis of conventional forms of zinc such as zinc pig, two commercial types of zinc powder, and zinc sheet.

TABLE IV

QUALITATIVE COLORIMETRIC ANALYSIS FOR IRON	
Zinc Material	Fe (ppm)
Zinc Pig	3.0
Zinc Fibers Electroformed from Pig	1.5
Zinc Powder, Type A	11.0
Zinc Powder, Type B	6.5
Zinc Sheet	18.0

(Accuracy of method is ± 0.5 ppm)

High purity is important from the standpoint of reducing gassing couples formed between the zinc and other metals present as impurities. Iron is a good example of a metal which forms a gassing couple with zinc in alkaline media. It will be seen from Table IV that there is a significant reduction in iron concentration in the zinc fibers and needles as compared with the other forms of zinc analyzed. The zinc sheet contained the greatest concentration of iron of about 18 ppm while the two samples of zinc powder contained 6.5 and 11 ppm respectively. It will be seen that the zinc fibers and needles represent the purest form of zinc containing only about 1.5 ppm of iron and thus would result in substantial reduction of gassing and wasteful corrosion of the zinc anode in a galvanic cell.

High surface area anodes for use in galvanic cells may be readily fabricated using the zinc fibers and needles of the invention by conventional compression molding techniques. The individual fibers or needles are placed within a suitable mold of the size and configuration desired and then compressed under a suitable pressure, say about 40 psi. Before applying pressure, the fibers or needles should be thoroughly intermingled with one another so that they are arranged in randomly orientated fashion within the mold with each of the fibers or needles making contact with as many neighboring fibers or needles as possible. It will be readily seen that the interconnected skeletal zinc fiber mat produced in accordance with the invention is advanta-

geous for use in this molding procedure since the fibers or needles are thoroughly intermingled and joined to one or more neighboring fibers in the mat. Upon the application of pressure, the intermingled fibers or needles readily interlock or interknit with one another producing an anode compact of high strength and cohesiveness.

Anode compacts so produced have been found to possess a number of advantages over anodes of the prior art. They possess a high strength and cohesiveness and are capable of supporting their own weight and consequently they do not require the use of a gelling agent such as carboxymethyl cellulose as employed in conventional gelled powder anodes. Moreover, the zinc fibers and needles contain only trace amounts of metallic impurities and therefore there is less tendency for the establishment of local corrosion couples which might otherwise result in wasteful anode corrosion and gassing during storage of the cells.

A series of polarization tests were conducted in order to demonstrate the superior performance capabilities of anode compacts made in accordance with the invention. The performance of the anode compacts was compared in the test with that of conventional flat zinc sheet anodes, sprayed zinc anodes (molten zinc sprayed onto a perforated zinc grid), and gelled powder anodes consisting of zinc powder suspended in a carboxymethyl cellulose gel. The anode compacts used in the test were made from zinc fibers electroformed from a methanol solution of zinc chloride. The weight of zinc was the same (0.80 gram) in both the anode compacts and gelled powder anodes tested. The tests were performed in a polytetrafluoroethylene cell holder using a large excess of a 35.8 per cent by weight potassium hydroxide electrolyte solution containing 4.48 per cent by weight of zinc oxide. The anodes were held in a vertical position with an anode face of about 0.78 square inch of "apparent area" exposed to the electrolyte. A large zinc cathode and a cadmium reference electrode were used in the cell. Current was provided by a 60-cycle a.c. interrupter of the type disclosed in the Kordes et al publication, (Journal of the Electrochemical Society, vol. 107, pages 480-483, June 1960). Substantially resistance-free potential readings were taken and recorded. A Keithley electrometer was used to make these readings.

Polarization curves for all the anodes tested at a temperature of 25°C. are shown in FIG. 5. Both the anode compacts and gelled powder anodes were also tested at low temperatures of about -20°C. and the polarization curves obtained in these tests are shown in FIG. 6. Each of the curves plotted represents the average of three individual runs. The drop in potential measured at a

given value of current below the potential obtained with no imposed anodic current is interpreted as being largely due to concentration overpotential although an activation overpotential component is included. The point in the curves where the potential experiences a sudden drop downward is taken as the limiting current, i.e., i_{lim} . It will be seen from the polarization curves in FIGS. 5 and 7 that the anode compacts of zinc fibers exhibited superior performance under conditions of high rate discharge and low temperature as compared with the other types of zinc anodes tested.

FIG. 15 shows a typical alkaline zinc galvanic dry cell employing an anode compact made in accordance with the invention. The cell comprises a cupped metallic can 22 surrounded by an insulating jacket 24. The extremities of the jacket are crimped around the outer edges of an insulated top cover 26 and an outer bottom metal cover 28. A paper washer 30 electrically insulates the can 22 from the bottom cover 28. Snugly fitted within the can 22 is a tubular cathode 32, the innermost surfaces of which are lined with a paper separator 34. Secured to the top of can 22 is a metal cap 36 serving as the positive cathode terminal.

The cathode used in the cell may be composed of manganese dioxide or other oxidic depolarizer material. Preferably, the cathode is of the cement-bonded type such as disclosed and claimed in U.S. Pat. No. 2,962,540 issued to K. Kordes on Nov. 29, 1960.

Separated from the top of can 22 by means of separator 34 and the plastic insulating disc 38 is the anode compact 40 of the invention. The anode compact is made by compression molding the zinc fibers or needles into cylindrical form as more particularly shown in FIG. 8.

The electrolyte for the cell is suitably a concentrated solution of potassium hydroxide, i.e., 30 to 35 per cent by weight solution of KOH. The electrolyte is absorbed into the anode compact and soaks the separator 34.

Suitably the closure for the cell may be of the type disclosed and claimed in U.S. Pat. No. 3,042,734 issued to J.L.S. Daly et al on July 3, 1962. Such a closure comprises an inner metal bottom 42 sealed within the open end of can 22 by means of a nylon gasket 44 having a central opening 46. This opening is of a diameter slightly smaller than the external diameter of a rivet 48 so that when the rivet is driven through the opening 46 the gasket will be radially compressed between the inner bottom member 42 and the rivet head, thereby furnishing a tight mechanical seal thereat. Prior to driving rivet 48 through the cover and gasket, the same is passed through a central opening in the anode collector 50. This anode collector may be formed by a pair of rod-like members 52 formed integrally with a head plate 54 in which the central opening is provided for the rivet 48, the pair of rod-like members 52 being embedded within the anode compact 40.

Illustrative of the practice of the invention, an anode compact for use in a D-size alkaline zinc-manganese dioxide galvanic dry cell of a construction such as shown in FIG. 7 may be made by compression molding 15.5 grams of zinc fibers into a cylindrical shape approximately 1.6 inches high and 0.85 inch in diameter. Such an anode compact has a void volume of about 85.8 percent of the total volume which is more than sufficient for the subsequent absorption of the electrolyte.

FIG. 9 shows a typical miniature button type alkaline zinc galvanic dry cell employing an anode compact of the invention. The cell comprises a metallic cup 56 which serves as the positive terminal. Within the cup 56 and in contact with its bottom wall is a thin wafer-like cathode 58. The cathode may be composed of any oxidic depolarizer material such as manganese dioxide, nickel oxide or silver oxide, for example. The anode is in the form of a thin pellet 60 and is disposed on top of the cathode 58 separated therefrom by at least one layer of a suitable separator material 62. A metallic top closure 64 is placed within the open end of the cup 56 and is pressed downwardly into contact with the top of the anode pellet 60. The top closure 64 is sealed around its outer periphery by a generally L-shaped plastic insulating grommet 66 and serves as the negative terminal of the cell.

The anode pellet used in the button type cell of FIG. 9 is made by compression molding the zinc fibers or needles as described hereinabove. FIG. 10 shows the anode pellet prior to assembly in the cell.

One of the most outstanding features of the invention is that the anode compacts can be readily fabricated using the zinc fibers and needles without the need for any suspension or gelling agent such as used in gelled powder anodes of the prior art. The elimination of the gelling agent is highly advantageous from the standpoint of providing optimum volumetric cell efficiency since the gelling agent used in prior anodes, i.e., carboxymethyl cellulose, is electrochemically inactive and performs no useful purpose other than to support the zinc powder. Its elimination thus allows for more active material to be incorporated into the anode structure and consequently the cell discharge capabilities are substantially increased.

Still other advantages are derived from the elimination of the gel in sealed secondary or rechargeable alkaline zinc galvanic dry cells. It has been found that the carboxymethyl cellulose gel is readily oxidized and tends to break down upon repeated cycling, that is, charge and discharge, and thus destroys the mechanical integrity of the anode body. It has been furthermore found that the presence of carboxymethyl cellulose in concentrated potassium hydroxide electrolyte containing zincate results in hydrogen gas evolution at the zinc interface during charging. The degree to which this reaction occurs is directly dependent on the concentration of carboxymethyl cellulose. The exact nature of this reaction has not been established but it is thought that it may be associated with the transport of zincate ions to the metal interface where reduction takes place, i.e., the carboxymethyl cellulose renders it more difficult for the zincate ions to reach the site for reduction. Another serious problem encountered with prior gelled powder anodes is that, under conditions of overcharge, the gel network tends to prohibit rapid oxygen recombination with the anode material and consequently dangerous internal gas pressures may develop in the sealed cells.

A series of experiments have been conducted to demonstrate the superior performance of alkaline zinc galvanic cells using anodes fabricated in accordance with the invention. In one such experiment, a number of D-size primary alkaline zinc-manganese dioxide dry cells were made, some with conventional gelled powder anodes, i.e., zinc powder in a carboxymethyl cellulose gel, and others with anode compacts of compressed inter-

locked zinc fibers fabricated in the manner as set forth hereinabove. The same amount of zinc was used in both types of cells, i.e., the zinc fibers were equivalent in weight to the zinc powder used in the gelled powder anodes. A 41 per cent by weight solution of potassium hydroxide was used as the electrolyte in all of the cells tested. Performance of the two types of cells was compared by progressively switching each of the cells for 15-second intervals across load resistors of 10, 2, 1, 0.5, 0.337 and 0.252 ohms. The voltages were continuously recorded on a potentiometric recorder. The voltage at the end of each 15-second interval was then used together with the known load resistor to calculate the current. Testing was conducted at temperatures of 25°C., 0°C. and -20°C. The voltage versus current relationship of the cells tested is shown in FIG. 11. It will be readily seen that for all the temperatures at which the cells were tested, the cells employing the interlocked zinc fiber anode compacts exceeded the performance of the cells employing the gelled zinc powder anodes of the prior art.

In another series of experiments, the superior performance capabilities of a primary alkaline zinc-manganese dioxide dry cell employing a zinc fiber anode compact versus an identical cell using a gelled zinc powder anode under conditions of heavy drain discharge were demonstrated. Again the same weight of zinc was used in both types of cells and the cells were otherwise identical in that they employed the same type of cathode, electrolyte and separator. During the test, the cells were continuously discharged across a one-ohm resistor. A comparison of the discharge voltage of the two types of cells tested is shown in FIG. 12. The discharge curves for both cells are essentially the same during the first 6 hours of discharge. At this time, however, a rapid drop in cell voltage was observed from the cell employing the gelled zinc powder anode. When duplicate cells employing the gelled anode were tested, a similar rapid drop in cell voltage was observed although the time at which this drop occurred varied from 4.5 to 6 hours depending upon the individual cell. It will be seen that there is no rapid voltage drop in the discharge curve for the cell employing a zinc fiber anode compact but rather the drop in voltage is gradual throughout the period of test.

The rapid voltage drop observed with the dry cells employing the gelled zinc powder anode on one-ohm discharge after 4.5 to 6 hours was associated with the polarization of the anode. On the other hand, practically all of the cell voltage decline previous to this time was associated with the polarization of the manganese dioxide cathode. In order to demonstrate this a reference electrode was placed in one of the cells employing the gelled powder anode and the potential of the working electrodes was recorded while the cell was continuously discharged across the one-ohm resistor. FIG. 13 shows the gelled zinc powder anode potential and compares this with the cell voltage on discharge. Similar potential measurements between a reference electrode and each of the two working electrodes in a cell employing a zinc fiber anode compact indicate that essentially all of the cell voltage decline on one-ohm discharge is associated with polarization of the manganese dioxide cathode.

The following conclusions can be drawn from the above series of experiments comparing the discharge performance of alkaline zinc-manganese dioxide dry

cells employing a zinc fiber anode with cells employing a gelled zinc powder anode.

- I. For conventional gelled zinc powder anode cells;
 - a. Essentially all of the cell voltage decline of 0.7 volt is due to the polarization of the manganese dioxide cathode. Only about 0.1 volt can be attributed to the polarization of the zinc anode.
 - b. Essentially all of the rapid voltage drop that occurs between 0.7 volt and 0.1 volt is due to the polarization of the gelled zinc powder anode.
- II. For zinc fiber anode cells;
 - a. No rapid polarization of the zinc anode comparable to that seen with the gelled zinc powder anode cells is observed at 0.7 volt.
 - b. Essentially all of the decline in cell voltage over the first 20 hours of discharge is associated with the polarization of the manganese dioxide cathode. Cell capacity is limited by this polarization and could be improved by use of a superior manganese dioxide cathode material.

III. Substitution of the zinc fiber anode for the gelled anode in an alkaline zinc-manganese dioxide dry cell results in increasing the cell capacity during the first 20 hours of discharge (FIG. 12) from 5.9 to 10.3 ampere hours. The additional capacity is obtained at cell voltages below 0.7 volt due to the polarization of the manganese dioxide cathode which masked the true capability of the zinc fiber anode as far as the cell potential is concerned. In spite of this, however, the zinc fiber anode demonstrated its capability to sustain high rate discharge for much longer periods of time than the gelled zinc powder anode.

In the manufacture of prior alkaline zinc galvanic dry cells of the type using a gelled zinc powder anode, it has become the common practice to amalgamate the zinc powder prior to formation of the gelled anode. This is necessary in order to prohibit the evolution of gas generated particularly during storage of the cells due to the establishment of local corrosion couples formed between the zinc and other metals present as impurities. As indicated above, iron is a good example of a metal which forms a corrosion couple with zinc although other metal impurities are capable of forming such couples in the alkaline media. Gassing couples can also be established with zinc by the migration of impurities through the electrolyte from the cathode to the anode. The establishment of these corrosion or gassing couples is a particularly troublesome problem in the case where the cells are hermetically sealed in order to prevent the loss of electrolyte due to leakage or evaporation. With such sealed cells it is generally necessary to provide some means for adequately venting the gases formed by these corrosion or gassing couples as well as those gases generated during use of the cell such as upon charging or overcharging in the case of a rechargeable cell, for example.

Amalgamation of the zinc powder prior to fabricating the gelled powder anode with usually about 8 per cent by weight of mercury has proven effective in prohibiting or substantially reducing the evolution of gas caused by the establishment of local gassing couples due to the presence of impurities in the zinc. It has now been found, however, that the level of amalgamation required with the present anodes may be reduced below that necessary with the gelled powder anode. This is at least partially due to the fact that the zinc fi-

bers and needles contain only trace amounts of impurities, notably iron for example. Reduction in the level of amalgamation in the case of the present anodes, however, depends largely upon the nature of the cathode material. If the cathode material contains only a limited amount of major impurities which might otherwise migrate through the cell electrolyte to the anode and establish local gassing couples thereat, then the level of amalgamation in the case of the present anodes may be substantially reduced below that required for the gelled powder anode.

In order to demonstrate the possible reduction in the level of amalgamation for anodes made in accordance with invention, another series of experiments was conducted using D-size sealed alkaline zinc-manganese dioxide galvanic dry cells. In these experiments, the cells were constructed without the standard manganese dioxide cathode so as to effectively isolate the anode and its electrolyte. Any gas evolution occurring during the test was thus solely attributable to the establishment of

cells similar to those just described was constructed using a standard gelled powder anode, i.e., zinc powder suspended in a carboxymethyl cellulose gel. The weight of the zinc powder was equivalent to that of the zinc fibers or needles used in making the anode compacts and the zinc powder was amalgamated with the standard 8 per cent by weight of mercury. The test cells were then placed in the bottom of a Pyrex beaker filled with paraffin oil so that any leaks in the sealed cell system could be easily detected by gas bubbling through the paraffin oil. A Pyrex tube having an open bottom end and equipped with a stopcock was placed within the beaker surrounding the cell and its pressure gauge. An extremely sensitive pressure test apparatus was thus provided for measuring the quantity of gas evolved from the cells. The sensitivity of the measurements was exceedingly high in that 7×10^{-6} moles of gas could be easily detected. This is equivalent to 1.4×10^{-5} grams of hydrogen or a local couple current of 0.2 milliamperes per hour magnitude. The cells were then placed on

TABLE V

	ANODE SHELF DATA Pressure (Psig) After Storage at 24°C. (months)						Pressure (Psig) After Storage at 54°C. (months)					
	1	2	3	4	5	30	1	2	4	6	8	30
Unamalgamated	7	15	20	27	33	>100						
Zinc Fibers												
Amalgamated (0.28% Hg)	0	7	12	19	25	>100						
Zinc Fibers												
Amalgamated (0.28% Hg)	0	2	7	14	20	>100						
Zinc needles												
Amalgamated (2.0% Hg)	0	0				40						
Zinc needles												
Amalgamated (3.0% Hg)	0	0				4						
Zinc needles												
Amalgamated (4.0% Hg)	0	0				2						
Zinc needles												
Amalgamated (5.0% Hg)	0	0				2						
Zinc needles												
Amalgamated (6.0% Hg)	0	0				0						
Zinc needles												
Amalgamated (7.0% Hg)	0	0				0						
Zinc needles												
Amalgamated (8.0% Hg)							4	5	5	5	5	10
Zinc needles												
Amalgamated (8.0% Hg)	0	0				0	7	8	8	8	8	12
Zinc Powder—CMC												
Anode gel												

local corrosion or gassing couples due to impurities in the anode. A total of 26 cells were used in the test. The cell closures were modified to accommodate a pressure gauge so that the internal gas pressure could be determined at any time during the test. The anodes were fabricated from compressed interlocked zinc fibers or needles, some of which were unamalgamated and other of which were amalgamated with various amounts of mercury up to 8 per cent by weight of mercury. Amalgamation was accomplished from an ethylene diamine complex of mercury. The weight of zinc fibers or needles for all the anodes was the same, i.e., 15.5 grams, and the anodes were cylindrical as shown in FIG. 8. A 41 per cent by weight solution of the potassium hydroxide was used as the electrolyte for all the cells and the electrolyte volume was the same, i.e., 12.8 milliliters. The electrolyte was previously shaken thoroughly with zinc fibers for the purpose of removing any trace heavy metal impurities that may have been originally present in the potassium hydroxide solution. A control lot of

shelf storage within the test apparatus and were separated into two groups. One group of cells was maintained at a temperature of 24°C. while the other group was maintained at a temperature of 54°C. Pressure data were periodically obtained by measuring the quantity of gas evolved from the cells. The test was carried out for a period of up to 2½ years. Table V below summarizes the results of these tests.

It will be readily seen that the results shown in Table V amply demonstrate that the level of amalgamation for the anodes of the invention can be effectively reduced to as low as about 3 per cent by weight of mercury provided that a good quality cathode containing a minimum amount of impurities is used. Pressure readings of about 40 psi were selected as the maximum pressure to be tolerated in the alkaline zinc-manganese dioxide galvanic dry cells. Those cells in which the zinc fibers or needles were unamalgamated or amalgamated with only up to 2 weight per cent mercury gassed profusely after two years of storage. On the other hand the

gas pressure in the cells constructed with anodes in which the zinc fibers or needles were amalgamated with at least 3 per cent or more of mercury remained below the maximum selected level. It should be understood, of course, that these experiments were carried out under conditions wherein the effect of cathode impurities was deliberately circumvented by eliminating the cathode from each of the cells tested. Migration of a substance or substances originating as impurities in the cell cathode to the zinc anode with subsequent establishment of gassing couples can account for the major source of gassing in an alkaline zinc-manganese dioxide galvanic dry cell. Thus when a cathode of poor quality is used it may be necessary with anodes of the invention to substantially increase the level of amalgamation above the lower percentage demonstrated as feasible in these experiments.

Many different types of alkaline zinc galvanic cells have been made using anodes fabricated from the zinc fibers and needles in accordance with the invention. Besides the primary alkaline zinc galvanic dry cells used in the above experiments, a number of secondary or rechargeable galvanic dry cells have also been constructed. These cells differ from those of primary type only in the specific composition of the cathode material and the electrolyte.

Rechargeable alkaline zinc-nickel oxide galvanic dry cells employing the anode of the invention have been tested for prolonged periods of time with repeated cycling, i.e., charge and discharge, and have shown a superior performance in that the cells were capable of attaining a state of full charge after discharge over a greater number of cycles than possible with rechargeable cells employing the conventional gelled zinc powder anode. This is believed due to the fact that the anode of the invention more readily permits rapid oxygen recombination with the active material since there is no gelling agent which normally restricts the passage of gas throughout the anode structure. In addition, no oxidizable organic gelling agent is present to deteriorate.

The rechargeable alkaline zinc-nickel oxide galvanic dry cells described above were of the miniature button type construction using a zinc fiber anode pellet as illustrated in FIGS. 9 and 10.

One advantage in the manufacture of these miniature button type dry cells is that the anode pellet can be assembled in the cell container in the dry state followed by metering of the desired amount of electrolyte rather than by the more complicated procedure of metering a wet gelled powder anode into the cell container. Moreover, there is less tendency for leakage of the electrolyte which is a major problem with these button type cells since the anode pellet is highly absorbent and soaks up and holds the electrolyte.

As further illustrative of the invention, a number of miniature button type primary alkaline zinc-silver oxide galvanic dry cells employing an anode pellet in accordance with the invention have been made and tested. The cells were subjected to a continuous discharge across a 600 ohm load resistor. FIG. 14 shows the discharge performance at room temperature of such a cell compared with the performance of a similar cell using a gelled zinc powder anode.

In the manufacture of conventional rechargeable alkaline zinc galvanic dry cells, it is common to employ an electrolyte consisting of a concentrated solution of

potassium hydroxide, suitably a 30 to 35 per cent solution of KOH. It has now been found, however, that with such rechargeable dry cells employing the anode of the invention the cycle life can be substantially increased by using a more highly concentrated solution of potassium hydroxide together with a high concentration of zinc oxide dissolved therein. Specifically, the molar ratio of KOH to ZnO should be of the order of about 6 to 1. Analysis of these electrolytes falls in the range of about 45 to 50 per cent potassium hydroxide and 12.5 to 15 per cent zinc oxide. The improved performance of these electrolytes can be attributed to the reduction in the formation of zinc dendrites formed during cell charging.

With the electrolytes contemplated in accordance with the invention, the formation of zinc dendrites on charging may be substantially reduced and the cycle life of the cells significantly improved. It has been furthermore found that the formation of these zinc dendrites may be even further reduced by incorporating in the cell electrolyte one or more additives selected from the group consisting of lead, arsenic, molybdenum and tungsten. In the alkaline solution, these additives will be present as the plumbite, arsenate, molybdate and tungstate. These additives should be present in the cell electrolyte in an amount of at least 20 ppm although a concentration of at least 1,000 ppm is preferred.

Ideally then, electrolytes most suitable for use in rechargeable alkaline zinc galvanic dry cells employing an anode made in accordance with the invention are highly concentrated solutions of 40 to 45 per cent potassium hydroxide containing about 12.5 to 15 per cent zinc oxide dissolved therein and having added thereto, in an amount of at least 20 ppm one or more additives selected from the group consisting of lead, arsenic, molybdenum, and tungsten.

When using the above electrolytes in a rechargeable alkaline zinc galvanic dry cell, it has been found preferable to employ a separator system consisting of multiple layers of a non-woven open pore material which is highly retentive of the electrolyte. This separator system is resistant to the penetration of zinc dendrites formed at the anode and thus serves to further improve the cycle life of the cell. Suitable separator materials for this purpose include Viskon-Vinyon* or other synthetic fiber batts.

*Viskon-Vinyon — composite separator consisting of cellulosic fiber material and a copolymer of vinyl chloride and vinyl acetate.

A number of miniature button type rechargeable alkaline zinc-nickel oxide galvanic dry cells utilizing the electrolytes of the invention have been made. The cell construction was basically the same as that shown in FIG. 9. The anodes for each cell were fabricated by compression molding zinc needles into the form of a wafer-like pellet (FIG. 10). The electrolyte composition was varied from a standard solution of 35 per cent KOH plus 1.5 per cent ZnO to electrolyte compositions containing 47.5 per cent KOH and 12.5 per cent ZnO with and without the addition of 1,000 ppm of lead. The separator used in the cells employing the electrolytes of the invention consisted of ten layers of 0.008 inch Viskon-Vinyon. The cells were subjected to deep discharge to 0.9 volt at the 1 ½ hour rate followed by constant current charging at the 4-hour rate plus 50 per cent minimum overcharge. The cells were considered to have reached the end of their useful cycle life when the cell capacity dropped off to 50 per cent of the ini-

tial capacity. Table VI below shows the results of these tests.

TABLE VI

EFFECTS OF ELECTROLYTE ADDITIVES	
Electrolyte Composition	Cycle life to 50% of Initial Capacity
A. 35% KOH + 1 1/2% ZnO	12
B. 47% KOH + 12 1/2% ZnO	65
C. 47% KOH + 12 1/2% ZnO + 1000 ppm Pb (added as PbO)	129

It will be readily seen from the table above that the electrolytes of the invention when used in the rechargeable cells produce a considerable improvement in cycle life. The cells employing the present electrolyte (B) without the addition of lead exhibited more than five-fold improvement in cycle life over the standard electrolyte (A) whereas the addition of lead to the present electrolyte (C) resulted in nearly a two-fold further improvement, thus demonstrating the effectiveness of these additives.

A further advantage derived from the use of the electrolytes of the invention is that when one of the selected additives, e.g., lead, is incorporated into electrolyte B, there is a substantial repression of gas evolution (hydrogen). This is particularly significant in those cases where the zinc fiber anode is used in conjunction with a poor quality cathode material.

Still another advantage of the present electrolytes when used in a sealed rechargeable dry cell employing an anode compact of the invention is that oxygen liberated during charging and particularly on overcharging can be rapidly recombined with the active zinc material without the buildup of dangerous gas pressure. The anode compact possesses at least about 85 per cent void volume and provides an excellent semiwet high surface area structure for rapid recombination of the oxygen gas evolved. It has been further found that the addition of zinc oxide to the anode compact aids in maintaining the desirable high concentration of zincate ions at this site during charging and overcharging. Thus the zinc oxide serves as overcharge protection.

What is claimed is:

1. An alkaline galvanic cell having an anode, a cathode and an alkaline electrolyte in contact therewith, said anode comprising a porous, electrolyte absorbent,

cohesive, self-supporting body of intermingled and interlocked zinc filaments characterized by having a thin elongated central spine portion with at least a few polydirectional side growths of granular, dendritic or platelet form, the thin elongated central spine portion consisting essentially of one or more single crystals preferentially orientated with an *a* axis parallel to the axis of the filament, said filaments having a length of from about 1/8 to about 4 inches, an average diameter of about 0.006 inch, and a specific surface area of between about 0.4 and 0.6 square meter per gram, said filaments being further characterized in that they are stable and nonpyrophoric.

2. The alkaline galvanic cell in accordance with claim 1 wherein the filaments are zinc fibers having a thin elongated central spine portion with a number of polydirectional side growths and having a length of from about 1/8 to about 2 inches.

3. The alkaline galvanic cell in accordance with claim 1 wherein the filaments are zinc needles having a thin smooth elongated central spine portion with only a few poly-directional side growths and having a length of from about 1/8 to about 4 inches.

4. The alkaline galvanic cell in accordance with claim 1 wherein the filaments contain less than about 1.5 parts per million of iron.

5. The alkaline galvanic cell in accordance with claim 1 wherein the filaments are amalgamated with at least about 3 per cent by weight of mercury.

6. The alkaline galvanic cell in accordance with claim 1 wherein the cathode is an oxidic compound selected from the group consisting of manganese dioxide, nickel oxide and silver oxide.

7. The alkaline galvanic cell in accordance with claim 1 wherein the alkaline electrolyte is a concentrated solution of potassium hydroxide.

8. The alkaline galvanic cell in accordance with claim 1 wherein the alkaline electrolyte comprises an aqueous solution of from about 40 to 45 per cent potassium hydroxide and 12.5 to 15 per cent zinc oxide.

9. The alkaline galvanic cell in accordance with claim 1 wherein the alkaline electrolyte contains at least about 20 parts per million of an additive selected from the group consisting of plumbites, arsenates, molybdates and tungstates.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,844,838 Dated October 29, 1974

Inventor(s) Demetrios V. Louzos

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Name of inventor - "Demetrois" should read -- Demetrios --

Column 2, line 41 (page 5, line 8 of application),
"crystal" should read -- central -- .

Column 2, line 51 (page 5, line 18 of application),
"neeldes" should read -- needles -- .

Column 2, line 63 (page 6, line 1 of application),
"of" should read -- or --; same line, "or"
should read -- of -- .

Column 3, line 17 (page 6, line 22 of application),
"of" should read -- or -- .

Column 5, line 51 (page 13, line 14 of application), "of"
(second occurrence) should read -- or -- .

Column 7, line 30 (page 17, line 5 of application),
"of" should read -- or -- .

Column 9, line 21 (page 20, line 27 of application),
"It will" should read -- It will thus -- .

Column 9, line 24 (page 20, line 30 of application),
"[1Y0]" should read -- [100] -- .

Column 9, head of last column of Table II (page 21 of applica-
tion), "Zn fiber direction" should read
-- Zn fiber orientated with its long direction -- .

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,844,838 Dated October 29, 1974

Inventor(s) Demetrios V. Louzos

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 30 (page 24, line 5 of application),
"coupled" should read -- couples -- .

Column 13, line 8 (page 29, line 7 of application),
"7" should read -- 6 -- .

Column 13, line 12 (page 29, line 11 of application),
"15" should read -- 7 -- .

Column 22, line 42, claim 9, (claim 39, line 2 of application),
"1" should read -- 8 -- .

Signed and Sealed this

thirtieth Day of December 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks