

RECHARGEABLE ZINC-AIR BATTERY WITH PERFORATED-SHELL ACTIVE PARTICLES

BACKGROUND OF THE INVENTION

1. TECHNICAL FIELD

[0001] The present invention relates to the field of energy storage, and more particularly, to zinc-based batteries.

2. DISCUSSION OF RELATED ART

[0002] Zinc-air batteries show promising capabilities as high energy density electrochemical power sources. Zinc secondary electrodes specifically are attractive anodic candidates having a negative potential of 1.215V vs. the standard hydrogen electrode and a high theoretical capacity of 820 Ah/kg. Additionally, the advantages of the secondary zinc electrode are low toxicity, low cost, good availability of the raw material and fewer concerns regarding the disposal or recycling of the electrode.

SUMMARY OF THE INVENTION

[0003] The following is a simplified summary providing an initial understanding of the invention. The summary does not necessarily identify key elements nor limit the scope of the invention, but merely serves as an introduction to the following description.

[0004] One aspect of the present invention provides a powder comprising: a plurality of perforated shells having a size of at least 100nm and comprising openings smaller than 10nm, wherein the shells are electrically conductive and/or comprise an electrically conductive coating, and zinc and/or zinc oxide which resides at least partially within the shells.

[0005] One aspect of the present invention provides a method comprising: wetting with a Zn solution a plurality of perforated shells having a size of at least 100nm and comprising openings smaller than 10nm, wherein the shells are electrically conductive material and/or comprise an electrically conductive coating, wherein the wetting is carried out by at least partial penetration of the Zn solution through the openings, and coating Zn at least partly internally in the shells by application of electric current to the shells.

[0006] These, additional, and/or other aspects and/or advantages of the present invention are set forth in the detailed description which follows; possibly inferable from the detailed description; and/or learnable by practice of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] For a better understanding of embodiments of the invention and to show how the same may be carried into effect, reference will now be made, purely by way of example, to the accompanying drawings in which like numerals designate corresponding elements or sections throughout.

[0008] In the accompanying drawings:

[0009] **Figure 1** is a high-level schematic illustration of perforated shell particles in a powder, according to some embodiments of the invention

[0010] **Figure 2** is a high-level schematic illustration of an electrode made of the powder, with only a first layer of perforated shell particles illustrated, according to some embodiments of the invention.

[0011] **Figure 3** is a high-level schematic illustration of powder being pressed and sintered to for the electrode active material, according to some embodiments of the invention.

[0012] **Figure 4** is a high-level schematic illustration of a zinc-air electrochemical cell comprising the electrode, according to some embodiments of the invention.

[0013] **Figure 5** is a high-level flowchart illustrating a method, according to some embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0014] In the following description, various aspects of the present invention are described. For purposes of explanation, specific configurations and details are set forth in order to provide a thorough understanding of the present invention. However, it will also be apparent to one skilled in the art that the present invention may be practiced without the specific details presented herein. Furthermore, well known features may have been omitted or simplified in order not to obscure the present invention. With specific reference to the drawings, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the present invention only, and are presented in the cause of

providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

[0015] Before at least one embodiment of the invention is explained in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is applicable to other embodiments that may be practiced or carried out in various ways as well as to combinations of the disclosed embodiments. Also, it is to be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting.

[0016] Embodiments of the present invention provide efficient and economical methods and mechanisms for preparing zinc-air batteries and thereby provide improvements to the technological field of energy storage. Powders, electrodes, zinc-air batteries and corresponding methods are provided. Powders comprise perforated shells having a size of at least 100nm and comprising openings smaller than 10nm. The shells are electrically conductive and/or comprise an electrically conductive coating. Powders further comprise zinc and/or zinc oxide which resides at least partially within the shells. Methods comprise wetting the shells with a zinc solution to yield at least partial penetration of the zinc solution through the openings, and coating zinc internally in the shells by application of electric current to the shells. Upon electrode preparation from the powder, cell construction and cell operation, zinc is oxidized to provide energy and the shells retain formed ZnO therewith, providing sufficient volume for the associated expansion and maintaining thereby the mechanical stability and structure of the electrode – to enable many operation cycles of the rechargeable zinc-air batteries.

[0017] **Figure 1** is a high-level schematic illustration of perforated shell particles **110** in a powder **100**, according to some embodiments of the invention. Powder **100** comprises a plurality of perforated shells **110** having a size of at least 100nm and comprising openings **115** smaller than 10nm, with shells **110** being electrically conductive (e.g., made of

electrically conductive material such as Ni, Sn, C in various forms, TiN or combinations thereof) and/or comprise an electrically conductive coating **112** (e.g., a carbon-based coating in various carbon forms, e.g., graphite or graphene). Powder **100** further comprises zinc **120** and/or zinc oxide **125** which reside at least partially within shells **110**. The volumes of perforated shells **110** are configured to sustain at least a 30% volume increase of Zn oxidation to ZnO.

[0018] Shells **110** may have few or many openings **115**, zinc **120** may be at least partly internally coated in shells **110** after penetrating shells **110** through openings **115**, e.g., in a Zn solution that is used to wet powder **100**. Zinc oxide **125** may comprise zinc oxide particles **125** which are at least partly within shells **110**, and may form additional particles in powder **100**.

[0019] In certain embodiments, shells **110** may be formed around zinc (and/or zinc oxide) particles, e.g., by coating or by inserting the particles into a conductive matrix, as described below.

[0020] **Figure 2** is a high-level schematic illustration of an electrode made of powder **100**, with only a first layer of perforated shell particles **110** illustrated, according to some embodiments of the invention.

[0021] In various embodiments, shells **110** may be at least partly agglomerated, may be pressed, and are sintered (or fused) and attached to a current collector **90** to form an electrode **130**.

[0022] **Figure 3** is a high-level schematic illustration of powder **100** being pressed and sintered to for the electrode active material, according to some embodiments of the invention. In various embodiments, shells **110** may be uniform or variable in shape and may comprise e.g., spherical, ellipsoid and/or rod-shaped shells **110**, as well as partially-symmetrical shapes, non-symmetrical shapes or combinations thereof. Zn and/or ZnO may be partly deposited outside of shells **110**, as illustrated schematically by numerals **121** and **126**, respectively. For example, some of the Zn solution may wet shells **110** externally and Zn may be coated on shells externally, and/or some ZnO particles may exit shells and/or form outside shells **110**. **Figure 3** further illustrates schematically internal spaces **111** in the powder particles, which shrink **113** upon reduction of Zn to ZnO. It is noted that shells **110** are configured to be large enough, with respect to the volume of internally coated Zn,

to allow for the expansion of ZnO formed by Zn oxidation. Powder **100** may be pressed and sintered in either oxidized or reduced state, or in an intermediate state (illustrated schematically with some ZnO particles remaining outside shells **110**) to yield electrode **130**.

[0023] **Figure 4** is a high-level schematic illustration of a zinc-air electrochemical cell **140** comprising electrode(s) **130**, according to some embodiments of the invention. Zinc-air battery **140** comprising cell(s) **140** may be formed from one or more electrode **130** (made of perforated shells **110** containing Zn **120** and/or ZnO **125** and shown in a highly schematic manner with enlarged shells **110**) and further comprise at least one air electrode **142** and alkaline electrolyte **143**. Cathodes **142** may be air cathodes, e.g., as taught by U.S. Patents Nos. 8,142,938 and 9,941,516, incorporated herein by reference in their entirety, comprising a catalyst attached to a PTFE (Polytetrafluoroethylene) skin on a network to which a current collector is attached. Cathodes **142** may be other types of cathodes operable in zinc-based batteries. Alkaline electrolyte **143** may comprise KOH and/or NaOH, as non-limiting examples. Contacts **141** are illustrated schematically for electrodes **130**, **142**.

[0024] Batteries **140** may be used as secondary, rechargeable batteries, with shells **110** supporting repeated expansion and contraction of the active material (Zn) in their internal volumes, thus protecting electrode **130** from mechanical stress and structural instability during multiple charging and discharging cycles. Perforated shells **110** are further configured to maintain at least a significant part (e.g., 50%, 70%, 90% or other values) of the active material within shells **110** during multiple charging and discharging cycles to maintain over time the structural stability of electrode **130**.

[0025] In various embodiments, shells **110** may be embedded within a conductive matrix, possibly a porous conductive matrix for further mechanical stabilization and for ensuring good electrical conductivity. In certain embodiments, shells **110** may be partly or fully coated by conductive coating **112**. In certain embodiments, at least some, or possibly all perforations **115** may be closed after introduction of Zn into shells **110**, to prevent exit of Zn **120** and/or ZnO **125** from shells **110** upon operation. In certain embodiments, coating **112** and/or the conductive matrix may at least partly close perforations **115**.

[0026] In various embodiments, shells **110** may be formed by any of electroless deposition, electrical deposition (e.g., electroplating), spraying, brushing, printing, dipping, spin-

coating, vapor deposition, sputtering or combinations thereof. Shells **110** may be understood as pockets that receive and hold the active material during operation. Shells **110** may be stiff, maintaining a free space to contain ZnO particles, or shells **110** may comprise flexible pockets that can somewhat expand (e.g., within a somewhat flexible matrix) to accommodate for the increase in volume from Zn to ZnO during the discharging of the battery. Shells **110** may be configured to support mechanically small encapsulated zinc reaction zones (pockets) within electrode **130** which prevent mechanical (large scale) stresses to electrode **130** as a whole. In certain embodiments, shells **110** and/or the zinc reaction zones and/or openings **115** therein may be formed during the electrode production process, e.g., using active materials, additives, binders (e.g., polytetrafluoroethylene (PTFE), related PFEs, fluorinated ethylene propylene (FEP); polyvinylidene fluoride (PVDF); Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP); ethylene vinyl acetate (EVA), low density polyethylene (LDPE), polypropylene (PP), and equivalent binders), stabilizers and/or pore formers encapsulated within shells **110**. Openings **115** may be configured to allow penetration of zinc solution into shells **110** and/or to maintain ionic conductivity across shell **110** to Zn/ZnO active material.

[0027] In various embodiments, coating **112** may comprise any form of carbon (e.g., graphite, graphene, nanotubes or combinations thereof), as well as any of: a metallic coating such as bismuth or indium, a metal alloy coating, a conductive polymer (possibly polymeric ink), a polymer with electronic conductive filler such as metal, carbon, graphite metal oxide, metal carbide or metal nitride or a combination of these materials. Electronic conductivity may be increased by adding a metallic mesh, expanded foil or carbon cloth within the electrode structure.

[0028] For example, as presented below, electronically conductive coating **112** may comprise a material with a high over-potential for hydrogen evolution. For example, shells **110** may comprise zinc particles having a particle size between 20-400 μ m, coated with a suitable metal coating such as bismuth or tin using conventional techniques such as electrolytic bath plating, yielding a coating thickness of 0.1-5 μ m. Coating **112** may be configured to be formed as a non-perfect, non-sealing coating. In another example, polymeric coating **112** (e.g., an organic electronically conductive material, e.g., graphite or

graphene) may be applied onto anodic zinc particles **110**. Coating **112** may be applied to particles **110** e.g., in solution, possibly using a coating precursor.

[0029] Electrode **130** may be formed by mixing shells **110** (e.g., modified and/or coated zinc particles) with other non-coated anodic particles and fusing the particles together by applying pressure to the particles or heat or a combination of both. During the heating process, pore formers may be applied or used to increase the pocket size leading to a more porous structure. Resulting zinc electrode **130** may be structured as zinc with anodic particles **110** partially coated with a conductive coating. Anodic particles **110** may be individually coated to form a sort of imperfect pocket or broken egg shell structure. Conductive coating **112** may be selected to have a low melting temperature such that the coated anodic particles may be pressed together as a cake and then sintered at a suitable temperature to form a porous three-dimensional electrode structure. Optionally, conductive particles or non-coated anodic particles or materials, e.g., calcium hydroxide, may be incorporated into this structure to reduce solubility of the zinc. In certain embodiments, during the cake formation and the sintering process, the individual additive particles may be surrounded by coated zinc, forming a complex three-dimensional structure in which the oxides or additives are in contact with metal-coated zinc particles **110**.

[0030] Certain embodiments comprise the formation of anodic particles **110** within a porous structure that already contains pores or pockets (e.g., a metal foam, a metal sponge, a metal matrix, a collection of porous particles, a broken-shell structure, a skeleton, a supporting framework or a combination thereof), and serves as support for the formation of particles **110** from a particle precursor. The particle precursor may comprise zinc ions that are delivered to the porous structure within a liquid. Once inside the structure, the zinc ions may be reduced to form zinc particles. Reduction of the zinc ions may be conducted chemically or electrochemically. The formed zinc particles are protected by the porous structure.

[0031] In certain embodiments, shells **110** may be at least 100nm in diameter and openings **115** may be smaller than 10nm. In various embodiments, shells **110**, and/or the zinc particles presented above, may range in size between 10nm and 1000µm, e.g., be in any of the ranges of: 100-300nm, 300nm-1µm, 1-3µm, 3-10µm, 10-30µm, 30-100µm or combinations thereof, and have various size distributions (e.g., low size distribution or

possibly monodispersed, high size distribution etc.). Coating **112** may cover shells **110** to various extents, e.g., between any of 0.01-99.99%, 0.01-50%, 50-99.99% or 100% of the shell area may be coated. Coating **112** may be at least partly internal as well as external and may have a regular or an irregular coating pattern. Perforations **115** and/or perforations of coating **112** may have a regular or an irregular perforation pattern and/or shape.

[0032] In various embodiments, one or more ZnO particles **125** may be present within each shell **110**, and may have small or large contact area with inner walls of shells **110**, maintaining electrical contact therewith.

[0033] **Figure 5** is a high-level flowchart illustrating a method **200**, according to some embodiments of the invention. The method stages may be carried out with respect to powders **100**, electrodes **130** and cells **140** described above, which may optionally be configured to implement method **200**. Method **200** may comprise the following stages, irrespective of their order.

[0034] Method **200** comprises wetting with a Zn solution a plurality of perforated shells (stage **230**), the shells formed from electrically conductive material (e.g., Ni, Sn, C in various forms, TiN or combinations thereof) and/or are coated by an electrically conductive coating, e.g., a carbon-based coating. (stage **210**), have a size of at least 100nm and are perforated (stage **220**) to have openings smaller than 10nm. Wetting **230** is carried out to reach at least partial penetration of the Zn solution through the openings. Method **200** further comprises coating Zn at least partly internally in the shells by application of electric current to the shells (stage **240**).

[0035] Methods **200** may optionally comprise pressing the powder (stage **248**) and further comprise sintering (or fusing) the powder of the shells to form an electrode and using the electrode in a zinc-air battery (stage **250**).

[0036] Method **200** may further comprise electrochemically oxidizing the internally coated Zn to form ZnO particles which are and/or stay at least partly within the shells (stage **242**) – either or both in a preparatory stage (before forming the electrode in stage **250**) or during operation of the battery. Complementarily, the openings may be configured to retain at least part of the ZnO within the shells (stage **244**). The volumes of the perforated shells may be configured to sustain at least a 30% volume increase during Zn oxidation to ZnO (stage **246**).

[0037] Advantageously, disclosed batteries **140** provide a large number of cycles, overcoming prior art limitations of zinc air batteries due to structural instability as prior art electrodes become spongy, suffer from dendrite growth and structural changes.

EXAMPLES

EXAMPLE 1

[0038] Ten grams of non-coated Zinc Grillo brand battery powder is mixed with 10 grams of bismuth-coated zinc Grillo powder. The mixed powder is then placed within a 10cm by 10 cm die and a 10 to 20 ton pressure is applied for 1 minute. The pressed electrode is then gently removed and transferred on a thin metal plate to an oven which is heated at 300°C. After 15 minutes, the plate is removed and allowed to cool to room temperature. The coated anodic particles are coated to form a sort of broken egg-shell structure (thus a non-perfect coating), and are sintered to an electrode.

EXAMPLE 2

[0039] Zinc particles (Grillo brand BC 40-0/200Bi/200Ln) are coated in a tin electroplating bath to form 1-5 μm thick tin coating. 20 grams of the coated particles are added to 5 grams of zinc oxide powder. The powder is mixed in a mechanical rotating mixer for 1 hour. To this, 0.5gram FEP powder (fluorinated ethylene propylene copolymer) produced by Dupont is added and the powder is mixed for an additional hour. The mixture is poured into a die of size 8 cm by 8 cm evenly on top of a precut silicone release paper. A tin coated mesh is placed onto the powder within the die. The head of the die is placed above the powder and a 15 ton pressure is applied for 20 seconds. The electrode cake is gently removed from the die and the silicone release paper removed. The cake is transferred to a 250°C oven on a brass plate coated with release coating such as Teflon for a sinter period of 15 minutes. The tin as well as the FEP melts at this temperature and upon cooling becomes a handleable electrode. The electrode is released from the brass plate.

EXAMPLE 3

[0040] 20 grams of polymer- (Dag EB-005) coated anodic particles are added to 8 grams of non-coated zinc particles and then placed for 1 hour in a tumbler mixer to ensure

homogenous mixing. The mixed powder is then placed within a 10 cm by 10 cm die and a 10 to 20 ton pressure is applied for 1 minute. The pressed electrode is then gently removed and transferred on a thin metal plate to an oven which is heated to 140°C. After 6 minutes the plate is removed and allowed to cool to room temperature. The electrode has transformed to a single block electrode which is connected via a three-dimensional conductive structure.

[0041] The polymeric coating may be an organic material with electronically conductive particles such as graphite. A commercial suitable thermoplastic polymeric material may be Dag EB-005 brand conductive coating produced by Henkel. The Dag EB-05 can be sprayed onto zinc particles such as Grillo with particle size of 100-400 microns to form a coating with thickness of 2-3 microns. The particles may be sprayed lightly and then dried while undergoing continuous movement in a heated air bath or a vibrating plate such that the particles are in constant motion to eliminate caking of the particles. The spraying and drying process is repeated until a sufficiently thick coating is achieved. The coating is left to dry for 1 hour at room temperature.

EXAMPLE 4

[0042] The anodes as described above are incorporated into a battery as follows. A flat square block of the zinc anode described in Example 1 is cut to an area size 50 mm x 50 mm, with thickness of ~2 mm and is situated between two air electrodes (one on each side) at a distance of 3 mm, as described in US patent 8,142,938 such that the catalyst side is facing the zinc electrode and the PTFE porous film faces the air, within a fitting block. Electrolyte (KOH concentration 350-500 gram per liter of water) flows in the gaps between the air electrode and the zinc electrode under the forced pressure of a diaphragm pump at a flow rate 0.01-0.1 L/min. The electrolyte may include efficiency-improving additives, such as stannate salt, glucose, poly-acrylic acid or polyacrylates, etc. Typical working temperature lies in the range from 10 to 40 °C, preferable discharge and charge current draw lies in the range of 1-30 mA/cm², at voltage 1.0-1.2 V.

[0043] In the above description, an embodiment is an example or implementation of the invention. The various appearances of "one embodiment", "an embodiment", "certain

embodiments" or "some embodiments" do not necessarily all refer to the same embodiments. Although various features of the invention may be described in the context of a single embodiment, the features may also be provided separately or in any suitable combination. Conversely, although the invention may be described herein in the context of separate embodiments for clarity, the invention may also be implemented in a single embodiment. Certain embodiments of the invention may include features from different embodiments disclosed above, and certain embodiments may incorporate elements from other embodiments disclosed above. The disclosure of elements of the invention in the context of a specific embodiment is not to be taken as limiting their use in the specific embodiment alone. Furthermore, it is to be understood that the invention can be carried out or practiced in various ways and that the invention can be implemented in certain embodiments other than the ones outlined in the description above.

[0044] The invention is not limited to those diagrams or to the corresponding descriptions. For example, flow need not move through each illustrated box or state, or in exactly the same order as illustrated and described. Meanings of technical and scientific terms used herein are to be commonly understood as by one of ordinary skill in the art to which the invention belongs, unless otherwise defined. While the invention has been described with respect to a limited number of embodiments, these should not be construed as limitations on the scope of the invention, but rather as exemplifications of some of the preferred embodiments. Other possible variations, modifications, and applications are also within the scope of the invention. Accordingly, the scope of the invention should not be limited by what has thus far been described, but by the appended claims and their legal equivalents.

CLAIMS

What is claimed is:

1. A powder comprising:
 - a plurality of perforated shells having a size of at least 100nm and comprising openings smaller than 10nm, wherein the shells are electrically conductive and/or comprise an electrically conductive coating, and
 - zinc and/or zinc oxide which resides at least partially within the shells.
2. The powder of claim 1, wherein the shells are at least partly agglomerated.
3. The powder of claim 1, wherein the zinc is at least partly internally coated in the shells.
4. The powder of claim 1, wherein the zinc oxide comprises zinc oxide particles which are at least partly within the shells.
5. The powder of any one of claims 1-4, wherein volumes of the perforated shells are configured to sustain at least a 30% volume increase of Zn oxidation to ZnO.
6. The powder of any one of claims 1-5, wherein the shells are conductive and made of at least one of Ni, Sn, C, TiN or combinations thereof.
7. The powder of any one of claims 1-6, wherein the shells are coated by a carbon-based coating.
8. An electrode made of the powder of any one of claims 1-7, sintered and attached to a current collector.
9. A zinc-air battery comprising at least one of the electrode of claim 8, at least one air electrode and alkaline electrolyte.
10. A method comprising:
 - wetting with a Zn solution a plurality of perforated shells having a size of at least 100nm and comprising openings smaller than 10nm, wherein the shells are electrically conductive material and/or comprise an electrically conductive coating, wherein the wetting is carried out by at least partial penetration of the Zn solution through the openings, and
 - coating Zn at least partly internally in the shells by application of electric current to the shells.

11. The method of claim 10, further comprising sintering a powder of the shells to form an electrode and using the electrode in a zinc-air battery.
12. The method of claim 11, further comprising pressing the powder prior to the sintering.
13. The method of any one of claims 10-12, further comprising electrochemically oxidizing the internally coated Zn to form ZnO particles which are at least partly within the shells.
14. The method of claim 13, wherein the openings are configured to retain at least part of the ZnO within the shells.
15. The method of any one of claims 10-14, wherein volumes of the perforated shells are configured to sustain at least a 30% volume increase during Zn oxidation to ZnO.
16. The method of any one of claims 10-15, further comprising forming the perforated shells from at least one of Ni, Sn, C, TiN or combinations thereof.
17. The method of any one of claims 10-16, further comprising coating the shells by a carbon-based coating.