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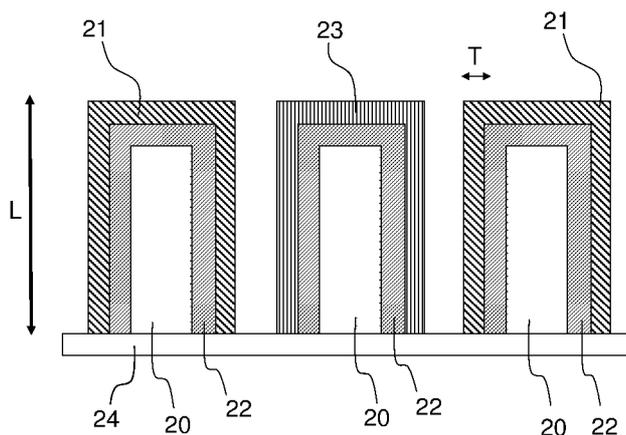
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(54) **Title:** THREE-DIMENSIONAL BATTERIES AND METHODS OF MANUFACTURING THE SAME



(57) **Abstract:** Various methods and apparatus relating to three-dimensional battery structures and methods of manufacturing them are disclosed and claimed. In certain embodiments, a three-dimensional battery comprises a battery enclosure, and a first structural layer within the battery enclosure, where the first structural layer has a first surface, and a first plurality of conductive protrusions extend from the first surface. A first plurality of electrodes is located within the battery enclosure, where the first plurality of electrodes includes a plurality of cathodes and a plurality of anodes, and wherein the first plurality of electrodes includes a second plurality of electrodes selected from the first plurality of electrodes, each of the second plurality of electrodes being in contact with the outer surface of one of said first plurality of conductive protrusions. Some embodiments relate to processes of manufacturing energy storage devices with or without the use of a backbone structure or layer.

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THREE-DIMENSIONAL BATTERIES AND METHODS OF MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

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[0001] This application claims priority under 35 U.S.C. section 119(e) to: (i) U.S. Provisional Application No. 60/884,836, entitled "Electrodes For Three Dimensional Lithium Batteries And Methods Of Manufacturing Thereof," filed on January 12, 2007; (ii) U.S. Provisional Application No. 60/884,828, entitled "Three-Dimensional Batteries and Methods of
10 Manufacturing Using Backbone Structure," filed on January 12, 2007; and (iii) U.S. Provisional Application No. 60/884,846, entitled "Three-Dimensional Lithium Battery Separator Architectures," filed on January 12, 2007; all of which are hereby incorporated by reference herein in their entirety.

15 BACKGROUND OF THE INVENTION

1. TECHNICAL FIELD OF THE INVENTION

[0002] Implementations consistent with the principles of the invention generally relate to the field of battery technology, more specifically to three-dimensional energy storage systems and
20 devices, such as batteries and capacitors, and methods of manufacturing thereof.

2. BACKGROUND

[0003] Existing energy storage devices, such as batteries, fuel cells, and electrochemical capacitors, typically have two-dimensional laminar architectures (e.g., planar or spiral-wound laminates) with a surface area of each laminate being roughly equal to its geometrical footprint
25 (ignoring porosity and surface roughness).

[0004] Fig. 1 shows a cross sectional view of an existing energy storage device, such as a lithium-ion battery. The battery 15 includes a cathode current collector 10, on top of which a

cathode 11 is assembled. This layer is covered by a separator 12, over which an assembly of an anode current collector 13 and an anode 14 are placed. This stack is sometimes covered with another separator layer (not shown) above the anode current collector 13, and is rolled and stuffed into a can to assemble the battery 15. During a charging process, lithium leaves the cathode 11 and travels through the separator 12 as a lithium ion into the anode 14. Depending on the anode 14 used, the lithium ion either intercalates (e.g., sits in a matrix of an anode material without forming an alloy) or forms an alloy. During a discharge process, the lithium leaves the anode 14, travels through the separator 12 and passes through to the cathode 11.

[0005] Three-dimensional batteries have been proposed in the literature as ways to improve battery capacity and active material utilization. It has been proposed that a three-dimensional architecture may be used to provide higher surface area and higher energy as compared to a two dimensional, laminar battery architecture. There is a benefit to making a three-dimensional energy storage device due to the increased amount of energy that may be obtained out of a small geometric area.

[0006] The following references may further help to illustrate the state of the art, and are therefore incorporated by reference as non-essential subject matter herein: Long *et. al.*, "Three-Dimensional Battery Architectures," *Chemical Reviews*, (2004), 104, 4463-4492; Chang Liu, FOUNDATIONS OF MEMS, Chapter 10, pages 1-55 (2006); Kanamura *et. al.*, "Electrophoretic Fabrication of LiCoO_2 Positive Electrodes for Rechargeable Lithium Batteries," *Journal of Power Sources*, 97-98 (2001) 294-297; Caballero *et al.*, " $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ thick-film electrodes prepared by electrophoretic deposition for use in high voltage lithium-ion batteries," *Journal of Power Sources*, 156 (2006) 583-590; Wang and Cao, "Li⁺-intercalation Electrochemical/Electrochromic Properties Of Vanadium Pentoxide Films By Sol Electrophoretic Deposition,"

Electrochimica Acta, 51, (2006), 4865 - 4872; Nishizawa *et al.*, "Template Synthesis of Polypyrrole-Coated Spinel LiMn_2O_4 Nanotubules and Their Properties as Cathode Active Materials for Lithium Batteries," *Journal of the Electrochemical Society*, 1923 - 1927, (1997); Shembel *et. al.*, "Thin Layer Electrolytic Molybdenum Oxysulfides For Lithium Secondary Batteries With Liquid And Polymer Electrolytes," *5th Advanced Batteries and Accumulators, ABA-2004*, Lithium Polymer Electrolytes; and Kobrin *et. al.*, "Molecular Vapor Deposition - An Improved Vapor-Phase Deposition Technique of Molecular Coatings for MEMS Devices," *SEMI Technical Symposium: Innovations in Semiconductor Manufacturing (STS: ISM), SEMICON West 2004, 2004 Semiconductor Equipment and Materials International*.

10 [0007] It would be desirable to make three-dimensional electrochemical energy devices that may provide significantly higher energy and power density, while addressing the above issues or other limitations in the art.

SUMMARY OF THE INVENTION

[0008] Various methods and apparatus relating to three-dimensional battery structures and methods of manufacturing them are disclosed and claimed. In certain embodiments, a three-dimensional battery comprises a battery enclosure, and a first structural layer within the battery enclosure, where the first structural layer has a first surface, and a first plurality of conductive protrusions extend from the first surface. A first plurality of electrodes is located within the battery enclosure, where the first plurality of electrodes includes a plurality of cathodes and a plurality of anodes, and wherein the first plurality of electrodes includes a second plurality of electrodes selected from the first plurality of electrodes, each of the second plurality of electrodes being in contact with the outer surface of one of said first plurality of conductive protrusions.

[0009] Other aspects and advantages of the present invention may be seen upon review of the figures, the detailed description, and the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Some embodiments of the invention are described with reference to the following figures.

[0011] Fig. 1 is a generic cross-section of an existing two-dimensional energy storage device
5 such as a lithium ion battery.

[0012] Fig. 2 is a schematic illustration of a backbone structure according to an embodiment of the invention.

[0013] Figs. 3A-3D are schematic illustrations of some shapes into which backbone structures may be assembled according to certain embodiments of the invention.

10 [0014] Figs. 4A-4E depict a schematic representation of a process for manufacturing a backbone structure using a subtractive reactive ion etch process, according to an embodiment of the invention.

[0015] Figs. 5A-5D depict a schematic representation of a process for manufacturing a backbone structure using a subtractive electrochemical etch process, according to an embodiment
15 of the invention.

[0016] Figs. 6A-6C depict a schematic representation of a process for manufacturing a backbone structure using a subtractive stamping process, according to an embodiment of the invention.

[0017] Figs. 7A-7D depict a schematic representation of a process for manufacturing a
20 backbone structure using an additive electrochemical deposition, electroless deposition, or electrophoretic deposition process, according to an embodiment of the invention.

[0018] Figs. 8A-8E depict a schematic representation of a process for manufacturing a backbone structure using an additive extrusion process, according to an embodiment of the invention.

[0019] Figs. 9A-9C depict a schematic representation of a process for manufacturing a backbone structure using a sequential deposition and assembly process, according to an
5 embodiment of the invention.

DETAILED DESCRIPTION

[0020] Certain embodiments of the invention relate to the design of a three-dimensional lithium-ion battery. Existing energy storage devices, such as batteries, fuel cells, and electrochemical capacitors, typically have two-dimensional laminar architectures (e.g., planar or spiral-wound laminates) with a surface area of each laminate being roughly equal to its geometrical footprint (ignoring porosity and surface roughness). A three-dimensional energy storage device can be one in which an anode, a cathode, and/or a separator are non-laminar in nature. For example, if electrodes protrude sufficiently from a backplane to form a non-laminar active battery component, then the surface area for such a non-laminar component may be greater than twice the geometrical footprint of its backplane. In some instances, given mutually orthogonal X,Y,Z directions, a separation between two constant-Z backplanes should be at least greater than a spacing between electrodes in an X-Y plane, divided by the square root of two.

[0021] Some embodiments of the invention relate to the use of a backbone structure for the manufacture of three-dimensional energy storage devices, such as batteries, capacitors, and fuel cells. The backbone structure may be used for the purpose of providing mechanical stability, electrical connectivity, and increased surface area per unit geometrical area. By way of example, the backbone structure may be made in the shape of pillars by wire-bonding aluminum on a flat substrate, which may be subsequently coated with a cathode or anode material for the purpose of assembling a battery. Examples of backbone formation using various materials, shapes, and methodologies are presented herein, among other embodiments.

[0022] Three-dimensional energy storage devices may produce higher energy storage and retrieval per unit geometrical area than conventional devices. Three-dimensional energy storage devices may also provide a higher rate of energy retrieval than two-dimensional energy storage

devices for a specific amount of energy stored, such as by minimizing or reducing transport distances for electron and ion transfer between an anode and a cathode. These devices may be more suitable for miniaturization and for applications where a geometrical area available for a device is limited and/or where energy density requirement is higher than what may be achieved
5 with a laminar device.

[0023] Some embodiments of the invention include a mechanically stable, electrically conductive backbone structure that ends up being a part of the final assembled energy storage device. A backbone material typically does not take an active part in electrochemical reactions of the energy storage device, and may enhance mechanical and electrical robustness.

10 [0024] The backbone material may also act as a high surface area substrate for manufacturing the high surface area electrochemical device. Mechanical robustness may increase the lifetime of the device, since active materials that constitute the device are typically porous electrodes with relatively lower mechanical stability. Electrical conductivity may enhance or maintain a power density of the device (e.g., by decreasing resistivity) while also equalizing current
15 distribution between electroactive species.

[0025] A backbone structure may be made in any shape that provides higher surface area relative to geometrical area, such as pillars, posts, plates, waves, circles, diamonds, spirals, staircase structures, and so forth. The backbone structure may be made out of any material that may be shaped, such as metals, semiconductors, organics, ceramics, and glasses. The backbone
20 structure may serve to provide: (i) rigidity to active electrodes in an energy storage device, such as anodes and cathodes in a lithium ion battery; (ii) electrical connectivity to tall three-dimensional structures; and (iii) increased surface area per unit geometrical area. Desirable materials include semiconductor materials such as silicon and germanium. Carbon-based

organic materials may also be used to form backbone structures for three-dimensional shaping. Metals, such as aluminum, copper, nickel, cobalt, titanium, and tungsten, may also be used for backbone structures.

[0026] In some embodiments, a backbone structure is made out of a metal, semiconductor,

5 organic material, ceramic, or glass using a subtractive formation technique. These materials may be processed by reactively etching a substrate using a selective etch mask and a plasma etch process. Alternatively, or in conjunction, electrochemical etching, stamping, or electrical discharge machining may be used to selectively remove material preferentially in areas where these materials are not desired.

10 [0027] In other embodiments, a backbone structure is made out of a metal, semiconductor,

organic, ceramic, or glass using an additive formation technique. These materials may be processed by making a sacrificial mold using a technique such as conventional lithography, and depositing a backbone material using techniques such as electrochemical deposition, electroless deposition, electrophoretic deposition, vacuum assisted filling, stencil assisted filling, and so
15 forth. In certain cases, the backbone structure may be assembled directly using a wirebonding process. In other cases, the backbone structure may be made on a flat plate using conventional lithography and deposition techniques, and subsequently assembled by "pick and place" and soldering or gluing techniques.

[0028] In other embodiments, a backbone material may be shaped using printing techniques,

20 such as three-dimensional printing and inkjet printing, to form a backbone structure using single or multiple layers of printing to obtain a desired shape and thickness. Alternatively, or in conjunction, the backbone material may be assembled in the form of layered sheets, with sacrificial layers deposited in between. After stacking of the sheets is substantially complete, a

resulting structure is cut into pieces of a desired height, assembled together, and the sacrificial material is released to provide the backbone structure.

[0029] In the case of an electrically conductive backbone structure, an active material may be directly assembled on top of and around the backbone structure by various techniques, such as
5 electrochemical deposition, electroless deposition, co-deposition in an organic or inorganic matrix, electrophoretic deposition, mechanical filling and compacting, and vacuum assisted flow deposition.

[0030] In case of an electrically non-conductive backbone structure, a conducting layer may be deposited by various techniques, such as electrochemical or electroless deposition, vapor assisted
10 vacuum deposition such as Atomic Layer Deposition (ALD) and Chemical Vapor Deposition (CVD), sputter deposition, evaporation, and electrophoretic deposition. This conductive layer may be subsequently removed in order to remove an electrical connection between an anode and a cathode. This removal may be accomplished using techniques such as sputter etching, ion milling, and liftoff. In addition, techniques such as chemical dissolution may be used with
15 standard techniques such as lithography to protect areas that do not need to be removed.

[0031] Fig. 2 illustrates an exemplary concept of a backbone structure 20 used in the formation of a three-dimensional battery. Fig. 2 shows a cross-sectional schematic of two positive electrodes 21 and a negative electrode 23. In this embodiment, the backbone structure 20 includes a non-conductive base 24 of a common material on which a conductive material 22 has
20 been deposited and removed in the areas where it is not needed in order to separate the electrodes 21 and 23. It is apparent from comparing Fig. 2 and Fig. 1 that a surface area for the electrodes 21 and 23 in Fig. 2 is relatively higher as compared to the surface area for the electrodes shown in Fig. 1, calculating this area as a product of a length L and a thickness T of the electrodes 21

and 23. It should be noted that the thickness, and therefore related properties such as conductivity, of various features (such as electrodes and backbone structure protrusions) according to certain embodiments may be varied locally (e.g., from electrode to electrode or from protrusion to protrusion) based on current-carrying requirements or other relevant performance specifications.

[0032] Some examples of three-dimensional architectures that are capable of use with certain embodiments of the present invention, and that have cathodes and anodes protruding from the same backplane, are shown in Figs. 3A-3D. Fig. 3A shows a three-dimensional assembly with cathodes and anodes in the shape of pillars, Fig. 3B shows a three-dimensional assembly with cathodes and anodes in the shape of plates, Fig. 3C shows a three-dimensional assembly with cathodes and anodes in the shape of concentric circles, and Fig. 3D shows a three-dimensional assembly with cathodes and anodes in the shape of waves. Other configurations, such as honeycomb structures and spirals might also be used with certain embodiments of the present invention. In Figs. 3A-3D, cathodes 30 and anodes 31 protrude from the same backplane and are alternating in a periodic fashion. However, in other embodiments the cathodes 30 may protrude from a different backplane than anodes 31.

[0033] Figs. 4A-4E depict a schematic representation of an overall process flow for manufacturing a backbone structure using a subtractive reactive ion etch process according to certain embodiments. The process involves using a substrate 40 that may be shaped using a directional plasma source to form a volatile gaseous by-product, thereby facilitating its removal. A non-limiting example of the substrate 40 is one formed of silicon, which may be single-crystal or polycrystalline in nature. A masking layer 41 is deposited on top of the substrate 40 by methods such as vacuum deposition, thermal oxidation, surface coating, and wet chemical

deposition. In the case of silicon as the substrate 40, a thermally grown silicon dioxide layer of a particular thickness may serve as the masking layer 41. This layer 41 may be subsequently patterned by standard patterning techniques such as lithography in order to provide a pattern suitable for further processing to create the backbone structure. In some embodiments of the invention, the masking layer 41 may be covered with a second masking layer 42 that is used to pattern the first masking layer 41 (see Figs. 4A-4B). In this case, the first masking layer 41 is patterned by using the second masking layer 42 as a stencil (see Fig. 4C). For the silicon/silicon dioxide case, a standard photoresist may be used as the second masking layer 42. The second masking layer 42 may be patterned with standard optical lithography techniques. The second masking layer 42 may be selectively removed using selective wet or dry methods, leaving behind the patterned first masking layer 41 (see Fig. 4D). This combination of the substrate 40 and the patterned first masking layer 41 is subjected to a directional plasma 43 in a controlled environment in order to transfer the image of the first masking layer 41 onto the substrate 40 (see Fig. 4D). This reactive etch process in the presence of a directional plasma source may provide excellent anisotropic etching of the substrate 40 while etching the masking layer 41 itself at a very low rate. After the reactive etch of the substrate 40 is substantially complete, the masking layer 41 may be removed to leave the patterned substrate 40 behind, thereby forming the backbone structure (see Fig. 4E).

[0034] The following example further explains concepts described with reference to Figs. 4A-4E. Single-crystal or polycrystalline silicon may be used as the substrate 40 that may be etched directionally in the presence of a plasma. The first masking layer 41 may be a thermally grown silicon dioxide layer of a particular thickness. A standard photoresist, such as AZ4620™ and AZP4620™ (commercially available from Clariant Corporation), may be used as the second

masking layer 42. This layer 42 may be spin coated on top of the silicon dioxide layer, and subsequently patterned with standard optical lithography techniques. The areas of the photoresist that are exposed to light may be developed away using a developer solution, such as AZ400K™ (commercially available from Clariant Corporation). This patterned structure is

5 dipped in a solution of HF, NH₃F, and water (Buffered Oxide Etch), wherein exposed silicon dioxide surfaces are dissolved. The remaining photoresist may be selectively removed by using a compatible organic solvent, such as N-methyl-2-Pyrrolidone, leaving behind the patterned silicon dioxide layer. This combination of the silicon and patterned silicon dioxide may be subjected to a directional fluoride plasma source in order to etch an image of the silicon dioxide

10 layer onto the substrate 40. The directionality of the plasma 43 is controlled by a bias voltage between an anode and a cathode in a conventional plasma reactive ion etcher. A difference in rate between etch of silicon and silicon dioxide causes a pattern to be transferred to the substrate 40 without much etching in a lateral direction. After the reactive etch of silicon is substantially complete, the masking layer 41 may be removed by immersion in the Buffered Oxide Etch

15 solution to leave the patterned substrate 40 behind. In some cases, a stop layer can be added to the bottom of the substrate 40 to facilitate complete etching and isolation of the cathode and anode backbone structures.

[0035] In some embodiments, the patterned substrate 40 is electrically conductive, in which case the resulting backbone structure is ready for further processing of active materials. In

20 certain other embodiments, the backbone structure is electrically non-conductive. In this case, further processing by deposition of a conductive layer may be performed by various methods.

[0036] Figs. 5A-5D depict a schematic representation of a process for manufacturing a backbone structure using a subtractive electrochemical etch process according to certain

embodiments. In these particular embodiments, a substrate 50 is patterned using a electrically insulating masking layer 51 that is deposited on top of the substrate 50 by methods such as vacuum deposition, thermal oxidation, surface coating, and wet chemical deposition. This layer 51 is subsequently patterned by standard patterning techniques such as lithography in order to provide a pattern suitable for further processing to create the backbone structure. In some 5 embodiments of the invention, the masking layer 51 is covered with a second masking layer 52 that is used to pattern the first masking layer 51 (see Figs. 5A-5B). In this case, the first masking layer 51 is patterned by using the second masking layer 52 as a stencil. The second masking layer 52 is selectively removed using selective wet or dry methods, leaving behind the patterned 10 first masking layer 51 (see Fig. 5B). The combination of the substrate 50 and the first masking layer 51 is placed in an electrochemical cell 53 that has a counter electrode 54 and a nozzle 55 that delivers a solution used to electrochemically remove a material in areas that are exposed to the solution (see Fig. 5C). In certain embodiments, the whole workpiece may be dipped into the solution that may dissolve the material that is in contact with the solution. However, the 15 illustrated process may be more isotropic in nature, and typically an amount of material removed in the depth direction D may be substantially the same as the amount of material removed in each side of the width direction W. A dip-tank solution may be used for making features in which gaps G in the resulting backbone structure are significantly narrower than the width W. A DC power source 56 may be used to apply a potential that is sufficient to remove the material in 20 contact with the solution. The process is substantially complete when essentially the desired amount of material is removed, which may be controlled based on the rate of etching that has been previously determined. In certain other cases, a current may be monitored, and a drop in the current may correspond to an end-point of the electrochemical reaction. After the reaction is

substantially complete, the workpiece is removed, and the masking layer 51 may be removed to leave the patterned substrate 50 behind, thereby forming the backbone structure.

[0037] The following example further explains concepts described with reference to Figs. 5A-

5D. One example of the substrate 50 for electrochemical patterning is a copper sheet. A sheet of

5 the desired thickness may be used as the substrate 50, and may be patterned using the electrically

insulating masking layer 51 (e.g., AZ4620TM or AZP4620TM photoresist) that is deposited on top

of the substrate 50 by spin coating. This layer 51 may be exposed to light in the presence of a

photomask that blocks light to areas in which the resist should be left behind. The workpiece

may be placed in a solution that selectively removes the exposed areas. The combination of the

10 substrate 50 and the first masking layer 51 is placed in the electrochemical cell 53 that has the

counter electrode 54 (e.g., platinum) and the nozzle 55 that delivers the electrochemical etch

solution used to electrochemically remove the metal in areas that are exposed to the solution. A

combination of 10 wt% sulfuric acid and 1 wt% hydrogen peroxide may be delivered through the

nozzle 55 to the workpiece. The DC power source 56 may be used to apply an anodic potential

15 to the substrate 50, which removes copper in areas where the solution comes in contact with the

copper anode and the platinum cathode at the same time, thereby forming a local electrochemical

cell. After the reaction is substantially complete, the workpiece may be removed, and the

masking layer 51 may be removed with N-methyl-2-pyrrolidone to leave the patterned substrate

50 behind.

20 [0038] Figs. 6A-6C depict a schematic representation of a process for manufacturing a

backbone structure using a subtractive stamping process according to certain embodiments. A

mandrel 60 is pre-fabricated with patterns that are inverted from a desired backbone pattern, and

the mandrel 60 is coated with a thin release layer 61 that may be used to facilitate removal of the

mandrel 60 after processing. The release layer 61 may be, for example, an organic material that may be vapor-deposited uniformly into three-dimensional features. This material may have additional properties of having either poor adhesion or the ability to be selectively etched without etching the mandrel 60 or a backbone material. For example, a stainless steel mandrel coated
5 with a thin layer of copper deposited by chemical vapor deposition may act as an adequate stamping device for a process where a material that is used as a mold is thermally curable photoresist (see Fig. 6A). The combination of the mandrel 60 and the release layer 61 is contacted with a sheet of moldable material 62 that is on top of a substrate 63. Pressure is applied in order to transfer the pattern to the moldable material 62 (see Fig. 6B). This
10 combination is hardened by curing into place the moldable material 62 using temperature or other means, such as light, in case the substrate 63 is transparent. The release layer 61 is removed by suitable means while separating the mandrel 60 and the resulting backbone structure that includes the molded material and the substrate 64 (see Fig. 6C).

[0039] In certain other embodiments of the invention, additive processes may be used to
15 process a backbone structure of an energy storage device. Figs. 7A-7D depict a schematic representation of a process for manufacturing the backbone structure using an additive electrochemical deposition process according to certain embodiments. This process may be referred to as a LIGA process in the art, which in German stands for "lithography, galvanof
forming and molding (Abformung)." In this process, a conductive or non-conductive substrate
20 70 is used. In case of a non-conducting substrate, a conducting layer 71 is deposited. Photoresist 72 is coated on top of this substrate 70, and is patterned by standard lithography techniques using a photomask 73 to leave behind the photoresist 72 in areas where a backbone material is not to be deposited (see Figs. 7A and 7B). The workpiece is placed in an electroplating bath with a

potential enough to reduce metallic ions present in solution to form a metal 74 (see Fig. 7C).

The metallic ions are reduced at a conductive surface and are not deposited where the photoresist 72 is present. When the process is substantially complete, the workpiece including components 70, 72, and 74 is removed from a plating cell, and the photoresist 72 is removed to leave the backbone structure (including components 70 and 74) behind (see Fig. 7D).

[0040] The following example further explains concepts described with reference to Figs. 7A-7D. In this process, a silicon wafer may be used as the semi-conductive substrate 70. Copper may be deposited using sputter deposition to create the conductive layer 71 on top of the silicon.

A positive or negative tone photoresist 72 (e.g., AZ4620™ or AZP4620™) may be coated on top of this substrate 70 and patterned by standard lithography techniques to leave behind the

photoresist 72 in areas where a backbone material is not to be deposited. This workpiece may be placed in a nickel electroplating bath including 1 M nickel sulfate, 0.2 M nickel chloride, 25 g/l boric acid, and 1 g/l sodium saccharin, along with a platinum counter electrode and a potential enough to reduce nickel ions present in the solution to Ni metal 74. The metal ions are reduced

at a conductive surface and are not deposited where the photoresist 72 is present. When the process is substantially complete, the workpiece including the silicon wafer 70, photoresist 72, and nickel metal 74 may be removed. Subsequently, the photoresist 72 may be removed using N-methyl-2-pyrrolidone to leave the backbone structure including components 70 and 74

behind. The remaining copper metal in the area where the photoresist 72 was present may be removed by a chemical etch involving 2% sulfuric acid and 1% hydrogen peroxide.

[0041] Figs. 8A-8E depict a schematic representation of a process for manufacturing a backbone structure using an additive extrusion process according to certain embodiments. A mandrel 80 is pre-fabricated with patterns that are inverted from a desired backbone pattern, and

the mandrel 80 is coated with a thin release layer 81 that may be used to facilitate removal of the mandrel 80 after processing (see Fig. 8A). This mandrel 80 also has openings either at the edges or on top of each opening 85 in order to facilitate the addition of a material that may be made into a mold. The release layer 81 may be, for example, an organic material that may be vapor-

5 deposited uniformly into three-dimensional features. This material may have additional properties of having either poor adhesion or the ability to be selectively etched without etching the mandrel 80 or a backbone material. For example, a stainless steel mandrel coated with a thin layer of copper deposited by chemical vapor deposition may act as an adequate stamping device for a process where a material that is used as the moldable material 82 is a thermally curable

10 photoresist. The combination of the mandrel 80 and the release layer 81 is contacted with a substrate 83 (see Fig. 8B). The moldable material 82 is extruded into the openings 85 and filled (see Fig. 8C). Any residual material within the openings 85 is cleaned out at this time (see Fig. 8D). This combination is hardened by curing into place the moldable material 82 using temperature or other means, such as light, in case the substrate 83 is transparent. The release

15 layer 81 is removed by suitable means while separating the mandrel 80 and the resulting backbone structure that includes the molded material 82 and the substrate 83 (see Fig. 8E). Depending on the requirements of each particular implementation, release layer 81 may not be necessary (e.g., if the mandrel/mold 80 itself satisfies the required characteristics that would otherwise be satisfied by a release layer). In certain embodiments, the mandrel/mold 80 may be

20 released by dissolution.

[0042] Figs. 9A-9C depict a schematic representation of an exemplary process for manufacturing a backbone structure using a sequential deposition and assembly process according to certain embodiments. In this process, alternating layers of backbone material and a

sacrificial material are assembled. An example of a set of materials that may be assembled together are sheets of polyethylene terephthalate (PET) 90 interspersed with copper foils 91. The resulting stack thus includes PET/copper/PET/copper/PET (see Fig. 9A). The layers are diced to a thickness substantially corresponding to a height of a backbone structure H, spirally wound within their axes, and assembled onto a substrate 92 using epoxy glue (see Fig. 9B). A sacrificial PET layer is removed by selectively etching it away in a selective chemical etch solution containing sodium hypochlorite (NaOCl). This leaves behind two spirally wound copper substrates, one for cathode backbone and another for anode backbone with gaps in the middle which will house active materials and separators for an electrochemical energy device (see Fig. 9C).

[0043] Once a backbone structure is available, materials that are involved in electrochemical reactions, also called active materials, may be loaded onto the backbone structure. This may be done by several different methods. An anode backbone and a cathode backbone may be separate from each other, but each electrode may be electrically conductive by itself. This lends to electrochemical deposition techniques and electrophoretic deposition techniques as viable options for adding the active materials. For example, in the case of a lithium-ion battery, a cathode material, such as LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}(\text{Ni}_x\text{Co}_y\text{Al}_z)\text{O}_2$, LiFePO_4 , or Li_2MnO_4 may be electrophoretically deposited onto a conductive substrate. Electrophoretic deposition may also be performed for V_2O_5 films. Cathode materials may also be co-deposited along with a polypyrrole matrix. In addition, certain cathode materials for lithium-ion batteries may be electrochemically deposited, such as molybdenum oxysulfides. In certain embodiments, cathode formation comprises electrophoretic deposition of LiCoO_2 until a layer thickness between 1 micron and 300 microns is formed. In certain embodiments, the layer thickness is between 5

microns and 200 microns, and in certain embodiments, the layer thickness is between 10 microns and 150 microns. With regards to anode materials, electrochemical deposition may be used for plateable anode materials, such as tin, electrophoretic deposition may be used to assemble graphite, and an electrophoretic resist deposition followed by pyrolysis may form a carbon
5 anode. Other suitable anode materials may include titanates, silicon, and aluminum. Similar layer thicknesses apply to anode formation as described above. Suitable separator materials may include polyethylenes, polypropylenes, TiO_2 , SiO_2 , Al_2O_3 , and the like.

[0044] While some embodiments have been described with reference to energy storage devices, it should be recognized that the backbone structures described herein may be useful in
10 various other types of devices to provide increased surface area per unit geometrical area (or per unit weight or volume). These other types of devices may involve various types of processes during their operation, such as heat transfer, chemical reactions, and diffusion.

[0045] While the invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and
15 equivalents may be substituted without departing from the true spirit and scope of the invention as defined by the appended claims. In addition, many modifications may be made to adapt a particular situation, material, composition of matter, method, operation or operations, to the objective, spirit, and scope of the invention. All such modifications are intended to be within the scope of the claims appended hereto. In particular, while the methods disclosed herein have
20 been described with reference to particular operations performed in a particular order, it will be understood that these operations may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the invention. Accordingly, unless

specifically indicated herein, the order and grouping of the operations is not a limitation of the invention.

CLAIMS

[0046] What is claimed is:

1. A three-dimensional battery, comprising:

a battery enclosure;

5 a first structural layer within the battery enclosure, said structural layer having a first surface;

a first plurality of conductive protrusions extending from said first surface of said first structural layer; and

10 a first plurality of electrodes within the battery enclosure, the first plurality of electrodes including a plurality of cathodes and a plurality of anodes, wherein the first plurality of electrodes includes a second plurality of electrodes selected from the first plurality of electrodes, each of the second plurality of electrodes being in contact with the outer surface of one of said first plurality of conductive protrusions.

15

2. The three-dimensional battery of claim 1, wherein the second plurality of electrodes is fewer than the first plurality of electrodes.

3. The three-dimensional battery of claim 2, the second plurality of electrodes consisting of a
20 plurality of anodes.

4. The three-dimensional battery of claim 2, the second plurality of electrodes consisting of a plurality of cathodes.

25 5. The three-dimensional battery of claim 1, wherein the first plurality of the electrodes is the same as the second plurality of electrodes.

6. The three-dimensional battery of claim 2, further comprising:

a second structural layer within the battery enclosure, said second structural layer having

30 a second surface;

a second plurality of conductive protrusions extending from said second surface of said second structural layer; and

a third plurality of electrodes selected from the first plurality of electrodes, each of the third plurality of electrodes being in contact with the outer surface of one of said second plurality of conductive protrusions.

5

7. The three-dimensional battery of claim 6, the third plurality of electrodes consisting of a plurality of anodes.

10 8. The three-dimensional battery of claim 6, the third plurality of electrodes consisting of a plurality of cathodes.

15 9. The three-dimensional battery of claim 1, wherein said first plurality of conductive protrusions surround a base material protruding from said first surface of said first structural layer.

10. The three-dimensional battery of claim 9, wherein said base material and said first structural layer comprise the same material.

20 11. The three-dimensional battery of claim 1, wherein each of said second plurality of electrodes comprises a layer overlying the outer surface of one of said first plurality of conductive protrusions.

25 12. The three-dimensional battery of claim 1, wherein said first plurality of conductive protrusions comprise fins protruding at least 50 microns from said first structural layer and having a thickness smaller than 20 microns.

13. The three-dimensional battery of claim 1, wherein said first plurality of conductive protrusions comprise pillars protruding at least 50 microns from said first structural layer.

30

14. The three-dimensional battery of claim 10, wherein each of said second plurality of electrodes comprises a layer overlying the outer surface of one of said first plurality of conductive protrusions.
- 5 15. The three-dimensional battery of claim 10, wherein said first plurality of conductive protrusions comprise fins protruding at least 50 microns from said first structural layer and having a thickness smaller than 20 microns.
16. The three-dimensional battery of claim 10, wherein said first plurality of conductive
10 protrusions comprise pillars protruding at least 50 microns from said first structural layer.
17. The three-dimensional battery of claim 13, each of said pillars being substantially cylindrical.
- 15 18. The three-dimensional battery of claim 16, each of said pillars being substantially cylindrical.
19. The three-dimensional battery of claim 6, wherein said second plurality of conductive protrusions is electrically insulated from said third plurality of conductive protrusions.
20
20. The three-dimensional battery of claim 1, wherein said first plurality of conductive protrusions comprise fins protruding at least 50 microns from said first structural layer and having an aspect ratio between approximately 2.5:1 and 500:1.
- 25 21. The three-dimensional battery of claim 1, further comprising a separator between at least one of said cathodes and one of said anodes.
22. A method for manufacturing a three-dimensional battery, comprising:
providing a first structural layer, said structural layer having a first surface;
30 forming a first plurality of conductive protrusions extending from said first surface of said first structural layer;

forming a first plurality of electrodes, wherein each of the first plurality of electrodes contacts the outer surface of one of said first plurality of conductive protrusions.

23. The method of claim 22, wherein forming said first plurality of electrodes comprises
5 forming a plurality of cathodes by electrophoretic deposition.
24. The method of claim 22, wherein forming said first plurality of electrodes comprises forming a plurality of anodes by electrophoretic deposition.
- 10 25. The method of claim 22, further comprising:
forming a plurality of non-active backbone protrusions extending from said first surface of said structural layer; and wherein forming a first plurality of conductive protrusions comprises forming a conductive layer overlying an outer surface of each of said non-active backbone protrusions.
- 15 26. The method of claim 22, wherein forming said first plurality of electrodes comprises varying the thickness of each of said first plurality of electrodes.
27. The method of claim 25, wherein forming the first plurality of electrodes comprises forming
20 a plurality of cathodes by electrophoretic deposition.
28. The method of claim 25, wherein forming the first plurality of electrodes comprises forming a plurality of anodes by electrophoretic deposition.
- 25 29. The method of claim 27, wherein forming the plurality of cathodes comprises electrophoretic deposition of LiCoO_2 .
30. The method of claim 25, further comprising separating the conductive layer between each of the plurality of non-active backbone protrusions.

30

31. The method of claim 27, wherein the step of forming each of said cathodes comprises electrophoretic deposition of LiCoO_2 until a layer thickness between approximately 1 micron and approximately 300 microns is formed.

- 5 32. The method of claim 25, further comprising:
- providing a second structural layer, said second structural layer having a second surface substantially opposing said first surface;
 - forming a second plurality of conductive protrusions extending from said second surface of said second structural layer and substantially parallel to said first plurality of
 - 10 conductive protrusions; and
 - forming a second plurality of electrodes, wherein each of said second plurality of electrodes contacts the outer surface of one of said second plurality of conductive protrusions.

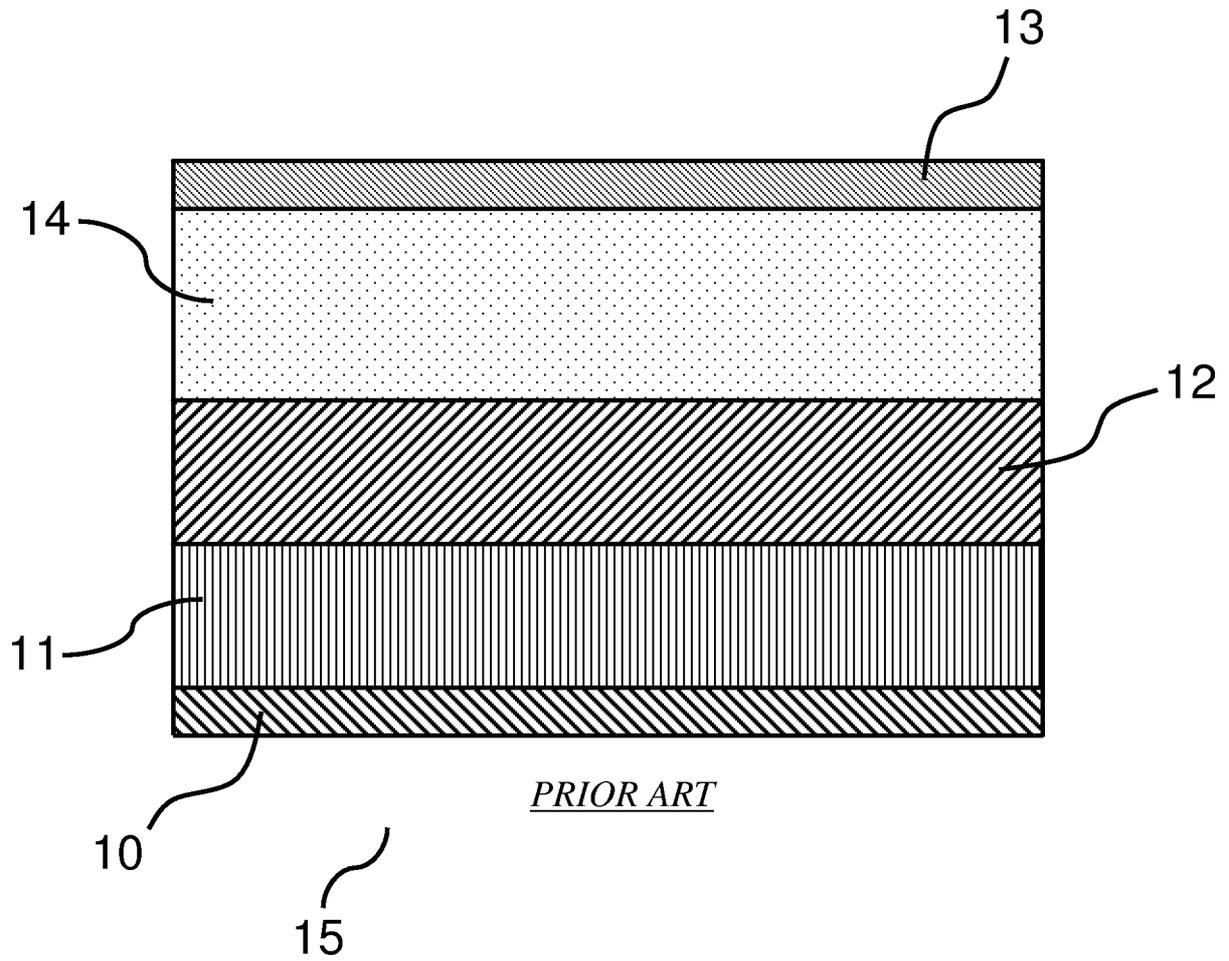


Figure 1

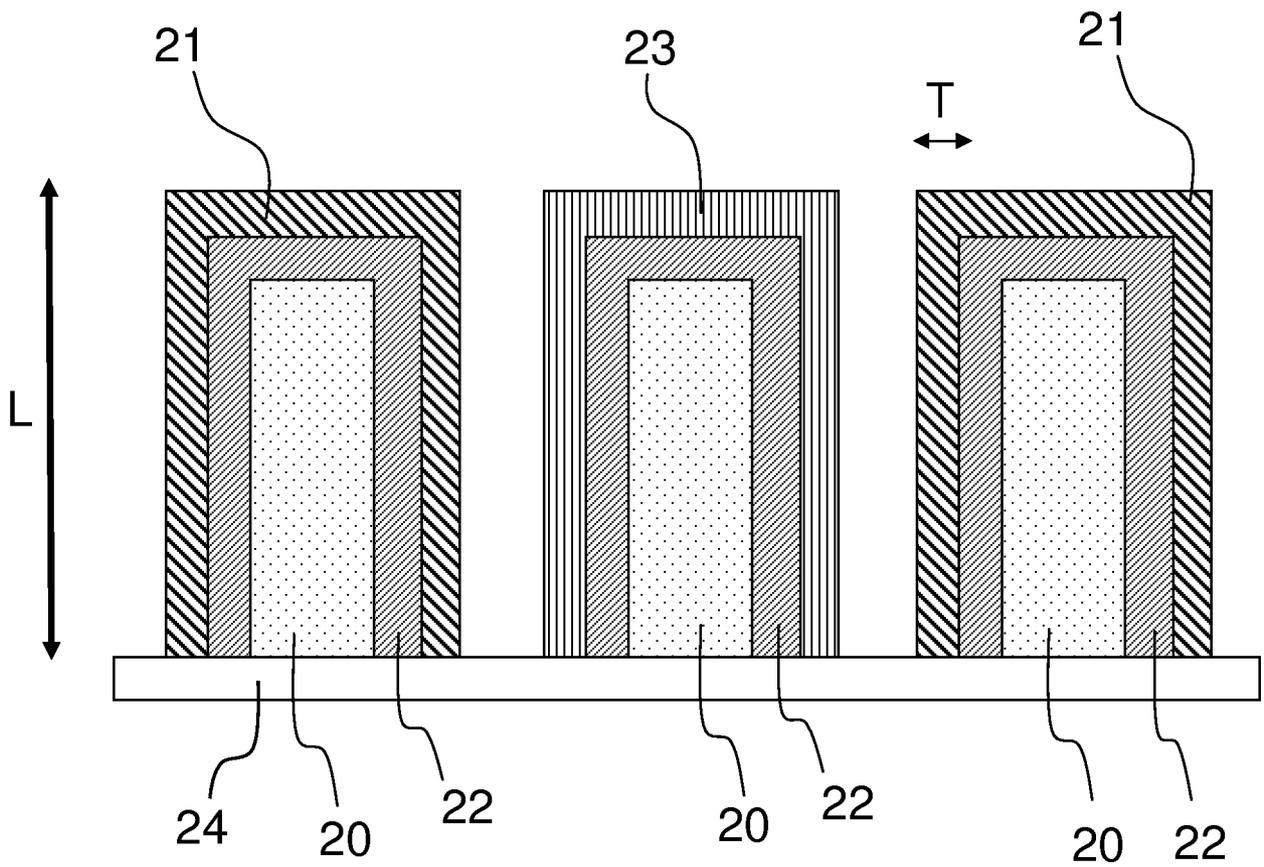


Figure 2

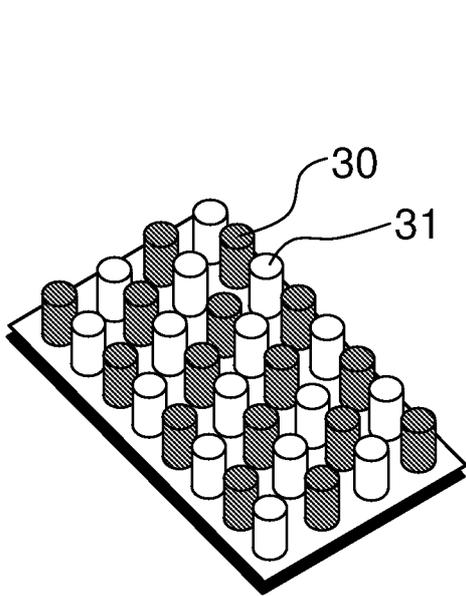


Fig. 3A

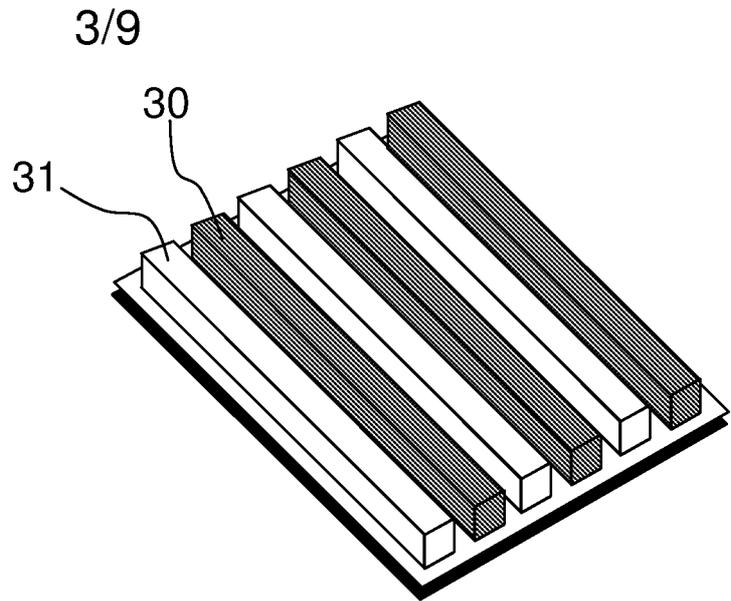


Fig. 3B

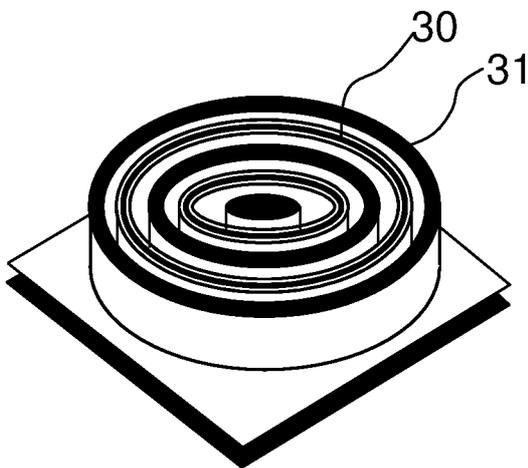


Fig. 3C

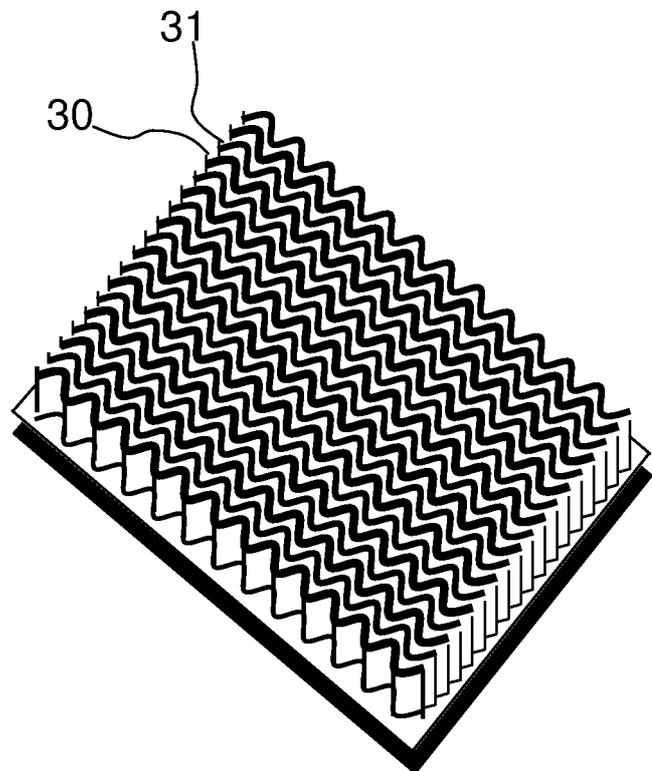


Fig. 3D

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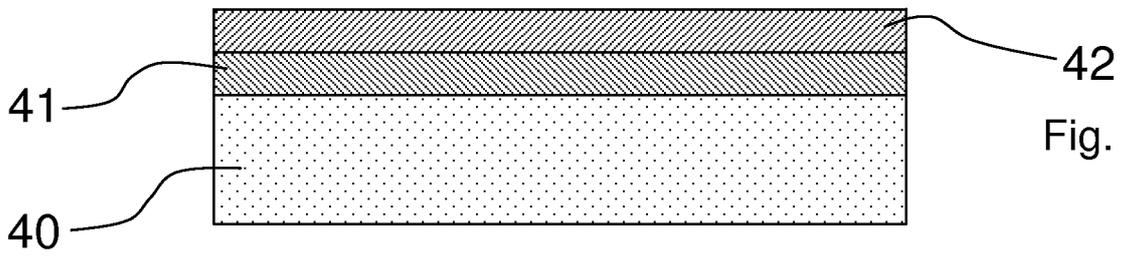


Fig. 4A

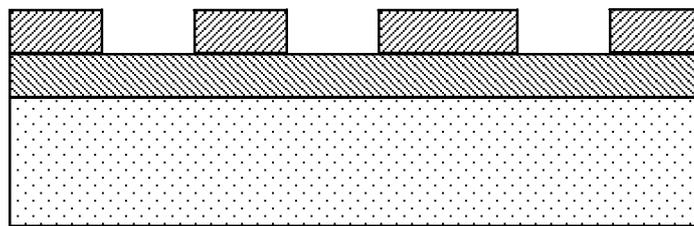


Fig. 4B

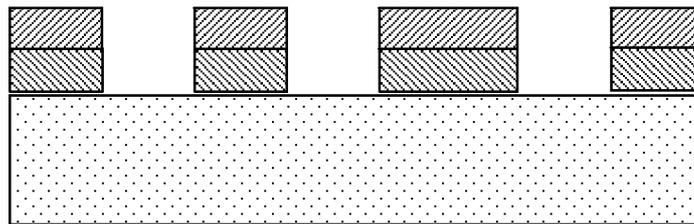


Fig. 4C

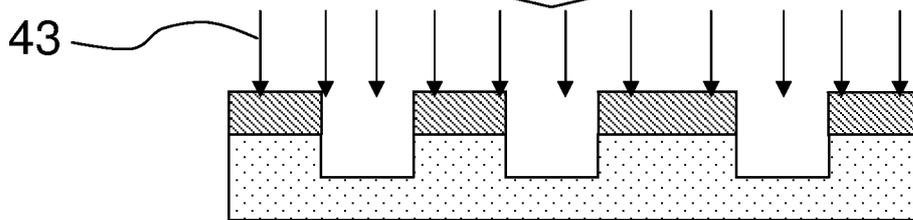


Fig. 4D

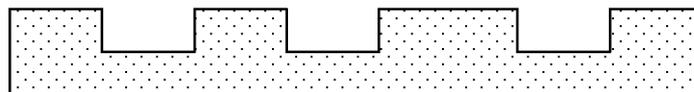


Fig. 4E

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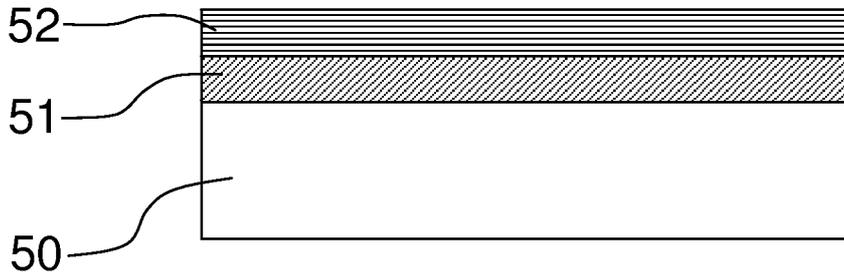


Fig. 5A

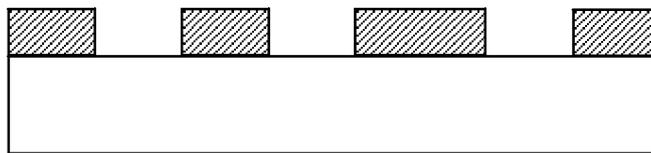


Fig. 5B

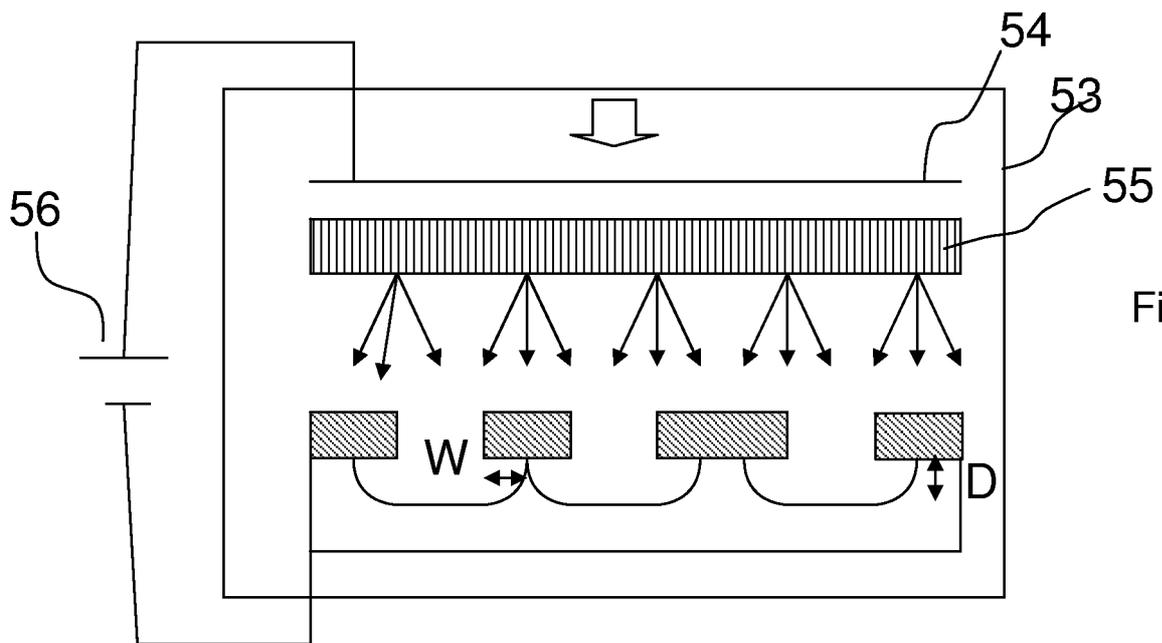


Fig. 5C

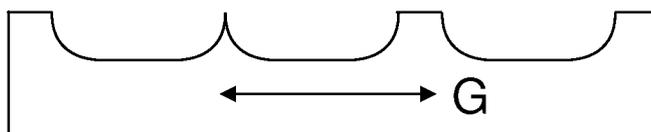


Fig. 5D

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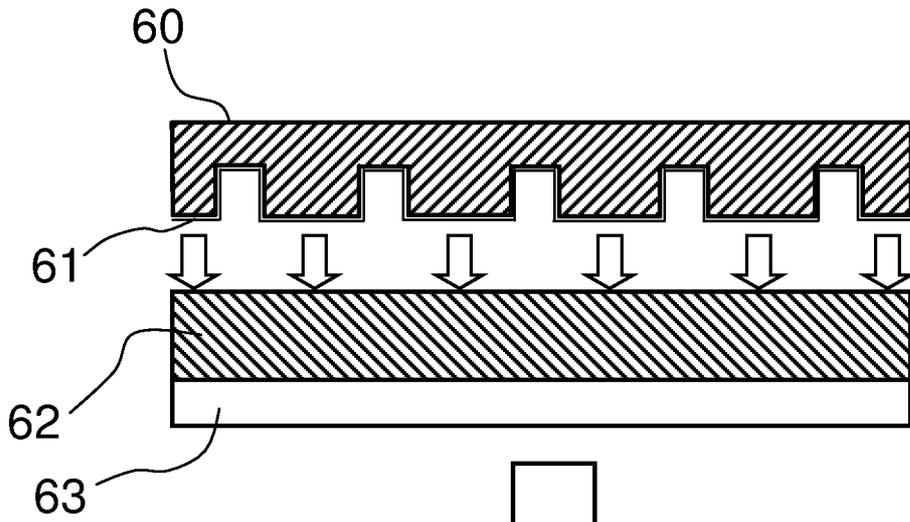


Fig. 6A

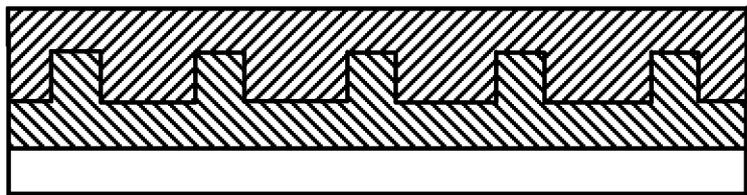
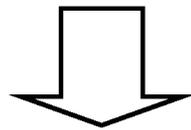


Fig. 6B

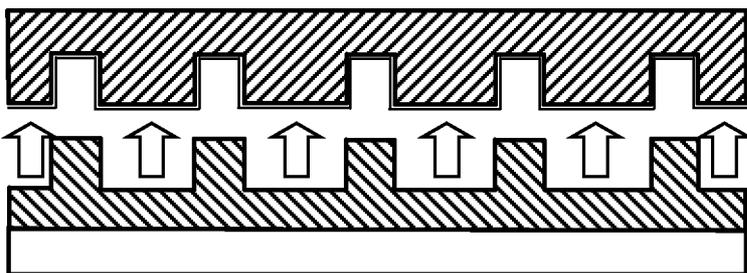
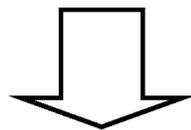
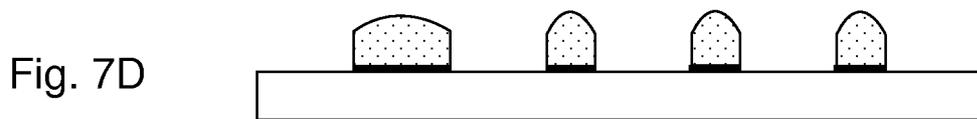
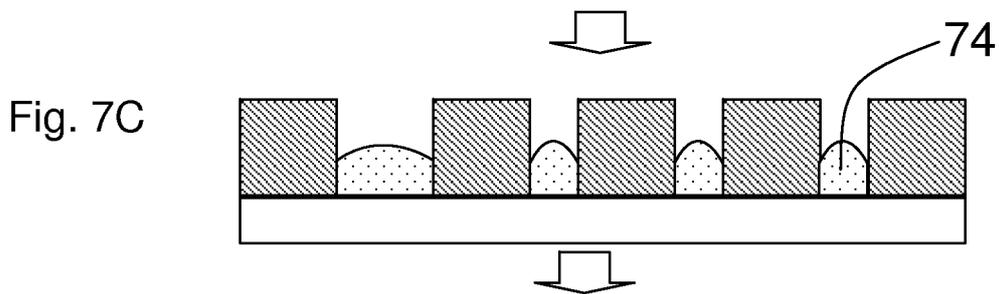
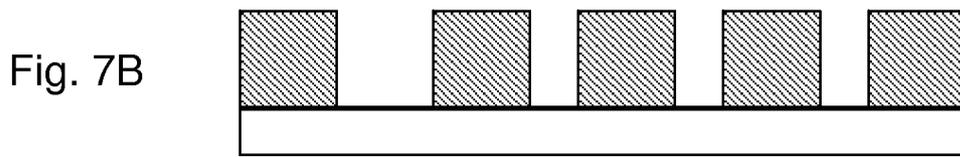
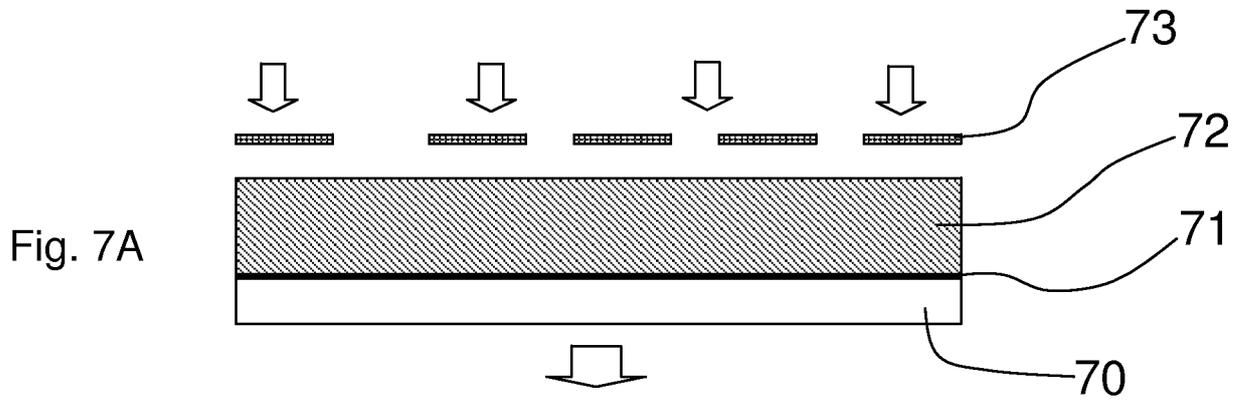
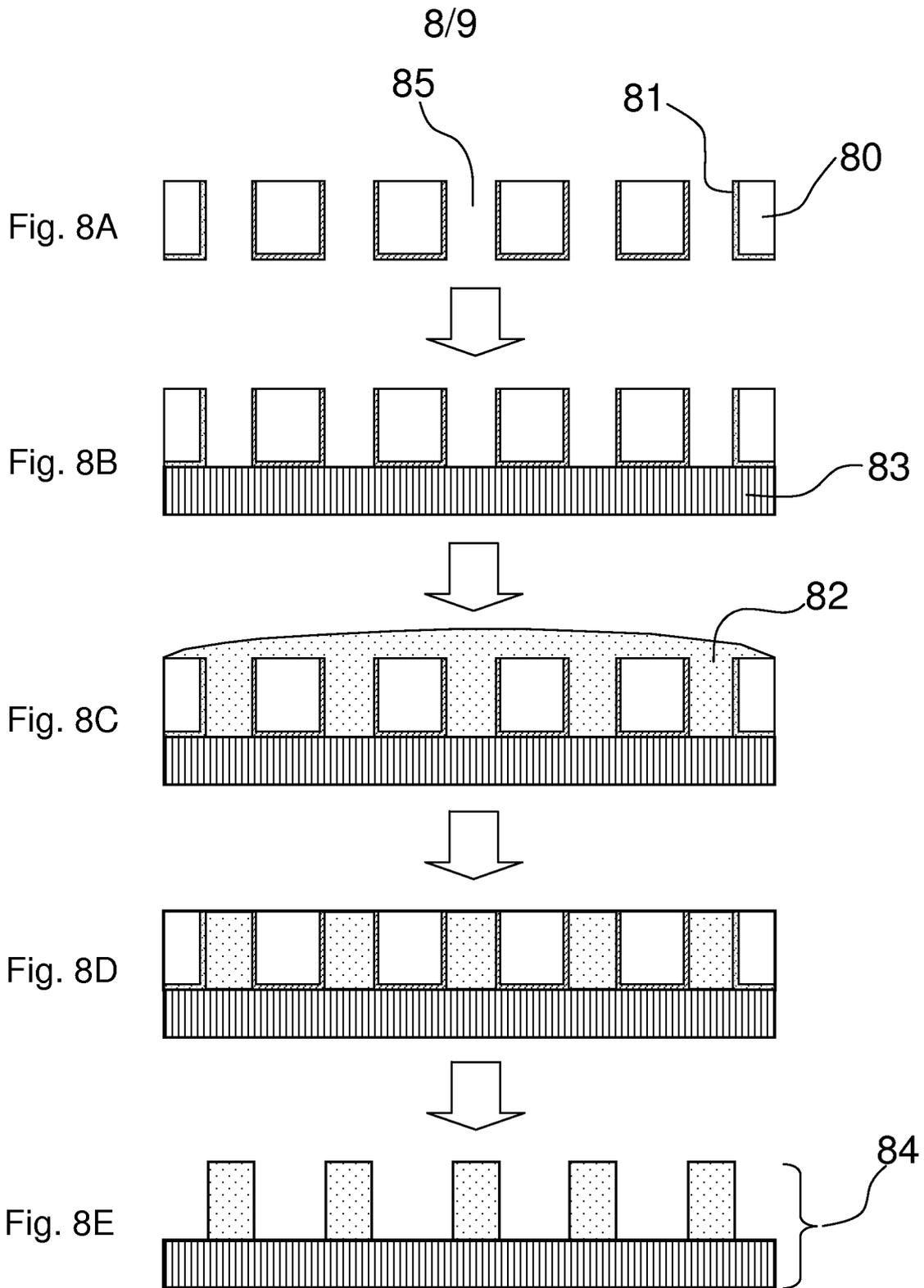


Fig. 6C

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Fig. 9A

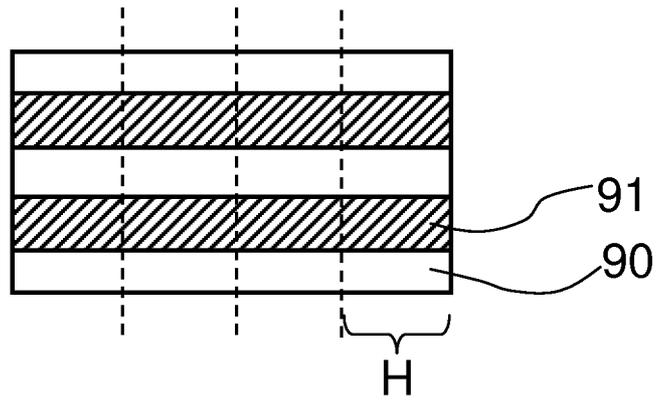


Fig. 9B

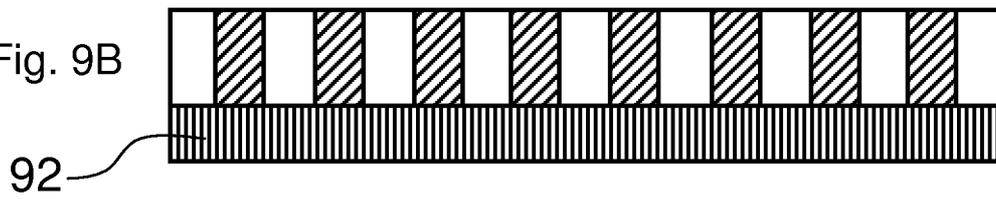
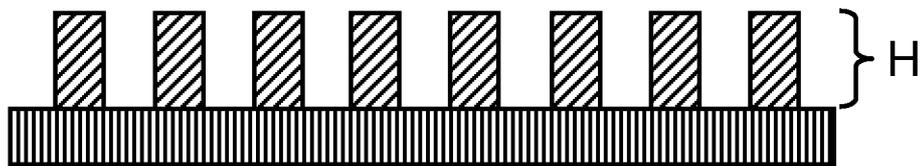


Fig. 9C



INTERNATIONAL SEARCH REPORT

International application No
PCT/US 08/50942

<p>A CLASSIFICATION OF SUBJECT MATTER IPC(8) - H01 M 6/00 (2008 04) USPC - 429/122 According to International Patent Classification (IPC) or to both national classification and IPC</p>		
<p>B FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) USPC - 429/122</p>		
<p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 429/209 - see keywords below</p>		
<p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST (USPT, PGPB, EPAB, JPAB), google com Search Terms Used battery, cathodes, anodes, electrodes, protrusions, plurality, pillars, housing, casing, enclosure, cathode, anode, second, three dimensional, lithium, cobalt, oxide, electrophoretic, deposition, interlocking</p>		
<p>C DOCUMENTS CONSIDERED TO BE RELEVANT</p>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	UA 6,432,585 B1 (Kawakami et al) 13 August 2002 (13 08 2002) entire document, especially Abstract, col 5, ln 15-28, col 13, ln 6-14, col 15, ln 11-22, col 16, ln 15-39, col 26, ln 52-62, col 32, ln 38-66, col 57, ln 16-20	1-32
Y	US 5,294,504 A (Otagawa et al) 15 March 1994 (15 03 1994) entire document, especially Abstract, col 9, ln 18-23, FIG 8	1-32
A	US 6,878,173 B2 (Miyahisa et al) 12 April 2005 (12 04 2005) entire document, especially Abstract	1-32
A	US 6,498,406 B1 (Honuchi et al) 24 December 2002 (24 12 2002) entire document, especially Abstract	1-32
<p><input type="checkbox"/> Further documents are listed in the continuation of Box C <input type="checkbox"/></p>		
<p>Special categories of cited documents</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure use exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>		
<p>Date of the actual completion of the international search 19 April 2008 (19 04 2008)</p>		<p>Date of mailing of the international search report 16 MAY 2008TJ</p>
<p>Name and mailing address of the ISA/AJS Mail Stop PCT, Attn ISA/US, Commissioner for Patents P O Box 1450, Alexandria, Virginia 22313-1450 Facsimile No 571-273-3201</p>		<p>Authorized officer Lee W Young PCT HlpdBsk 571 272-4300 PCTOSP 571 272 7774</p>