



(51) International Patent Classification:

H01M 4/70 (2006.01) *H01M 10/04* (2006.01)
H01M 4/04 (2006.01) *H01M 10/28* (2006.01)
H01M 4/76 (2006.01) *H01M 10/38* (2006.01)
H01M 4/78 (2006.01)

(21) International Application Number:

PCT/US2016/021342

(22) International Filing Date:

8 March 2016 (08.03.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/130,041 9 March 2015 (09.03.2015) US

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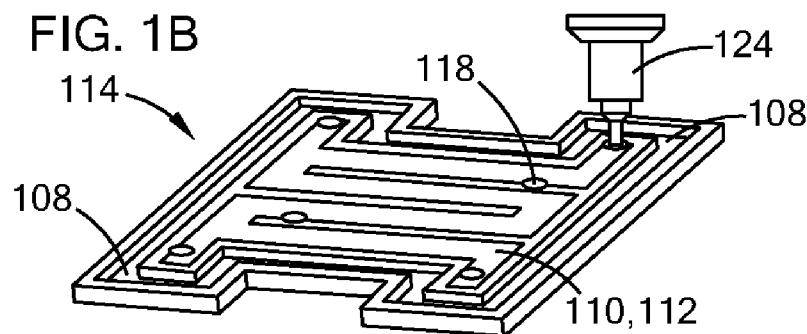
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF MAKING AN ELECTRODE STRUCTURE AND A MICROBATTERY CELL



(57) Abstract: An electrode structure for a rechargeable microbattery cell comprises a patterned current collector having a trench therein. The trench comprises a predetermined 2D shape and depth, and an electrode is disposed within the trench. The electrode has the predetermined 2D shape. The trench may comprise a surface roughness of from about 0.001 mm to about 0.1 mm. A method for manufacturing an electrode structure for a rechargeable microbattery cell comprises forming a trench having a predetermined 2D shape and depth in a conductive substrate, thereby creating a patterned current collector. One or more surfaces of the trench may be roughened. The trench is filled with an electrode formulation to form an electrode. An electrode structure comprising the electrode having the predetermined 2D shape in the patterned current collector is thereby created.

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METHOD OF MAKING AN ELECTRODE STRUCTURE AND A MICROBATTERY CELL

RELATED APPLICATION

[0001] The present patent document claims the benefit of priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Serial No. 62/130,041, filed on March 9, 2015, and hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] The present disclosure is directed generally to battery technology and more particularly to a method of fabricating rechargeable microbattery cells having arbitrary shapes.

BACKGROUND

[0003] Energy storing microdevices have potential applications in autonomous microelectronics, including microrobotics, sensors, photovoltaics, displays, and biomedical devices. The next-generation of autonomous microelectronic devices may require power systems that enable more flexible integration among dissimilar building blocks with different sizes, shapes and functionalities (*e.g.*, actuating, sensing, lighting, bending, and stretching).

[0004] Direct-write assembly is a microscale 3D printing technique that enables the fabrication of features ranging from simple lines to complex 3D architectures by the deposition of highly concentrated inks through fine deposition nozzles of typically 1-250 μm in diameter. The application of this technology to microbattery fabrication in arbitrary form factors has not been previously explored.

[0005] Conventional Li-ion battery techniques, including canning, crimping and pouching, have not been demonstrated for microbatteries with arbitrary form factors. Recently, microbattery designs in planar and three-dimensional (3D) motifs based on micro- and nanostructured architectures have been demonstrated by conventional lithography, colloidal templating methods, and printing, but microbattery fabrication in arbitrary form factors with scalable processibility has long been a challenge.

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BRIEF SUMMARY

[0006] An electrode structure for a rechargeable microbattery cell comprises a patterned current collector having a trench therein. The trench comprises a predetermined 2D shape and depth, and an electrode is disposed within the trench. The electrode has the predetermined 2D shape. The trench may comprise a surface roughness of from about 0.001 mm to about 0.1 mm.

[0007] A method for manufacturing an electrode structure for a rechargeable microbattery cell comprises forming a trench having a predetermined 2D shape and depth in a conductive substrate, thereby creating a patterned current collector. One or more surfaces of the trench may be roughened. The trench is filled with an electrode formulation to form an electrode. An electrode structure comprising the electrode having the predetermined 2D shape in the patterned current collector is thereby created.

[0008] A method for manufacturing a rechargeable battery cell comprises forming an inner trench and an outer trench surrounding the inner trench in each of two conductive substrates. First and second patterned current collectors are thereby created from the conductive substrates. Each of the inner trenches is filled with an electrode formulation, and thus a first electrode is formed in the first patterned current collector and a second electrode is formed in the second patterned current collector. A separator is deposited on the first electrode or the second electrode. A packaging material is deposited in each of the outer trenches to form a first sealing structure on the first patterned current collector and a second sealing structure on the second patterned current collector. The first patterned current collector is stacked on the second patterned current collector in a face-to-face configuration, and the first sealing structure comes into contact with the second sealing structure. The first sealing structure is bonded to the second sealing structure, thereby forming a microbattery cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIGs. 1A-1E show a perspective view of an exemplary microbattery fabrication process.

[0010] FIG. 2 shows cross-sectional schematic of an exemplary fabricated microbattery cell.

[0011] FIG. 3 shows a conductive substrate patterned by laser micromachining to include trenches of various shapes and sizes for microbattery fabrication.

[0012] FIG. 4 shows scanning electron microscope (SEM) images of high-resolution microtrench patterns for electrodes and packaging materials used to form donut-shaped cells, H-shaped cells, and shield-shaped cells.

[0013] FIG. 5 shows exemplary materials for forming the anode and cathode.

[0014] FIG. 6 shows viscosity versus shear rate for 3 wt.% solutions of cellulose acetate phthalate (CAP) and hydroxylpropyl methylcellulose (HPMC), and a mixed solution of CAP and HPMC, where CAP:HPMC = 9:1 by weight.

[0015] FIG. 7 shows elastic modulus versus shear stress for lithium titanate (LTO) and lithium manganese nickel oxide (LNMO) electrode formulations.

[0016] FIG. 8 shows SEM images of LTO (top) and LNMO (bottom) electrodes formed by, in this example, doctor blading into microtrenches (50 μm deep) of varying widths from 100 μm to 1 mm at a 100- μm increment with a 100- μm wall spacing.

[0017] FIG. 9 shows SEM images of the surface of stainless steel substrates before (left image) and after (right image) laser cutting.

[0018] FIG. 10 shows optical images of LTO films (top) and LNMO films (bottom) doctor-blade coated on bare, smooth-surface stainless steel substrates.

[0019] FIG. 11 shows viscosity versus shear rate (left plot) and elastic modulus versus shear stress (right plot) for an exemplary silicone ink used for adhesive and packaging materials.

[0020] FIG. 12 shows the printing of adhesive structures in the form of silicone dots. An optical image captured during printing using a silicone ink and a 100 μm -diameter nozzle is shown on the left, and an SEM image of a dot array printed on a silicon substrate is shown on the right. The inset shows a magnified SEM image of a dot printed at a dwell time of 50 milliseconds and lifting speed of 10 mm s^{-1} .

[0021] FIG. 13 shows printing of a packaging material comprising a silicone ink to form a sealing (or packaging) structure.

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[0022] FIG. 14 shows a schematic diagram (left image) and an SEM image (right) of an exemplary fill-hole (or access hole) structure.

[0023] FIG. 15 shows an optical image of exemplary fabricated microbattery cells with different shapes and sizes produced from a single conductive sheet ($40 \times 50 \times 0.076 \text{ mm}^3$).

[0024] FIG. 16 shows high magnification optical images of exemplary fabricated microbattery cells having different shapes and sizes.

[0025] FIG. 17 shows materials volume fraction versus electrode depth or thickness (left image) and cell width (right image) for square microbattery cells.

[0026] FIG. 18 shows voltage versus capacity for the LTO half-cell (left plot) and LNMO half-cell (middle plot) measured by coin cell geometries (2030 cells) of varying the charge-discharge rate. The right plot shows cyclability of the LTO and LNMO half-cells measured at 1C.

[0027] FIG. 19 illustrates the performance of an exemplary LTO-LNMO full cell measured by coin cell geometry (2030 cells). The left plot shows the charge (Li transfer from LNMO to LTO) and discharge curves of the LTO-LNMO full-cell battery at a series of rates from 1 to 100C, where the charge and discharge rate are same. The right plot shows the cyclability of the LTO-LNMO full cell measured at 1C.

[0028] FIG. 20 shows trench depth versus number of laser passes for laser cutting carried out on a stainless steel substrate.

[0029] FIG. 21 shows exemplary drawings for laser cut layers including all layers (left figure) and each layer separately (right figures).

DETAILED DESCRIPTION

[0030] A novel approach has been developed for fabricating customized, rechargeable lithium (Li) ion microbatteries having arbitrary form factors. The new method is highly scalable and can be used to create microbatteries having arbitrary shapes and sizes (e.g., from about 1 mm to 100 cm in lateral dimension). Using the approach described herein, Li-ion microbattery cells can be created in a wide range of geometries (e.g. square, shield, ribbon, and ring) with sizes as small as 2 mm $\times$ 2 mm wide and 0.3 mm thick.

[0031] Referring to FIG. 1A, a method for manufacturing an electrode structure for a rechargeable microbattery cell entails forming a trench having a predetermined two-dimensional (2D) shape and depth in a conductive substrate, thereby creating a patterned current collector. The trench is then filled with an electrode formulation to create an electrode having the predetermined 2D shape, as shown schematically in FIG. 1B. The electrode may have a thickness that is substantially the same as the depth of the trench. The electrode structure formed by this process may be a cathode structure or an anode structure, depending on the electrode formulation selected to fill the trench.

[0032] The trench may comprise a surface roughness of from about 0.001 mm to about 0.1 mm, or from about 0.01 mm to about 0.1 mm, which may promote good adhesion between the electrode and the patterned current collector. The surface roughness may be imparted during fabrication, either during formation of the trench or by an additional post-forming roughening step. The surface roughness may be present on a bottom surface of the trench and/or on one or more (or all) walls of the trench. The surface roughness may be an average surface roughness R_a , measured using methods known in the art.

[0033] Advantageously, the trench may be formed by laser cutting, which may be effective in both carving out the desired geometry and producing the desired surface roughness. Laser cutting may also be referred to as laser machining or laser micromachining. In this technology, a laser is employed to cut partially or entirely through a workpiece, which in this disclosure is a conductive substrate that is typically flat. Laser cutting typically entails directing the output of a high-power laser to the workpiece using laser optics and a computer numerical controlled (CNC) motion control system. Upon reaching the conductive substrate, the laser beam may melt, burn and/or vaporize a local region of the substrate. To create a cut of the desired geometry, the laser beam may be moved along a continuous predetermined path while in contact with the substrate.

[0034] In the present disclosure, laser cutting may be used to form one or more trenches in the conductive substrate each having a depth less than the thickness of

the conductive substrate. Laser cutting may also be used to cut entirely through the conductive substrate (e.g., to form alignment holes for cell assembly) or to cut partially or entirely through other components of the microbattery cell.

[0035] The process of forming the trench may be aided by wet etching, which may be effective to carve out trench structures faster than laser cutting alone. However, wet etching may not yield the desired surface roughness. For this reason, it may be beneficial to use wet etching in conjunction with laser cutting, where laser cutting serves as the final step in the trench forming process.

[0036] The conductive substrate is electrically conductive and may comprise one or more conductive materials such as a metal, metal alloy, carbon, conductive polymer, or a conductive metal oxide. Advantageously, the conductive substrate comprises stainless steel, which has a high resistance to oxidation during laser machining and very good mechanical strength and flexibility. FIG. 9 shows SEM images of the surface of an exemplary stainless steel substrate before (left image) and after (right image) laser cutting.

[0037] The trench may be filled with the electrode formulation using any of a number of deposition techniques, including three-dimensional (3D) printing, doctor blading, screen printing, ink jet printing or aerosol jet printing of the electrode formulation.

[0038] 3D printing is a layer-by-layer printing technique that enables the fabrication of features ranging from simple lines to complex 3D architectures by the deposition of highly concentrated inks through fine deposition nozzles. The print quality of this technique may be influenced by nozzle diameter, ink rheology, ink dispensing pressure and printing speed. 3D printing, as described in detail in International Patent Application Serial Nos. PCT/US2014/043860, filed June 24, 2014, PCT/US2014/063810, filed November 4, 2014, and PCT/US2014/065899, filed November 17, 2014, may be employed for the fabrication of the electrode structures described here and other microbattery cell components (e.g., adhesive materials, packaging or sealing materials, etc.). The above-referenced patent publications are hereby incorporated by reference in their entirety. As an alternative to 3D printing,

doctor blading may be used for the filling step. Advantages of doctor blading are that it does not require G-code generation or any aligning steps.

[0039] The predetermined 2D shape may have any desired 2D geometry. For example, the predetermined 2D shape may be a polygon, such as a triangle, square, rectangle, pentagon, hexagon, or in general any n -sided shape, where n may be an integer from 3 to 50, or from 3 to 20. In other examples, the predetermined 2D shape may be an H-shape, a V-shape, or a zig-zag shape. In addition or alternatively, the predetermined 2D shape may include one or more curved portions. For example, the predetermined 2D shape may be a circle, a ring (or donut), an oval, or another curved shape comprising a single continuous curved portion. In another example, the predetermined 2D shape may include two or more curved portions, such as a sine wave or a shield shape as shown in FIG. 4 (upper right corner), which has four curved portions. In other cases, the predetermined 2D shape may comprise one or more sides (the sides being substantially straight) in conjunction with one or more curved portions.

[0040] FIGs. 1A-1E show a perspective view of an exemplary microbattery fabrication process, where the patterned current collector and electrode are formed in FIGs. 1A and 1B. FIG. 2 shows a cross-sectional schematic of an exemplary fabricated microbattery after an anode structure and a cathode structure formed as described above are sandwiched together with a separator in between. The entire microbattery fabrication process is described in detail below. In this example, a current collector including a trench having an H-shape (250 μm wide, 50 μm deep, 100 μm spacing) is prepared using laser micromachining. The electrode formulation (anode or cathode formulation) is filled into the trench by doctor blading, and then additional packaging trenches are formed by laser micromachining, as discussed below. No spacer for doctor blading is required because the trench walls serve as spacers.

[0041] FIG. 3 shows a conductive sheet or substrate (40 $\times$ 50 $\times$ 0.076 mm³) including a number of trenches of various sizes and shapes produced by laser micromachining. Shown are eleven square trenches (2 $\times$ 2 $\times$ 0.076 mm³), nine spherical trenches (3 mm in diameter, 76 μm thick), seven H-shaped trenches (4 $\times$ 4 $\times$ 0.076 mm³), five donut- or ring-shaped trenches (inner diameter is 2 mm; outer

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diameter is 5 mm, 76 μm thick), five shield cells ($5 \times 6 \times 0.076 \text{ mm}^3$), and two ribbon cells ($2 \times 13 \times 0.076 \text{ mm}^3$). Generally speaking, each trench may have a width of from about 0.1 to 1 mm, and a depth of from about 0.01 mm and 0.5 mm.

[0042] FIG. 4 shows SEM images of patterned current collectors including trenches for electrodes (250-500 μm wide, 50 μm thick) and trenches for packaging materials (250 μm wide, 50 μm thick) used in exemplary ring- or donut-shaped, H-shaped, and shield-shaped cells. Edges of each shape are fully cut except for twelve holding points (25 μm wide, 76 μm thick) so that the electrode structures can be easily separated from the conductive sheet by manual force. The alignment of the electrode structures and other microbattery components during cell assembly is carried out using aligning fixture, holes, and pins.

[0043] The electrode formulation (*e.g.*, anode or cathode formulation) used to infill the trenches may comprise an electrochemically active material such as a lithium-based metal oxide and/or carbon (*e.g.*, graphite). Exemplary anode and cathode materials are shown in FIG. 5 and may include any of the following: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO), lithium cobalt oxide (LiCoO_2), lithium iron phosphate (LiFePO_4), vanadium oxide (V_2O_5 , LiV_3O_8), manganese oxide (MnO_2), tin-based oxides and composite alloys. In the examples described in this disclosure, LTO and LNMO are employed to form the respective anode and cathode structures used in 3.2 V microbattery cells.

[0044] Graphite may be used as the electrochemically active material to increase the nominal cell voltage; however, graphite-based Li-ion battery cells may have safety concerns. LTO is believed to ensure safer operation due to a minimal risk of Li-metal plating due to accidental overcharging. Other advantages of LTO include the absence of solid electrolyte interface (SEI) formation, and a stable and long cycle life due to low volume change during charge/discharge cycling. LNMO is believed to be advantageous to form the cathode because of its high working voltage (4.7 V) and theoretical capacity of 146.7 mAh g⁻¹. Generally, LNMO is known to show 20% and 30% higher energy density than LiCoO_2 and LiFePO_4 , respectively. In some cases, it

may be advantageous to add a conductive additive, such as carbon (e.g., carbon black) to the electrode formulation.

[0045] The electrode formulation (or electrode ink) may comprise a powder dispersed in a binder solution that includes a binder. Typically, the solids loading of the electrode formulation is from about 40-70%. The powder may have an average or nominal particle size of from about 0.1 micron to about 30 microns. Typically, the average particle size is from about 0.1 micron to about 20 microns, from about 0.1 to about 10 microns, or from about 0.5 micron to about 5 microns. In the examples in the present disclosure, the particle size of the LTO powders is smaller than 1 micron and the particle size of LNMO particles is smaller than 20 microns. Notably, the particle size represents a secondary size after particle agglomerating or sintering. The primary particle size is smaller than 500 nanometers.

[0046] The binder solution may be a mixture solution of *N*-methyl-2-pyrrolidone (NMP) and water, and the binder may comprise one or more water-compatible polymers selected from the group consisting of: cellulose acetate phthalate (CAP), (hydroxylpropyl) methylcellulose (HPMC), hydroxyl propyl cellulose, sodium carboxy methyl cellulose, poly(acrylic acid), polyvinylpyrrolidone, and polyethylene glycol. For example, the binder solution may include any of the above-mentioned polymers and CAP, where a mixing percentage of the polymer (e.g., HPMC) to the CAP is from about 10% to about 50% by weight.

[0047] In one example, the electrode formulation may be synthesized by dispersing the LTO (or LNMO) powder and carbon black as a conductive additive along with a binder in an NMP solution, followed by concentrating to the desired solids loading (e.g., about 60 wt.%). The weight ratios of the powder, carbon black, and binder are 81:10:9 for the exemplary LTO ink and 71:17:12 for the exemplary LNMO ink.

[0048] The electrode formulations may be prepared using polyvinylidene fluoride (PVDF), which is a frequently-used binder for Li-ion batteries. However, PVDF may be incompatible with highly concentrated inks (e.g., 60 wt.% solids) due to ink instability induced by moisture absorption from ambient air. Accordingly, a switch to water-compatible binders may be beneficial. For example, a mixed solution (3 wt.%) of

cellulose acetate phthalate (CAP) and hydroxylpropyl methylcellulose (HPMC) dissolved in a mixed solvent (97:3 by weight) of *N*-methyl-2-pyrrolidone (NMP) and water provides good binding properties. Water-soluble binders are also known to form dense electrodes after drying without using any mechanical pressing, which is often required to densify PVDF-based electrode films.

[0049] The viscosity of the binder solution can be adjusted by varying the mixing ratio of CAP and HPMC. A 9:1 (CAP:HPMC) weight ratio is employed in the exemplary electrode formulation, where CAP serves as the main binder and HPMC serves as the viscosifier. FIG. 6 shows viscosities of the (3 wt.%) solutions of CAP and HPMC, and a mixed solution of CAP:HPMC = 9:1 by weight. Using this binder composition, LTO and LNMO anode/cathode formulations have been prepared with high solids loadings (~ 60 wt%). The electrode formulations exhibit excellent shelf life in air without noticeable rheological changes over several months. It is noted that the amount of binder employed in the electrode formulation could be reduced by using solely a high viscosity binder (e.g. HPMC); however, this may inhibit the electrochemical performance of the battery cells due to the delamination of the electrode from the current collector after electrolyte soaking.

[0050] The LTO and LNMO inks typically exhibit a viscosity of about 10^2 Pa-s and an elastic modulus of about 10^4 Pa. FIG. 7 shows elastic moduli of the LTO and LNMO inks. These electrode formulations exhibit shear thinning behavior when shear rate is increased, yielding at a high shear rate and exhibiting a plateau elastic modulus at low values of shear stress. FIG. 8 shows SEM images of an LTO electrode (top) and a LNMO electrode (bottom) filled by doctor blading into trenches (50 μ m deep) of varying widths from 100 μ m to 1 mm at a 100- μ m increment with a 100- μ m wall spacing.

[0051] The high solids-loading electrode formulations sufficiently fill the microtrenches without exhibiting large crack formation or delamination. It is believed that patterned current collectors including trenches formed by laser cutting have textured or roughened surfaces that promote enhanced adhesion between the electrode and the current collector.

[0052] FIG. 10 shows optical images of LTO films (top) and LNMO films (bottom) doctor-blade coated on bare, smooth-surface stainless steel substrates. Notably, the formation of large cracks is observed for the films coated onto the bare, smooth surfaces when the film thickness exceeds 50 μm .

[0053] As would be understood from the preceding description, an electrode structure for a rechargeable microbattery cell, such as a Li-ion microbattery cell, comprises a patterned current collector having a trench therein, where the trench comprises a predetermined 2D shape and depth. An electrode comprising the predetermined 2D shape is disposed within the trench. The patterned current collector is formed from the conductive substrate as described above, and thus comprises a conductive material, also as set forth above. The trench, electrode, and predetermined 2D shape may have any of the characteristics described previously.

[0054] The above description is focused on the fabrication of electrode structures for use in rechargeable microbattery cells. Also described is a method for manufacturing a rechargeable microbattery cell, such as a Li-ion microbattery cell in arbitrary form factors, and the fabrication of flexible microbattery modules based on the fabricated cells.

[0055] In the description of microbattery fabrication that follows, it should be understood that the order in which the steps are described does not limit the order in which the steps are carried out. As would be recognized by one of ordinary skill in the art, the order of various steps can be changed. For example, the inner trenches may be formed before or after the outer trenches are formed. In another example, the filling of the inner trenches with an electrode formulation may occur before or after the outer trenches are formed, and before or after the outer trenches are filled with the packaging material.

[0056] Referring again to FIGs. 1A-1B, the method comprises forming an inner trench 106,206 and an outer trench 108,208 surrounding the inner trench 106,206 in each of two conductive substrates 102,202, thereby creating first and second patterned current collectors 104,204. The two conductive substrates may be separate

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conductive sheets or different portions of a single conductive sheet that are eventually separated for cell assembly.

[0057] The inner trenches 106,206 and the outer trenches 108,208 of the first and second patterned current collectors 104,204 may be formed in the same way as and have any of the characteristics of the trenches described above. The two conductive substrates 102,202 and the first and second patterned current collectors 104,204 may also have any of the characteristics described above for the conductive substrate and the patterned current collector, respectively.

[0058] As illustrated in FIG. 1B, each of the inner trenches 106,206 is filled with an electrode formulation 110,210 to form a first electrode 112 in the first patterned current collector 104 and a second electrode 212 in the second patterned current collector 204. The electrode formulations 110,210 used to fill the inner trenches 106,206 may be the same or different electrode formulations and may comprise any of the electrode formulations described elsewhere in this disclosure. Depending on the electrode formulation 110,210 used to fill the inner trenches 106,206, a cathode structure 114 and an anode structure 214 may be formed. For example, the first patterned current collector 104 containing the first electrode 112 may form the cathode structure 114, and the second patterned current collector 204 containing the second electrode 212 may form the anode structure 214.

[0059] Referring now to FIG. 1C, a separator 116 is deposited on the first electrode 112 or the second electrode 212. Depositing the separator 116 may entail executing a pick-and-place maneuver using a pre-formed membrane film. Alternatively, the separator 116 may be formed by a solution processing method such as spray coating, doctor blading, screen printing, ink jet printing, or aerosol jet printing, followed by drying.

[0060] When the separator 116 comprises a pre-formed membrane, the method may further include fabricating adhesive structures 118 comprising an adhesive material on the first or second electrode prior to positioning the pre-formed membrane film, as shown in FIGs. 1B and 1C. The adhesive structures 118 may be formed by 3D

printing, which entails extrusion of a suitable ink formulation through a deposition nozzle 124.

[0061] A packaging material 120,220 may be deposited in each of the outer trenches 108, 208 to form a first sealing structure 122 on the first patterned current collector 104 and a second sealing structure 222 on the second patterned current collector 204, as shown in FIG. 1D. When the microbattery cell 100 is assembled, the first sealing structure 122 comes into contact with the second sealing 222 structure, as illustrated in FIG. 1E. It should be noted that, depending on the 2D shape of the electrode, an additional trench may be present on each patterned current collector for forming an additional sealing structure. This may be understood in reference to the top left image of FIG. 4, which shows a ring-shaped cell where the electrode is surrounded by an outer sealing structure and also surrounds an inner sealing structure. Thus, the term “first sealing structure” as used herein may refer to any or all sealing structures present on the first patterned current collector, and the term “second sealing structure” refers to any or all sealing structures present on the second patterned current collector.

[0062] The first patterned current collector 104 including the first electrode 112 and the second patterned current collector 204 including the second electrode 212 may be stacked in a face-to-face configuration in an aligning fixture with the separator 116 in between, and the first sealing structure 122 may be bonded to the second sealing structure 222. A microbattery cell 100 having an arbitrary shape is thus formed. The bonding may entail heating the sealing structure at a temperature of from about 100°C to 200°C (e.g., 150°C) for a time period that may extend from 10 min to 60 min (e.g., 30 min) in order to cure the packaging material. Packaging that provides effective sealing is critical to containing the electrolyte solution, blocking moisture and oxygen permeation, and preventing damage from physical impact.

[0063] After the bonding, the microbattery cell may be heated for an additional time period in a vacuum environment to remove all moisture from the battery cell. For example, the fabricated cells may be vacuum dried at from 120°C to 200°C (e.g., 180°C) for 12-20 hours (e.g., 16 hours) and then transferred into an argon-filled

glove box. An electrolyte solution may be added to the cell through a fill-hole 126 (Fig. 1E), as described below.

[0064] Although it may be advantageous to form the adhesive structures and sealing structures by 3D printing, other deposition techniques such as doctor blading or screen printing may also be used. The adhesive material and the packaging material may comprise a polymer, such as silicone, polyurethane, or epoxy.

Experiments have been carried out using a silicone ink formulation (SS-153, Silicone solutions) that is heat curable (150°C, 30 min), solvent-free (100% solid), one-part silicone-based composition as the adhesive and packaging materials. The apparent viscosity and plateau elastic modulus of the silicone ink are measured as 500 Pa·s and 1.05×10^{-5} Pa, respectively, as shown in FIG. 11.

[0065] Printed adhesive structures in the form of printed dots may be used to adhere a PVDF membrane (an exemplary separator) onto the electrode-filled patterned current collectors. 3D printed dots have been optimized by printing a silicone dot array, as shown in FIG. 12. The left image shows an optical image captured during printing of the silicone ink using a 100-μm nozzle. The right image shows SEM images of the printed dot array (12 × 12) formed on a Si wafer using varying dwell times and lifting speeds of the deposition nozzle. The inset in the right shows the magnified SEM image of a dot printed at a dwell time of 50 milliseconds and a lifting speed of 10 mm s⁻¹.

[0066] The size of the printed dots decreases when the dwell time is decreased. A minimal dot dimension of 150 μm in width and 200 μm in height is achieved at a dwell time of 50 milliseconds and a lifting speed of 10 mm s⁻¹. Different numbers and distributions of dots may be used for cells with different shapes and size. Also, the printed adhesive structures may be formed to have geometries other than dots, such as strips or lines.

[0067] FIG. 13 shows printing of the exemplary silicone ink that may be used for packaging. The left image shows an optical image captured during printing of the silicone ink into a packaging trench (250 μm wide, 50 μm deep) in a patterned current collector using a 200-μm nozzle. The right image shows SEM images of silicone

structures having different numbers of printed layers after being formed layer by layer in the trenches.

[0068] The exemplary silicone ink formulation used herein may enable microscale 3D printing to be carried out with reliable stop and start capability. SEM images show that the printed features are safely pinned into the microtrenches. High aspect ratio features having three layers and five layers are also demonstrated via layer-by-layer printing. Notably, the printed silicone, which is secured in the trenches, serves as a robust packaging material and sealing structure for the assembled cells.

[0069] After fabrication of the bonded microbattery cell, the method may further include forming a fill-hole (or access hole) in one of the first and second patterned current collectors to allow an electrolyte solution to be flowed into the microbattery cell. Once the microbattery cell is filled with an appropriate amount of the electrolyte solution, the access hole may be sealed to contain the electrolyte solution in the microbattery cell.

[0070] FIG. 14 shows a schematic cross-sectional diagram (left image) and an SEM image (right) of an exemplary fill-hole design. The fill-hole may be sealed using a two-step drop-casting method with inner and outer fill-hole sealants. The fill-hole is designed to hold sealants well and may be fully cut so that it extends to the separator where the electrolyte solution can easily penetrate into the entire volume of the cell. A low-viscosity UV-curable epoxy that enables good adhesion on the electrolyte solution-contaminated surface may be drop cast into the fill-hole to form an inner fill-hole sealant. A high-viscosity UV-curable silicone or hermetic sealant that enables good sealing against moisture and oxygen permeation may then be drop cast onto the inner fill-hole sealant to form an overlying outer fill-hole sealant, thereby ensuring a secure seal of the fill-hole.

[0071] After sealing the fill-hole, individual microbattery cells may be separated from a sheet comprising patterned current collector sheets using gentle manual force to break the cell holding points (which may be about 25 μm wide and 76 μm thick). The number of the cell holding points for a given microbattery cell may depend on the size of the cells, where more holding points may be required for larger cells.

[0072] To demonstrate the flexibility of the microbattery fabrication technology, various microbattery shapes have been produced using a current collector sheet patterned to include trenches of various 2D shapes and sizes, including eleven square trenches ($2 \times 2 \times 0.3 \text{ mm}^3$), nine spherical trenches (3 mm in diameter, 0.3 mm thick), seven *H*-shaped trenches ($4 \times 4 \times 0.3 \text{ mm}^3$), five donut-shaped or ring-shaped trenches (i.d. = 2 mm, o.d. = 5 mm, 0.3 mm thick), five shield-shaped trenches ($5 \times 6 \times 0.3 \text{ mm}^3$), and two ribbon trenches ($2 \times 13 \times 0.3 \text{ mm}^3$). Fabricating other shapes of interest in any size scale is possible by simply changing the current collector patterns and printing parameters. FIG. 15 shows an optical image of fabricated microbattery cells having different shapes and sizes produced from the current collector sheet ($40 \times 50 \times 0.076 \text{ mm}^3$), and FIG. 16 shows high magnification optical images of several of the fabricated cells.

[0073] FIG. 17 shows materials volume fraction for an exemplary 2-mm square cell as a function of electrode thickness or depth (left image) and cell width (right image). The materials volume fraction in the 2-mm cell is 6.4% for electrode, 45.7% for current collector, 5.5% for separator, 8.3% for electrolyte, and 34.2% for packaging. Materials fraction is affected by the electrode thickness and cell size, and the latter is the major factor. In some embodiments, the microbattery cell may include a materials volume fraction of about 1-8% for the electrode, about 42-48% for the current collector, about 3-8% for the separator, about 6-10% for the electrolyte and about 33-35% for the packaging. In other embodiments, the microbattery cell may include a materials volume fraction of about 1-18% for the electrode, about 40-45% for the current collector, about 2-10% for the separator, about 5-20% for the electrolyte and about 12-42% for the packaging.

[0074] To demonstrate electrochemical performance, half-cells are characterized using coin cell geometry (2032 cells). FIG. 18 shows voltage versus capacity for an LTO half-cell (left plot) and LNMO half-cell (middle plot) measured by varying the charge-discharge rate. The right plot shows cyclability of the LTO and LNMO half-cells measured at 1C. C is a dimensionless measure of the rate of charge/discharge of a battery. A battery discharged at a 1C rate is discharged in 1 hour with a constant

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current. A battery discharged at an nC rate is discharged with a current n times the 1C current. Half-cells show the typical characteristics of LTO electrodes with a discharge plateau at about 1.5 V versus Li/Li⁺ with a nominal discharge capacity of 165 mAh g⁻¹ at 1C. LNMO electrodes exhibit two distinguishable discharge pseudoplateaus at 4.7 V and 4.6 V, and a small loping plateau centered at 4.0 V with a nominal discharge capacity of 131 mAh g⁻¹ at 1C. The former two are ascribed to Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ redox couples, while the latter is associated with Mn³⁺/Mn⁴⁺ redox couple.

[0075] FIG. 19 shows the LTO-LNMO full cell performances measured by coin cell geometry (2032 cells). The left plot shows the charge (Li transfer from LNMO to LTO) and discharge curves of the LTO-LNMO full-cell battery at a series of rates from 1 to 50C (the charge and discharge rate are same). The right plot shows the cyclability of the LTO-LNMO full cell measured at 1C.

[0076] Charge-discharge curves with small hysteresis and flat voltage profile centered at 3.18 V with a discharge capacity of 121.8 mAh g⁻¹, 83% to theoretical value (147 mAh g⁻¹), is obtained at 1C. Up to 70 cycles at 1C shows about 6% capacity loss. Voltage plateau and discharge capacity decrease with increasing discharge rate as usual but the battery exhibits high voltage (3.1 V) and capacity (60 mAh g⁻¹) at a rate as high as 30C. This high rate performance may be attributed to the stable electrodes that are formed using a water-compatible binder as well as the trench geometry for the electrodes which may promote effective current collection.

[0077] The electrochemical performance of microbattery cells fabricated with 3D printed sealants were also tested. The cells were stable in ambient atmosphere for several hours, after which time there was some deterioration of hermetic sealing. The chemical compatibility, mechanical properties, and rheology of sealants are of key importance for good cell packaging. Based on the platform microbattery fabrication techniques described herein, we are under developing better sealant materials to improve long-term stability of printed microbatteries.

[0078] Batteries are inherently opaque and rigid; however, miniature battery cells in arbitrary form factors may enable new functionalities, including semitransparency, bending, conformal folding, and stretching. The above-described method may thus

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further entail forming a flexible microbattery module. The method may comprise fabricating a plurality of the microbattery cells, and supporting the microbattery cells on or in a flexible structure such that the microbattery cells are spaced apart from each other. The flexible structure may comprise an elastomeric material. The microbattery cells may be connected in series or in parallel to form the flexible microbattery module. The flexible structure may be partly or fully optically transparent. It may be beneficial for the microbattery cells to comprise a thickness of about 3 mm or less, about 2 mm or less, or about 1 mm or less. The microbattery cells may have any of the 2D shapes described above, and typically have a lateral size of from about 1 mm to about 100 cm.

EXAMPLES

Example 1: Ink Preparation

[0079] Four inks, including LTO for anode, LNMO for cathode, silicone for adhesive and packaging and UV-curable epoxy for fill-hole sealant, are used. Highly concentrated LTO inks are prepared by first dispersing 8.1 g of LTO powder (particle size < 1 into the microtrench pattern, UBE, Japan), 1 g of carbon black as a conductive filler, and 30 g a mixture of binder solution (3 wt.%, CAP:HPMC = 9:1 by weight) in a 97:3 mixture of *N*-methyl-2-pyrrolidone and deionized water. The ratio of materials used are powder:carbon:binder = 80:10:10 by weight. The mixture is sonicated for 30 min in a water bath, followed by concentrating *via* solvent evaporation on a hot plate at 150°C (solution temperature = 96°C) until the ink solids loading (powder + carbon + binder) reaches to ~ 50 wt.%. This ink is then further concentrated by vacuum (-100 KPa) drying at room temperature up to ~ 60 wt.% solids. LNMO inks are prepared using the same procedure except using LNMO powder (particle size < 0.5 µm, Aldrich). The ratio of materials used is powder:carbon:binder = 71:17:12 by weight and the final ink solids loading is 54 wt%. One-part, thermally curable (150°C, 30 min) silicone (SS-153, Silicon Solutions) is used as received for printing adhesive and packaging layers. UV-curable epoxy (Model, Company) is used as received for sealing fill-holes in the cells.

Example 2: Forming Patterned Current Collectors and Printed Structures

[0080] Patterned current collectors are formed by defining trenches (250 μm wide, 50 μm deep, 100 μm spacing) in stainless steel sheets (76-127 μm thick) by laser micromachining. FIGs. 20 and 21 show exemplary laser cutting parameters and laser cut drawings applicable to this and other examples. Table 1 below includes the cutting conditions for each layer of the drawings shown in FIG. 21. Each layer was cut with 20 passes, and the laser cut line-to-line spacing is 2 microns. Note that two sets are required for layers 1-5. The total laser cutting time for the anode and cathode is 13 hours.

Table 1. Laser Cut Drawings and Cutting Time

Laser Cut Drawings	Cutting Conditions	Time (min)
Layer 1 - Trenches for electrode	100% PWR, 20 cm/s, 25 KHz	192.0
Layer 2 - Trenches for packaging	100% PWR, 20 cm/s, 25 KHz	123.0
Layer 3 - Release cut except holding points	100% PWR, 20 cm/s, 25 KHz	55.0
Layer 4 - Aligning guideline for printing	100% PWR, 20 cm/s, 25 KHz	0.1
Layer 5 - Holes and borders	100% PWR, 20 cm/s, 25 KHz	16.0
Layer 6 - Logos and remarks	100% PWR, 20 cm/s, 25 KHz	0.1
Layer 7 - Outer fill holes (i.d. 600 μm)	100% PWR, 20 cm/s, 25 KHz	6.7
Layer 8 - Inner fill holes (i.d. 200 μm)	100% PWR, 20 cm/s, 25 KHz	1.3
Layer 9 - Separator	100% PWR, 20 cm/s, 25 KHz	0.3

[0081] The patterned current collectors are cleaned by sonicating in water for 5 min, followed by filling with suitable electrode formulations using doctor blading. No spacer is required because the walls between trenches serve as the spacer. The resultant structures are then heat-treated at 120°C for 30 min. Adhesive and packaging materials are printed using a 3-axis micropositioning stage (ABL 900010, Aerotech Inc., Pittsburgh, PA), whose motion is controlled by computer-aided design software (RoboCAD, 3D Inks, Stillwater, OK). The silicone ink is housed in separate syringes (3 mL barrel, EFD Inc., East Providence, RI), which are attached by luer-lok to (a) a

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tapered plastic nozzle (200 μm in diameter) for printing packaging and (b) a tapered metal nozzle (1000 μm in diameter) for printing adhesive dot arrays. An air-powered fluid dispenser (800 ultra dispensing system, EFD Inc.) is used to pressurize the barrel and control the ink flow rate. The typical printing speed for this ink is ~ 10 mm/s at ~ 500 psi. Silicone adhesive structures are printed on top of trench walls using a 100- μm nozzle.

Example 3: Cell Assembly

[0082] Aligning hole patterns are produced on a separator sheet (pore size = 0.2 μm , Whatman) by laser cutting. Then, the separator sheet is placed onto the anode-filled patterned current collector using an aligning fixture, a 1 kg weight is placed on the separator sheet, and the structure is heat-treated at 120°C under the pressure of the 1 kg weight for 1 h to cure the silicone adhesive structures. The excess section of the separator is then laser cut and removed. A silicone ink is used as a packaging material and printed into the packaging trenches to finish the anode portion of the cell. Separately, the cathode portion is prepared by doctor blading of the LMNO ink, followed by printing the silicone packaging ink. Cell assembly is carried out by stacking the LTO and LNMO parts in a face-to-face configuration using the aligning fixture, followed by heat-treating at 120°C also under the pressure of a 1.0 kg weight for 1 h to bond them together. The assembled cell is then vacuum (~ 100 KPa) dried at 180°C overnight. Finally, an electrolyte solution with 1.0 M LiPF_6 in 50:50 mixture of ethylene carbonate (EC) and dimethyl carbonate is filled into the cell through a fill-hole (200 μm inner diameter and 600 μm outer diameter) using repeated light vacuuming and unvacuuming in an argon-filled glove box, followed by sealing the fill-holes using a UV-curable epoxy sealant followed by a UV-curable silicone.

Example 4: Characterization

[0083] All electrochemical measurements are carried out in ambient air, and electrochemical data is collected with a commercial potentiostat (SP150, Biologic Co.). For the half-cell test, the LTO and LNMO electrodes are laser cut into circles of 13 mm diameter and tested using a conventional coin cell geometry using LiPF_6 solution in EC:DMC = 50:50 by volume. A piece of lithium foil (1 mm thick, Model,

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Company) serves as both the counter and reference electrodes. Cyclic voltammetry and galvanic charge/discharge are performed to check the electrochemical reactivity and rate capability. For the rate test, the charge and discharge rates are held constant over the range from 1C to 100C. The cycling life is also measured in constant current, and both the charge and discharge rates are fixed at 1C. The rate performance and cyclability for the LTO-LNMO full cells are also carried out using the same electrolyte solution and equipment. Ink rheology is measured in both shear viscometry and oscillatory modes using a controlled-stress rheometer (C-VOR, Malvern Instruments, Malvern, UK) equipped with C14 cup and bob at 25 °C in the presence of a solvent trap to prevent evaporation. The apparent ink viscosity (η) is acquired as a function of shear rate (0.01–500 s⁻¹) in a logarithmically ascending series. The shear storage (G') and viscous loss (G'') moduli are measured in an oscillatory mode as a function of controlled shear stress (10-10000 Pa) at a frequency of 1 Hz with increasing amplitude sweep. Microstructures of printed features are characterized using SEM (Hitach S-4700). Ink solids loading was obtained by drying the inks at 150 °C for 12 h in an oven.

[0084] Although the present invention has been described in considerable detail with reference to certain embodiments thereof, other embodiments are possible without departing from the present invention. The spirit and scope of the appended claims should not be limited, therefore, to the description of the preferred embodiments contained herein. All embodiments that come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein. Furthermore, the advantages described above are not necessarily the only advantages of the invention, and it is not necessarily expected that all of the described advantages will be achieved with every embodiment of the invention.

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CLAIMS

1. An electrode structure for a rechargeable microbattery cell, the electrode structure comprising:
a patterned current collector having a trench therein, the trench comprising a predetermined 2D shape and depth; and
an electrode disposed within the trench, the electrode comprising the predetermined 2D shape.
2. The electrode structure of claim 1, wherein the trench comprises a surface roughness of from about 0.001 mm to about 0.1 mm.
3. The electrode structure of claim 1 or 2, wherein a thickness of the electrode is substantially the same as the depth of the trench.
4. The electrode structure of any one of claims 1-3, wherein the depth of the trench is from about 0.01 mm and 0.5 mm.
5. The electrode structure any one of claims 1-4, wherein the trench has a width of from about 0.1 to 1 mm.
6. The electrode structure of any one of claims 1-5, wherein the predetermined 2D shape is an n-sided shape, where n is an integer from 3 to 50.
7. The electrode structure of any one of claims 1-6, wherein the predetermined 2D shape comprises one or more curved portions.
8. The electrode structure of any one of claims 1-7, wherein the patterned current collector comprises a conductive material selected from the group consisting of: metal, metal alloy, carbon, conductive polymer, and conductive metal oxide, and wherein the conductive material may be coated on glass or a polymeric substrate.

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9. The electrode structure of claim 8, wherein the conductive material comprises stainless steel.

10. The electrode structure of any one of claims 1-9, wherein the electrode comprises an electrochemically active material selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO), lithium cobalt oxide (LiCoO_2), lithium iron phosphate (LiFePO_4), vanadium oxide (V_2O_5 , LiV_3O_8), manganese oxide (MnO_2), tin-based oxides and composite alloys.

11. The electrode structure of any one of claims 1-10, wherein the electrochemically active material comprises a lithium-based metal oxide selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO), lithium cobalt oxide (LiCoO_2) and lithium iron phosphate (LiFePO_4).

12. The electrode structure of claim 11, wherein the lithium-based metal oxide is selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO).

13. A method for manufacturing an electrode structure for a rechargeable microbattery cell, the method comprising:

forming a trench having a predetermined 2D shape and depth in a conductive substrate, thereby creating a patterned current collector; and

filling the trench with an electrode formulation to form an electrode having the predetermined 2D shape, thereby forming an electrode structure for a rechargeable microbattery cell.

14. The method of claim 13, wherein forming the trench comprises roughening one or more surfaces of the trench.

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15. The method of claim 13 or 14, wherein forming the trench comprises laser cutting.

16. The method of any one of claims 13-15, wherein forming the trench further comprises wet etching, the laser cutting being carried out after the wet etching.

17. The method of any one of claims 13-16, wherein filling the trench comprises 3D printing, doctor blading, screen printing, ink jet printing or aerosol jet printing of the electrode formulation.

18. The method of any one of claims 13-17, wherein a thickness of the electrode is substantially the same as the depth of the trench.

19. The method of any one of claims 13-18, wherein the predetermined 2D shape is an n-sided shape, where n is an integer from 3 to 50.

20. The method of any one of claims 13-19, wherein the predetermined 2D shape comprises one or more curved portions.

21. The method of any one of claims 13-20, wherein the conductive substrate comprises a conductive material selected from the group consisting of: metal, metal alloy, carbon, conductive polymer, and conductive metal oxide.

22. The method of claim 21, wherein the conductive material comprises stainless steel.

23. The method of any one of claims 13-22, wherein the electrode comprises an electrochemically active material selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO), lithium cobalt oxide (LiCoO_2), lithium iron phosphate (LiFePO_4), vanadium

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oxide (V_2O_5 , LiV_3O_8), manganese oxide (MnO_2), tin-based oxides and composite alloys.

24. The method of any one of claims 13-23, wherein the electrochemically active material comprises a lithium-based metal oxide selected from the group consisting of: lithium titanate ($Li_4Ti_5O_{12}$; LTO), lithium manganese nickel oxide ($LiNi_{0.5}Mn_{1.5}O_4$; LNMO), lithium cobalt oxide ($LiCoO_2$) and lithium iron phosphate ($LiFePO_4$).

25. The method of claim 24, wherein the lithium-based metal oxide is selected from the group consisting of: lithium titanate ($Li_4Ti_5O_{12}$; LTO), lithium manganese nickel oxide ($LiNi_{0.5}Mn_{1.5}O_4$; LNMO).

26. The method of any one of claims 13-25, wherein the electrode formulation comprises a powder dispersed in a binder solution.

27. The method of claim 26, wherein the binder solution includes a binder comprising a water-compatible polymer.

28. The method of claim 27, wherein the water-compatible polymer is selected from the group consisting of: cellulose acetate phthalate (CAP), (hydroxylpropyl) methylcellulose (HPMC), hydroxyl propyl cellulose, sodium carboxy methyl cellulose, poly(acrylic acid), polyvinylpyrrolidone, and polyethylene glycol.

29. The method of claim 28, wherein the binder comprises HPMC and CAP, a mixing percentage of the HPMC to the CAP being from about 10% to about 50% by weight.

30. A method for manufacturing a rechargeable microbattery cell, the method comprising:

forming an inner trench and an outer trench surrounding the inner trench in

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each of two conductive substrates, thereby creating first and second patterned current collectors;

filling each of the inner trenches with an electrode formulation to form a first electrode in the first patterned current collector and a second electrode in the second patterned current collector;

depositing a separator on the first electrode or the second electrode;

depositing a packaging material in each of the outer trenches to form a first sealing structure on the first patterned current collector and a second sealing structure on the second patterned current collector;

stacking the first patterned current collector on the second patterned current collector in a face-to-face configuration, the first sealing structure coming into contact with the second sealing structure; and

bonding the first sealing structure to the second sealing structure, thereby forming a microbattery cell.

31. The method of claim 30, further comprising:

forming an access hole in one of the first and second patterned current collectors;

flowing an electrolyte solution into the microbattery cell through the access hole after the bonding; and

sealing the access hole to contain the electrolyte solution in the microbattery cell.

32. The method of claim 30 or 31, wherein forming the inner and outer trenches comprises roughening one or more surfaces of the inner and outer trenches.

33. The method of any one of claims 30-32, wherein forming the inner and outer trenches comprises laser cutting.

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34. The method of claim 33, wherein forming the inner and outer trenches further comprises wet etching, the laser cutting being carried out after the wet etching.

35. The method of any one of claims 30-34, wherein filling the inner trenches with the electrode formulation comprises 3D printing, doctor blading, screen printing, ink jet printing or aerosol jet printing.

36. The method of any one of claims 30-35, wherein depositing the separator comprises spray coating, doctor blading, screen printing, ink jet printing, or aerosol jet printing using a membrane solution, followed by drying.

37. The method of any one of claims 30-35, wherein depositing the separator comprises executing a pick-and-place maneuver using a pre-formed membrane film.

38. The method of claim 37, further comprising, prior to depositing the separator, fabricating one or more adhesive structures comprising an adhesive material on the first or second electrode to adhere to the pre-formed membrane film.

39. The method of claim 38, wherein fabricating the adhesive structures comprises 3D printing.

40. The method of any one of claims 30-39, wherein depositing the packaging material comprises 3D printing, doctor blading or screen printing.

41. The method of any one of claims 30-40, wherein the stacking is carried out in an aligning fixture.

42. The method of any one of claims 30-41, wherein the bonding comprises heating at a temperature of from about 100°C to 200°C for a time period of 10 min to 120 min.

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43. The method of any one of claims 30-42, further comprising, after the bonding, heating the microbattery cell for an additional time period in a vacuum environment.

44. The method of any one of claims 30-43, wherein a thickness of the electrode is substantially the same as the depth of the trench.

45. The method of any one of claims 30-44, wherein the two conductive substrates comprise a conductive material selected from the group consisting of: metal, metal alloy, carbon, conductive polymer, and conductive metal oxide.

46. The method of claim 45, wherein the conductive material comprises stainless steel.

47. The method of any one of claims 30-46, wherein the electrode formulation comprises a lithium-based metal oxide.

48. The method of claim 47, wherein the lithium-based metal oxide is selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO), lithium cobalt oxide (LiCoO_2) and lithium iron phosphate (LiFePO_4).

49. The method of claim 47 or 48, wherein the lithium-based metal oxide is selected from the group consisting of: lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$; LTO), lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LNMO).

50. The method of any one of claims 30-49, wherein the electrode formulation comprises a powder dispersed in a binder solution.

51. The method of claim 50, wherein the binder solution includes a binder comprising a water-compatible polymer.

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52. The method of claim 51, wherein the water-compatible polymer is selected from the group consisting of: cellulose acetate phthalate (CAP), (hydroxylpropyl) methylcellulose (HPMC), hydroxyl propyl cellulose, sodium carboxy methyl cellulose, poly(acrylic acid), polyvinylpyrrolidone, and polyethylene glycol.

53. The method of claim 51 or 52, wherein the binder comprises HPMC and CAP, a mixing percentage of the HPMC to the CAP being from about 10% to about 50% by weight.

54. The method of any one of claims 30-53, wherein each of the inner and outer trenches comprises a width of from about 0.1 to 1 mm.

55. The method of any one of claims 30-54, wherein the depth of each of the inner and outer trenches is from about 0.01 mm to 0.5 mm.

56. The method of any one of claims 30-55, wherein one or both of the inner and outer trenches comprises a surface roughness of from about 0.001 mm to about 0.1 mm.

57. The method of any one of claims 30-56, further comprising:
forming a plurality of the microbattery cells;
supporting the microbattery cells on or in a flexible structure, the microbattery cells being spaced apart from each other; and
interconnecting the microbattery cells in series or parallel, thereby forming a flexible microbattery module.

58. The method of claim 57, wherein the flexible structure comprises an elastomeric material.

59. The method of claim 57 or 58, wherein the flexible structure is semi- or fully optically transparent.

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60. The method of any one of claims 30-59, wherein the microbattery cells comprise a thickness of about 3 mm or less.

61. The method of any one of claims 30-60, wherein the microbattery cells comprise a lateral size of from about 1 mm to about 100 cm.

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FIG. 1A

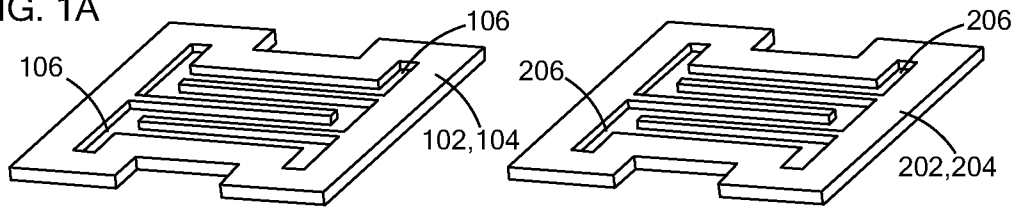


FIG. 1B

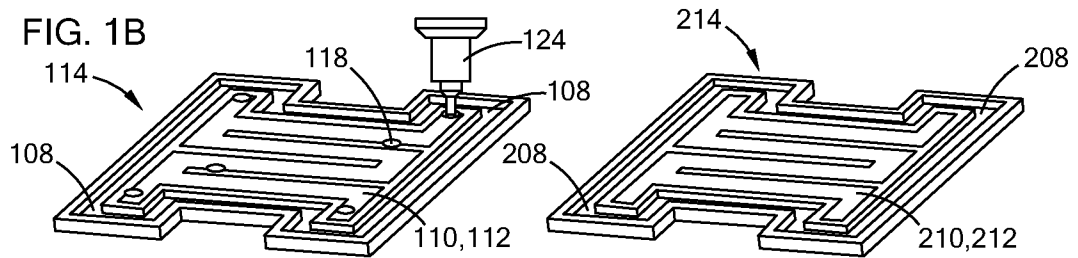


FIG. 1C

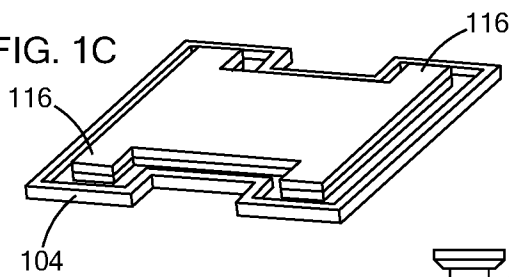


FIG. 1D

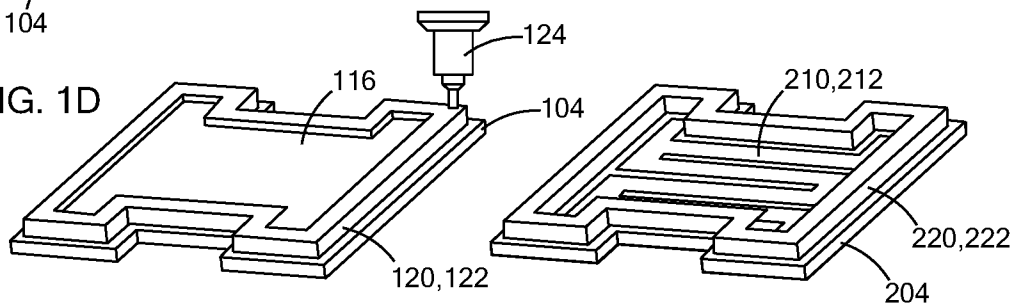
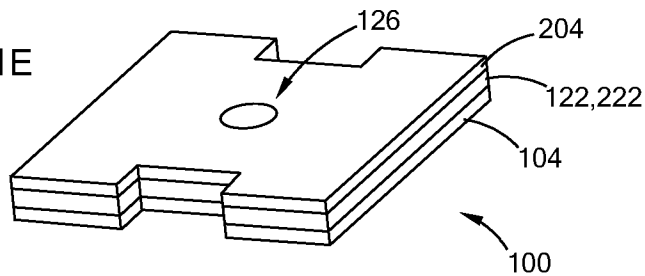


FIG. 1E



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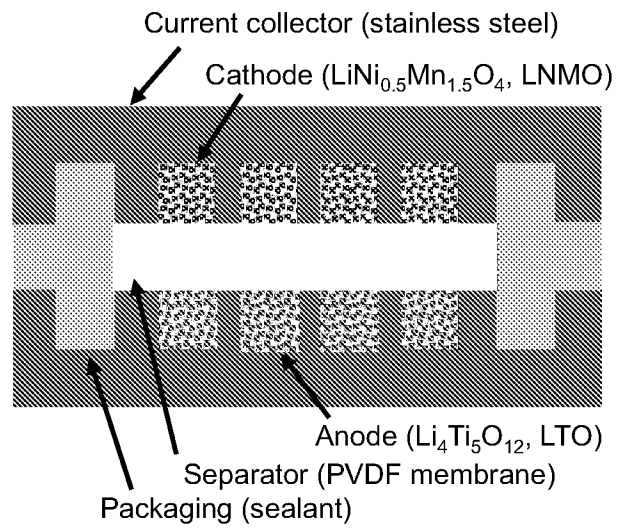


FIG. 2

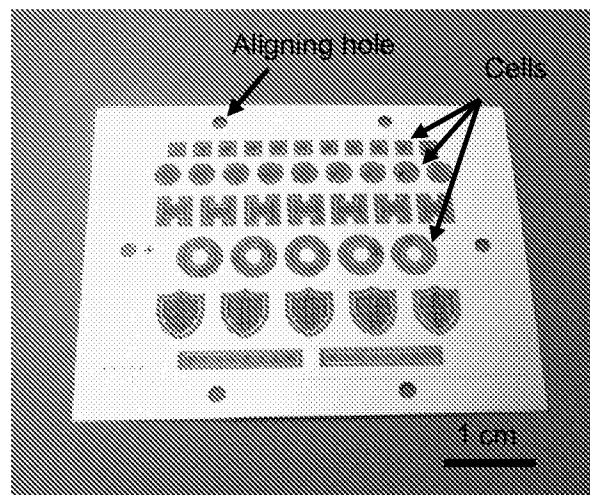


FIG. 3

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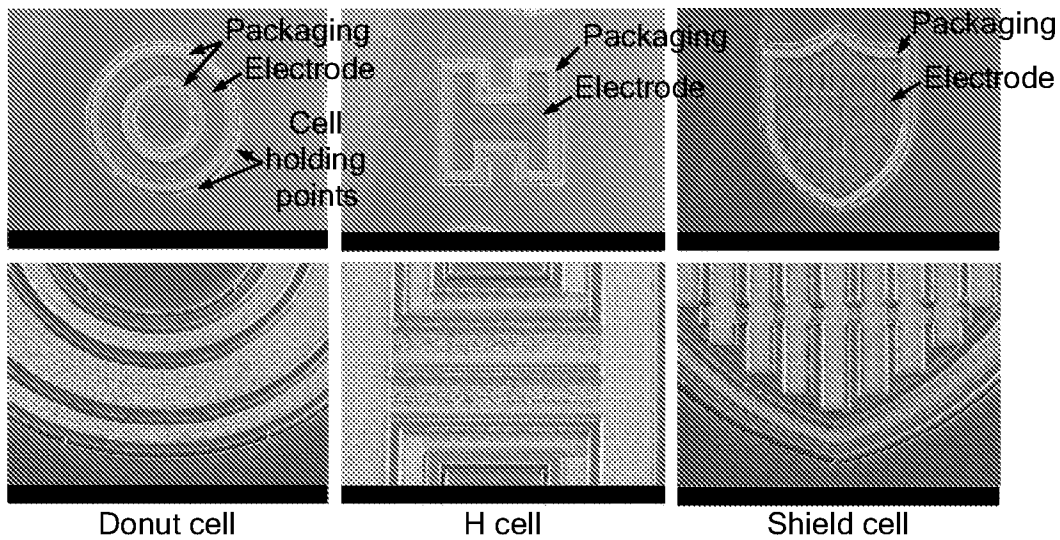


FIG. 4

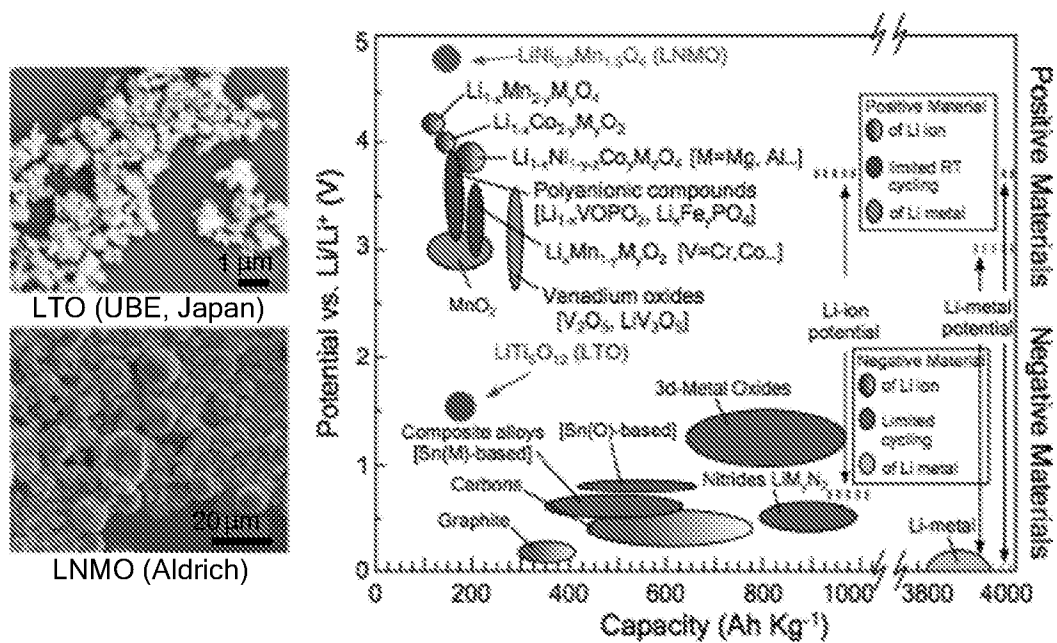


FIG. 5

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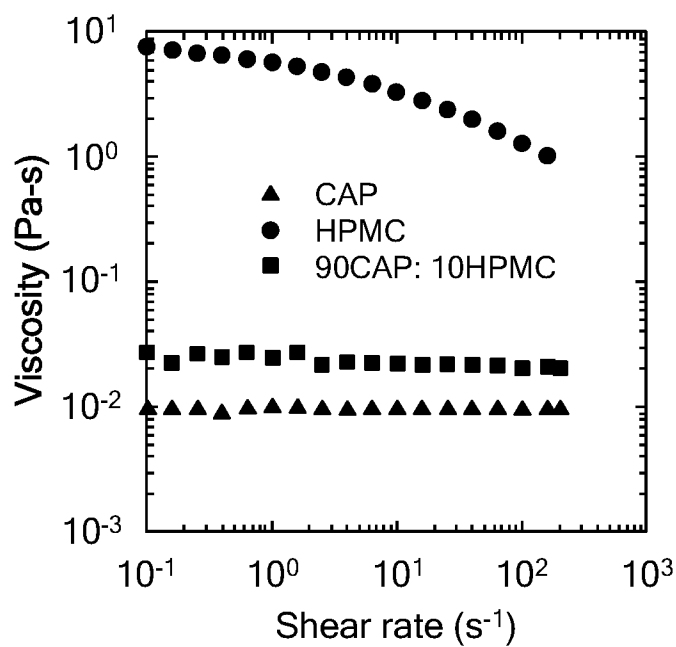


FIG. 6

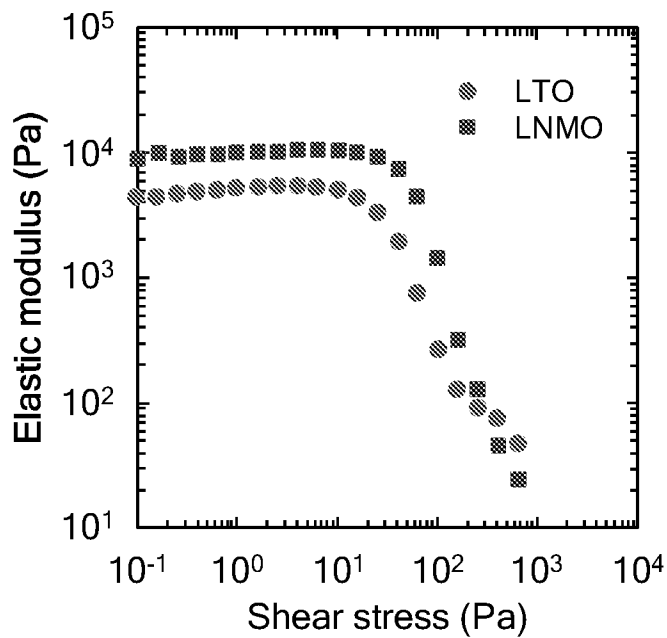


FIG. 7

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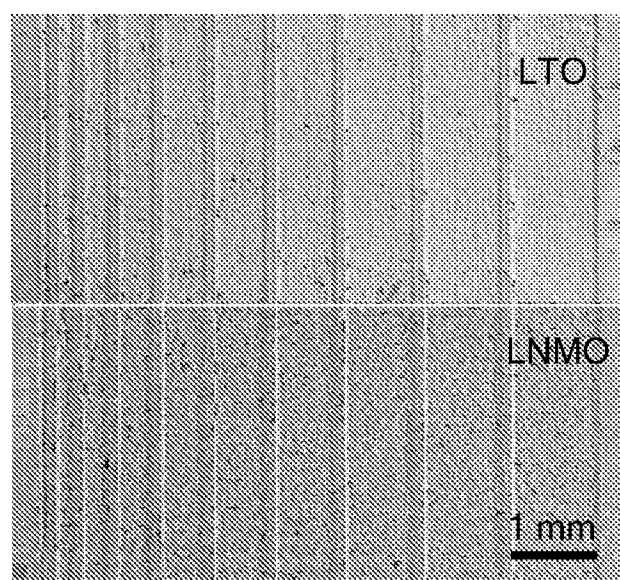


FIG. 8

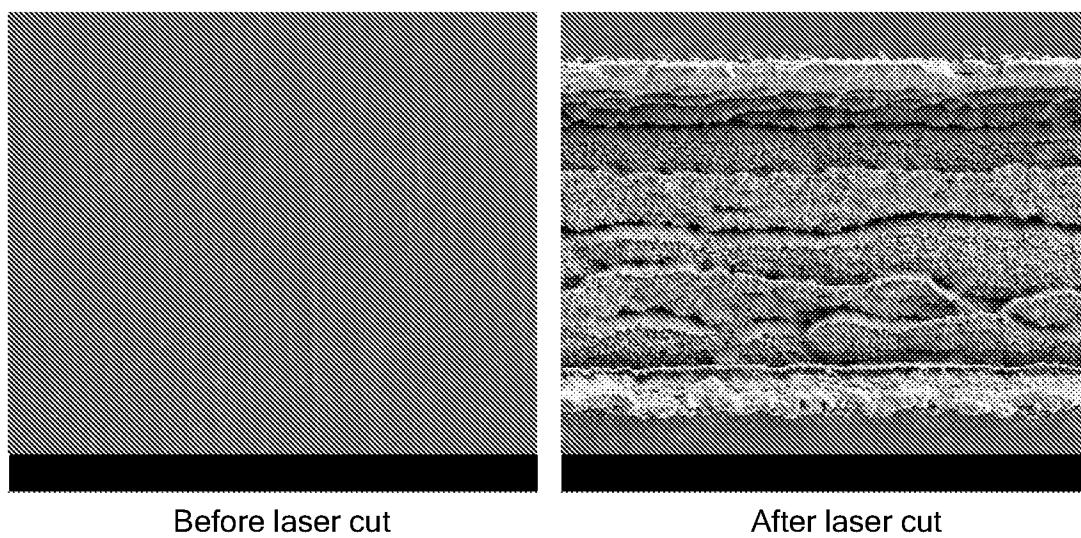


FIG. 9

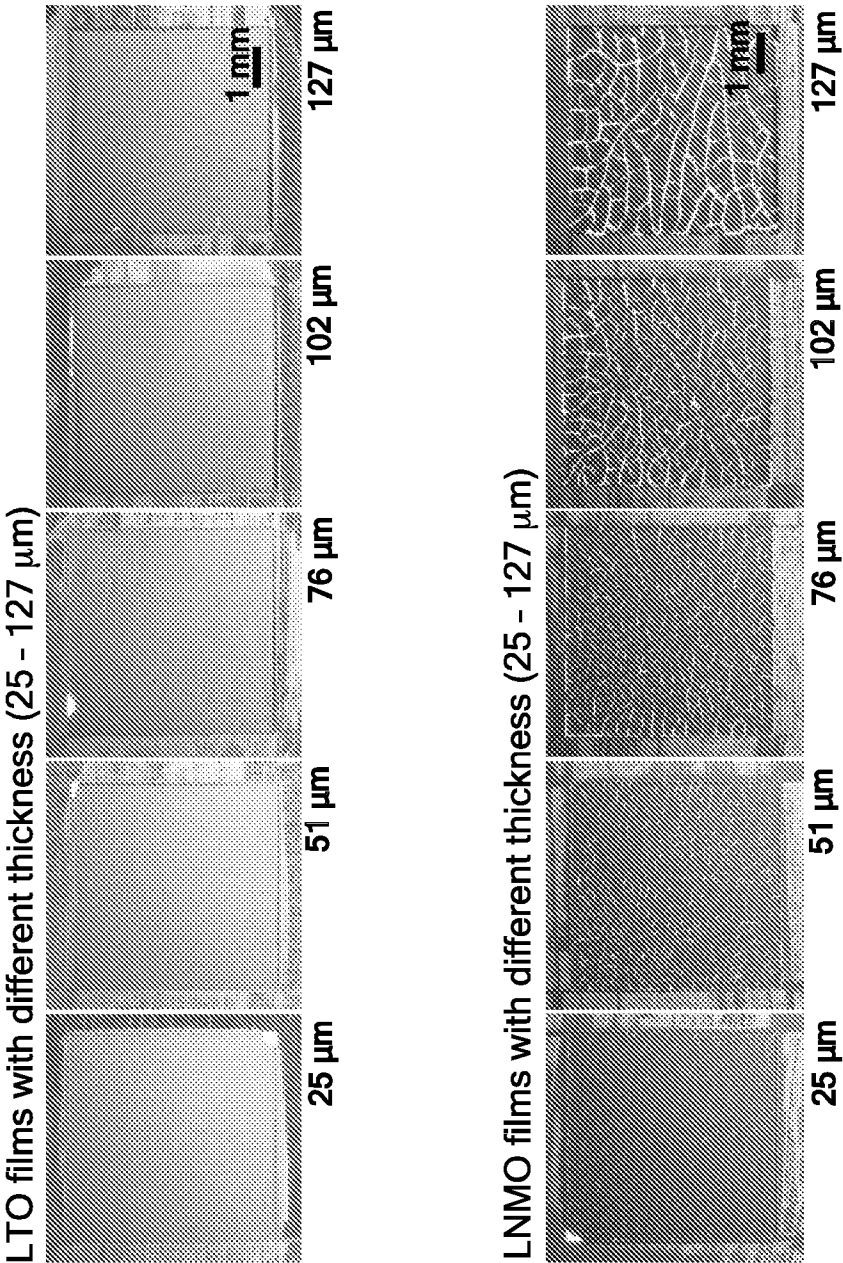


FIG. 10

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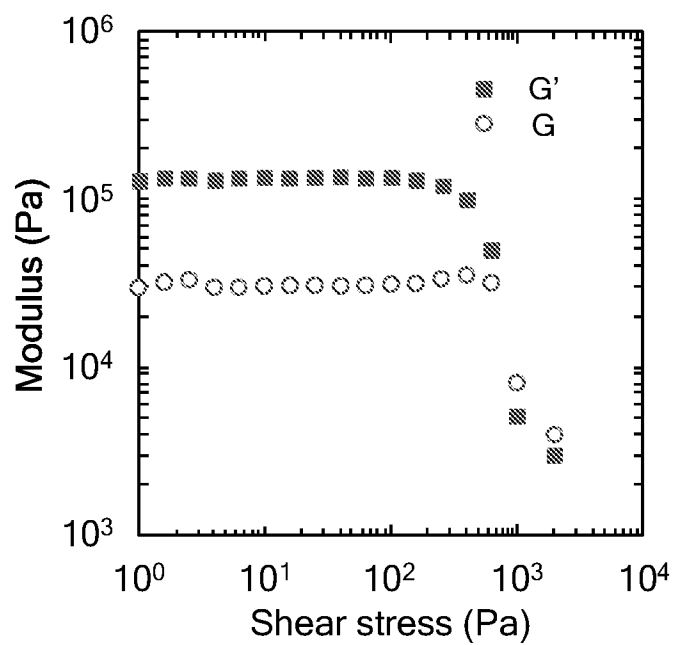
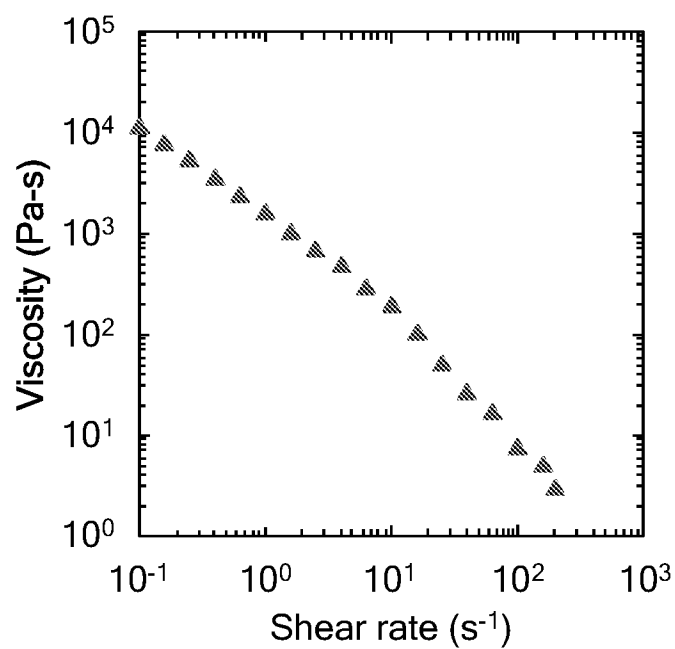


FIG. 11

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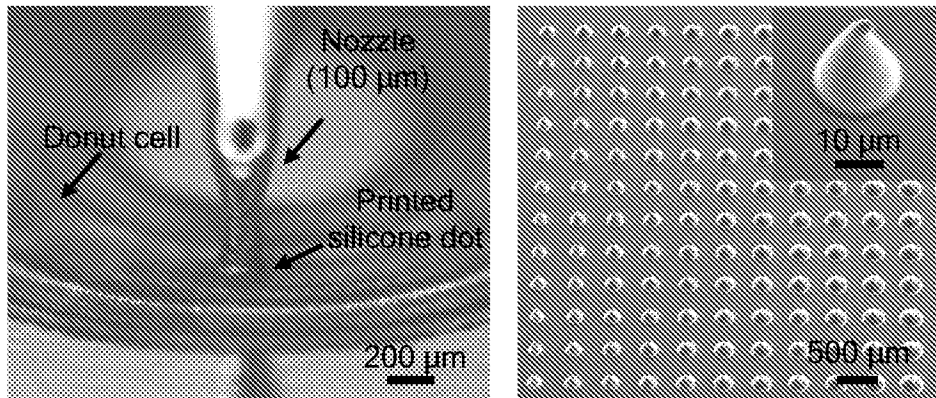


FIG. 12

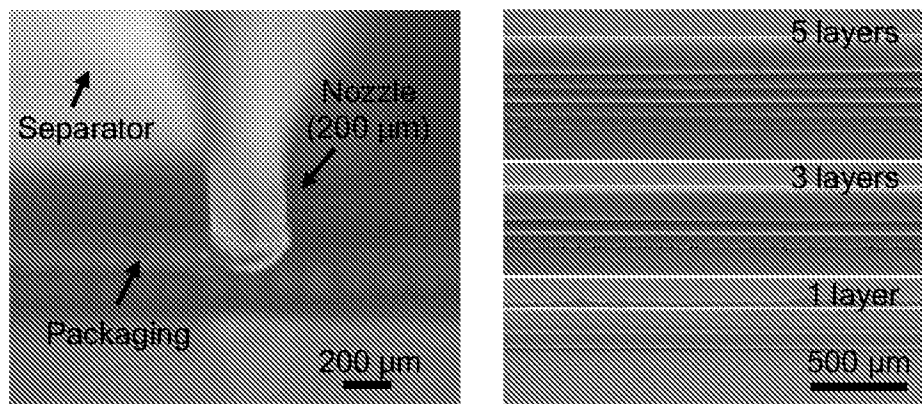


FIG. 13

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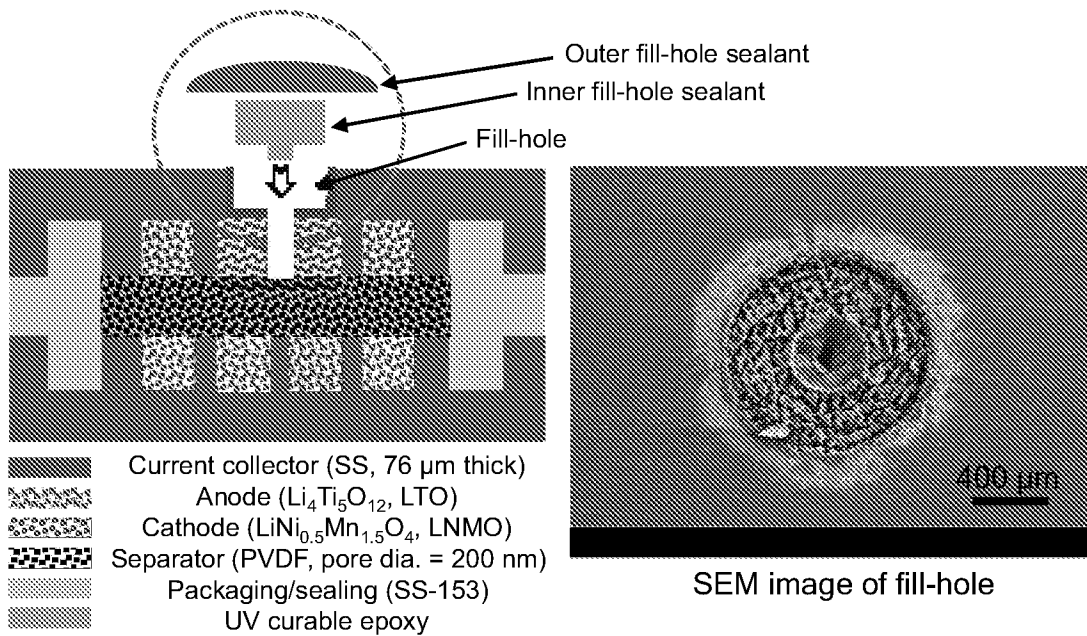


FIG. 14

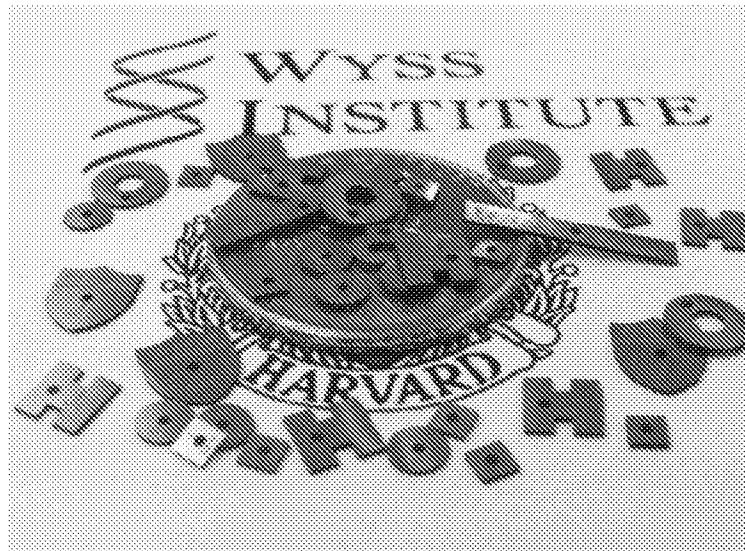


FIG. 15

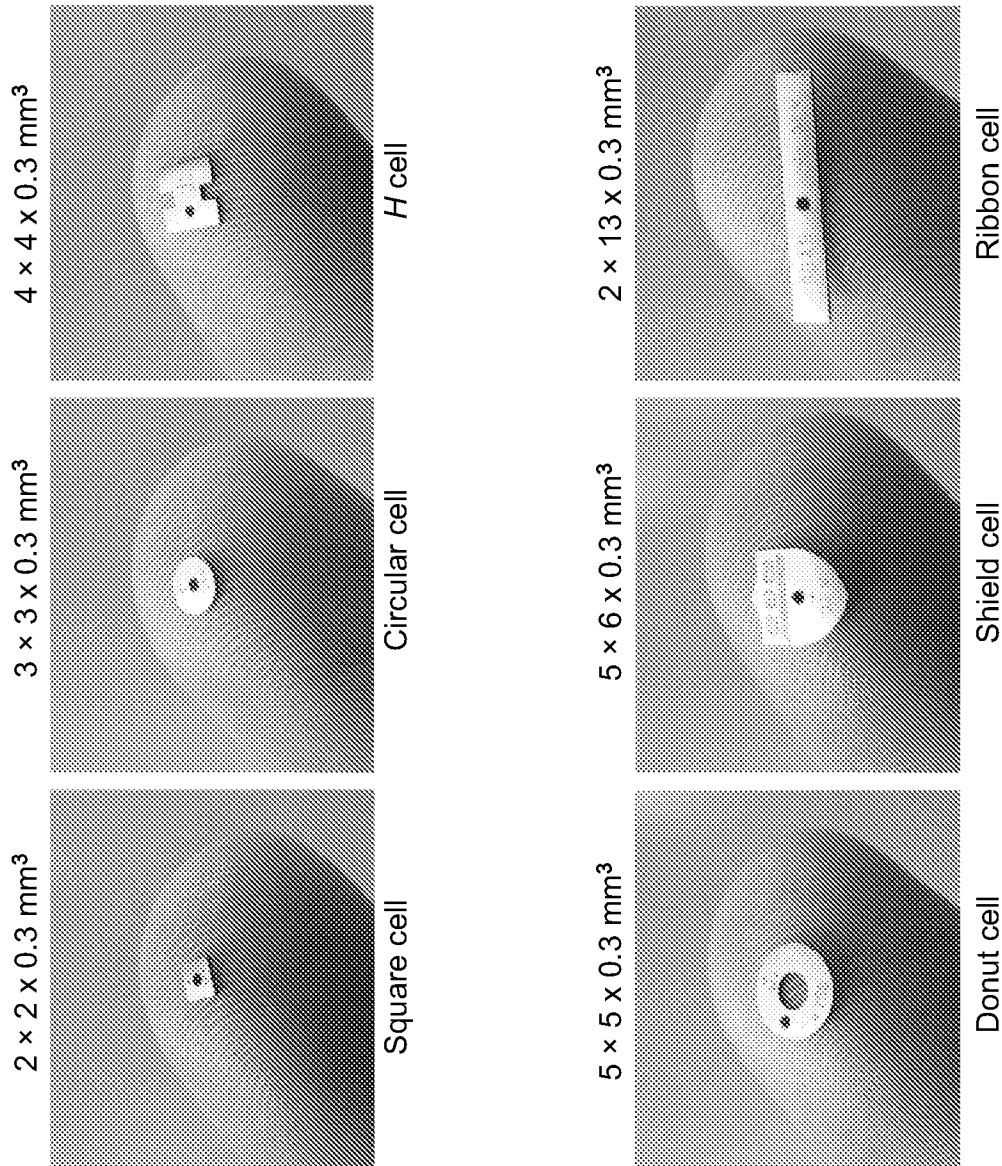


FIG. 16

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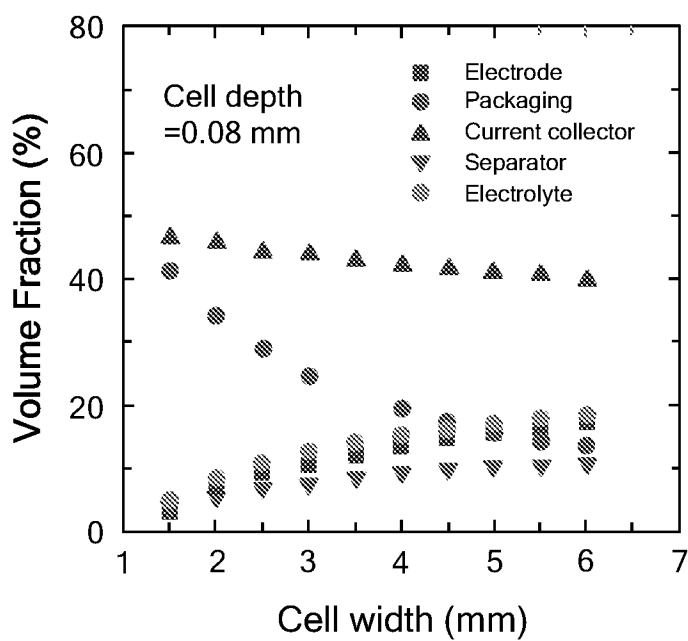
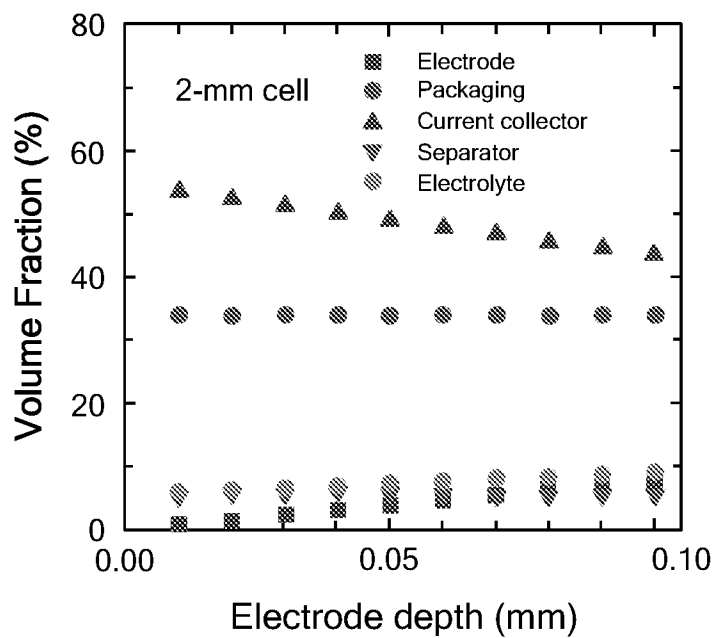


FIG. 17

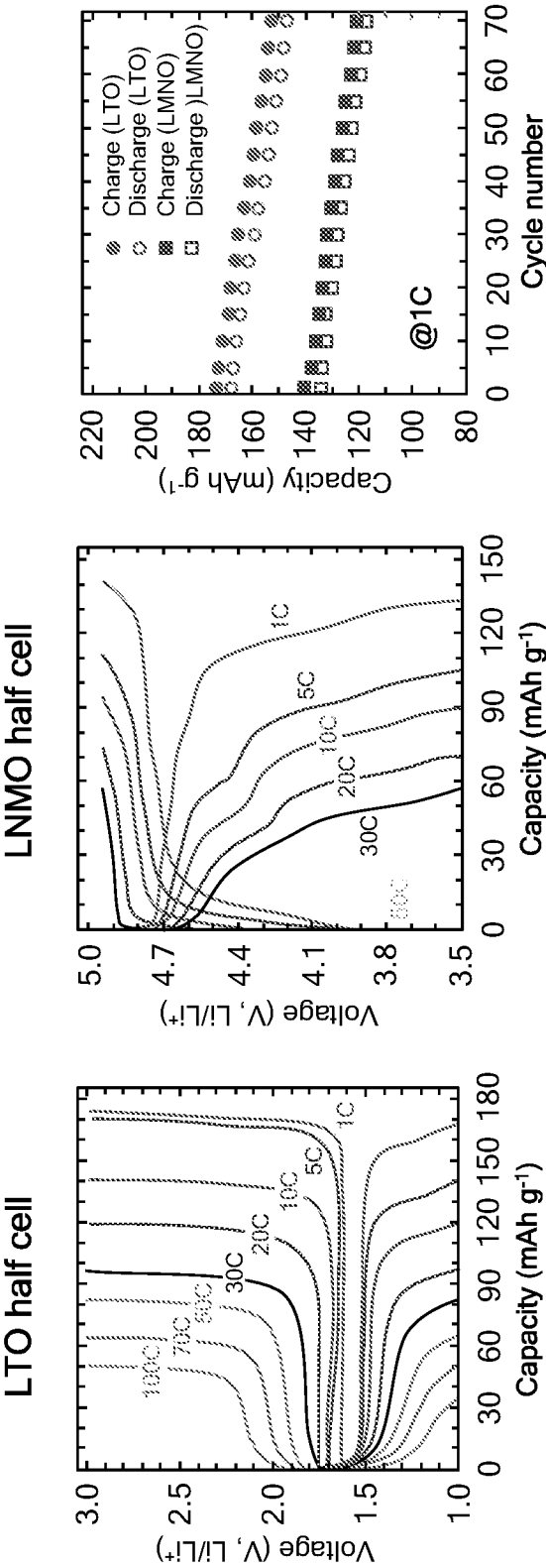


FIG. 18

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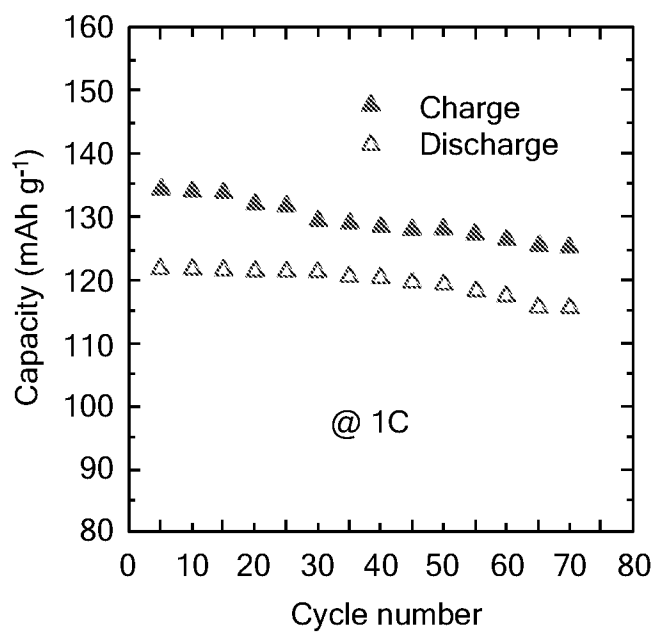
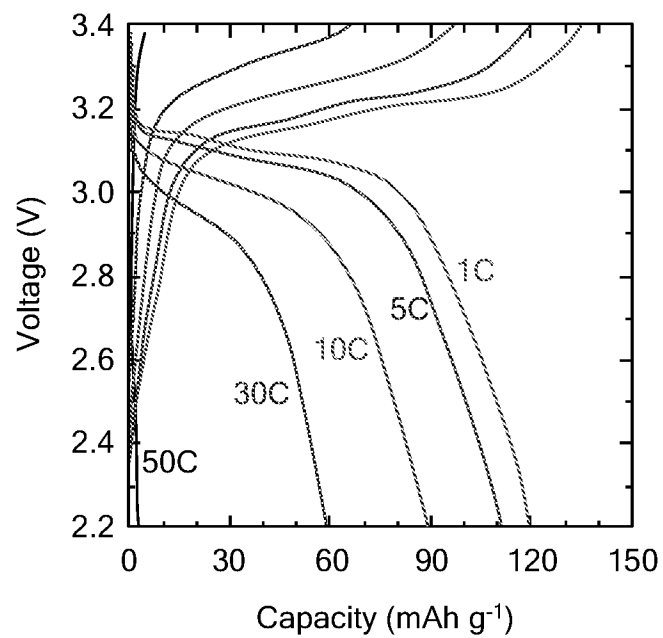
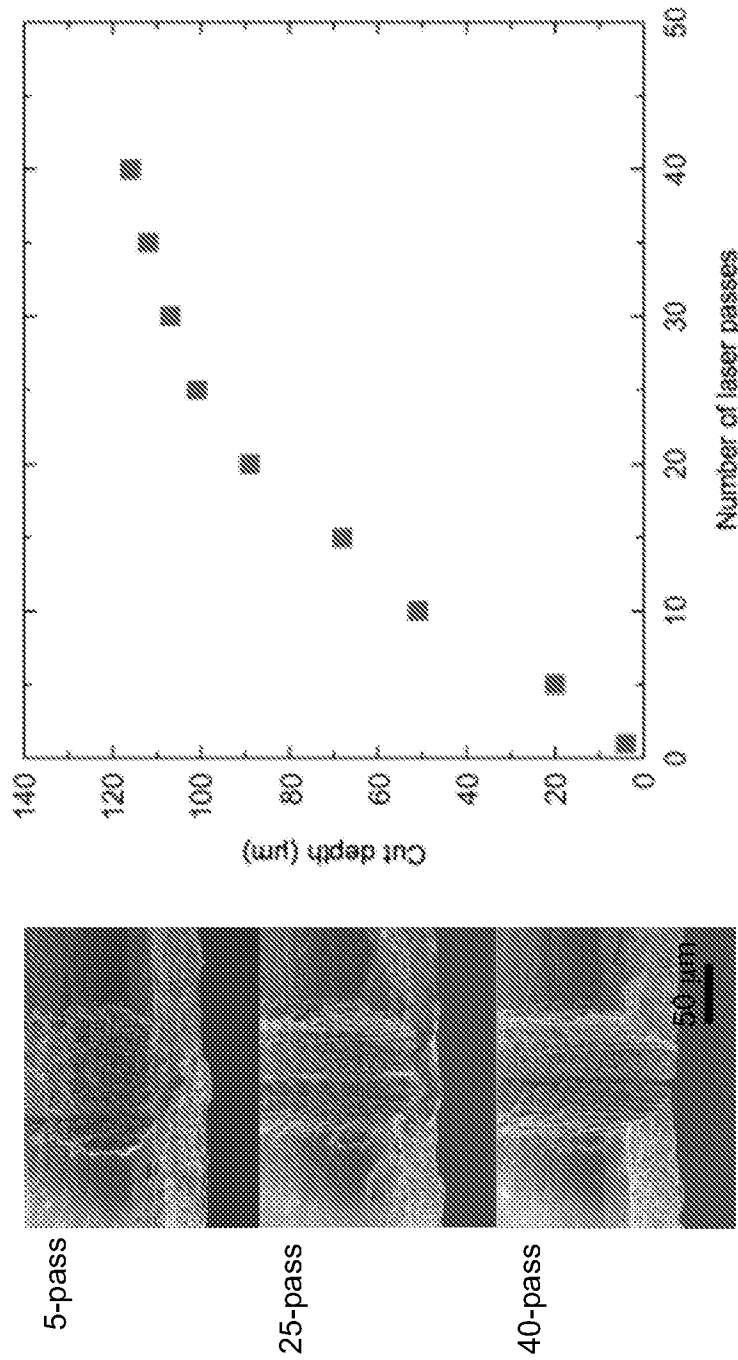


FIG. 19



Laser cut conditions: PWR 100%, 20 cm/sec, laser cut line-to-line spacing (2 μm)
Substrate is stainless steel sheet (127 μm thick)

FIG. 20

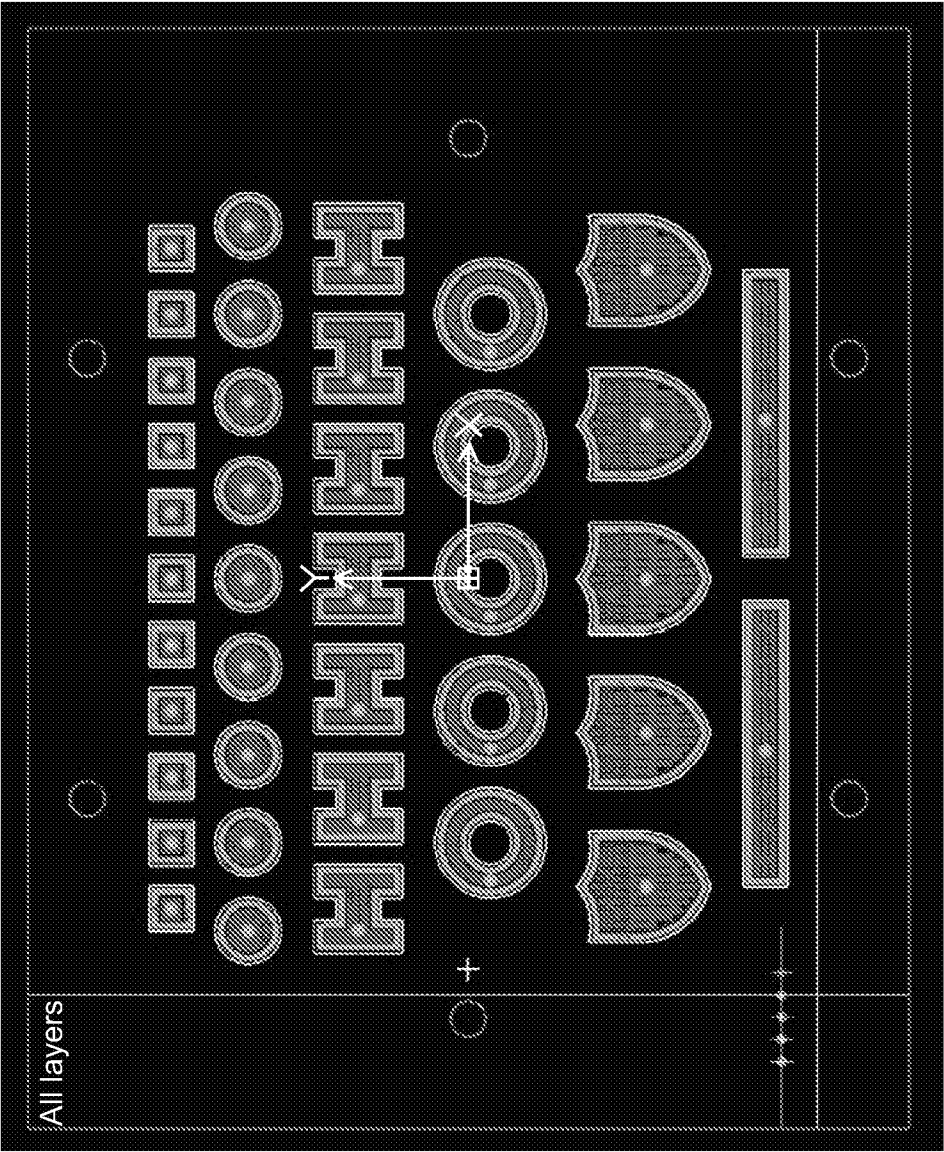


FIG. 21A

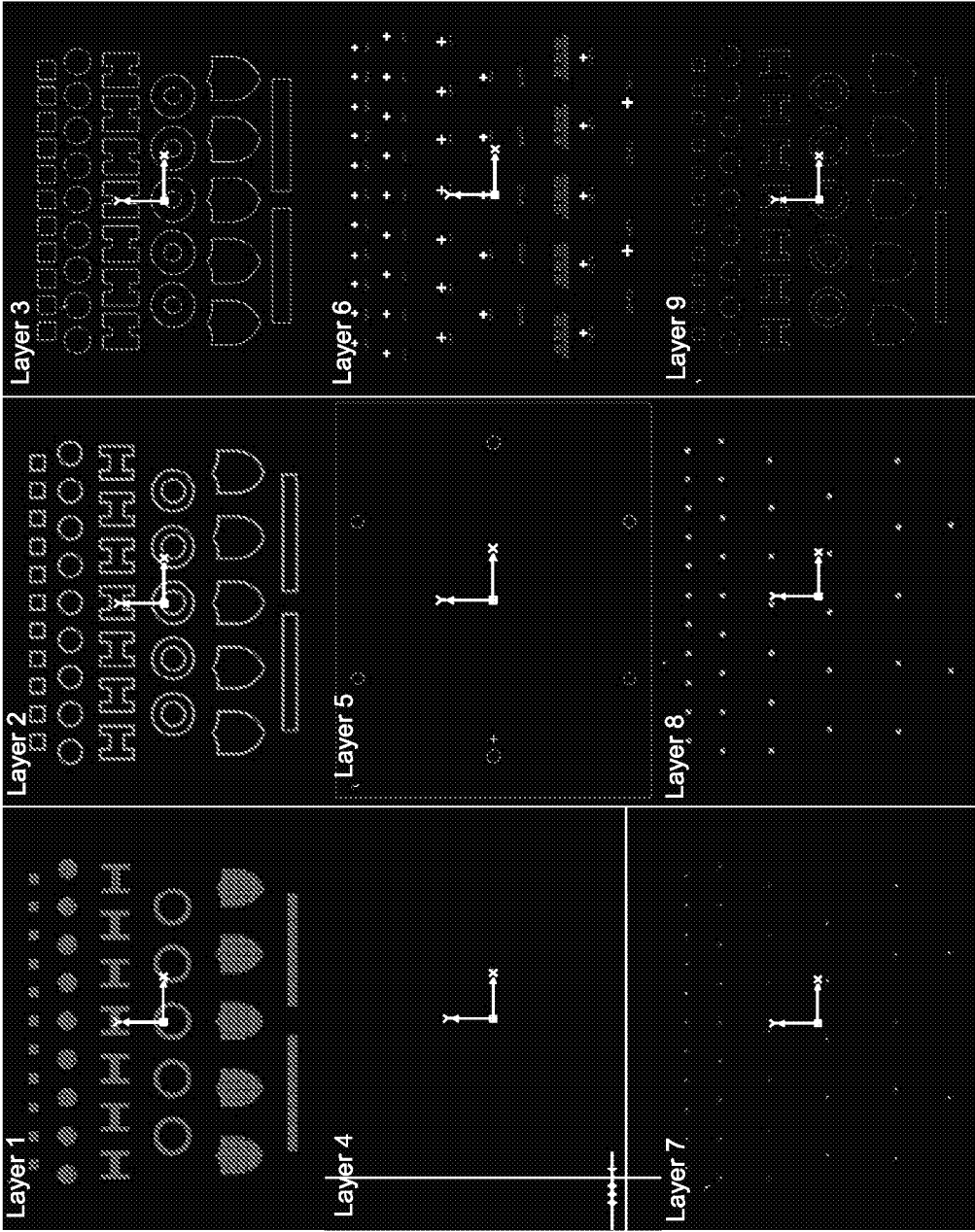


FIG. 21B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/021342

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/70, H01M 4/04, H01M 4/76, H01M 4/78, H01M 10/04, H01M 10/28, H01M 10/38 (2016.01)

CPC - H01M 4/70, H01M 4/0404, H01M 4/76, H01M 4/78, H01M 10/0436, H01M 10/126 (2016.02)

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)

IPC(8) - H01M 4/04, 4/70, 4/76, 4/78, 10/04, 10/28, 10/38 (2016.01)

CPC - H01M 4/0404, 4/70, 4/76, 4/78, 10/0436, 10/126, 10/283, 10/287 (2016.02)

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

USPC 29/873, 623.200, 623.100; 429/139, 163, 174, 180, 185, 209, 246, 517 (keyword delimited)

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

Orbit, Google Patents, Google Scholar

Search terms used: recharge, battery, microbattery, current collector, trench, channel, recess, seal, adhesive, surface roughness, electrode, hole

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 2013/0095381 A1 (OUKASSI et al) 18 April 2013 (18.04.2013) entire document	1, 3, 13
Y		2, 14, 15, 30-32
Y	US 2007/0031733 A1 (KOGETSU et al) 08 February 2007 (08.02.2007) entire document	2, 14, 15, 32
Y	US 2014/0199597 A1 (TAIWAN SEMICONDUCTOR MANUFACTURING CO., LTD) 17 July 2014 (17.07.2014) entire document	30-32
A	US 2011/0086246 A1 (FURUKAWA et al) 14 April 2011 (14.04.2011) entire document	1-3, 13-15, 30-32
A	US 2007/0134549 A1 (NATHAN et al) 14 June 2007 (14.06.2007) entire document	1-3, 13-15, 30-32

☐ 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 application or patent but 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	

Date of the actual completion of the international search

03 May 2016

Date of mailing of the international search report

11 MAY 2016

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/021342

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-12, 16-29, 33-61
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.