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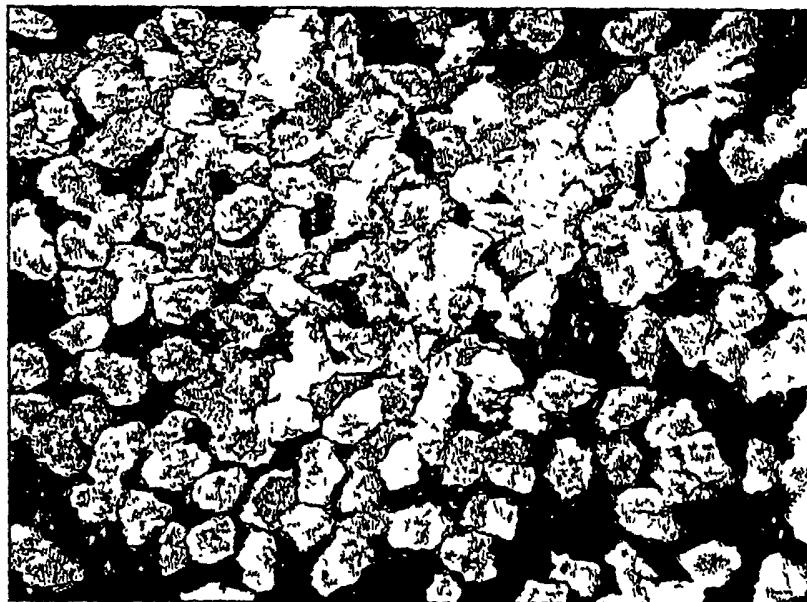
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(54) Title: ZINC ANODE MATRIX FOR RECHARGEABLE ALKALINE BATTERY



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(57) Abstract: An anode paste material (10) for use in zinc-based batteries that is designed to reduce zinc ion diffusion and resultant electrode shape change as well as zinc dendrite formation while optionally allowing for hydrogen permeability through the matrix comprising a regenerated cellulose film (12) containing domains of hydrogen permeable polymer, particles of zinc and zinc oxide (20) surrounded by hydrocarbon beads (14).



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## Zinc Anode Matrix for Rechargeable Alkaline Battery

Technical Field

This invention relates to a paste material used in a rechargeable, alkaline, zinc-based battery and more particularly this invention relates to a matrix for zinc particles in an anode for a zinc-silver secondary battery.

Background of the Invention

In modern electronics, there is a need for high performance, rechargeable batteries. A silver-zinc battery, having one of the highest energy densities both per unit weight and per unit volume plus extremely high discharge rates, appears to be an ideal solution to this need. However, a zinc-based battery has historically presented many challenges for the battery manufacturer. One of these challenges involves containing zincate diffusion within the battery. This is a particularly severe problem because zinc is extremely soluble in the strongly alkaline environments routinely used as the electrolyte in these types of batteries. The presence of  $KZn(OH)_x$  where  $x=1$  to 3 presents a double-edged sword for the battery designer. On the upside, the high solubility allows for rapid current spikes typically unattainable with other battery systems. However, this high solubility diffuses zinc ions into undesired locations within the battery. Upon re-plating, this zinc diffusion leads to the well-known phenomena of electrode shape change and the presence of zinc dendrites within the batteries. This shape change includes an agglomeration of the zinc towards the center of the battery while simultaneously depleting

zinc from the edges. Dendrites can readily be formed due to the zinc concentration gradients within the battery. Their tree-like structures have as their most undesirable effect the rupture of the separator membranes leading to 5 battery shorting.

Researchers in this area have tried various approaches to control the electrode shape change and to reduce the zinc dendrite formation. They can be classified into five different categories. The first approach involves taking 10 into account the redistribution of zinc by starting out with zinc depleted at the center and agglomerated at the edges. The second approach attempts to deal with the issue by modifying the electric field experienced by the zinc so that the edges experience a stronger electric field than 15 the center. A third approach involves attempts to decrease the solubility of the zinc by complexing it with other agents. The fourth approach involves attempts to contain the solubility of zinc by encapsulating it in a matrix, typically a matrix involving gelling agents. The fifth and 20 final approach involves attempts to make a separator resistant to zinc dendrites. Encapsulation is the most promising of the approaches to improve anode performance.

#### Statement of the Prior Art

25 Encapsulation has focused on using agents that swell easily in the presence of the electrolyte. In U.S. Patent No. 5,686,204, Bennet et al use crosslinked CARBOPOL acrylic acid as a gelling agent possessing high absorbency. In U.S. Patent No. 4,368,244 Danzig uses paste material 30 composed of diacetone acrylamide and acrylic acid. Sehm in U.S. Patent No. 4,778,737 teaches zinc surrounded by acrylamide and acrylate polymers.

Polyethylene oxide (PEO) has been disclosed in several patents as a gelling agent, including U.S. Patent No. 5,384,214 by Sugihara et al who use a surfactant made of PEO and a perfluoroalkyl chain. Similarly, Getz et al in U.S. Patent No. 5,464,709 use a methoxylated polyethylene oxide (Carbowax 550).

Still others have researched the use of crosslinked vinyl alcohols as preferred gelling agents. Thus, Ito et al in U.S. Patent No. 5,525,444 disclose an electrode with a paste made from a vinyl alcohol crosslinked to a moiety containing COOX groups. Suga et al in U.S. Patent No. 5,382,482 place zinc in direct contact with a crosslinked polymer, such as in the crosslinking of polyvinyl alcohol and dimethyldiethoxysilane.

Polyacrylic acid is used by Shinoda et al in U.S. Patent No. 5,376,480 while Goldstein in U.S. Patent No. 5,206,096 discloses a mixture of organic inhibitors and a gelling agent such as polyacrylic acid, carboxymethyl cellulose and hydrolyzed polyacrylonitrile. Kordesh et al in U.S. Patent No. 5,281,497 teach crosslinked starch as the preferred gelling agent.

Finally, Suga et al in U.S. Patent No. 5,348,820 suggest a polymer layer which is in contact with the zinc, said polymer having an oxygen permeability constant greater than  $10^{-13} \text{ cm}^3 \text{ cm}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ .

None of the above patents address certain peculiarities of zinc electrodes. First, there is the tendency of zinc to expel the gelling agent upon re-plating. This creates void spaces for zinc ion diffusion. Second, there are significant density changes when zinc is discharged to zinc oxide and vice versa. Finally, these patents do not address the hydrogen production that occurs

1 during overcharge. All of these effects, acting separately and in concert, contribute to the breach of the initial zinc matrix.

5 Statement of the Invention

The present invention provides a material that surrounds the zinc in a three-dimensional lattice matrix which induces the zinc to re-plate in the same mesh size as it was originally assembled. Second, the material has been 10 designed to be mechanically stable despite zinc cycling. Third, the anode paste of the invention remains electrically interconnected during the entire charge cycle. Finally, the anode has high ionic transport, excellent accommodation to zinc density changes and, optionally, high 15 hydrogen transport.

The material used as the anode paste component is of comparable grain size to the zinc particle grain size. When the paste is mixed with zinc, zinc oxide and electrolyte, the material is formed into a three- 20 dimensional lattice matrix of comparable mesh size to the zinc mesh size, which serves to diminish electrode shape change as well as zinc dendrite formation. The occurrence of zinc ion diffusion is also minimized. The anode paste material contains polymer beads encapsulated by cellulose, 25 and optionally, intermixed with a hydrophobic polymer of hydrogen permeability greater than  $1 \times 10^{-13} \text{ cm}^3 \text{ cm}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ .

The anode paste material contains cellulose as a gelling agent. Cellulose in the form of regenerated cellulose has been a widely used separator for zinc-based 30 batteries. Some of the reasons for this include its low electrical impedance as well as its excellent ion transport in alkaline environments. In the presence of alkaline

electrolyte cellulose can swell considerably. As a powder, cellulose is often used as a gelling agent. Cellulose is the principal constituent in the matrix material of the invention. Cellulose, with a degree of polymerization between 200 and 1200, can be used, so long as it is made soluble. This cellulose can also be crosslinked by a variety of methods.

Despite its advantages, cellulose is limited in its ability to accommodate zinc density changes and to transport hydrogen. If cellulose powder acts as the sole gelling agent, zinc ions readily permeate through the gel. Additionally, cellulose possesses one of the lowest hydrogen permeability coefficients of known polymers.

To compensate for these limitations, the anode matrix of the present is a two-component material that incorporates small hydrocarbon beads encapsulated in a cellulose matrix.

#### Brief Description of the Drawings

Figure 1 is a schematic view of an anode matrix grain.

Figure 2 is a schematic view of zinc and zinc oxide particles surrounded by the anode matrix material.

Figure 3 is a schematic view of a network of zinc oxide particles on a current collector; and

Figure 4 is a micrograph of the matrix material.

#### Detailed Description of the Invention

Referring now to Figures 1 and 2 the anode matrix paste is composed of a paste 10 of cellulose particles 12 which are cohesively joined, but interrupted with hydrocarbon beads 14 that are uniformly embedded within the

particles. The paste 10 is pressed as a paste into a conductive support 16 such as a silver or copper screen or layer of extended metal. The hydrocarbon beads 14 mechanically reinforce the resulting anode matrix material

5 10. The beads 14 should be formed of a material that can withstand strongly alkaline environments, suitably a hydrocarbon aliphatic resin such as polyethylene or polypropylene. Additionally, the beads 14 should be small enough as to constitute part of a framework that maintains 10 the original matrix grain size. Preferably, there should be between ten and fifty hydrocarbon beads 14 per zinc/zinc oxide matrix grain 20. As the zinc re-plates, these beads help to contain the zinc within the initial zinc grain cavities 18 as shown in Figure 3.

15 The density of zinc, which is present when the battery is fully charged, is 7.14 while the density of zinc oxide, which is present when the battery is fully discharged, is 5.67. Thus, an agent is needed that conforms to the varying density of zinc while maintaining the zinc in 20 place. Density changes are accommodated by using cellulose as a gelling agent.

To allow for hydrogen transport out of the zinc grains during fast charging, the anode material may optionally contain from 10 to 50% by weight of a hydrophobic polymer 25 having a hydrogen permeability greater than  $1 \times 10^{-13} \text{ cm}^3 \text{cm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ . Substances possessing this permeability include, but are not limited to, ethyl cellulose, cellulose acetate, polymethyl pentene, polydimethyl siloxane, polyphenyl oxide, and gutta percha. The hydrophobic agent can be 30 mixed with the cellulose component in the manner described in co-pending patent application, Serial No. \_\_\_\_\_ entitled RECOMBINANT SEPARATOR filed concurrently herewith

(Attorney Docket No. 968-20-003), the disclosure of which is expressly incorporated by reference. In the three-component system of the invention, the polymeric beads are uniformly distributed throughout the sheet while the 5 cellulose and hydrogen transport agent are phase separated. This phase separation allows for macroscopic behavior characteristic of the separate constituents. The cellulose and the hydrophobic agent are dissolved, either separately or concurrently, and the polymeric beads are added as a 10 fine suspension to this medium. The material is then cast, coagulated, rinsed and dried.

To assure that zinc re-plates in the same mesh size as originally assembled, the material is ground to a particle size that approximates the zinc mesh size. The material 15 then surrounds the zinc, forming a lattice that not only induces the zinc to remain in place, but also allows for ion movement out of the matrix, preventing hydrogen accumulation on the zinc surface and at the same time contracting and expanding in response to any changes in 20 zinc density.

This invention works optimally when the matrix material is mixed with zinc and zinc oxide. Electrical connectivity needs to be maintained throughout the battery cycle. A totally discharged battery may lose all of its 25 metallic zinc and fail to maintain properly arranged nucleation sites, thus leading to a tendency of the zinc to migrate outside of its initially established boundaries on subsequent cycles. However, a fully charged battery will convert all zinc oxide into zinc causing it to lose 30 conductivity for the following reason. Zinc oxide, though a semiconductor, serves to interconnect all zinc grains via channels formed by coating the matrix material. The

network of zinc oxide particles 20, shown as high impedance resistors in Figure 3, should be maintained, particularly at the end of the charging cycle. Thus, a charging scheme is desired whereby the battery is charged between 10% and 5 90% of its total capacity. The battery should be cathode limited to stay within this range. Preferable mixing ratios of zinc oxide to zinc are in the range of 5 to 40% by weight.

Example 1

10 40 grams of microcrystalline cellulose (MCC, Aldrich 31,069-7) is placed in solution of 2 kg of 5% LiCl/DMAC and heated to 120 degrees Celsius for 15 minutes. The cooled solution affords a clear solution of MCC. 50 grams of ethyl cellulose (EC) is dissolved in 1000 ml DMAC separately. MCC and EC solutions are combined in 2/1 weight ratio by dry polymer weight. 20 g of polyethylene beads (Quantum Inc.) are added and stirred for 15 minutes. 120 ml of the combined solution is placed on a 10x10 glass tray. A humidifier providing water over the glass tray 15 yields a gelled product containing phases of MCC and EC and uniformly distributed polyethylene beads. This gel is then washed with water repeatedly until all DMAC and LiCl are removed. The gel is then dried, forming a sheet. This sheet is then ground via conventional means to obtain 20 powder having a mesh size approximate to that of the zinc 25 mesh size.

A micrograph of the anode matrix material is shown in Figure 4. Magnification is 20x.

A typical matrix material loading would be:

30 Zinc 25.2 g  
Zinc oxide 8.8 g  
KOH (1.38 s.g.) 10.5 g

Matrix Material 1.5 g

Above materials are combined into a paste and said paste is used as the negative electrode with a silver current collector.

5 Said sheet is tested for resistance to zinc migration as follows. A cavity with two compartments has a regenerated cellulose separator dividing the two compartments. One compartment contains 20 ml of a saturated amount of zinc in electrolyte while the other 10 compartment has 20 ml of plain electrolyte. The migration of zinc from the saturated side of the zinc-free side is detected at stated time intervals via atomic absorption spectroscopy. Results reported are in ppm of Zn.

Table 1

15	Minutes	Without Paste	With Paste
	30	600	240
	60	760	260
	400	15,200	8400
	1400	38,000	25,000

20 Example 2

40 grams of microcrystalline cellulose (MCC, Aldrich 31,069-7) is placed in a solution of 2 kg of 5% LiCl/DMAC and heated to 120 degrees Celsius for 15 minutes. The cooled solution affords a clear solution of MCC. The 25 solution is reacted with 18 g of NaOH and 36 g diiodododecane for 16 hours. 50 grams of ethyl cellulose (EC) is dissolved in 1000 ml DMAC separately. MCC and EC solutions are combined in a 2/1 weight ratio by dry polymer weight. 20 g of polyethylene beads (Quantum Inc.) are added.

10 Material is then treated as in Example 1.

It is to be realized that only preferred embodiments of the invention have been described and that numerous

substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

## Claims

1. An anode paste for an alkaline battery comprising; cellulose particles and grains of metal anode material, said particles containing a dispersion of hydrocarbon beads and said particles surrounding said grains to form a supported cavity.

5 2. An anode paste according to claim 1 in which the paste further contains grains of semiconductive metal oxide forming a conductive path through the paste.

10 3. An anode paste according to claim 2 in which the metal is zinc.

4. An anode paste according to claim 3 in which the metal oxide is zinc oxide.

5 5. An anode paste according to claim 1 in which the cellulose particles film further contain polymeric domains of material having a hydrogen permeability of at least  $10^{-13} \text{cm}^3 \text{cm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ .

6. An anode paste according to claim 5 in which the hydrogen permeable material is present in an amount of 10 to 60 parts by weight per 100 parts of cellulose.

20 7. An anode paste according to claim 6 in which the hydrogen permeable material is selected from the group consisting of cellulose ethers, cellulose esters, polymethylpentene, polysiloxanes, polyphenylene oxides and hydrocarbon elastomers.

25 8. An anode paste according to claim 7 in which the hydrogen permeable material is ethyl cellulose.

9. An anode paste according to claim 1 which the hydrocarbon beads are selected from polyalkylene resins of 10 monomers containing 2 to 8 carbon atoms.

10. An anode paste according to claim 1 in which the hydrocarbon beads are selected from the group consisting of polyethylene and polypropylene.

11. An anode paste according to claim 1 which the cellulose has a degree of polymerization from 200 to 1200.

12. An anode paste according to claim 1 in which 20 to 50 hydrocarbon beads per cellulose particle are present for each metal grain.

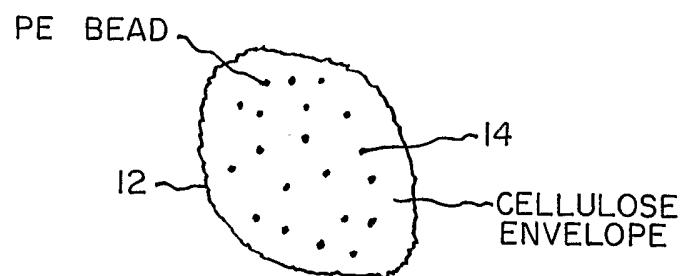
13. An anode paste according to claim 12 in which an anode grain comprises a dispersion of hydrocarbon beads in cellulose.

14. An anode paste according to claim 13 in which the anode grains are approximately the same size as the metal grains.

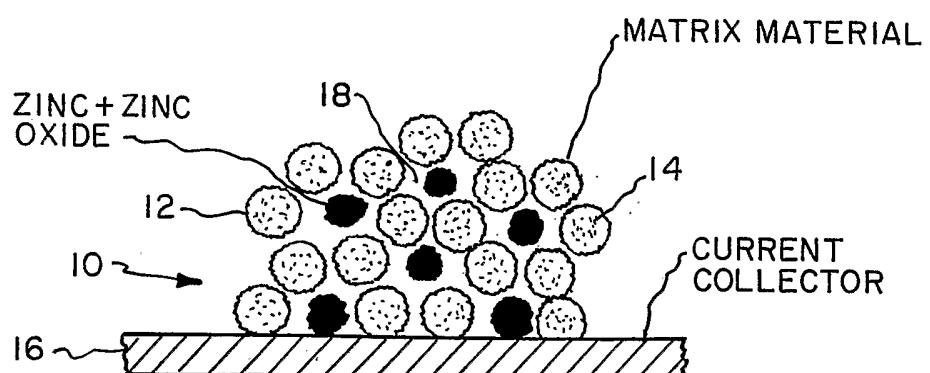
15. An anode paste according to claim 14 in which the anode grains form a lattice surrounding the metal and metal oxide grains.

16. An anode paste according to claim 3 in which the metal oxide is present in an amount of 5 to 40% by weight of the metal.

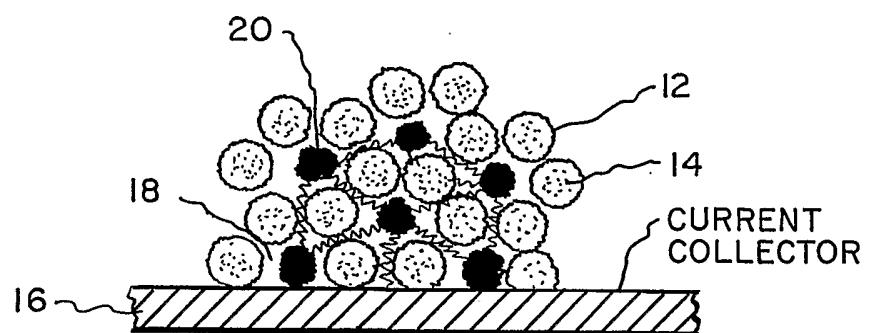
17. An anode paste according to claim 1 in which the matrix material is present in an amount of 1 to 15% by weight of the metal and metal oxide.



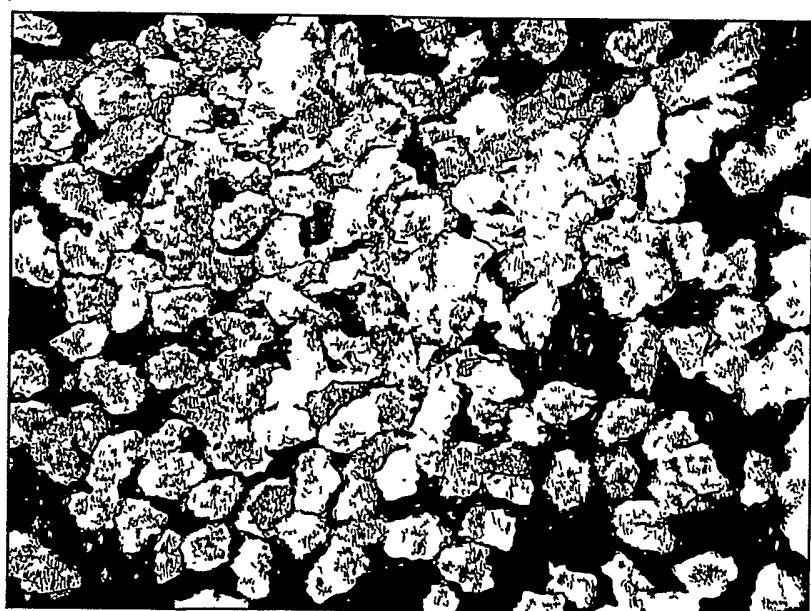
*Fig. 1.*



*Fig. 2.*



*Fig. 3.*



*Fig. 4.*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/12441

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 4/42, 4/48

US CL :429/229, 231

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/229, 231

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

search terms: alkaline battery, anode, cellulose, zinc oxide, hydrocarbon

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,300,371 A (TOMANTSCHGER et al) 05 April 1994, col. 13, lines 10-21, col. 16, lines 25-65	1-17
Y	US 5,795,679 A (KAWAKAMI et al) 18 August 1998, col. 7, lines 39-44, col. 16, lines 60-67	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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