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(54) Title: STABLE METAL PLATING IN "ANODE-FREE" SOLID-STATE BATTERIES ENABLED BY SEEDED NUCLEATION

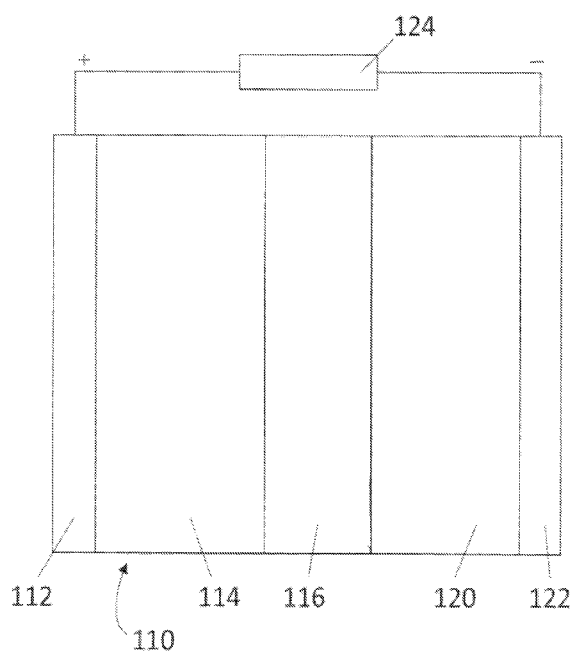


FIG. 1

(57) Abstract: A structure for making an electrochemical device is disclosed. The structure comprises a solid-state electrolyte material having a first surface comprising metal clusters, and a current collector in contact with the first surface of the solid-state electrolyte material. In one embodiment, the structure further comprises an electrode comprising an electroactive species, wherein the electrode is in contact with a second surface of the solid-state electrolyte material. The electroactive species can be electrodeposited on the solid current collector by passing formation current through the unformed structure. In the electrodeposition process, the electroactive species is depleted from the electrode and can be deposited onto the current collector. In one embodiment, after formation, an interfacial layer of the electrodeposited electroactive species can function as an anode of the electrochemical device and the electrode can function as a cathode of the electrochemical device.

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Stable Metal Plating In "Anode-Free" Solid-State Batteries Enabled By Seeded Nucleation

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application is based on, claims benefit of, and claims priority to U.S. Patent Application No. 63/426,817 filed on November 21, 2022, which is hereby incorporated by reference herein in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under Grant Number DGE 1841052 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0003] The invention relates to anode-free manufacturing in which a structure is fabricated with a bare current collector replacing the conventional anode, and a metal anode is then formed electrochemically on the first charge cycle by electroplating a metal contained within the cathode between a solid-state electrolyte and the current collector.

2. Description of the Related Art

[0004] Solid-state batteries (SSBs) show potential to offer higher energy densities than current state-of-the-art Li-ion batteries, while also alleviating safety concerns. For these energy density increases to be realized, it is necessary to utilize a thin (<25 μm) Li metal (Li^0) anode. Manufacturing of SSBs with thin Li metal anodes is complicated by the high reactivity of Li^0 , which forms a thin passivation layer even in controlled environments. The passivation layer on Li^0 also hinders the formation of a low-resistance interface between Li^0 and the solid-state electrolyte (SSE), which has been shown to impact Li^0 cycling performance. However, state-of-the-art cathodes such as NMC, NCA, and LFP are produced in the fully lithiated state, any Li^0 in the as-manufactured SSB will be excess and diminish the energy density. Therefore, it is highly desirable to manufacture " Li^0 -free" ('anode-free') SSBs to avoid handling of highly reactive Li^0 during manufacturing and as well as remove excess Li^0 in the cell. In " Li^0 -free" cells, the anode current collector (CC) is bare when the cell is assembled

until Li^0 is plated *in-situ* at the CC/SSE interface during the first charging step using stored Li from the cathode active material. The “ Li^0 -free” cell architecture could increase energy density above that of conventional SSBs by eliminating excess Li^0 as well as decreasing cell costs by simplifying the manufacturing process.

5 **[0005]** However, *in-situ* plating of the Li^0 anode comes with a myriad of challenges. One is the necessity to achieve intimate contact at the CC/SSE interface before the first *in-situ* plating step. Without conformal contact between the CC and SSE during plating, hot spots with amplified local current density will form, leading to short-circuiting of the cell. Thus far, all demonstrated “ Li^0 -free” cells rely on high
10 pressure or high temperature CC/SSE bonding steps.

[0006] Another obstacle to stable operation of “ Li^0 -free” cells is the growth morphology of the *in-situ* plated Li^0 anode. It has been shown that in “ Li^0 -free” cells, Li^0 forms isolated islands, which then grow and eventually merge to form a uniform film. However, it has been demonstrated that this island growth mode of Li^0 can lead
15 to fracture of the current collector, through which Li^0 may extrude and cause capacity loss.

[0007] Therefore, what is needed is an improved method for enabling stable lithium metal plating in cells without the requirement of current collector / solid-state electrolyte bonding wherein the method also prevents fracture of the current collector
20 during plating.

SUMMARY OF THE INVENTION

[0008] The present disclosure provides a structure for making an electrochemical device. The structure comprises a solid-state electrolyte material having a first surface comprising metal clusters, and a current collector in contact with the first
25 surface of the solid-state electrolyte material. In one embodiment, the structure further comprises an electrode comprising an electroactive species, wherein the electrode is in contact with a second surface of the solid-state electrolyte material. The electroactive species can be electrodeposited on the solid current collector by passing formation current through the unformed structure. In the electrodeposition
30 process, the electroactive species is depleted from the electrode and can be deposited onto the current collector at a formation current density between $1 \mu\text{A}/\text{cm}^2$

and 10 mA/cm². In one embodiment, after formation, an interfacial layer of the electrodeposited electroactive species can function as an anode of the electrochemical device and the electrode can function as a cathode of the electrochemical device.

5 **[0009]** The present disclosure also provides a method of making an electrochemical device. The method can comprise: (a) providing a solid-state electrolyte material having a first surface and a second surface; (b) forming metal clusters on the first surface of the solid-state electrolyte material to form a modified surface of the solid-state electrolyte material; (c) placing the modified surface of the solid-state electrolyte material in contact with a current collector; (d) placing the
10 second surface of the solid-state electrolyte material in contact with an electrode comprising an electroactive species to form a layered structure; and (e) passing a current through the layered structure to create an interfacial layer comprising the electroactive species between the solid-state electrolyte material and the current
15 collector, wherein the interfacial layer can function as an anode of the electrochemical device and the electrode can function as a cathode of the electrochemical device.

[0010] In one embodiment, the present invention provides a method of electrodeposition of an alkali metal on a solid-state electrolyte surface. The
20 homogeneous deposition of the alkali metal is enabled by heterogeneous nucleation sites on the solid-state electrolyte surface. Heterogeneous nucleation sites take the form of metal clusters, which are formed by sputtering the metal to produce a uniform layer and then annealing the sample to transform the uniform layer into a textured, clustered morphology. Without the annealing step to change the metal layer from
25 uniform to clustered, the homogeneous plating of the alkali metal is compromised (i.e., the cell short circuits). The solid-state electrolyte may comprise a lithium-ion conducting ceramic (e.g., LLZO) where the alkali metal deposited will be lithium, or the solid-state electrolyte may comprise a sodium-ion conducting ceramic (e.g., NASICON) where the alkali metal deposited is sodium. The clustered metal
30 interlayer on the solid-state electrolyte surface may be gold, silver, tin, aluminum, magnesium, silicon, zinc, bismuth, or germanium.

[0011] Applications of the present disclosure include, without limitation, a method for electrodeposition of alkali metal on a solid state electrolyte surface, and solid state electrolyte technology that can be used for the development of solid state batteries.

[0012] Advantages of the present disclosure include, without limitation, the use of a solid-state electrolyte instead of a liquid electrolyte; patterning is done directly on the electrolyte; and the pattern is formed through heat treatment.

[0013] These and other features, aspects, and advantages of the present disclosure will become better understood upon consideration of the following detailed description, drawings, and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 shows a schematic of a lithium metal battery.

[0015] FIG. 2 shows SEM images of Au-coated LLZO surface with Au layer deposited in panel (a) after heat-treatment (Au-Flat) and in panel (b) before heat-treatment (Au-Clusters), as well as AFM images of the LLZO surface with in panel (c) Au-Flat and in panel (d) Au-Clusters, where R_a is average roughness.

[0016] FIG. 3 shows in panel (a) a schematic of in situ Li plating in a cell with Au-Flat interlayer; in panel (b), a schematic of in situ Li plating in a cell with Au-Clusters interlayer; in panel (c), "Spalling"-type failure of LLZO after in situ Li plating of Au-Flat cell; in panel (d), Li islands formed on Au-coated LLZO surface upon initial in situ Li plating of Au-Clusters cell, in panel (e) a schematic showing hypothesized Cu/LLZO contact with Au-Flat leading to current focusing; in panel (f), a schematic showing hypothesized Cu/LLZO contact with Au-Clusters leading to distributed current; and in panel (g), potential response upon initial in situ plating for Au-Flat (red) and Au-Clusters (blue) cells. The sudden drop of polarization voltage for the Au-Flat cell, likely corresponding to short-circuiting, is marked by a red star. A blue star marks the charge passed for the Au-Clusters cell corresponding to the SEM image in panel d.

[0017] FIG. 4 shows in panel (a), a schematic of a cell with in situ plated Li metal electrode denoting the positions of center, middle, and edge used in FIB/SEM characterization; in panel (b), SEM of LLZO surface at 1%, 5% and 10% state-of-charge (SOC) during plating both in the center of the sample (i-iii) and the edge (iv-

vi); in panel (c), a cross-sectional SEM image after FIB milling of cell at 100% SOC in center of the sample showing position of Cu CC, in situ Li, and LLZO as seen in part d; and in panel (d), cross-sectional SEM images at 10%, 50%, and 100% SOC at center, middle, and edge positions of in situ plated Li. All scale bars in c are 50 μm .

5 **[0018]** FIG. 5 shows in panel (a), potential response during stripping of in situ plated Li, with inset showing polarization up to 1 V wherein each symbol (circle, square, triangle, diamond, and inverted triangle) represents a GEIS measurement superimposed during the DC stripping at 0.2 mA cm^{-2} ; in panel (b), GEIS spectra collected at the indicated points in a; in panel (c), ex situ cross-sectional SEM images
10 of the LLZO/in situ Li/Cu interface at the corresponding points to a and b wherein all scale bars in c are 50 μm ; and in panel (d), ex situ SEM of the LLZO surface after polarization to 1 V showing differing residual Li at center of sample vs edges.

[0019] FIG. 6 shows in panel (a), potential response during plating and stripping of in situ plated Li at 0.2 mA cm^{-2} and 60°C showing 97.4% recovery during stripping of
15 in situ plated Li; in panel (b), an inset of graph a showing potential response during in situ plating of Li upon initial cell assembly (black) and after plating 3.3 mAh cm^{-2} then stripping to 1 V polarization (red), where all plating and stripping was carried out at 0.2 mA cm^{-2} and 60°C; in panel (c), ex situ cross-sectional SEM images of the
20 LLZO/in situ Li/Cu interface after plating 3.3 mAh cm^{-2} , stripping to 1 V polarization, then re-plating 3.3 mAh cm^{-2} ; and in panel (d), cycling at 0.2 mA cm^{-2} with capacity 3.3 mAh cm^{-2} at 2.5 MPa and 60°C. Full CE data vs. cycle data is shown in Fig. 20.

[0020] FIG. 7 shows an AFM image of 3D height profile of Au coated glass slide.

[0021] FIG. 8 shows a voltage profile during plating for air exposed Au-Clusters cell compared to non-air exposed Au-Clusters cell.

25 **[0022]** FIG. 9 shows SEM images of the Au-coated LLZO surface heat treated at in panel (a), 400°C and in panel (b), 600°C. In panel (c), voltage profiles upon Li plating for the corresponding samples.

[0023] FIG. 10 shows in panel (a), SEM image of the Au-Flat sample with corresponding EDS mapping of panel (b), Au, and panel (c), O; in panel (d), SEM
30 image of the Au-Clusters sample in the center of the pellet with corresponding EDS mapping of panel (e), Au, and panel (f) O; and in panel (g), SEM image of the

Au-Clusters sample at the edge of the pellet with corresponding EDS mapping of panel (h), Au and panel (i), O.

[0024] FIG. 11 shows SEM images of LLZO surface with Au layer applied in panel (a), post-HT at center of LLZO sample, in panel (b), post-HT at edge of LLZO sample, in panel (c), pre-HT at center of LLZO sample, and in panel (d), pre-HT at edge of LLZO sample.

[0025] FIG. 12 shows XPS spectra of surface of in panel (a), Au-flat and in panel (b), Au-Clusters samples. Spectra were acquired at 3 different points on each sample.

[0026] FIG. 13 shows potential response upon *in situ* Li plating for Au-Clusters (blue) and Au-Flat (red) cells. Time $t = 0$ is defined as the onset of application of galvanostatic current. Prior to time $t = 0$, the cell was at open circuit conditions and the recorded potential is the open circuit potential.

[0027] FIG. 14 shows SEM images of Au-Flat cell after short-circuiting showing in panel (a), Li extruding from a crack on the LLZO surface, and in panel (b), FIB milled cross section of the crack pictured in panel (a).

[0028] FIG. 15 shows magnified image of the sample pictured in Fig. 4 panel bii at 5% SOC illustrating the morphology of the Li fracture surface with Au particles below.

[0029] FIG. 16 shows FIB cuts at varying locations for an *in situ* plated Li anode with capacity 3.3 mAh cm^{-2} .

[0030] FIG. 17 shows SEM/EDS of FIB-milled cross section of cell after *in situ* Li plating. EDS shows that the light phase in the *in situ* plated Li corresponds to an Au rich phase.

[0031] FIG. 18 shows cross-sectional SEM of sample shown in Figure 4 at 10% SOC at the edge of the sample, showing differing Au morphology in the *in situ* plated Li layer.

[0032] FIG. 19 shows a cross-sectional SEM of sample shown in Figure 5 showing detail of in panel (a), center of sample and in panel (b), middle of sample, where voids have formed.

[0033] FIG. 20 shows Coulombic efficiency versus cycle number for data shown in Figure 6 panel (d).

DETAILED DESCRIPTION OF THE INVENTION

[0034] Before the present invention is described in further detail, it is to be understood that the invention is not limited to the particular embodiments described. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The scope of the present invention will be limited only by the claims. As used herein, the singular forms "a", "an", and "the" include plural embodiments unless the context clearly dictates otherwise.

[0035] It should be apparent to those skilled in the art that many additional modifications beside those already described are possible without departing from the inventive concepts. In interpreting this disclosure, all terms should be interpreted in the broadest possible manner consistent with the context. Variations of the term "comprising", "including", or "having" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, so the referenced elements, components, or steps may be combined with other elements, components, or steps that are not expressly referenced. Embodiments referenced as "comprising", "including", or "having" certain elements are also contemplated as "consisting essentially of" and "consisting of" those elements, unless the context clearly dictates otherwise. It should be appreciated that aspects of the disclosure that are described with respect to a system are applicable to the methods, and vice versa, unless the context explicitly dictates otherwise.

[0036] As used herein, a "cell" or "electrochemical cell" is an electrochemical device that contains the electrodes and an electrolyte. As used herein, "electrochemical cells" are contemplated as being rechargeable cells, also referred to as secondary cells, unless the context clearly dictates otherwise. In an electrochemical cell or electrochemical device, the "anode" is defined as the electrode that undergoes oxidation, therefore losing electrons, during discharge. The "cathode" is defined as the electrode that undergoes reduction, therefore gaining electrons, during discharge. These electrochemical roles are reversed in an electrochemical cell or electrochemical device during the charging process, but the "anode" and "cathode" electrode designations herein remain the same. As used

herein, "formation" is the process that includes the step of charging of the battery for the first time. This charging may be accomplished using a "formation current". An "unformed" structure has not yet undergone the first charging of the "formation" process.

5 **[0037]** Numeric ranges disclosed herein are inclusive of their endpoints. For example, a numeric range of between 1 and 10 includes the values 1 and 10. When a series of numeric ranges are disclosed for a given value, the present disclosure expressly contemplates ranges including all combinations of the upper and lower bounds of those ranges. For example, a numeric range of between 1 and 10 or
10 between 2 and 9 is intended to include the numeric ranges of between 1 and 9 and between 2 and 10.

15 **[0038]** One embodiment of a method of the invention allows for anode-free manufacturing in which an unformed structure is fabricated with a bare current collector replacing the conventional anode, and a metal anode is then formed electrochemically on the first charge cycle by electroplating a metal contained within the cathode between a solid-state electrolyte and the current collector using a formation current.

20 **[0039]** Figure 1 shows a non-limiting example of a lithium metal battery 110 that may be manufactured using an embodiment of the present disclosure. The lithium metal battery 110 of Figure 1 includes a first current collector 112 (i.e., aluminum) in contact with a cathode 114. A solid-state electrolyte 116 is arranged between the cathode 114 and an anode 120, which is in contact with a second current collector 122 (i.e., copper). The first current collector 112 and the second current collector 122 of the lithium metal battery 110 may be in electrical communication with an electrical
25 component 124. The electrical component 124 could place the lithium metal battery 110 in electrical communication with an electrical load that discharges the battery or a charger that charges the battery.

30 **[0040]** The first current collector 112 and the second current collector 122 can comprise a conductive metal or any suitable conductive material. In some embodiments, the first current collector 112 and the second current collector 122 may be a single material comprising a metal or a metal alloy. If a single material, the first

current collector 112 and the second current collector 122 can comprise a material selected from the group consisting of nickel, molybdenum, titanium, zirconium, tantalum, alloy steel, stainless steel, nickel based super alloys (e.g., Inconel), cobalt based super alloys, copper, iron, aluminum, or mixtures, combinations and alloys thereof. In some embodiments, the first current collector 112 and the second current collector 122 have a thickness between 1 nanometer and 100 micrometers, between 10 nanometers and 60 micrometers, or between 900 nanometers and 25 micrometers. It is to be appreciated that the thicknesses depicted in Figure 1 are not drawn to scale. Further, it is to be appreciated that the thickness of the first current collector 112 and the second current collector 122 may be different.

[0041] In some embodiments, a suitable cathode 114 of the lithium metal battery 110 is a lithium host material capable of storing and subsequently releasing lithium ions. An example cathode active material is a lithium metal oxide wherein the metal is one or more aluminum, cobalt, iron, manganese, nickel and vanadium. Non-limiting example lithium metal oxides are LiCoO_2 (LCO), LiFeO_2 , LiMnO_2 (LMO), LiMn_2O_4 , LiNiO_2 (LNO), $\text{LiNi}_x\text{Co}_y\text{O}_2$, $\text{LiMn}_x\text{Co}_y\text{O}_2$, $\text{LiMn}_x\text{Ni}_y\text{O}_2$, $\text{LiMn}_x\text{Ni}_y\text{O}_4$, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and others. Another example cathode active material is a lithium-containing phosphate having a general formula LiMPO_4 wherein M is one or more of cobalt, iron, manganese, and nickel, such as lithium iron phosphate (LFP) and lithium iron fluorophosphates. Another example cathode active material is a cathode active material having a formula $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, wherein $x+y+z = 1$ and $x:y:z = 1:1:1$ (NMC 111), $x:y:z = 4:3:3$ (NMC 433), $x:y:z = 5:2:2$ (NMC 522), $x:y:z = 5:3:2$ (NMC 532), $x:y:z = 6:2:2$ (NMC 622), or $x:y:z = 8:1:1$ (NMC 811). Many different elements, e.g., Co, Mn, Ni, Cr, Al, or Li, may be substituted or additionally added into the structure to influence electronic conductivity, ordering of the layer, stability on delithiation and cycling performance of the cathode materials. The cathode active material can be a mixture of any number of these cathode active materials. In other embodiments, a suitable material for the cathode 114 of the lithium metal battery 110 is porous carbon (for a lithium air battery), or a sulfur containing material (for a lithium sulfur battery). The cathode 114 may have a

thickness between 1 nanometer and 100 micrometers, between 10 nanometers and 50 micrometers, or between 100 nanometers and 10 micrometers

[0042] In some embodiments, a suitable anode 120 of the lithium metal battery 110 consists of *in situ* formed (e.g., electroplated) lithium metal. Another example anode 120 material consists essentially of *in situ* formed lithium metal. In other embodiments, a suitable anode 120 consists of *in situ* formed magnesium, sodium, or zinc metal. In other embodiments, a suitable anode 120 consists essentially of *in situ* formed magnesium, sodium, or zinc metal.

[0043] An example solid-state electrolyte 116 material for the lithium metal battery 110 can include any suitable solid electrolyte capable of conducting metal ions. For example, the solid-state electrolyte may be lithium phosphorous oxynitride (LiPON). The solid-state electrolyte may be an oxide based garnet such as lithium lanthanum zirconium oxide (LLZO), aluminum doped LLZO, gallium doped LLZO, niobium doped LLZO, or tantalum doped LLZO. The solid-state electrolyte may be a sodium super ionic conductor (NaSICON) such as lithium aluminum titanium phosphate (LATP). The solid-state electrolyte may be lithium super ionic conductor (LiSICON). The solid-state electrolyte may be a thio-LISICON. The solid-state electrolyte may be lithium aluminum germanium phosphate (LAGP). The solid-state electrolyte may be sulfide glass such as lithium phosphorous sulfide (LPS). The solid-state electrolyte may be sodium- β -alumina or sodium- β' -alumina. The solid-state electrolyte may be a polymer such as polyethylene oxide (PEO), polyacrylonitrile (PAN), or a crystalline thermoplastic polymer. The solid-state electrolyte may comprise a mixture of any of the electrolytes listed above. The solid-state electrolyte may have a thickness between 1 nanometer and 100 micrometers, between 100 nanometers and 50 micrometers, or between 1 micrometer and 25 micrometers.

[0044] In another embodiment of the lithium metal battery 110, the solid-state electrolyte 116 for the lithium metal battery 110 comprises a ceramic material having a formula of $\text{Li}_w\text{A}_x\text{M}_2\text{Re}_{3-y}\text{O}_z$,

wherein w is 5 – 7.5,

wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr, Ba, and any combination thereof,

wherein x is 0 – 2,

wherein M is selected from Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te, and any combination thereof,

wherein Re is selected from lanthanide elements, actinide elements, and any combination thereof,

wherein y is 0 – 0.75,

wherein z is 10.875 – 13.125, and

wherein the ceramic material has a garnet-type or garnet-like crystal structure.

In some embodiments of the solid-state electrolyte 116, M is Zr and A is Al and x is not 0, or M is Zr and A is Ga and x is not 0, or M is a combination of Zr and Ta. In one embodiment, the solid-state electrolyte comprises $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$.

[0045] As part of an anode-free method for manufacturing the lithium metal battery 110, we disclose a method of electrodepositing an electroactive species that utilizes a formation current to form films at a solid current collector/solid electrolyte interface in a layered structure comprising a current collector in contact with a solid-state electrolyte material having a modified surface and a second surface which is in contact with an electrode comprising an electroactive species. The current collector can be the current collector 122 of the lithium metal battery 110. The current collector 122 can be electrochemically blocking to the electroactive species. The term "blocking" as used herein can refer to a current collector comprising a material with sufficiently low electroactive species solubility as determined by the thermodynamic phase diagrams such that the material can be considered non-reactive with the electroactive species. The solid electrolyte can be the solid-state electrolyte 116 of the lithium metal battery 110. The electrode can be a lithiated cathode 114 of the lithium metal battery 110. The electroactive species can be lithium. The modified surface of the solid-state electrolyte material may be in contact with the current collector. The modified surface of the solid-state electrolyte material includes metal clusters formed on the first surface of the solid-state electrolyte material to form the modified surface of the solid-state electrolyte material. In one embodiment of the method, the modified surface of the solid-state electrolyte material

has an average roughness in a range of 10 nanometers to 200 nanometers, or in a range of 10 nanometers to 100 nanometers.

[0046] The present invention provides a structure for making an electrochemical device. The structure comprises a solid-state electrolyte material having a first surface comprising metal clusters, and a current collector in contact with the first surface of the solid-state electrolyte material. In one embodiment, the structure further comprises an electrode comprising an electroactive species, wherein the electrode is in contact with a second surface of the solid-state electrolyte material. The structure is unformed, and the electroactive species can be electrodeposited on the solid current collector by passing current through the structure. In the electrodeposition process, the electroactive species is depleted from the electrode and can be deposited onto the current collector at a formation current density between $1 \mu\text{A}/\text{cm}^2$ and $10 \text{ mA}/\text{cm}^2$. In one embodiment, after formation, an interfacial layer of the electrodeposited electroactive species can function as an anode of the electrochemical device and the electrode can function as a cathode of the electrochemical device.

[0047] In one embodiment of the structure, the metal clusters comprise a metal selected from the group consisting of gold, silver, tin, aluminum, magnesium, silicon, zinc, bismuth, germanium, and mixtures thereof. The metal clusters can comprise gold. By a cluster, we mean a discrete particle which may be flat or have sphere-like morphology. The cluster may range in diameter from $1 \text{ nm} - 100 \mu\text{m}$, and range in height from $1 \text{ nm} - 100 \mu\text{m}$. The cluster may range in diameter from $1 \text{ nm} - 100 \mu\text{m}$, and range in height from $1 \text{ nm} - 1000 \text{ nm}$.

[0048] In one embodiment of the structure, the current collector comprises a single material comprising a metal or a metal alloy. The current collector can comprise a material selected from the group consisting of nickel, molybdenum, titanium, zirconium, tantalum, alloy steel, stainless steel, nickel based super alloys, cobalt based super alloys, copper, aluminum, iron, or mixtures thereof.

[0049] In one embodiment of the structure, the current collector has a thickness between 1 nanometer and 100 micrometers.

[0050] In one embodiment of the structure, the solid-state electrolyte material comprises a material selected from the group consisting of lithium phosphorous oxynitride (LiPON), oxide based garnets, sodium super ionic conductors (NaSICON), lithium super ionic conductors (LiSICON), thio-LiSICONs, sulfide glass, argyrodite sulfide, polymers, or mixtures thereof.

[0051] In one embodiment of the structure, the solid-state electrolyte material is selected from the group consisting of lithium lanthanum zirconium oxide (LLZO), aluminum doped LLZO, gallium doped LLZO, niobium doped LLZO, tantalum doped LLZO, lithium aluminum titanium phosphate (LATP), lithium aluminum germanium phosphate (LAGP), lithium phosphorous sulfide (LPS), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), crystalline thermoplastic polymers, alkali metal cation-alumina, metal halides, or mixtures thereof.

[0052] In one embodiment of the structure, the solid-state electrolyte material comprises lithium lanthanum zirconium oxide (LLZO) or a derivative thereof.

[0053] In one embodiment of the structure, the solid-state electrolyte material comprises a ceramic material having a formula of $\text{Li}_w\text{A}_x\text{M}_z\text{Re}_{3-y}\text{O}_z$,

wherein w is 5 – 7.5,

wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr, Ba, and any combination thereof,

wherein x is 0 – 2,

wherein M is selected from Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te, and any combination thereof,

wherein Re is selected from lanthanide elements, actinide elements, and any combination thereof,

wherein y is 0 – 0.75,

wherein z is 10.875 – 13.125, and

wherein the ceramic material has a garnet-type or garnet-like crystal structure.

In one embodiment, M is a combination of Zr and Ta. In one embodiment, M is Zr, and A is Al, and x is not 0. In one embodiment, M is Zr, and A is Ga, and x is not 0.

[0054] In one embodiment of the structure, the solid-state electrolyte material is sodium- β -alumina and/or sodium- β'' -alumina.

[0055] In one embodiment of the structure, the solid-state electrolyte material has a thickness between 1 nanometer and 100 micrometers.

[0056] In one embodiment of the structure, the current collector is electrochemically blocking to the electroactive species.

5 **[0057]** In one embodiment of the structure, the electroactive species comprises an alkali metal. The electroactive species can comprise lithium. The electroactive species can comprise sodium.

10 **[0058]** In one embodiment of the structure, the electrode comprises a lithium host material is selected from the group consisting of (i) lithium metal oxides wherein the metal is one or more of aluminum, cobalt, iron, manganese, nickel and vanadium, and (ii) lithium-containing phosphates having a general formula LiMPO_4 wherein M is one or more of cobalt, iron, manganese, and nickel.

15 **[0059]** The present invention also provides a method of making an electrochemical device. The method can comprise: (a) providing a solid-state electrolyte material having a first surface and a second surface; (b) forming metal clusters on the first surface of the solid-state electrolyte material to form a modified surface of the solid-state electrolyte material; (c) placing the modified surface of the solid-state electrolyte material in contact with a current collector; (d) placing the second surface of the solid-state electrolyte material in contact with an electrode
20 comprising an electroactive species to form a layered structure; and (e) passing a current through the layered structure to create an interfacial layer comprising the electroactive species between the solid-state electrolyte material and the current collector, the interfacial layer functioning as an anode of the electrochemical device and the electrode functioning as a cathode of the electrochemical device. In one
25 embodiment of the method, passing the current through the layered structure is without conformal contact between the current collector and the solid-state electrolyte material. In one embodiment of the method, placing the second surface of the solid-state electrolyte material in contact with an electrode does not include a lamination step.

30 **[0060]** In one embodiment of the method, step (a) further comprises heat treating the solid-state electrolyte material at a temperature between 100°C and 700°C. In

one embodiment of the method, step (e) further comprises applying a pressure between 0.1 MPa and 10 MPa to the layered structure. In one embodiment of the method, step (e) further comprises applying pressure between 0.1 MPa and 10 MPa at a temperature between 25°C and 100°C to layered structure.

5 **[0061]** In one embodiment of the method, step (b) comprises sputtering a metal on the first surface of the solid-state electrolyte material to produce a uniform layer of the metal and annealing the uniform layer to transform the uniform layer into the metal clusters. Annealing the uniform layer can be performed at an annealing temperature below a melting point of the metal. Annealing the uniform layer can be performed at an annealing temperature between 100°C and 700°C, or between 10 300°C and 500°C in an inert atmosphere. The uniform layer can have a thickness between 1 and 1000 nanometers.

[0062] In one embodiment of the method, the metal clusters comprise a metal selected from the group consisting of gold, silver, tin, aluminum, magnesium, silicon, 15 zinc, bismuth, germanium, and mixtures thereof. The metal clusters can comprise gold.

[0063] In one embodiment of the method, the current collector comprises a single material comprising a metal or a metal alloy. In one embodiment of the method, the current collector comprises a material selected from the group consisting of nickel, 20 molybdenum, titanium, zirconium, tantalum, alloy steel, stainless steel, nickel based super alloys, cobalt based super alloys, copper, aluminum, iron, or mixtures thereof.

[0064] In one embodiment of the method, the current collector has a thickness between 1 nanometer and 100 micrometers.

25 **[0065]** In one embodiment of the method, the solid-state electrolyte material comprises a material selected from the group consisting of lithium phosphorous oxynitride (LiPON), oxide based garnets, sodium super ionic conductors (NaSICON), lithium super ionic conductors (LiSICON), thio-LiSICONs, sulfide glass, argyrodite-sulfide, polymers, or mixtures thereof. In one embodiment of the method, the solid-state electrolyte material is selected from the group consisting of lithium 30 lanthanum zirconium oxide (LLZO), aluminum doped LLZO, gallium doped LLZO, niobium doped LLZO, tantalum doped LLZO, lithium aluminum titanium phosphate

(LATP), lithium aluminum germanium phosphate (LAGP), lithium phosphorous sulfide (LPS), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), crystalline thermoplastic polymers, alkali metal cation-alumina, metal halides, or mixtures thereof. In one embodiment of the method, the solid-state electrolyte material comprises lithium lanthanum zirconium oxide (LLZO) or a derivative thereof.

[0066] In one embodiment of the method, the solid-state electrolyte material comprises a ceramic material having a formula of $\text{Li}_w\text{A}_x\text{M}_2\text{Re}_{3-y}\text{O}_z$,

wherein w is 5 – 7.5,

wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr, Ba, and any combination thereof,

wherein x is 0 – 2,

wherein M is selected from Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te, and any combination thereof,

wherein Re is selected from lanthanide elements, actinide elements, and any combination thereof,

wherein y is 0 – 0.75,

wherein z is 10.875 – 13.125, and

wherein the ceramic material has a garnet-type or garnet-like crystal structure.

In one embodiment, M is a combination of Zr and Ta. In one embodiment, M is Zr, and A is Al, and x is not 0. In one embodiment, M is Zr, and A is Ga, and x is not 0.

[0067] In one embodiment of the method, the solid-state electrolyte material is sodium- β -alumina and/or sodium- β'' -alumina.

[0068] In one embodiment of the method, the solid-state electrolyte material has a thickness between 1 nanometer and 100 micrometers.

[0069] In one embodiment of the method, the current collector is electrochemically blocking to the electroactive species.

[0070] In one embodiment of the method, the interfacial layer comprises a single material comprising a metal or a metal alloy. In one embodiment of the method, the interfacial layer comprises a material selected from the group consisting of lithium, sodium, silver, magnesium, silicon, zinc, bismuth, germanium, calcium, cobalt, iron, potassium, copper, gold, tin, aluminum, or alloys thereof, or mixtures thereof.

[0071] In one embodiment of the method, the interfacial layer comprises an alkali metal. The interfacial layer can comprise lithium. The interfacial layer can comprise sodium.

[0072] In one embodiment of the method, the electrode comprises a lithium host material is selected from the group consisting of (i) lithium metal oxides wherein the metal is one or more of aluminum, cobalt, iron, manganese, nickel and vanadium, and (ii) lithium-containing phosphates having a general formula LiMPO_4 wherein M is one or more of cobalt, iron, manganese, and nickel.

[0073] In one embodiment of the method, no dendrite penetration into the solid electrolyte material occurs during passing a current through the layered structure. In one embodiment of the method, passing the current through the layered structure is at current between $1 \mu\text{A}/\text{cm}^2$ and $10 \text{ mA}/\text{cm}^2$.

[0074] The interfacial layer can have a uniform thickness after passing a current through the layered structure. After passing a current through the layered structure, the interfacial layer can have complete surface contact with the solid-state electrolyte material. The interfacial layer can have a thickness between 1 nanometer and 100 micrometers. The interfacial layer can have a surface coverage of 5% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 70% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 80% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 85% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 90% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 95% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 97% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 98% or greater with the solid-state electrolyte material. The interfacial layer can have a surface coverage of 99% or greater with the solid-state electrolyte material.

[0075] In one aspect, the pressure can be applied to the layered structure at a pressure between 0.1 and 10 MPa, or between 0.2 and 10 MPa, or between 0.4 and 10 MPa, or between 0.6 and 10 MPa, or between 0.8 and 10 MPa, or between 1 and

10 MPa, or between 1.2 and 10 MPa, or between 1.4 and 10 MPa, or between 1.6 and 10 MPa, or between 1.8 and 10 MPa, or between 2 and 10 MPa, or between 0.1 and 5 MPa, or between 0.1 and 2 MPa, or between 0.1 and 1.8 MPa, or between 0.1 and 1.6 MPa, or between 0.1 and 1.4 MPa, or between 0.1 and 1.2 MPa, or between 0.1 and 1 MPa, or another range suitable for pressing the layered structure.

[0076] In one aspect, the layered structure can be pressed at a temperature between 25°C and 100°C, or between 50°C and 100°C, or another range suitable for pressing the layered structure.

[0077] In one embodiment of the method, the electroactive species comprises an alkali metal. In one embodiment of the method, the electroactive species comprises lithium. In one embodiment of the method, the electroactive species comprises sodium. In one embodiment of the method, the method eliminates nucleation overpotential for the electroactive species when creating the interfacial layer.

EXAMPLE

[0078] The following Example is provided in order to demonstrate and further illustrate certain embodiments and aspects of the present invention and is not to be construed as limiting the scope of the invention. The statements provided in the Example are presented without being bound by theory.

[0079] In this Example, we demonstrate stable lithium plating in “Li⁰-free” solid-state batteries enabled by seeded nucleation.

1a. Overview

[0080] In the “Li⁰-free” architecture, cells are manufactured with a bare anode current collector and the Li metal anode is plated in situ during the first charging step. While this architecture has many attractive qualities from manufacturing and energy density perspectives, stable Li plating in solid-state “Li⁰-free” cells can be challenging. It is generally accepted that the Li overpotential affects Li homogeneity in “Li⁰-free” cells. We demonstrate that the nucleation overpotential for Li plating in solid-state “Li⁰-free” cells using commercial current collectors can be eliminated by introducing metal clusters that guide Li nucleation. Au is used as model alloying metal cluster. Here, we demonstrate stable Li plating with thickness 16.5 μm (3.3 mAh cm⁻²) in oxide solid-state electrolyte “Li⁰-free” cells enabled by Au metal

clusters. It is shown that 97% of the in situ plated Li can be reversibly stripped at 60°C and 2.5 MPa. Conversely, Au interlayers which are flat and continuous instead of clustered in morphology consistently showed short-circuiting during in situ Li plating, limiting Li electrodeposition to $<0.1 \text{ mAh cm}^{-2}$. These results can help guide future studies of Li nucleation and growth at solid/solid interfaces, as well as offer alternative manufacturing pathways for “Li⁰-free” solid-state batteries.

1b. Introduction

[0081] Solid-state batteries (SSBs) have potential to offer higher energy densities than current state-of-the-art Li-ion batteries, while also alleviating safety concerns [Ref. 1–3]. For these energy density increases to be realized, a thin ($<25 \text{ }\mu\text{m}$) Li metal anode is required [Ref. 4]. Manufacturing of SSBs with thin Li metal anodes is complicated by the high reactivity of Li, which forms a thin passivation layer even in controlled environments [Ref. 5]. The passivation layer on Li also hinders the formation of a low-resistance interface between Li and the solid-state electrolyte (SSE), which has been shown to impact cell cycling performance [Ref. 6–8]. However, state-of-the-art cathodes like $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ are produced in the fully lithiated state, so any Li metal in the as-manufactured SSB will diminish the energy density [Ref. 9]. Therefore, it is highly desirable to manufacture “Li⁰-free” (“anode-free”) SSBs to avoid handling of highly reactive Li during manufacturing as well as remove excess Li in the cell. In “Li⁰-free” cells, the anode current collector (CC) is bare when the cell is assembled. Then, Li is plated in situ at the CC/SSE interface during the first charging step using stored Li from the cathode active material [Ref. 10,11]. The “Li⁰-free” cell architecture could increase energy density above that of conventional SSBs by eliminating excess Li as well as decrease cell costs by simplifying the manufacturing process [Ref. 11–13].

[0082] Wang *et al.* first demonstrated uniform in situ Li deposition and cycling in the solid-state system using a bare Cu CC, showing a high Coulombic efficiency of 99% [Ref. 14]. However, in situ plating of the Li anode comes with a myriad of challenges [Ref. 15,16]. One is the necessity to achieve intimate contact at the CC/SSE interface before in situ plating. Without conformal CC/SSE contact during plating, hot spots with amplified local current density may form, leading to short-

circuiting of the cell. Thus far, all demonstrated “Li⁰-free” cells rely on high pressure or temperature CC/SSE interface formation steps. “Li⁰-free” cells with the relatively soft SSE Li₆PS₅Cl utilize high- pressure pre-forming steps (225–520 MPa) and/or high-pressure cycling to maintain CC/SSE contact [Ref. 17–19]. However, the garnet Li₇La₃Zr₂O₁₂ (LLZO) SSE cannot be deformed easily at room temperature, so LLZO “Li⁰-free” cells require high-temperature (900°C) CC/SSE lamination [Ref. 14,15,20]. High pressure or temperature CC/SSE interface formation steps increase the complexity of “Li⁰-free” cell manufacturing and may chemically bond the CC to the SSE, which could affect the Li nucleation overpotential and therefore the homogeneity of plated Li.

[0083] Lowering the Li nucleation overpotential has been identified as an important endeavor to enable uniform Li plating in “Li⁰-free” cells [Ref. 21]. The work of Lee *et al.* on “Li⁰-free” SSBs hypothesized that decreasing the nucleation overpotential of Li both enables stable Li plating and improves the uniformity of Li deposition [Ref. 17]. In that study, a 10 μm Ag-C layer was interposed between the sulfide SSE and CC before performing warm isostatic pressing at 490 MPa to improve interfacial contact. Although it was theorized that the solubility of Ag with Li reduced the nucleation overpotential, the exact change in overpotential was not quantified by analyzing the voltage profile during Li electrodeposition. The Li nucleation overpotential is observed in the voltage profile when the voltage first goes below 0 V, then through a minima before reaching a higher steady-state value [Ref. 22,23]. This phenomenon has been well-studied in liquid electrolyte systems with varying interlayers imposed on CCs by Yan *et al.* [Ref. 24]. Common CC materials like Cu and Ni, which are insoluble with Li, show a distinct nucleation overpotential similar to what is observed in solid-state “Li⁰-free” cells with Cu or Ni CCs. Interlayers which can alloy with Li, including Ag and Au, were shown to have no nucleation overpotential for Li plating in liquid electrolyte cells. Yan *et al.* also showed that Au could be patterned on the CC to control the nucleation of Li and act as a seed for Li growth. While the effect of alloying interlayers on Li nucleation has been well-studied in conventional liquid-electrolyte systems, less is understood about the role of alloying interlayers in solid-state “Li⁰-free” cells. Both Kim *et al.*

and Krauskopf *et al.* investigated the role of alloy interlayers in the solid-state system using Au coated LLZO [Ref. 22,25]. These studies concur that Au interlayers are effective in reducing the nucleation overpotential for Li plating but did not address other factors that may contribute to the nucleation over-potential in solid-state systems. Another study using sulfide electrolyte “Li⁰-free” cells showed that a Te coating on the Cu CC could lower, but not eliminate, the nucleation overpotential [Ref. 19]. Importantly, mechanical contributions from the de-bonding of the CC/SSE interface are also expected to contribute to the nucleation overpotential in solid-state “Li⁰-free” cells [Ref. 14,15]. Therefore, it is desirable to eliminate the high pressure/temperature CC/SSE formation steps both from a manufacturing perspective and to further reduce the Li nucleation overpotential.

[0084] In this Example, we aimed to eliminate the nucleation overpotential in solid-state “Li⁰-free” cells by a two-prong approach: integrating metal clusters that promote Li nucleation at the LLZO surface combined with eliminating the high-temperature CC/SSE lamination step to remove the contribution of mechanical de-bonding to the nucleation overpotential. Crucially, we postulate that the metal clusters serve two purposes as both a means to promote Li nucleation similar to what was shown by Yan *et al.* in liquid electrolytes, and as points of electrical contact to evenly distribute the current across the CC/SSE interface. Owing to the ease of integration using a common sputtering technique, Au is used as a model cluster. In this Example, we demonstrate stable Li metal plating of 3.3 mAh cm⁻² in Cu/LLZO “Li⁰-free” cells with no CC/SSE lamination by imposing a clustered Au metal interlayer on the LLZO surface. By heating Au-coated LLZO, de-wetting of the Au occurs to form discrete Au clusters on the LLZO surface. We hypothesize that these Au agglomerates play an important role in providing uniformly distributed nucleation sites to enable homogeneous Li metal plating. It is shown that the Li nucleation overpotential can be eliminated in a solid-state “Li⁰-free” cell and that the voltage response during plating for this solid-state “Li⁰-free” cell closely matches that of Li plating in a liquid electrolyte system. First, the morphology of the Au-coated LLZO is characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The in situ formed Li anode morphology is examined during both

plating and stripping using focused-ion beam (FIB) milling combined with SEM and electrochemical impedance spectroscopy (EIS). The alloying/de-alloying of the metal interlayer is shown to be repeatable and reversible through multiple cycles of plating and stripping the in situ formed Li metal anode. These results illustrate the importance of controlled nucleation during in situ Li plating, as well as demonstrate the feasibility of stable Li plating in “Li⁰-free” cells without the requirement of CC/SSE lamination.

2. Experimental

2.1 Materials

[0085] LLZO billets (d = 12.7 mm) with composition $\text{Li}_{6.5}\text{La}_3\text{Ta}_{0.5}\text{Zr}_{1.5}\text{O}_{12}$ were densified using rapid-induction hot-pressing, as previously described [Ref. 26]. Each billet was cut into pellets ~2 mm thick using a diamond saw. X-ray diffraction (Rigaku Corp.) was used to confirm the phase purity of the LLZO pellets after hot-pressing. The pellets were ground with sandpaper up to 1,200 grit, followed by a sequence of polishing steps using diamond paste up to a final roughness of 0.1 μm . For Au-Clusters samples (cells with a clustered Au interlayer morphology as characterized in Characterization of Au interlayer section), one side of the polished pellet was Au coated at this point using a desktop sputtering system (Denton Desk V) with power of 20 mA for a time of 5 minutes. The estimated thickness of the Au layer is ~160 nm based on AFM measurements of an Au-coated glass slide using identical deposition parameters (see Fig. 7). Next, the pellets were heat treated to 400°C in an argon-filled glovebox (Vacuum Atmospheres Co.) with atmosphere < 1 ppm O₂, which has been shown previously to remove contaminants from the LLZO surface [Ref. 27]. The thick Li/LLZO interface was prepared by scraping the oxide layer on Li foil (Alfa Aesar) with thickness 750 μm before punching the Li into discs (d = 11 mm) and applying it to the uncoated LLZO surface. Discs (d = 12.7 mm) of 35 μm battery grade Ni foil (Targray) were pressed on the other surface of the Li foil, as well as placed onto the opposite surface of the LLZO pellet to protect the surface. These cells were conditioned at 170°C for 8 hours at ~1 MPa inside the glovebox to minimize the thick Li/LLZO interfacial resistance. At this point, Au-Flat samples (cells with a flat interlayer morphology as characterized in Characterization of Au interlayer section) were removed

from the glovebox in a sealed vial, and quickly transferred to the Au sputterer and Au coated using the same parameters as reported for Au-Clusters samples. It is estimated that the Au-Flat samples were exposed to air outside the glovebox for <30 seconds during transfer. To confirm that the brief exposure to air was not the reason for failure of Au-Flat cells, an Au-Clusters cell was exposed to air for the same amount of time before in situ Li plating. This cell exhibited stable Li deposition similar to Au-Clusters cells not exposed to air (see Fig. 8). To investigate the effect of the Au-Clusters size on Li plating, the heat treatment temperature was increased to 600°C. It was observed that the Au-Clusters increased in size but no significant differences in Li plating behavior were observed (see Fig. 9). Therefore, a 400°C heat treatment was utilized for all Au-Clusters samples henceforth. To complete the cell assembly, a battery-grade Cu foil (Targray) with thickness 10 μm ($d = 12.7 \text{ mm}$) was placed on the Au coated LLZO surface before cell testing and the stack was subjected to 2.5 MPa pressure.

2.2 Electrochemical Testing

[0086] Electrochemical testing was performed using a Biologic VMP-300 potentiostat/galvanostat. The cell stack described above was tested at a temperature of 60°C under 2.5 MPa pressure using a load frame (Imada, Inc.) with custom pressure clamp. Li was plated from the thick Li counter electrode to the bare Cu foil electrode using a current density of 0.2 mA cm^{-2} . During cycling experiments, Li was stripped from the in situ plated Li electrode using a current density of 0.2 mA cm^{-2} . Potentiostatic electrochemical impedance spectroscopy (PEIS) was performed on the cells as-assembled (before in situ plating), after in situ plating, and between stripping and plating during cycling experiments. An AC perturbation voltage of 5 mV was applied over a frequency range of 7 MHz to 1 Hz.

[0087] Operando galvanostatic electrochemical impedance spectroscopy (GEIS) was conducted during stripping of in situ plated Li at mA cm^{-2} and room temperature. These experiments were conducted at room temperature due to the loss of resolution in GEIS at elevated temperatures. An AC perturbation current of 0.015 mA cm^{-2} oscillating around the DC stripping current was applied over a frequency range of 7 MHz to 1 Hz.

2.3 Cross Sectional and Surface Analysis

[0088] To examine the Cu/Li/ LLZO interface, cross-sections were cut using focused ion beam (FIB) milling and imaged using a Thermo Fisher Helios G4 Plasma FIB UXe. FIB milling was conducted using an acceleration voltage of 30 kV, and an initial beam current of 0.5 μ A followed by a cleaning beam current of 0.2 μ A. The cross-sectional scanning electron microscope (SEM) images were obtained on the same system using an accelerating voltage of 3 kV and beam current of 0.2 nA. Energy-dispersive X-ray spectroscopy (EDS) was used to identify Au-rich phases in the in situ plated Li metal using the same system under an accelerating voltage of 8 kV and beam current of 1.2 nA. Surface SEM images were acquired using a TESCAN MIRA3 SEM using an accelerating voltage of 5 kV and beam intensity setting of 5. Surface EDS maps were acquired also using the TESCAN MIRA3 SEM using an accelerating voltage of 8 kV and beam intensity setting of 15. AFM images were acquired with a Veeco Dimension Icon AFM using a Bruker ScanAsyst-Air AFM tip. The data was analyzed using Nanoscope Analysis 2.0 software. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD. Survey scans used a pass energy of 160 eV, while core scans used a pass energy of 20 eV.

3. Results and Discussion

3.1 Characterization of Au Interlayer

[0089] In this Example, two distinct morphologies of Au on the LLZO surface were investigated. To form a clustered Au morphology on the LLZO surface, the LLZO was Au coated prior to a 400°C heat treatment which is typically performed to reduce the thick Li/LLZO interfacial resistance. These samples will be referred to as Au-Clusters. To examine how the Au morphology effects Li plating, a flat Au interlayer was also formed on the LLZO surface by coating the LLZO after the 400°C heat treatment. These samples will be referred to as Au-Flat. The morphology of the Au interlayers on the LLZO surface was characterized using SEM and AFM. SEM images (see Fig. 2 panel a) show that the surface of the Au-Flat LLZO is relatively uniform with some small particulate growth on the LLZO surface. EDS mapping of Au- Flat LLZO (see Figs. 10 panel a – 10 panel c) confirms that the Au is

distributed homogeneously over the surface. The particulate growth on the surface of the Au-Flat LLZO is likely Li_2CO_3 , which has previously been shown to form on the LLZO surface [Ref. 27]. This is supported by EDS mapping showing elevated O content corresponding to the particulate growth. The surface of the Au-Clusters LLZO (see Fig. 2 panel b) shows the Au layer has coarsened and separated into discrete islands of Au on the LLZO surface. This is confirmed by EDS mapping of the Au on the LLZO surface (Figs. 10 panel d – 10 panel f). This phenomenon has been observed previously when annealing Au thin films on silicon and glass surfaces [Ref. 28–31]. These previous studies demonstrated that the morphology of the Au formed depended on the duration of annealing, with the Au clusters coarsening as the annealing time is increased [Ref. 29].

[0090] The morphology of the Au layer was also examined using SEM at different locations on the LLZO surface to compare differences at the center of the pellet vs the edge. Au-Flat samples demonstrated consistent morphology regardless of location on the pellet (see Figs. 11 panel a, 11 panel b). However, it was observed that the Au-Clusters layer had different Au morphology at the edge vs the center of the LLZO pellet (see Figs. 11 panel c, 11 panel d). While the Au layer separated into discrete islands over the majority of the LLZO surface, near the edges the Au layer is mostly intact with a few small pinholes. EDS mapping confirms the identification of the Au layer on top of the LLZO (see Fig. 10 panel g – 10 panel i). It is hypothesized that densifying the LLZO through the rapid-induction hot-press method leads to variations in the density or grain morphology of the LLZO pellet. This may be due to gradients in temperature or pressure associated with the rapid-induction hot-pressing procedure. A previous study including electron back-scatter diffraction of the grain structure of rapid-induction hot-pressed Al-doped LLZO over a 6 mm radial section appears to show variation in microstructure with position [Ref. 32]. However, the different elemental doping of the Al-doped LLZO studied previously will likely lead to different grain characteristics in the Ta-doped LLZO here [Ref. 33]. In order to fully understand the behavior of Au on the LLZO surface during annealing, the density and grain morphology of Ta-doped hot-pressed LLZO should be fully characterized.

[0091] AFM was used to examine the 3D morphology of the Au interlayers observed with SEM. It can be seen in Fig. 2 panel c that the surface of the Au-Flat LLZO is mostly uniform in height with a few small variations that reach ~150 nm. The average roughness (R_a) of the Au-Flat sample was calculated to be 6.2 nm. This roughness value increases to 55.5 nm for the Au-Clusters sample. AFM imaging of the Au-Clusters surface (see Fig. 2 panel d) shows numerous small clusters with height around 500 nm, and a few clusters with height reaching 1,000 nm. X-ray photoelectron spectroscopy (XPS) was used to investigate surface chemistry differences in the Au-Flat and Au-Clusters samples (see Fig. 12). Both samples were found to have peaks corresponding to Au, C, and O, where C and O can be attributed to the previously discussed Li_2CO_3 formation on the LLZO surface. Interestingly, the Au-Clusters sample also shows a small (0.67 atomic percent) amount of Na. This Na may diffuse into the Au interlayer during the heat treatment from small impurities in the LLZO, as the Li_2CO_3 precursor used in solid-state synthesis of LLZO is known to contain a small amount of Na_2O . Next, the difference in Au interlayers will be correlated to electrochemical behavior during in situ Li plating.

3.2 Lithium Plating

[0092] To show the effect of Au morphology on in situ Li plating, cells with a Cu CC, Au-coated LLZO, and thick Li counter electrode were assembled (see Figs. 3 panel a, 3 panel b). This cell construction differs from previous reports of “ Li^0 -free” LLZO cells in that the Cu CC is placed on the surface instead of laminating at 900°C to produce conformal contact between Cu/LLZO [Ref. 14,15,20]. The open circuit voltage (OCV) of the Au-Flat cell was 1.8 V, while the OCV of the Au-Clusters cell was measured to be 1.1 V (see Fig. 13). The discrepancy in OCV values between the Au-Flat and Au-Clusters cell may be caused by the small amount of Na contained in the Au- Clusters interlayer, as shown by XPS measurements (see Fig. 12). The potential response of the cells upon application of a constant current (0.2 mA cm^{-2}) was recorded, and Fig. 3 panel c shows representative voltage profiles during initial in situ Li plating for both Au-Flat and Au-Clusters cells. Past works of in situ Li plating on bare CCs show a drop of potential below zero to a minimum, followed by a decrease in polarization to an asymptotic value [Ref. 15,20,22,23].

This initial drop in potential is sometimes referred to as the Li nucleation overpotential, meaning that it is the overpotential required to nucleate Li on a bare CC. In contrast, the Au-Clusters cell exhibits an alloying nucleation overpotential above 0 V before first plateauing at ~215 mV. This voltage dip is a well-known phenomenon of the overpotential needed to nucleate a new phase in a Li alloying material [Ref. 34,35]. Importantly, this alloying nucleation overpotential is distinct from what is typically seen in “Li⁰-free” cells at a potential below 0 V. The Li nucleation overpotential seen below 0 V represents the nucleation energy of Li on the CC, and from mechanical stresses associated with debonding the CC from the SSE [Ref. 14,15].

[0093] After the alloying nucleation overpotential is observed, the Au-Clusters cells show two lithiation plateaus consistent with previous studies of Au lithiation in liquid electrolyte systems [Ref. 24,36]. The two plateaus likely correspond to the formation of Li₂Au (~215 mV) and Li₃Au (~100 mV) [Ref. 37]. Using the capacity associated with each voltage plateau, the amount of active Au participating in the alloying reaction can be estimated. The voltage plateau at ~215 mV corresponds to a capacity of ~12 $\mu\text{Ah cm}^{-2}$, or 55 μg of active Au participating in the formation of Li₂Au. This corresponds to ~15% of the total Au estimated to have been deposited initially (see Fig. 7), indicating that most Au does not electrochemically alloy with Li. Therefore, the remaining ~85% of Au which does not electrochemically alloy with Li may chemically alloy with Li after in situ Li is plated or may remain as elemental Au due to kinetic limitations. It has been shown that at 60°C, a flat layer of Au will chemically alloy with Li without an electrochemical driving force [Ref. 38]. Therefore, Au which is not electrochemically lithiated initially may be chemically lithiated after in situ Li is plated. However, the morphology of the Au may limit the reactivity and kinetically limit the Li/Au reaction. Here, the Au is in the form of ~1 μm clusters, while the previous study showing chemical Au/Li alloying was performed using a thin (100 nm) flat layer of Au. The outer shell of the Au clusters may alloy with Li, while the inside remains as elemental Au. Further study of the lithiation mechanism of Au clusters at a solid/solid interface is contemplated to understand the limited electrochemical activity of the Au studied herein. The second

voltage plateau at ~ 100 mV corresponds to a capacity of $\sim 8 \mu\text{Ah cm}^{-2}$, or 25 μg of Au participating in the formation of Li_3Au . This indicates that not all Li_2Au formed may be converted to Li_3Au . After the second voltage plateau, the potential of the cell drops below zero, followed by a sustained negative potential indicating the onset of Li metal plating. While previous reports of “ Li^0 -free” cells exhibit an overpotential at this point associated with the nucleation of Li metal, the Au-Clusters cell does not show any nucleation overpotential below 0 V [Ref. 14,15,20]. This indicates that the overpotential required to nucleate Li on lithiated Au is negligible. Notably, the voltage profile of the Au-Clusters cell is distinctly similar to that of lithiation on Au coated Cu in liquid electrolyte cells [Ref. 24].

[0094] The Au-Flat cell has a different potential response, showing a steady slope instead of two distinct voltage plateaus. A previous study of LLZO SSE with a flat Au CC only recorded one voltage plateau at 200 mV with no secondary plateau, which was hypothesized to be due to kinetic limitations. Here, current focusing leading to localized increased current densities may cause similar kinetic limitations that prevent defined voltage plateaus during plating of Au-Flat cells. While the Au-Clusters cell does not show any nucleation overpotential, the nucleation overpotential for the Au-Flat cell cannot be accurately evaluated because failure occurs before a steady-state voltage can be achieved. The increase in voltage after the minimum for the Au-Flat cell may indicate a nucleation overpotential or may be due to Li filament growth through the LLZO leading to a decrease in cell resistance before failure. Post-mortem analysis of the Au-Flat cell after failure reveals “spalling”-type failure of the LLZO (see Fig. 3 panel b) as well as Li-filled cracks in the LLZO (see Fig. 14). These types of failure indicate increased local current density, likely caused by imperfect Cu/LLZO contact [Ref. 39]. Previous studies have shown that Li can be plated in situ at the Cu/LLZO interface without the presence of interlayers if conformal contact can be made through a high-temperature lamination process [Ref. 14]. It is likely that in the Au-Flat cells, where the Cu CC has been placed on the LLZO surface instead of bonded to the LLZO surface, lack of intimate and uniform Cu/LLZO contact leads to the formation of “hot-spots” and short-circuiting.

[0095] Conversely, the Au-Clusters cell shows stable in situ Li plating to the chosen capacity of 3.3 mAh cm^{-2} ($16.5 \text{ }\mu\text{m}$ thickness). This capacity of Li plated was chosen to match a typical cathode loading of 3 mAh cm^{-2} with an additional 10% of excess Li, assuming that during commercial cell operation the Li anode will not be fully depleted [Ref. 4,14]. While the Au-Flat cell shows failure indicative of local increased current density (see Fig. 3 panel b, at a similar amount of charge passed the Au-Clusters cell has multiple distributed Li islands ($<5 \text{ }\mu\text{m}$) on the LLZO surface (see Fig. 3 panel d). It is also evident that the surface morphology of the Au on the LLZO surface has changed after in situ Li plating (see Fig. 3 panel d) compared to Fig. 2 panel b (before charge is passed). The difference in Au morphology may be due to swelling of the Au during lithiation, as the conversion of Au to Li_3Au corresponds with an increase of 3.34x the original Au volume [Ref. 37].

[0096] Based on the different in situ Li plating behaviors exhibited by Au-Clusters vs Au-Flat cells, it is hypothesized that the Au interlayer morphology affects the current distribution across the LLZO surface. In Au-Flat cells, the Au-coated LLZO surface has little height variation as evidenced by Fig. 2 panel c. This may lead to disparity of Cu/LLZO contact across the LLZO surface, leading to some regions with increased local current density (see Fig. 3 panel e). In contrast, the non-continuous Au interlayer in Au-Clusters cells with Au height up to $\sim 1 \text{ }\mu\text{m}$ above the LLZO surface (see Fig. 2 panel d) may provide enhanced Cu/LLZO contact and seeded nucleation sites for in situ plating of Li (see Fig. 3 panel f). Due to the large number of Au clusters to act as seeds for Li nucleation, the current density is spread more evenly across the face of the LLZO, leading to stable Li deposition. Seeded nucleation of Li in a liquid electrolyte system was previously explored by Yan *et al.* [Ref. 24]. This work demonstrated that patterned Au on a Cu CC could act as a seed for Li deposition. It is hypothesized that for clustered Au on LLZO, the Au interlayer performs similarly to seed in situ Li deposition. The XPS results (see Fig. 12) show that there are also slight chemical differences in the Au-Flat and Au-Clusters interlayers, with the Au-Clusters interlayer containing 0.67 atomic percent Na. Previous work has shown that introducing an Na-K eutectic liquid between the Li and LLZO increased the maximum current density achievable without short-

circuiting [Ref. 40]. This same study also showed that the Li-Na system will not form liquid phases at room temperature (or 60°C), and therefore a similar effect to the Na-K eutectic liquid is not expected to enhance plating stability of Li in this current study. Therefore, we attribute the morphology of the Au layer to be the controlling factor in stable Li plating. Based on the consistent short-circuiting of Au-Flat cells, this type of Au interlayer was not studied further. To better understand the in situ Li plating behavior in Au-Clusters cells, the Li morphology was examined using focused ion beam milling and SEM.

[0097] The in situ plated Li morphology was examined as a function of state-of-charge (SOC) and position on the face of the cell (center, middle, or edge) (see Fig. 4 panel a). The Cu CC was removed from the face of the Au coated LLZO, and SEM was used to image the LLZO surface at 1, 5, and 10% SOC. As seen in Fig. 11 panel c – 11 panel d, the morphology of the Au interlayer for the Au-Clusters cells varies between the center and edges of the sample. Therefore, both the center and the edge of the LLZO surface were imaged using SEM at varying SOC. At 1% SOC in the center of the LLZO surface, the Au morphology has changed due to the onset of in situ Li plating as described previously (see Fig. 4 panel bi). Numerous small islands (< 5 µm) of in situ plated Li have formed. As the SOC is increased to 5%, a dimpled fracture morphology of the in situ Li is observed as a consequence of peeling of the Cu CC (see Fig. 4 panel bii). The dimpled fracture surface morphology is typical of ductile materials such as Li [Ref. 41]. It appears that at 5% SOC, the Li has started to form a continuous layer in the center, although the Au clusters are still visible beneath the fractured Li (see Fig. 15). At 10% SOC, the Au clusters are no longer visible beneath the fractured in situ plated Li (see Fig. 4 panel biii). It is believed that the contrast seen in this image is a result of surface topography, where the edges of the Li dimples are higher than the center, resulting in increased brightness at the edges. It is evident that the size of the dimples in the fracture surface have increased compared to the sample at 5% SOC. It is hypothesized that the increase in dimple size with SOC is due to a decrease in the volume fraction of inclusions in the Li, where the Au clusters may act as inclusions. In ductile materials, voids frequently nucleate at inclusions and spread until void linkup occurs, which

determines the size of the dimples on the fracture surface [Ref. 41]. When the inclusion volume fraction decreases as more in situ Li is plated and the amount of Au clusters remains the same, the dimple size may increase as shown in Fig. 4 panel b ii-iii.

5 **[0098]** The in situ plated Li morphology at the edge of the LLZO surface shows markedly different morphology than at the center of the LLZO surface. At 1% SOC, a few Li islands with diameter $\sim 5\ \mu\text{m}$ have formed. Compared to the center of the sample, there are fewer Li islands and each Li island is larger. The morphology of the islands in the center vs the edge of the LLZO surface also varies. While the
10 small islands in the center have relatively flat tops, the islands at the edge of the LLZO appear to be rough. As the SOC is increased to 5%, these islands grow in size to diameter $\sim 10\ \mu\text{m}$ before beginning to coalesce at 10% SOC. Although the Li shows signs of coalescence at 10% SOC, the surface coverage of Li on LLZO is not complete. It is also noted that on the edge of the sample, the Li does not have a
15 morphology consistent with a fracture surface, unlike at the center of the sample. This could be due to reduced pressure at the edge of the LLZO surface. Previous studies of in situ Li plating on the LLZO surface which used the same pressure fixture as in this Example showed using pressure-sensitive paper that the pressure was concentrated in the center of the sample [Ref. 15]. It is hypothesized that the
20 differences of in situ plated Li morphology at the edges of the LLZO surface vs. the center is due to both the differences in Au interlayer morphology shown previously, and perhaps inhomogeneity of pressure across the cell radially.

[0099] At 10% SOC a continuous layer of in situ plated Li metal had formed in the center of the cell, so for SOC $\geq 10\%$ cross-sections of the LLZO/ situ Li/Cu interface
25 were milled using a plasma focused ion beam (FIB) and examined using SEM. Previous studies have suggested that using plasma FIB milling with Xe-ion sources is less destructive to the Li morphology than traditional Ga-ion FIB milling, without the need to use cryogenic temperatures [Ref. 42]. FIB milling and SEM imaging were carried out at 10%, 50%, and 100% SOC in the center, middle and edge of the
30 cell. For each sample, 3 FIB cuts were made at the center, middle, and edge of the cell. Fig. 16 illustrates these cuts for a sample with $3.3\ \text{mAh cm}^{-2}$ of in situ Li plated,

and shows that the edge of the sample has the most variability in Li morphology, with more voids observed in the cross-section closest to the edge of the sample. Therefore, for cross-sections labeled “Edge” in Figs. 4–6, the FIB cut was made as close as possible to the edge of the sample for maximum variability in Li morphology to be observed. A typical cross-section of a cell at 100% SOC is shown in Fig. 4 panel c, and the orientation of the LLZO, Li, and CC in Fig. 4 panel c is the same as in the cross-sections in Fig. 4 panel d. The cross-section shows that the in situ plated Li is dense and conformal to the LLZO and CC in the center of the sample. Small, bright secondary phase particulates can also be observed in the in situ plated Li cross-section. These particulates are observed to be near the CC, near the LLZO surface, and interspersed throughout the in situ plated Li. EDS was performed on a cross-section of in situ plated Li and showed that the particulates are an Au-rich phase (see Fig. 17). Based on the charge passed during the alloying plateaus shown in Fig. 3 panel g, not all Au in the interlayer alloys with Li. Therefore, these particulates may be Au clusters that did not alloy with Li, or may be a partially lithiated Au phase.

[00100] Cross-sections shown in Fig. 4 panel d reveal the in situ plated Li to be homogeneous and uniform in thickness in the center and middle of the cells at 10%, 50%, and 100% SOC. Au-rich clusters are dispersed throughout the in situ plated Li cross-sections in the center and middle for all SOC examined, although the distribution of the clusters is not uniform. At 100% SOC, 3.3 mAh cm^{-2} of Li has been plated, which should correspond to a Li thickness of $16.5 \text{ }\mu\text{m}$. At both the center and middle of the sample, the thickness of the in situ plated Li layer is measured to vary between $16 - 18 \text{ }\mu\text{m}$ over the $200 \text{ }\mu\text{m}$ wide milled cross-sections. This indicates that there is some non-uniformity in the thickness of in situ plated Li. At the edge of the sample, voids are present in the in situ plated Li at 10%, 50%, and 100% SOC. At 10% SOC, differing morphology of the Au interlayer can be observed (see Fig. 18). In some places, thin bands of Au can be observed, which correspond to the flat Au morphology observed at the edge of the LLZO surface in Fig. 11. Other parts of the cross-section show Au particulates interspersed in the plated Li. The Au morphology, which is dependent on the position, may vary within the span of the $200 \text{ }\mu\text{m}$ cross-

sectional cuts, leading to varying Li morphology. At 100% SOC on the edge of the cell, the in situ plated Li thickness reaches 25 μm in some regions, while other regions have large voids. The combined surface and cross-sectional SEM measurements as SOC is increased reveal the effect of initial Li nucleate morphology on the homogeneity of the fully plated in situ Li. While many small and flat Li islands quickly merge into a continuous layer by 10% SOC in the center of the cell, large and uneven Li islands at the edge do not merge as the SOC is increased. This results in voids in the in situ plated Li at the edges, while the Li in the center and middle of the cell is dense and homogeneous. Next, the morphology of the in situ plated Li will be examined under anodic current (in situ Li stripping).

3.3 Lithium Stripping

[00101] With the in situ plated Li morphology characterized, the impact of morphology on stripping in situ plated Li was examined. Cells were stripped at 0.1 mA cm^{-2} to a cutoff voltage of 1 V at room temperature under 2.5 MPa pressure. While in situ Li was plated at 60°C, stripping was performed at room temperature to record *operando* galvanostatic electrochemical impedance spectra (GEIS) during the stripping process. At designated points, an AC current with magnitude 0.015 mA cm^{-2} was imposed in addition to the DC stripping current of 0.1 mA cm^{-2} to perform the GEIS measurements in *operando*. Under these conditions, 92% of the in situ plated Li was recovered during stripping. The impedance spectra were collected at five specific points during stripping: at 0% DOD (blue circle), 50% DOD (orange square), 75% DOD (yellow triangle), when the cell polarized to 2x the average voltage from 0%-50% DOD (purple diamond), and during polarization to 1 V (green inverted triangle). The potential response during stripping of in situ formed Li is shown in Fig. 5 panel a, and the corresponding Nyquist plots obtained through GEIS measurements are shown in Fig. 5 panel b. Some shifting of the impedance spectra is observed in the Nyquist plot at 50% and 75% DOD. While decreases in cell impedance can be evidence of soft short-circuiting, it is seen that in the final two GEIS measurements the bulk and grain boundary impedances still closely correspond with the initial measurement at 0% DOD. Therefore, the shifting in impedance spectra is likely due to temperature fluctuations in the glovebox during

testing. The potential response during stripping is similar to previous reports of stripping in situ Li using Cu/LLZO with no Au interlayer [Ref. 20]. First, a “quasi-stable” period of stripping is observed where the cell voltage remains steady during stripping. The GEIS spectra at 0%, 50%, and 75% SOC are included in this “quasi-stable” regime of stripping, where a small Li/LLZO interfacial resistance can be observed. The “quasi-stable” regime is then followed by an unstable voltage polarization of the cell where the Li/LLZO interfacial resistance increases quickly [Ref. 43]. The GEIS spectra marked by the purple diamond and green inverted triangle are included in this unstable regime, and this is supported by the increases in interfacial resistance represented at low frequencies in the Nyquist plot in Fig. 5 panel b. It is noted that while Li/LLZO interfacial resistance is usually represented by a semicircle in the Nyquist plot, the low frequency limit for GEIS measurements was limited to 1 Hz to avoid distortion of the DC stripping behavior by the long acquisition time of measurements below 1 Hz. The stripping behavior of the Au seeded in situ plated Li differs from previous studies in the unstable stripping regime during polarization to 1 V, as shown in the inset of Fig. 5 panel a. A plateau is visible at ~180 mV, likely corresponding to de-alloying of Li and Au. The de-alloying of Li from Au in liquid electrolytes has been studied using transmission electron microscopy, and while intermediate phases could not be identified, the final phase of Li de-alloying from Au was LiAu_3 . Therefore, it is likely that after polarization of the cell to 1 V, the lithiated Au is not completely transformed back to pure Au.

[00102] The morphology of the in situ plated Li was characterized by FIB milling at the interface with cross-sectional SEM for the first 3 selected points during stripping. At the last selected point during stripping (after polarization to 1 V), the morphology of the remaining Li was characterized by SEM of the LLZO surface. This is because after polarization to 1 V, there was no longer adhesion between the LLZO and Cu. In the center of the sample, Li is stripped homogeneously over the points observed (Fig. 5 panel c), and after stripping to 1 V polarization some Li particulates are still visible on the Au coated LLZO surface. After polarization to 1 V, the Au on the LLZO surface appears to have contracted compared to the lithiated Au (Fig. 4 panel bi) due to a decreased density after some de-alloying of Li. In the

middle of the sample, the Li is stripped with no voids over the first two points characterized at 50% and 75% SOC. This changes when the stripping of Li enters the unstable phase, corresponding to the accelerating formation of voids (marked by a purple diamond). At this point voids have formed in the in situ Li in the middle of the sample, but not at the center (Fig. 19). The preferential formation of voids in the Li at the middle of the sample may be due to lower pressure radially outwards from the center of the cell or may be caused by the closer position to the edge of the sample, where the Li stripping is limited. Cross-sectional SEM analysis of the Li at the edge of the sample during stripping shows large voids present, consistent with the morphology seen during in situ Li plating at the edge. After polarization to 1 V, large ($\sim 10\ \mu\text{m}$) spherules of Li are still present on the LLZO surface (Fig. 5 panel d). It appears that the limited recovery (8% irreversible) of in situ plated Li in this cell configuration is due to the Li at the edge of the sample, which has irregular morphology. This irregular morphology may lead to contact loss with the CC or LLZO during stripping, decreasing the accessible Li capacity. Electrochemical and cross-sectional SEM characterization in the previous sections showed that the Au clusters go through alloying/de-alloying transitions during plating and stripping, as well as some physical separation from the LLZO surface as in situ Li is plated. Next, we examine the feasibility of re-plating in situ Li in a cell that has been stripped to 1 V despite possible changes in Au cluster distribution.

3.4 Cycling Behavior

[00103] To investigate the repeatability of in situ Li plating after stripping, cells were plated and stripped at $0.2\ \text{mA cm}^{-2}$ to a cutoff voltage of 1 V at 60°C under 2.5 MPa pressure. In the first cycle at 60°C , 97.4% of the in situ plated Li is stripped, an increase of 5% compared to room temperature stripping at $0.1\ \text{mA cm}^{-2}$. After stripping, in situ Li plating is repeated, and $3.3\ \text{mAh cm}^{-2}$ of Li are re-plated with stable deposition behavior (see Fig. 6 panel a). The voltage profiles for in situ Li plating during the 1st and 2nd cycles are steady and nearly identical other than the initial voltage plateaus corresponding to Au alloying. When in situ Li is re-plated, the first voltage plateau is shortened, corresponding to a reduced capacity of $4\ \mu\text{Ah cm}^{-2}$ during re-plating compared to $10\ \mu\text{Ah cm}^{-2}$ during the first plating (see Fig. 6 panel

b). This first voltage plateau likely corresponds to the formation of Li_2Au , and the reduced capacity of this plateau may indicate that after cell polarization to 1 V some Li_2Au remains and is not de-alloyed from Li. Krauskopf *et al.* also found that Li could not be completely stripped from a formed Li_2Au alloy on the LLZO surface [Ref. 22].

5 The incomplete de-alloying of Li_2Au is also supported by the change in alloying nucleation overpotential behavior during re-plating of in situ Li. The first plating voltage profile shows an alloying nucleation overpotential before the plateau at ~215 mV corresponding to the nucleation of Li_2Au , as discussed earlier. Upon re-plating of Li, this nucleation overpotential disappears. Studies of Li alloys by Huggins have
10 shown that if some secondary phase is already present due to incomplete de-alloying, no nucleation over-potential is observed on the next cycle [Ref. 35]. Therefore, the presence of Li_2Au from incomplete de-alloying likely prevents the alloying nucleation overpotential on the re-plating of Li. The capacity of the second Au alloying plateau corresponding to the formation of Li_3Au remains constant for the
15 1st and 2nd Li platings at $7 \mu\text{Ah cm}^{-2}$. Therefore, it is likely that the reduced capacity corresponding to the first alloying plateau is caused by incomplete de-alloying of Li_2Au after cell polarization to 1 V. The consistent capacity of the Au alloying plateau corresponding to the formation of Li_3Au suggests that the repeated in situ plating of Li is enabled again by the Au clusters, similar to the first plating.

20 **[00104]** The morphology of the in situ plated Li was characterized after plating, stripped, and re-plating to examine where excess Li may accumulate and if re-plated Li was homogeneous (see Fig. 6 panel c). Cross-sectional SEM showed that at the center and middle of the sample, re-plated in situ Li was uniform and consistent with the morphology observed during the first plating (see Fig. 4 panel d). At the center
25 and middle of the sample, the re-plated in situ Li thickness was measured to range between 15–17 μm . However, the edge of the sample showed both large voids and regions where the Li thickness reached up to 32 μm . It appears that due to incomplete Li stripping at the edge of the sample, as evidenced in Fig. 5 panel d, some Li may accumulate at the edge of the sample after re-plating. To investigate
30 the CE of stripping in situ plated Li over multiple cycles, cells were cycled at 0.2 mA cm^{-2} with 3.3 mAh cm^{-2} of Li plated, followed by stripping to a voltage cutoff of 1 V at

60°C under 2.5 MPa pressure (see Fig. 6 panel d). A high first-cycle CE of 97.9% was recorded, increasing to 99.5% on the 15th cycle (see Fig. 20). As demonstrated in Fig. 5 panel d, the irreversibility during stripping is likely due to irregular Li morphology at the edges of the cell, leading to contact loss between the Li and CC or LLZO. Over each cycle, excess Li will remain after stripping in areas where there is poor contact between the Li and CC or LLZO. The build-up of this Li may enhance the contact between the plated Li and CC or LLZO by filling in gaps of contact, therefore producing the increase of CE over cycle that is shown in Fig. 20. It has been shown that relatively high (97.9%) first-cycle CE can be achieved, and that Li can be re-plated in situ even after polarizing the cell to 1 V and the Au clusters are redistributed during initial plating/stripping. The repeatability of Li plating after stripping shows promise for seeded Au interlayers to enable long cycle-life “Li⁰-free” batteries.

4. Conclusions

[00105] In this Example, we demonstrated stable Li metal plating of 16.5 μm (3.3 mAh cm⁻²) in LLZO “Li⁰-free” cells enabled by seeded nucleation of Li metal. Cells with a flat Au layer on the LLZO surface repeatedly short-circuited during in situ Li plating, limiting Li electrodeposition to <0.1 mAh cm⁻². Performing a heat treatment of the Au-coated LLZO transformed the flat Au layer into discrete clusters of Au, which may act as seeds for Li nucleation and lead to stable Li plating. The “Li⁰-free” cells were assembled without high temperature or pressure interface formation steps which are usually required to facilitate intimate CC/SSE contact. The protrusion of the Au clusters from the LLZO surface may create beneficial electrical contact between the CC/SSE, preventing localized current density increases. However, it was found that the Au morphology varied over the LLZO surface, and that this Au morphology influenced the morphology of the in situ plated Li. Over the majority of the LLZO surface, where the Au formed clusters, the Li plated uniformly and was able to be stripped nearly reversibly. Near the edge of the LLZO pellet where the Au layer remained mostly intact with a few pinholes, the Li plated irregularly with large voids in the micro-structure and was not able to be completely stripped. Clearly, the morphology of the Au layer impacts the morphology of the

plated Li, which in turn affects the reversibility of Li plating and stripping. We contemplate optimizing the heat treatment time and temperature of Au-coated LLZO to achieve the segregation of the Au layer across the entire surface of the LLZO. Cross-sectional SEM of in situ plated Li shows that Au clusters are present in the in situ plated Li throughout plating and stripping, and that the clusters are present both by the LLZO surface, current collector surface, and distributed in the Li. It was shown that the effect of the Au seed layer was repeatable over a second cycle after the in situ plated Li was stripped and the cell polarized to 1 V. Finally, it was shown that LLZO “Li⁰-free” cells cycled with a high CE of 97.9% on the first cycle, increasing to 99% on the 15th cycle.

[00106] For the first time, we have clearly demonstrated the elimination of the Li nucleation overpotential by interposing an alloying interlayer in a solid-state “Li⁰-free” cell using commercial Cu current collectors. Past studies of Li nucleation overpotential in solid-state “Li⁰-free” cells assume mechanical contributions to the nucleation overpotential, including CC/SSE delamination. This Example, which included an Au interlayer in a “Li⁰-free” cell with no CC/SSE lamination, showed a potential response during Li plating remarkably similar to what has been demonstrated in a liquid electrolyte system with different mechanical environment. These results motivate further examination of the contributions to Li nucleation overpotential, and how the nucleation overpotential in turn affects Li plating morphology and the reversibility of stripping. Finally, the demonstration of stable Li plating with no CC/SSE lamination or pre-formation steps challenges the previous assumption that intimate CC/SSE contact is needed to facilitate stable plating in “Li⁰-free” cells. While intimate CC/SSE contact is one path for stable Li plating, it is shown here that many distributed electrical contacts (Au seed clusters) can be sufficient to evenly distribute the current density across the cell. These findings can have important implications for manufacturing pathways of “Li⁰-free” cells.

[00107] REFERENCES:

1. P. Albertus, S. Babinec, S. Litzelman, and A. Newman, *Nat. Energy*, 3 (2018).

2. J. Janek and W. G. Zeier, *Nat. Energy*, 1 (2016).
3. K. B. Hatzell *et al.*, *ACS Energy Lett.*, 5 (2020).
4. M. J. Wang, E. Kazyak, N. P. Dasgupta, and J. Sakamoto, *Joule*, 5 (2021).
5. S. K. Otto, Y. Moryson, T. Krauskopf, K. Pepler, J. Sann, J. Janek, and A. Henss, *Chem. Mater.*, 33 (2021).
6. S. K. Otto, T. Fuchs, Y. Moryson, C. Lerch, B. Mogwitz, J. Sann, J. Janek, and A. Henss, *Energy Mater.*, 4 (2021).
7. A. Sharafi, H. M. Meyer, J. Nanda, J. Wolfenstine, and J. Sakamoto, *J. Power Sources*, 302 (2016).
10. A. Sharafi, S. Yu, M. Naguib, M. Lee, C. Ma, H. M. Meyer, J. Nanda, M. Chi, D. J. Siegel, and J. Sakamoto, *J. Mater. Chem. A*, 5 (2017).
9. V. Pimenta, M. Sathiya, D. Batuk, A. M. Abakumov, D. Giaume, S. Cassaignon, D. Larcher, and J. M. Tarascon, *Chem. Mater.*, 29 (2017).
15. J. Qian, B. D. Adams, J. Zheng, W. Xu, W. A. Henderson, J. Wang, M. E. Bowden, S. Xu, J. Hu, and J. G. Zhang, *Adv. Funct. Mater.*, 26 (2016).
11. R. V. Salvatierra, W. Chen, and J. M. Tour, *Adv. Energy Sustain. Res.*, 2 (2021).
12. S. Nanda, A. Gupta, and A. Manthiram, *Adv. Energy Mater.*, 11 (2021).
13. C. Heubner, S. Maletti, H. Auer, J. Hüttel, K. Voigt, O. Lohrberg, K. Nikolowski, M. Partsch, and A. Michaelis, *Adv. Funct. Mater.*, 31 (2021).
20. M. J. Wang, E. Carmona, A. Gupta, P. Albertus, and J. Sakamoto, *Nat. Commun.*, 11 (2020).
15. E. Kazyak, M. J. Wang, K. Lee, M. D. Thouless, J. Sakamoto, and N. P. Dasgupta, *Matter*, 5 (2022).
25. T. Fuchs, J. Becker, C. G. Haslam, C. Lerch, J. Sakamoto, F. H. Richter, and J. Janek, *Adv. Energy Mater.*, 13 (2022).
17. Y. G. Lee *et al.*, *Nat. Energy*, 5 (2020).

18. A. L. Davis, E. Kazyak, D. W. Liao, K. N. Wood, and N. P. Dasgupta, *J. Electrochem. Soc.*, 168 (2021).
19. Y. Wang *et al.*, *Adv. Mater.*, 35 (2022).
20. K. Lee, E. Kazyak, M. J. Wang, P. Neil, and J. Sakamoto, *Joule*, 6 (2022).
- 5 21. L. Qian, Y. Zheng, T. Or, H. W. Park, R. Gao, M. Park, Q. Ma, D. Luo, A. Yu, and Z. Chen, *Small*, 18 (2022).
22. T. Krauskopf, R. Dippel, H. Hartmann, K. Peppler, B. Mogwitz, F. H. Richter, W. G. Zeier, and J. Janek, *Joule*, 3 (2019).
23. M. Motoyama, M. Ejiri, and Y. Iriyama, *J. Electrochem. Soc.*, 162 (2015).
- 10 24. K. Yan, Z. Lu, H. W. Lee, F. Xiong, P. C. Hsu, Y. Li, J. Zhao, S. Chu, and Y. Cui, *Nat. Energy*, 1 (2016).
25. S. Kim *et al.*, *Adv. Energy Mater.*, 10 (2020).
26. N. J. Taylor, S. Stangeland-Molo, C. G. Haslam, A. Sharafi, T. Thompson, M. Wang, R. Garcia-Mendez, and J. Sakamoto, *J. Power Sources*, 396 (2018).
- 15 27. A. Sharafi, E. Kazyak, A. L. Davis, S. Yu, T. Thompson, D. J. Siegel, N.P. Dasgupta, and J. Sakamoto, *Chem. Mater.*, 29 (2017).
28. V. Švorčík, O. Kvítek, O. Lyutakov, J. Siegel, and Z. Kolská, *Appl. Phys. A Mater. Sci. Process.*, 102 (2011).
29. T. F. Young, J. F. Chang, and H. Y. Ueng, *Thin Solid Films*, 322 (1998).
- 20 30. X. Sun and H. Li, *Nanotechnology*, 24 (2013).
31. K. Jia, J. L. Bijeon, P. M. Adam, and R. E. Ionescu, *Plasmonics*, 8 (2013).
32. X. Liu *et al.*, *Nat. Mater.*, 20 (2021).
33. G. Han, B. Kinzer, R. Garcia-Mendez, H. Choe, J. Wolfenstine, and J. Sakamoto, *J. Eur. Ceram. Soc.*, 40 (2020).
- 25 34. C. Y. Wang, Y. S. Meng, G. Ceder, and Y. Li, *J. Electrochem. Soc.*, 155 (2008).

35. R. A. Huggins, *J. Power Sources*, 81-82 (1999).

36. P. Bach, M. Stratmann, I. Valencia-Jaime, A. H. Romero, and F. U. Renner, *Electrochim. Acta*, 164 (2015).

37. A. J. Leenheer, K. L. Jungjohann, K. R. Zavadil, and C. T. Harris, *ACS Nano.*, 10 (2016).

38. J. Wakasugi, H. Munakata, and K. Kanamura, *J. Electrochem. Soc.*, 164 (2017).

39. E. Kazyak, R. Garcia-Mendez, W. S. LePage, A. Sharafi, A. L. Davis, A. J. Sanchez, K. H. Chen, C. Haslam, J. Sakamoto, and N. P. Dasgupta, *Matter*, 2 (2020).

40. R. J. Y. Park, C. M. Eschler, C. D. Fincher, A. F. Badel, P. Guan, M. Pharr, B. W. Sheldon, W. C. Carter, V. Viswanathan, and Y. M. Chiang, *Nat. Energy*, 6 (2021).

41. T. H. Courtney, "Toughening Mechanisms and the Physics of Fracture." (2005), in: *Mech. Behav. Mater.*, Second Edition, Waveland Press, Inc., p. 506.

42. Y. Lu, C. Zhao, J. Hu, S. Sun, H. Yuan, Z. Fu, and X. Chen, *Sci. Adv.*, 8 (2022).

43. K. Eckhardt, T. Fuchs, S. Burkhardt, P. J. Klar, J. Janek, and C. Heiliger, *ACS Appl. Mater. Interfaces*, 14 (2022).

The citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

[00108] Thus, the present invention provides a method for anode-free manufacturing in which an unformed structure is fabricated with a bare current collector replacing the conventional anode, and a metal anode is then formed electrochemically on the first charge cycle by electroplating a metal contained within the cathode between a solid-state electrolyte and the current collector.

[00109] In light of the principles and example embodiments described and illustrated herein, it will be recognized that the example embodiments can be modified in arrangement and detail without departing from such principles. Also, the foregoing discussion has focused on particular embodiments, but other configurations are also contemplated. In particular, even though expressions such as "in one embodiment", "in another embodiment," or the like are used herein, these phrases are meant to generally reference embodiment possibilities, and are not intended to limit the invention to particular embodiment configurations. As used herein, these terms may reference the same or different embodiments that are combinable into other embodiments. As a rule, any embodiment referenced herein is freely combinable with any one or more of the other embodiments referenced herein, and any number of features of different embodiments are combinable with one another, unless indicated otherwise.

[00110] Although the invention has been described in considerable detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention can be used in alternative embodiments to those described, which have been presented for purposes of illustration and not of limitation. Therefore, the scope of the appended claims should not be limited to the description of the embodiments contained herein.

CLAIMS

What is claimed is:

1. A structure for making an electrochemical device, the structure comprising:
 - a solid-state electrolyte material having a first surface comprising metal clusters; and
 - a current collector in contact with the first surface of the solid-state electrolyte material.
2. The structure of claim 1 further comprising:
 - an electrode comprising an electroactive species, the electrode being in contact with a second surface of the solid-state electrolyte material.
3. The structure of claim 2 wherein the structure is unformed.
4. The structure of any of claims 1, 2, or 3 wherein:
 - the metal clusters comprise a metal selected from the group consisting of gold, silver, tin, aluminum, magnesium, silicon, zinc, bismuth, germanium, and mixtures thereof.
5. The structure of any of claims 1, 2, or 3 wherein:
 - the metal clusters comprise gold.
6. The structure of any of claims 1, 2, or 3 wherein:
 - the metal clusters have a diameter between 1 nm and 100 μm , and a height between 1 nm and 100 μm .
7. The structure of any of claims 1, 2, or 3 wherein:
 - the current collector comprises a single material comprising a metal or a metal alloy.

8. The structure of any of claims 1, 2, or 3 wherein:

the current collector comprises a material selected from the group consisting of nickel, molybdenum, titanium, zirconium, tantalum, alloy steel, stainless steel, nickel based super alloys, cobalt based super alloys, copper, aluminum, iron, or mixtures thereof.

9. The structure of any of claims 1, 2, or 3 wherein:

the current collector has a thickness between 1 nanometer and 100 micrometers.

10. The structure of any of claims 1, 2, or 3 wherein:

the solid-state electrolyte material comprises a material selected from the group consisting of lithium phosphorous oxynitride (LiPON), oxide based garnets, sodium super ionic conductors (NaSICON), lithium super ionic conductors (LiSICON), thio-LiSICONs, sulfide glass, argyrodite-sulfide, polymers, or mixtures thereof.

11. The structure of any of claims 1, 2, or 3 wherein:

the solid-state electrolyte material is selected from the group consisting of lithium lanthanum zirconium oxide (LLZO), aluminum doped LLZO, gallium doped LLZO, niobium doped LLZO, tantalum doped LLZO, lithium aluminum titanium phosphate (LATP), lithium aluminum germanium phosphate (LAGP), lithium phosphorous sulfide (LPS), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), crystalline thermoplastic polymers, alkali metal cation-alumina, metal halides, or mixtures thereof.

12. The structure of any of claims 1, 2, or 3 wherein:

the solid-state electrolyte material comprises lithium lanthanum zirconium oxide (LLZO) or a derivative thereof.

13. The structure of any of claims 1, 2, or 3 wherein:
the solid-state electrolyte material comprises a ceramic material having a formula of $\text{Li}_w\text{A}_x\text{M}_2\text{Re}_{3-y}\text{O}_z$,
wherein w is $5 - 7.5$,
wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr, Ba, and any combination thereof,
wherein x is $0 - 2$,
wherein M is selected from Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te, and any combination thereof,
wherein Re is selected from lanthanide elements, actinide elements, and any combination thereof,
wherein y is $0 - 0.75$,
wherein z is $10.875 - 13.125$, and
wherein the ceramic material has a garnet-type or garnet-like crystal structure.
14. The structure of claim 13, wherein M is a combination of Zr and Ta.
15. The structure of claim 13, wherein M is Zr, and A is Al, and x is not 0.
16. The structure of claim 13, wherein M is Zr, and A is Ga, and x is not 0.
17. The structure of any of claims 1, 2, or 3 wherein:
the solid-state electrolyte material is sodium- β -alumina and/or sodium- β'' -alumina.
18. The structure of any of claims 1, 2, or 3 wherein:
the solid-state electrolyte material has a thickness between 1 nanometer and 100 micrometers.
19. The structure of any of claims 2 or 3, wherein the current collector is electrochemically blocking to the electroactive species.

20. The structure of any of claims 2 or 3, wherein the electroactive species comprises an alkali metal.

21. The structure of any of claims 2 or 3, wherein the electroactive species comprises lithium.

22. The structure of any of claims 2 or 3, wherein the electroactive species comprises sodium.

23. The structure of any of claims 2 or 3 wherein:
the electrode comprises a lithium host material is selected from the group consisting of (i) lithium metal oxides wherein the metal is one or more of aluminum, cobalt, iron, manganese, nickel and vanadium, and (ii) lithium-containing phosphates having a general formula LiMPO_4 wherein M is one or more of cobalt, iron, manganese, and nickel.

24. A method of making an electrochemical device, the method comprising:

- (a) providing a solid-state electrolyte material having a first surface and a second surface;
- (b) forming metal clusters on the first surface of the solid-state electrolyte material to form a modified surface of the solid-state electrolyte material;
- (c) placing the modified surface of the solid-state electrolyte material in contact with a current collector;
- (d) placing the second surface of the solid-state electrolyte material in contact with an electrode comprising an electroactive species to form a layered structure; and
- (e) passing a current through the layered structure to create an interfacial layer comprising the electroactive species between the solid-state electrolyte material and the current collector, the interfacial layer functioning as an anode of the electrochemical device and the electrode functioning as a cathode of the electrochemical device.

25. The method of claim 24 wherein:

- step (a) further comprises heat treating the solid-state electrolyte material at a temperature between 100°C and 700°C.

26. The method of claim 24 wherein:

- step (e) further comprises applying a pressure between 0.1 MPa and 10 MPa to the layered structure.

27. The method of claim 24 wherein:

- step (e) further comprises applying pressure between 0.1 MPa and 10 MPa at a temperature between 25°C and 100°C to layered structure.

28. The method of claim 24 wherein:

step (b) comprises sputtering a metal on the first surface of the solid-state electrolyte material to produce a uniform layer of the metal and annealing the uniform layer to transform the uniform layer into the metal clusters.

29. The method of claim 28 wherein:

annealing the uniform layer is performed at an annealing temperature below a melting point of the metal.

30. The method of claim 28 wherein:

annealing the uniform layer is performed at an annealing temperature between 100°C and 700°C.

31. The method of claim 24 wherein:

the metal clusters comprise a metal selected from the group consisting of gold, silver, tin, aluminum, magnesium, silicon, zinc, bismuth, germanium, and mixtures thereof.

32. The method of claim 24 wherein:

the metal clusters comprise gold.

33. The method of claim 24 wherein:

the metal clusters have a diameter between 1 nm and 100 µm, and a height between 1 nm and 100 µm.

34. The method of claim 24 wherein:

the current collector comprises a single material comprising a metal or a metal alloy.

35. The method of claim 24 wherein:

the current collector comprises a material selected from the group consisting of nickel, molybdenum, titanium, zirconium, tantalum, alloy steel, stainless steel, nickel based super alloys, cobalt based super alloys, copper, aluminum, iron, or mixtures thereof.

36. The method of claim 24 wherein:

the current collector has a thickness between 1 nanometer and 100 micrometers.

37. The method of claim 24 wherein:

the solid-state electrolyte material comprises a material selected from the group consisting of lithium phosphorous oxynitride (LiPON), oxide based garnets, sodium super ionic conductors (NaSICON), lithium super ionic conductors (LiSICON), thio-LiSICONs, sulfide glass, argyrodite-sulfide, polymers, or mixtures thereof.

38. The method of claim 24 wherein:

the solid-state electrolyte material is selected from the group consisting of lithium lanthanum zirconium oxide (LLZO), aluminum doped LLZO, gallium doped LLZO, niobium doped LLZO, tantalum doped LLZO, lithium aluminum titanium phosphate (LATP), lithium aluminum germanium phosphate (LAGP), lithium phosphorous sulfide (LPS), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), crystalline thermoplastic polymers, alkali metal cation-alumina, metal halides, or mixtures thereof.

39. The method of claim 24 wherein:

the solid-state electrolyte material comprises lithium lanthanum zirconium oxide (LLZO) or a derivative thereof.

40. The method of claim 24 wherein:
the solid-state electrolyte material comprises a ceramic material having a formula of $\text{Li}_w\text{A}_x\text{M}_2\text{Re}_{3-y}\text{O}_z$,
wherein w is 5 – 7.5,
wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr, Ba, and any combination thereof,
wherein x is 0 – 2,
wherein M is selected from Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te, and any combination thereof,
wherein Re is selected from lanthanide elements, actinide elements, and any combination thereof,
wherein y is 0 – 0.75,
wherein z is 10.875 – 13.125, and
wherein the ceramic material has a garnet-type or garnet-like crystal structure.

41. The method of claim 40, wherein M is a combination of Zr and Ta.

42. The method of claim 40, wherein M is Zr, and A is Al, and x is not 0.

43. The method of claim 40, wherein M is Zr, and A is Ga, and x is not 0.

44. The method of claim 24 wherein:
the solid-state electrolyte material is sodium- β -alumina and/or sodium- β'' -alumina.

45. The method of claim 24 wherein:
the solid-state electrolyte material has a thickness between 1 nanometer and 100 micrometers.

46. The method of claim 24 wherein:
the interfacial layer has a thickness between 1 nanometer and 100 micrometers.
47. The method of claim 24 wherein:
the current collector is electrochemically blocking to the electroactive species.
48. The method of claim 24 wherein:
the interfacial layer comprises a single material comprising a metal or a metal alloy.
49. The method of claim 24 wherein:
the interfacial layer comprises a material selected from the group consisting of lithium, sodium, silver, magnesium, silicon, zinc, bismuth, germanium, calcium, cobalt, iron, potassium, copper, gold, tin, aluminum, or alloys thereof, or mixtures thereof.
50. The method of claim 24 wherein:
the interfacial layer comprises an alkali metal.
51. The method of claim 24 wherein:
the interfacial layer comprises lithium.
52. The method of claim 24 wherein:
the interfacial layer comprises sodium.

53. The method of claim 24 wherein:

the electrode comprises a lithium host material is selected from the group consisting of (i) lithium metal oxides wherein the metal is one or more of aluminum, cobalt, iron, manganese, nickel and vanadium, and (ii) lithium-containing phosphates having a general formula LiMPO_4 wherein M is one or more of cobalt, iron, manganese, and nickel.

54. The method of claim 24, wherein no dendrite penetration into the solid electrolyte material occurs during step (d).

55. The method of claim 24, wherein the interfacial layer has a uniform thickness after step (d).

56. The method of claim 24, wherein the interfacial layer has a surface coverage of 5% or greater with the solid-state electrolyte after step (d).

57. The method of claim 24, wherein the interfacial layer has a surface coverage of 70% or greater with the solid-state electrolyte after step (d).

58. The method of claim 24, wherein the interfacial layer has complete surface contact with the solid-state electrolyte material after step (d).

59. The method of claim 24, wherein passing the current through the layered structure is at current between $1 \mu\text{A}/\text{cm}^2$ and $10 \text{mA}/\text{cm}^2$.

60. The method of claim 24, wherein passing the current through the layered structure is without conformal contact between the current collector and the solid-state electrolyte material.

61. The method of claim 24, wherein placing the second surface of the solid-state electrolyte material in contact with an electrode does not include a lamination step.

62. The method of claim 24, wherein the electroactive species comprises an alkali metal.

63. The method of claim 24, wherein the electroactive species comprises lithium.

64. The method of claim 24, wherein the electroactive species comprises sodium.

65. The method of claim 24, wherein the method eliminates nucleation overpotential for the electroactive species when creating the interfacial layer.

66. The method of claim 24, wherein the modified surface of the solid-state electrolyte material has an average roughness in a range of 10 nanometers to 200 nanometers.

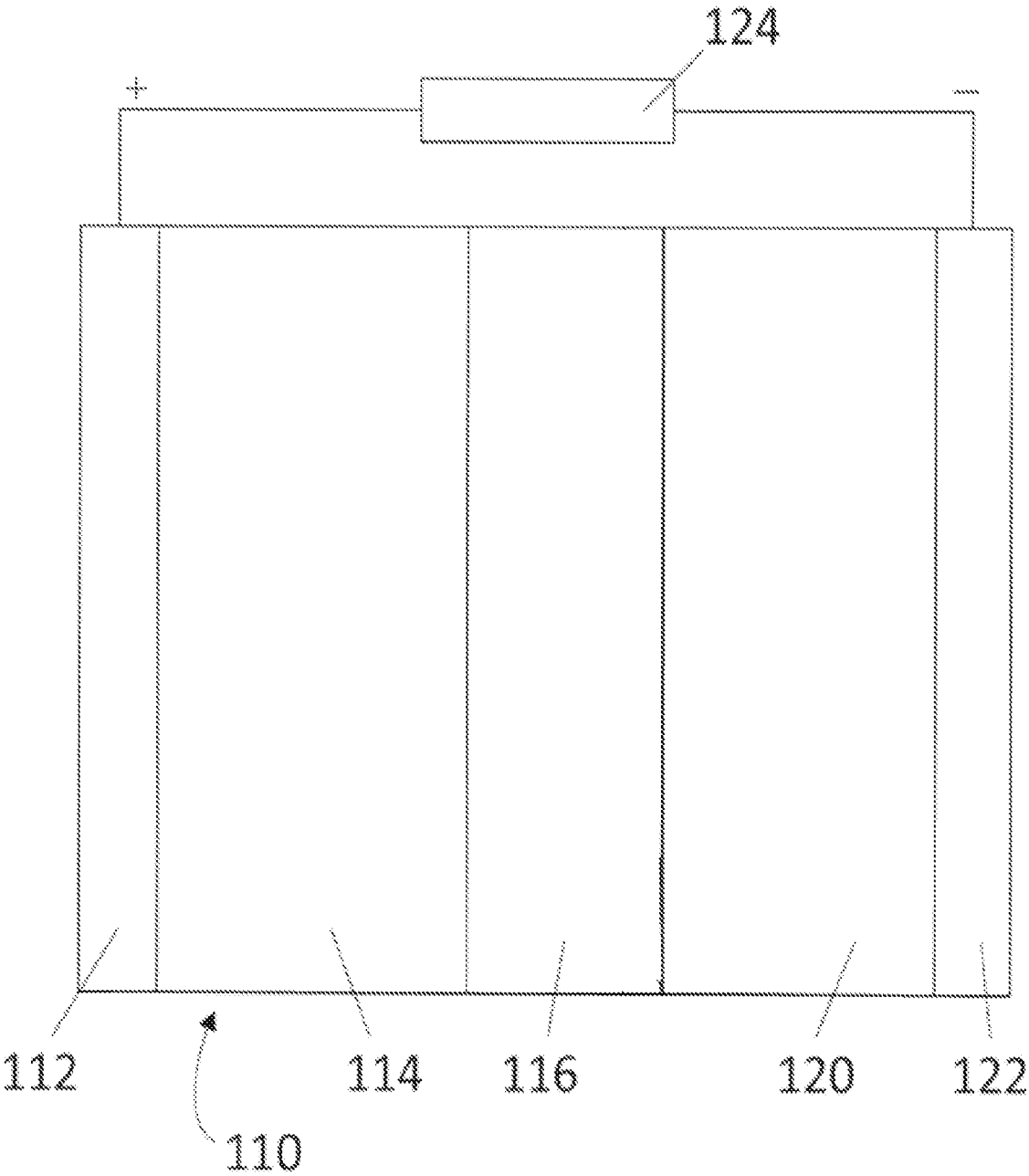


FIG. 1

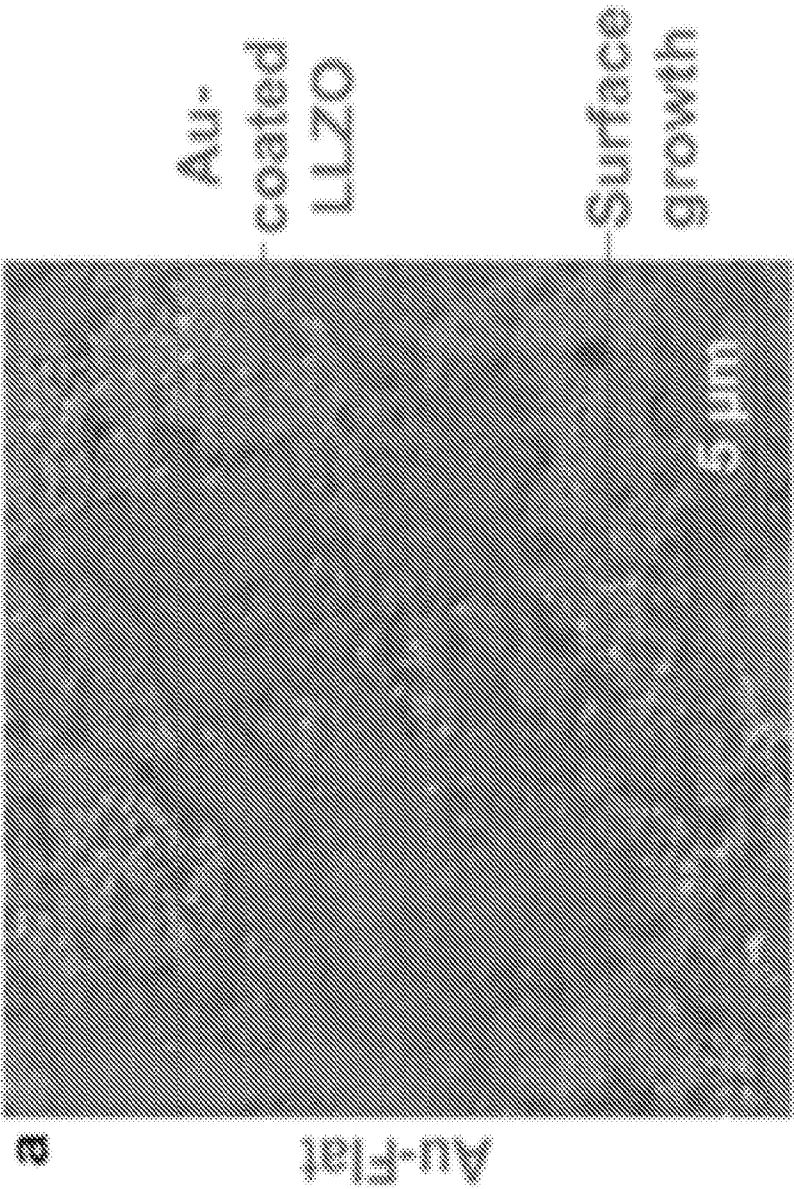


Figure 2

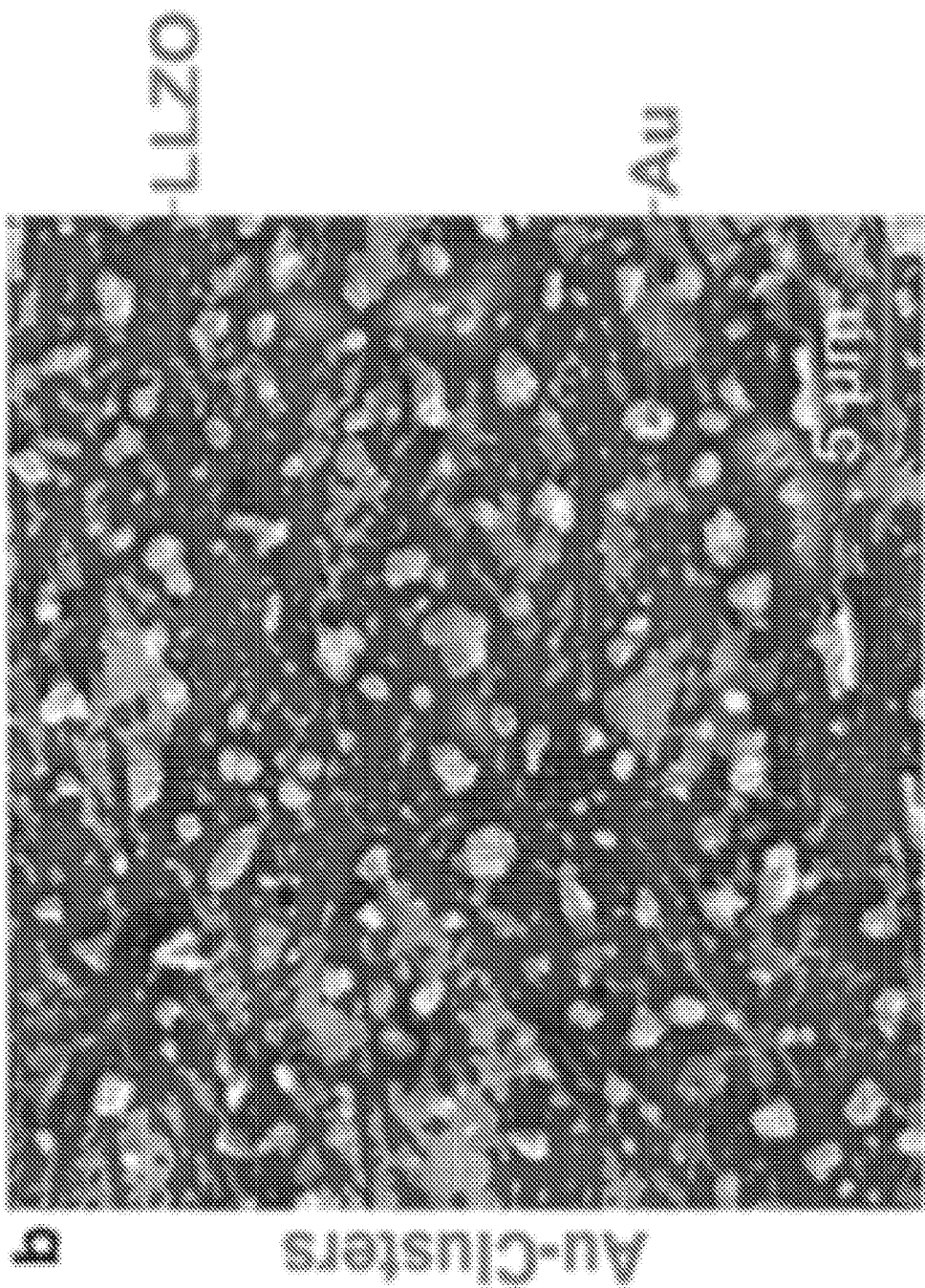


Figure 2 (continued)

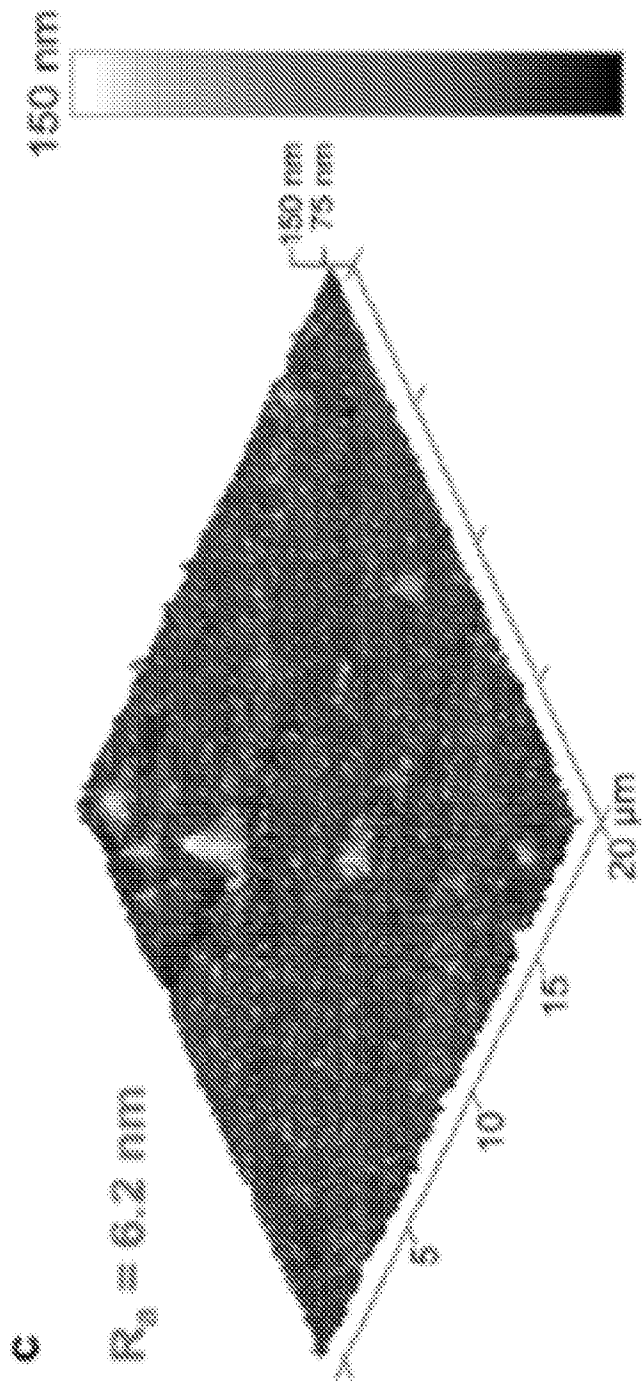


Figure 2 (continued)

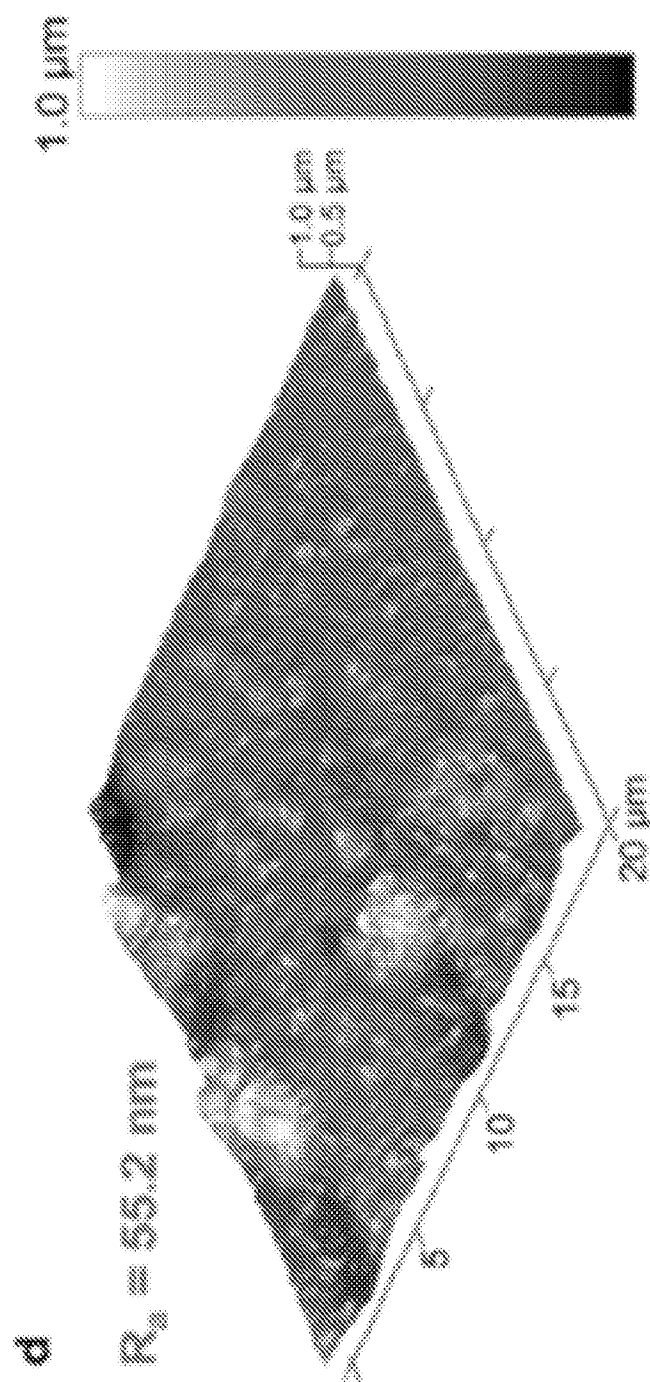


Figure 2 (continued)

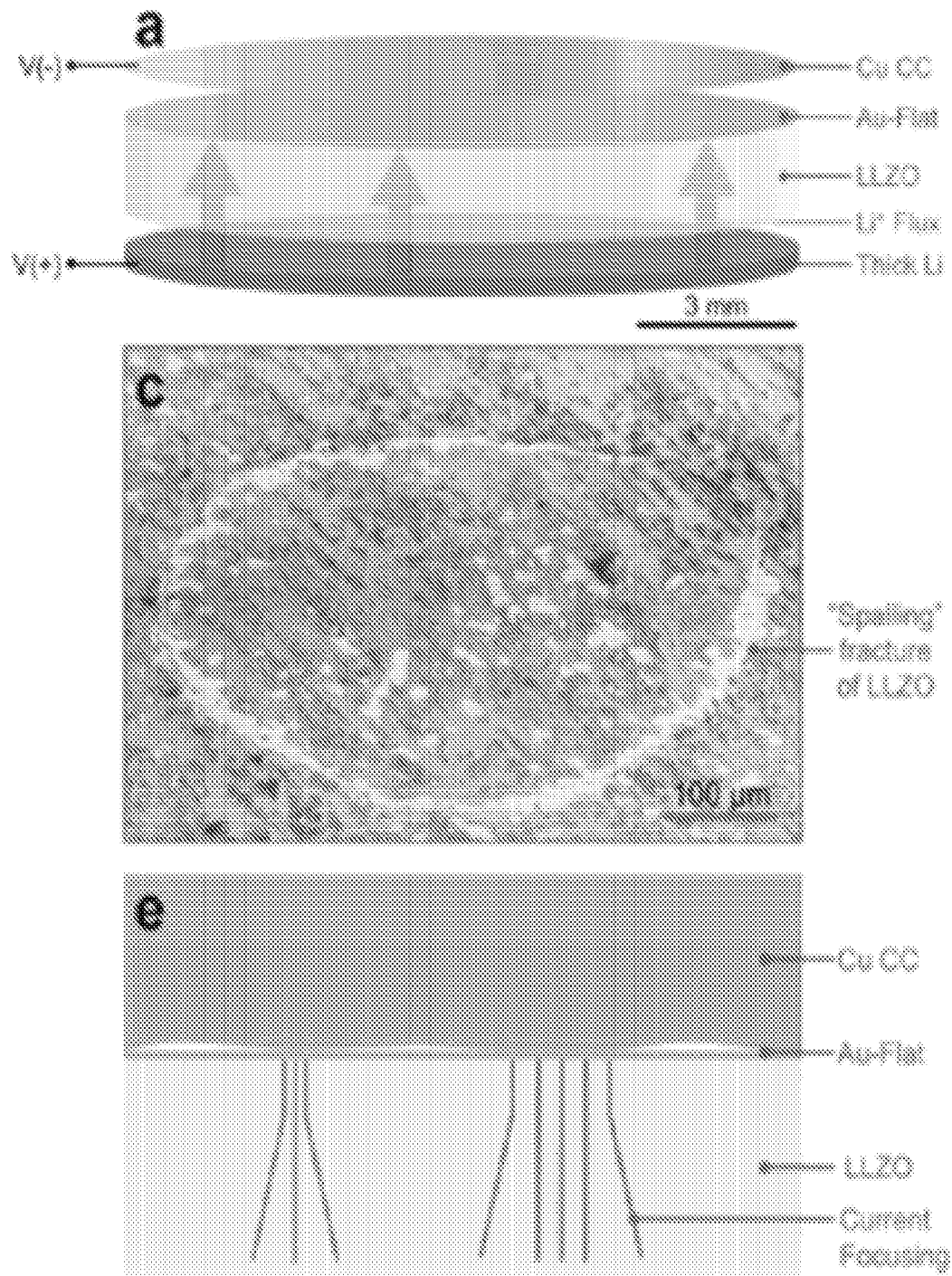


Figure 3

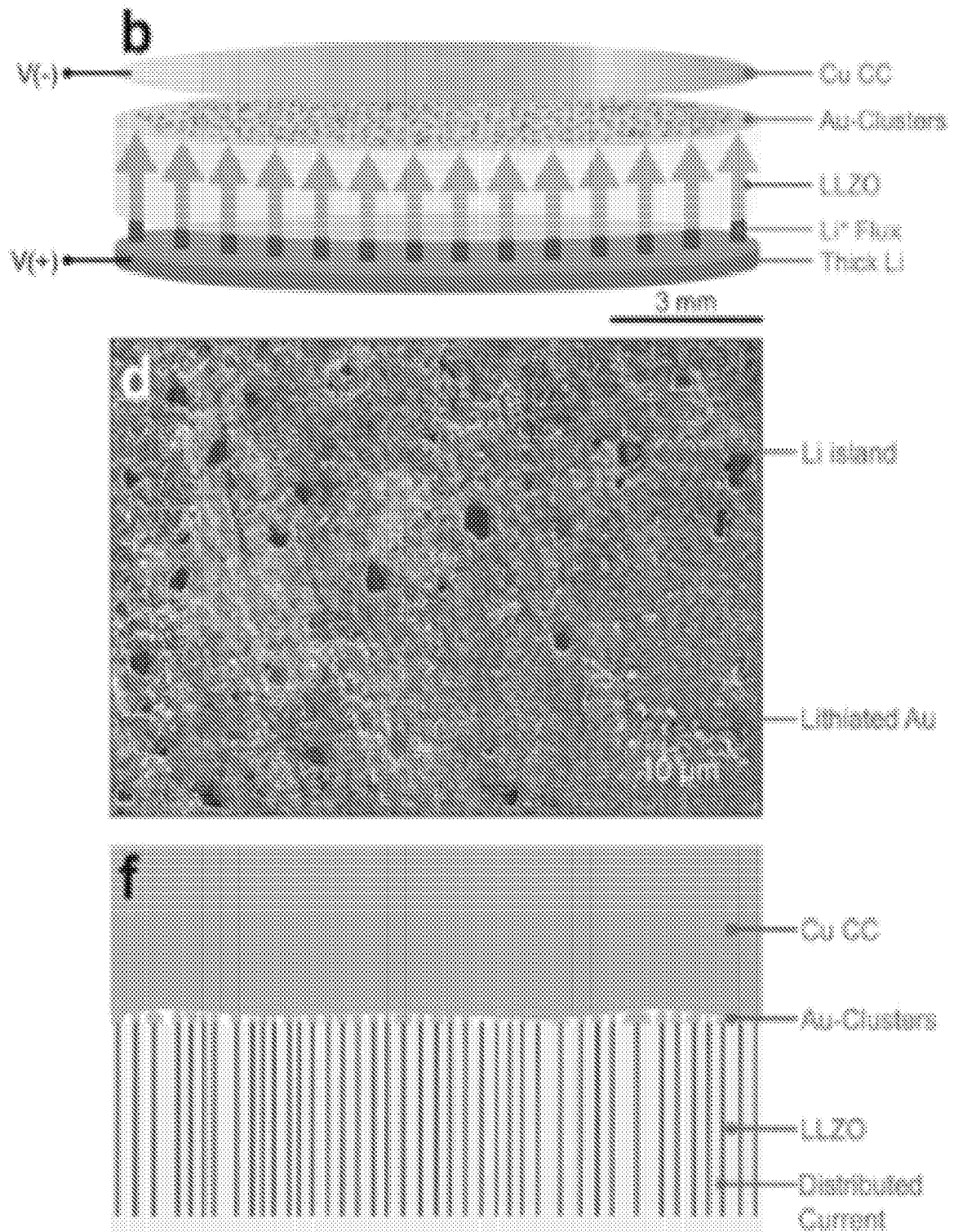


Figure 3 (continued)

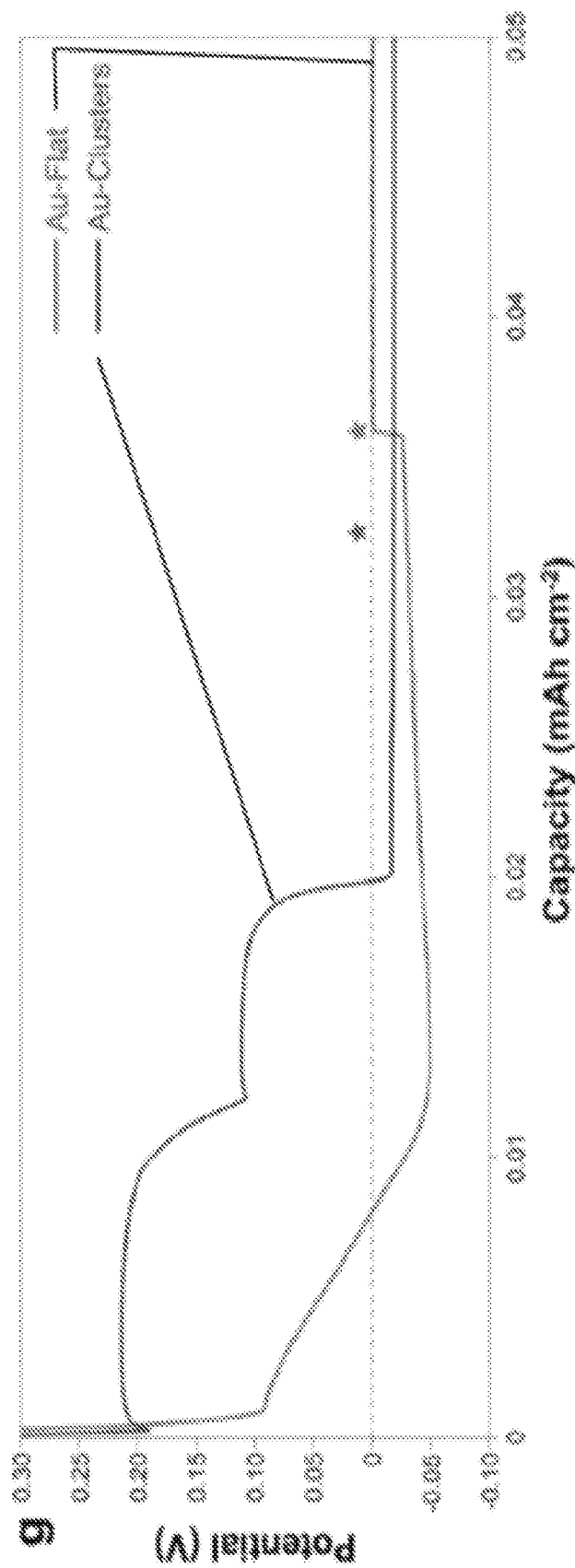


Figure 3 (continued)

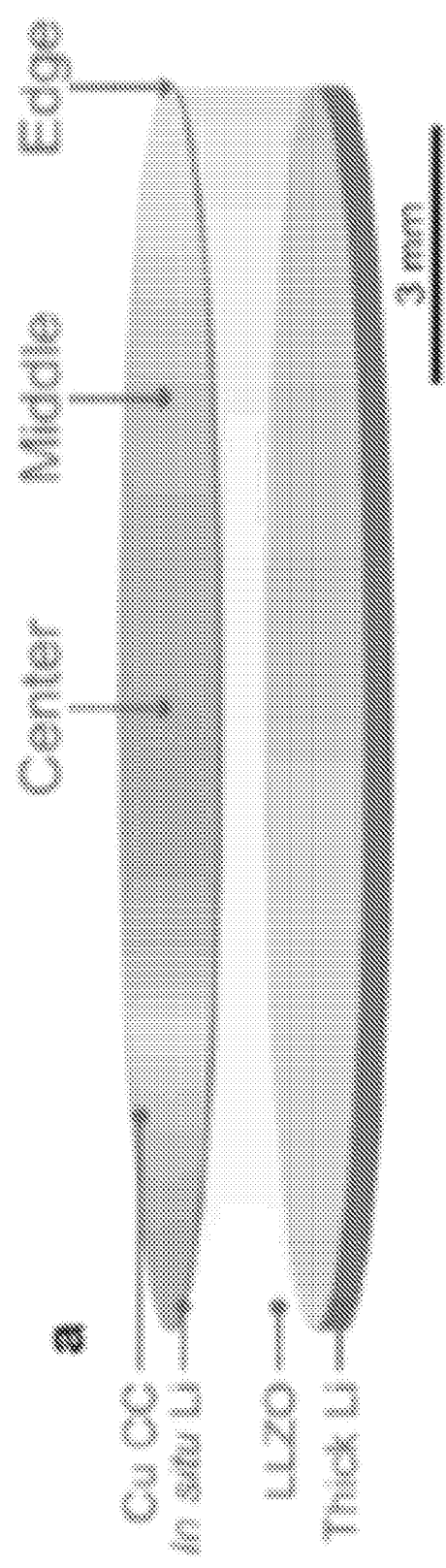


Figure 4

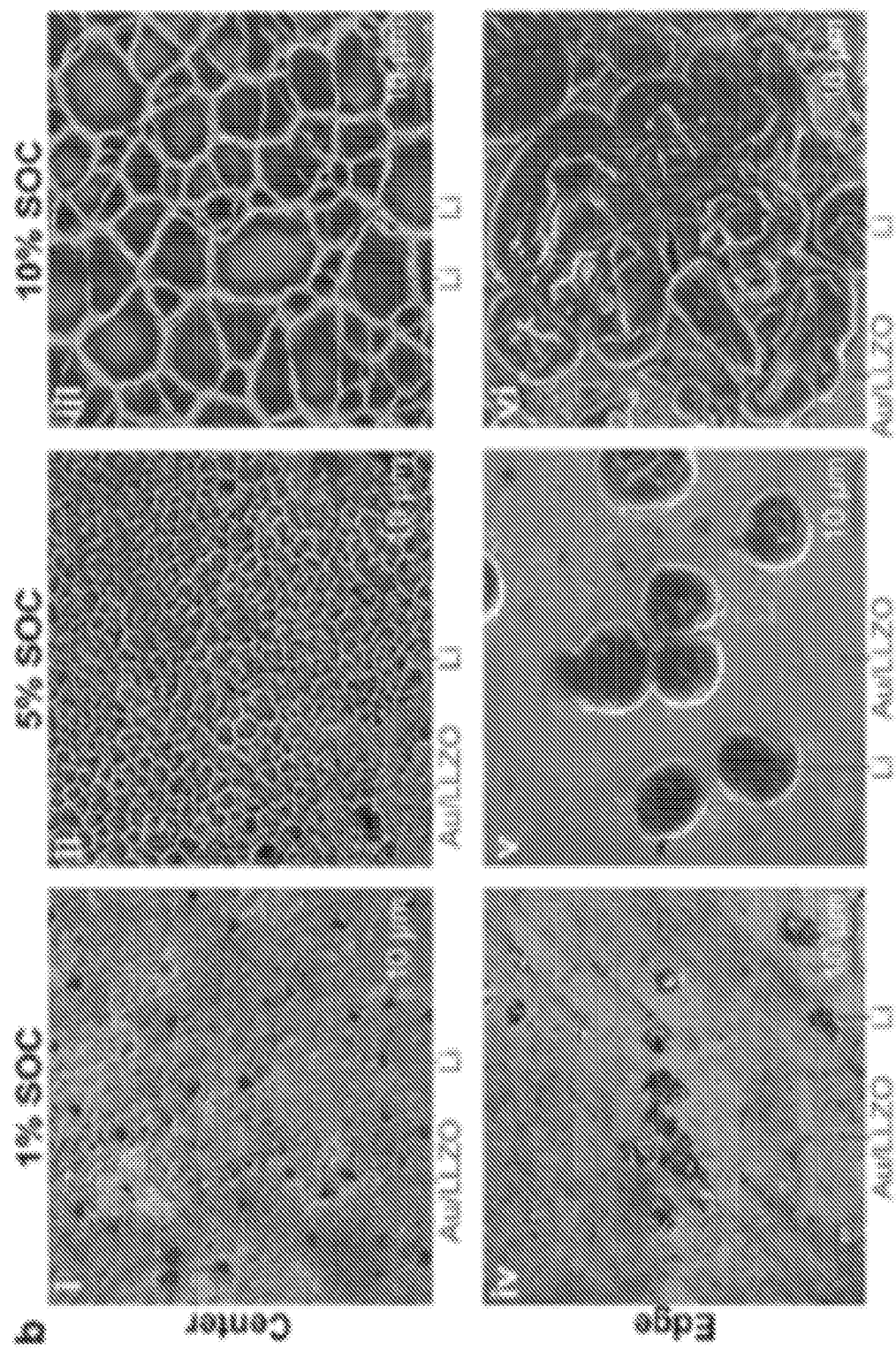


Figure 4 (continued)

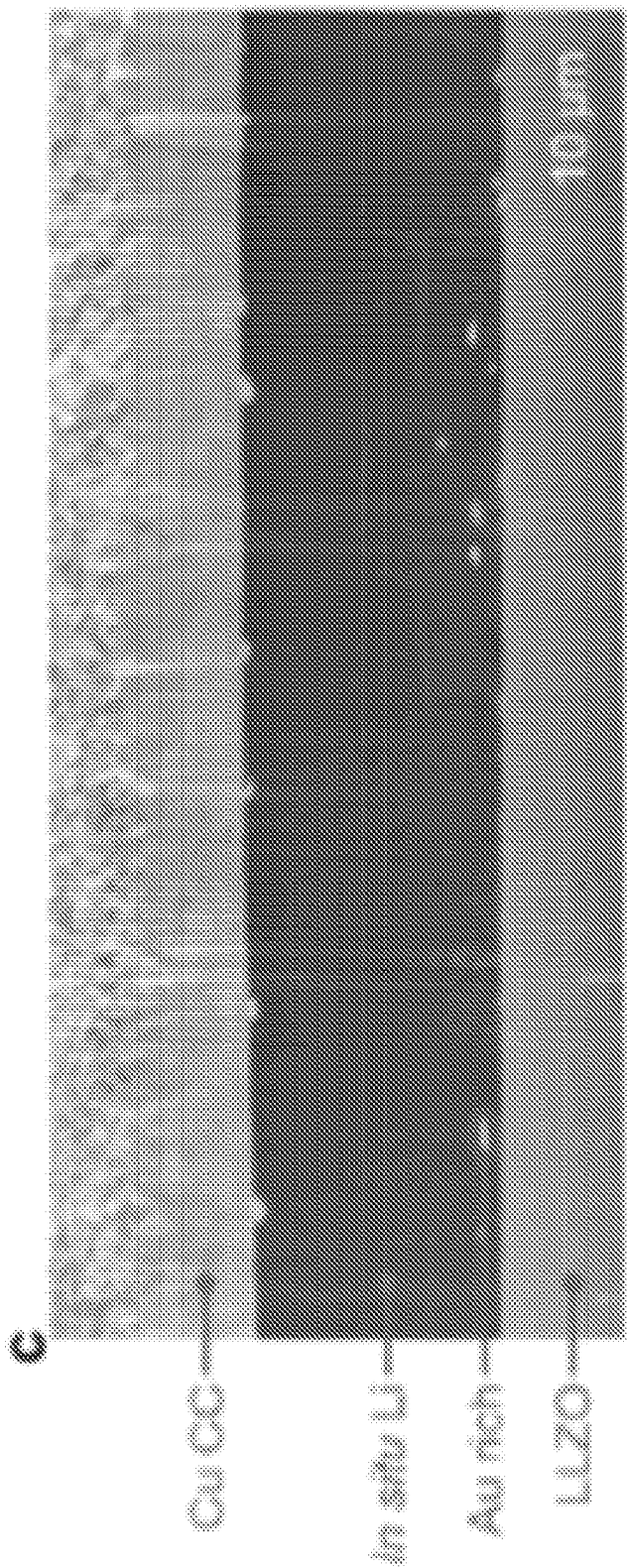


Figure 4 (continued)

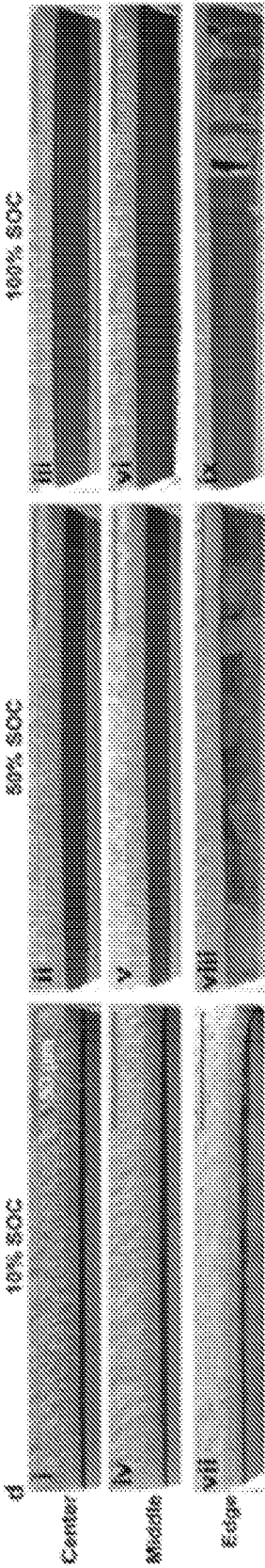


Figure 4 (continued)

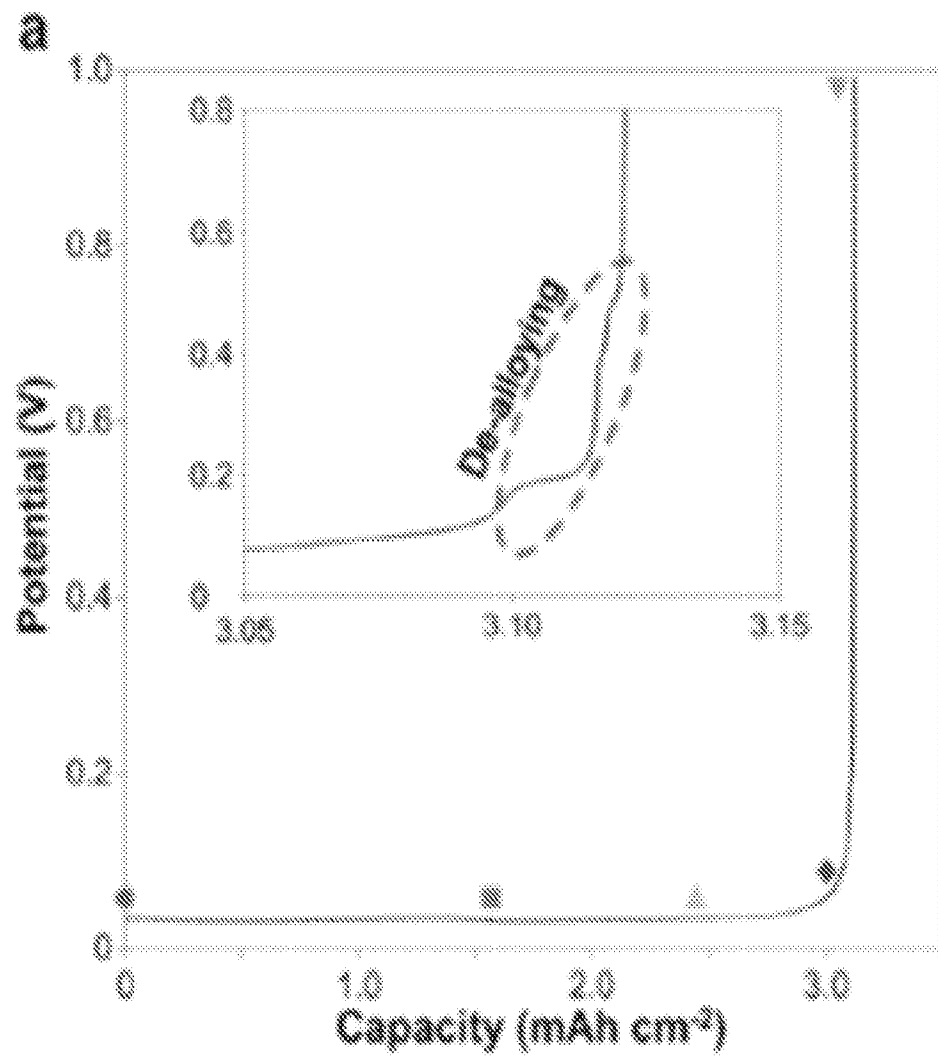


Figure 5

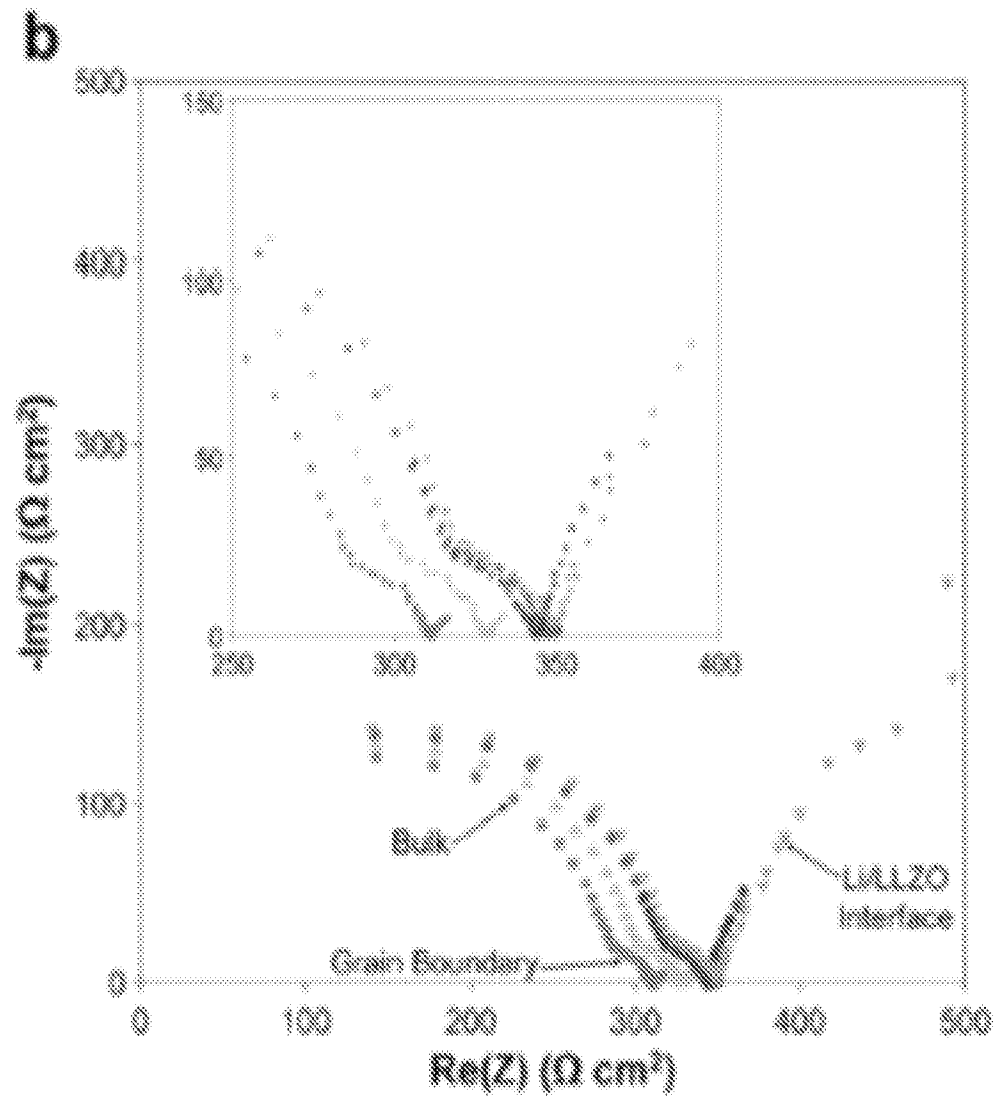


Figure 5 (continued)

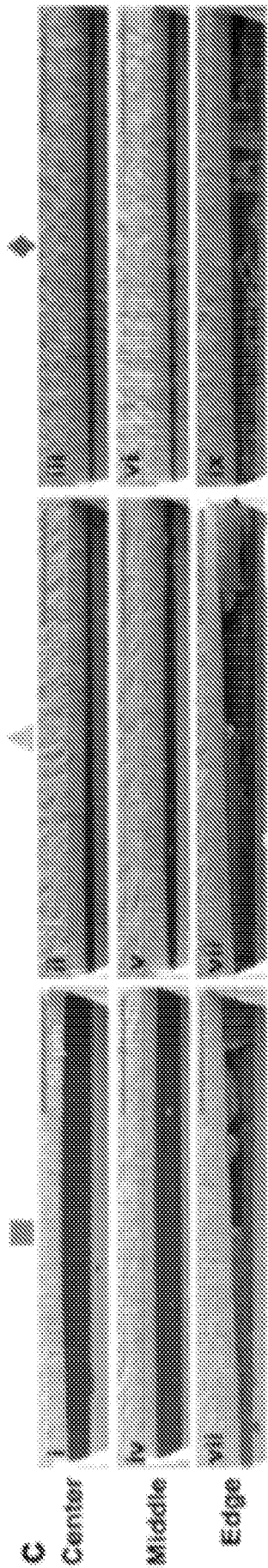


Figure 5 (continued)

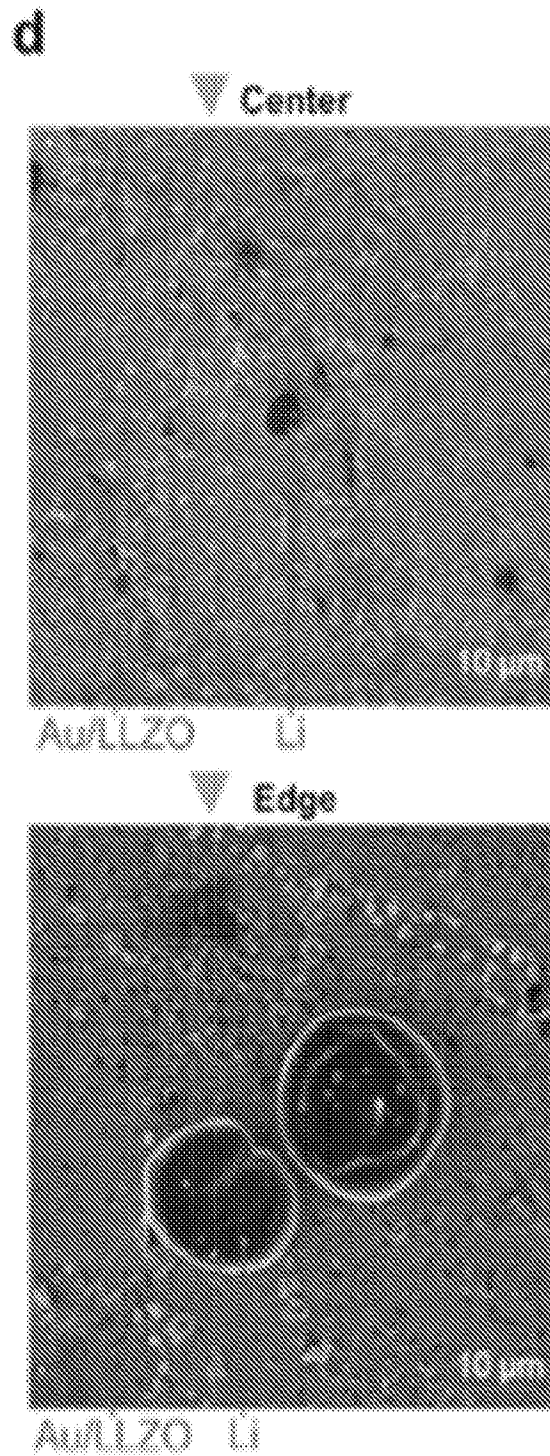


Figure 5 (continued)

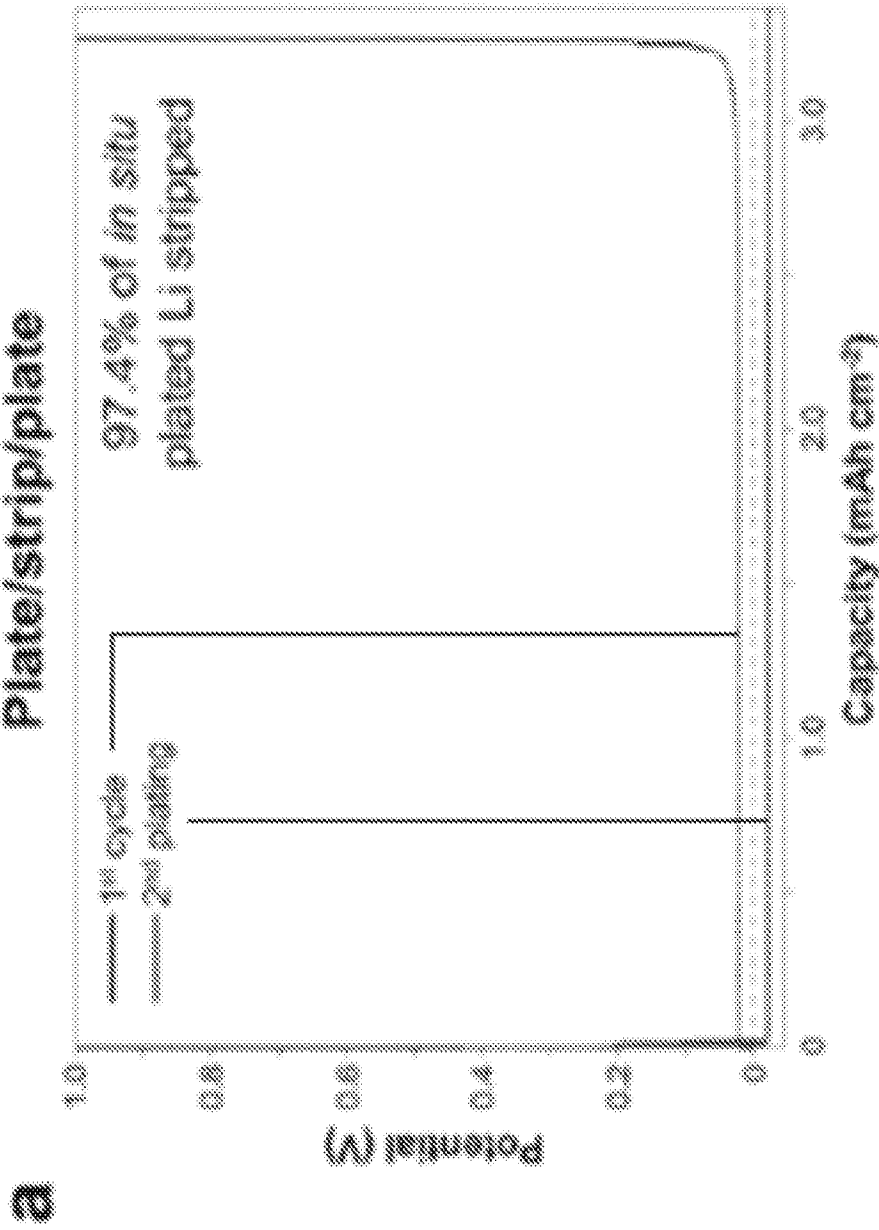


Figure 6

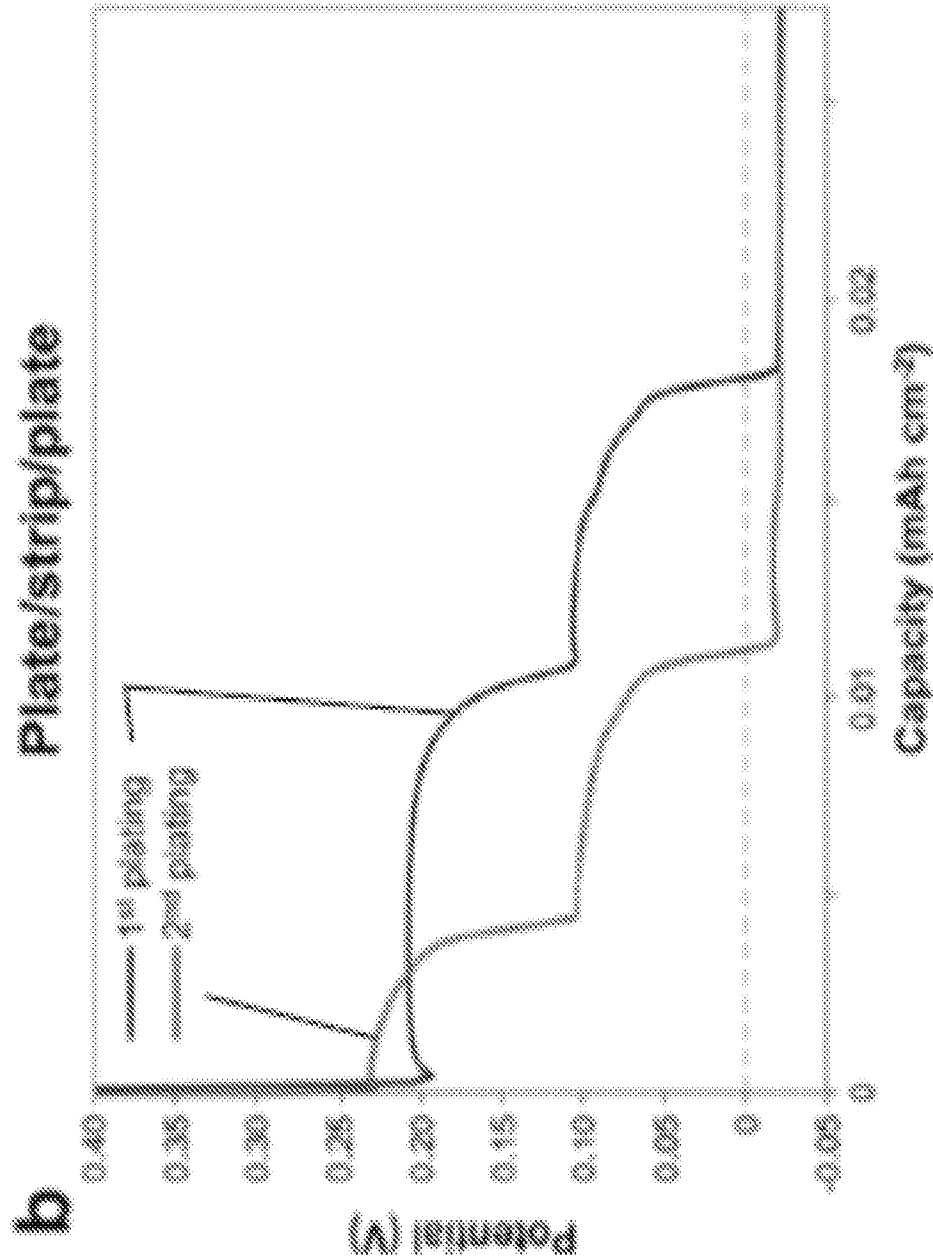


Figure 6 (continued)

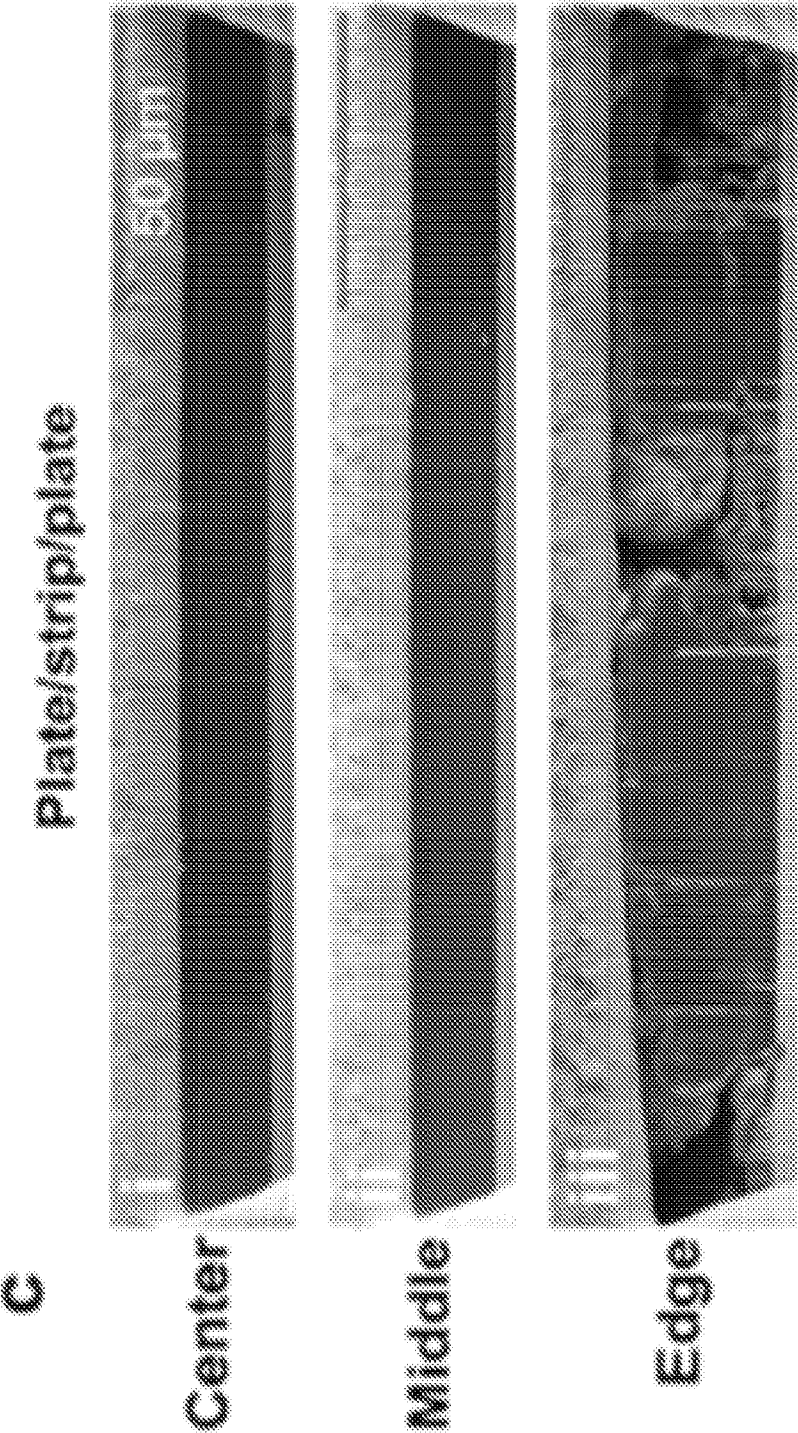


Figure 6 (continued)

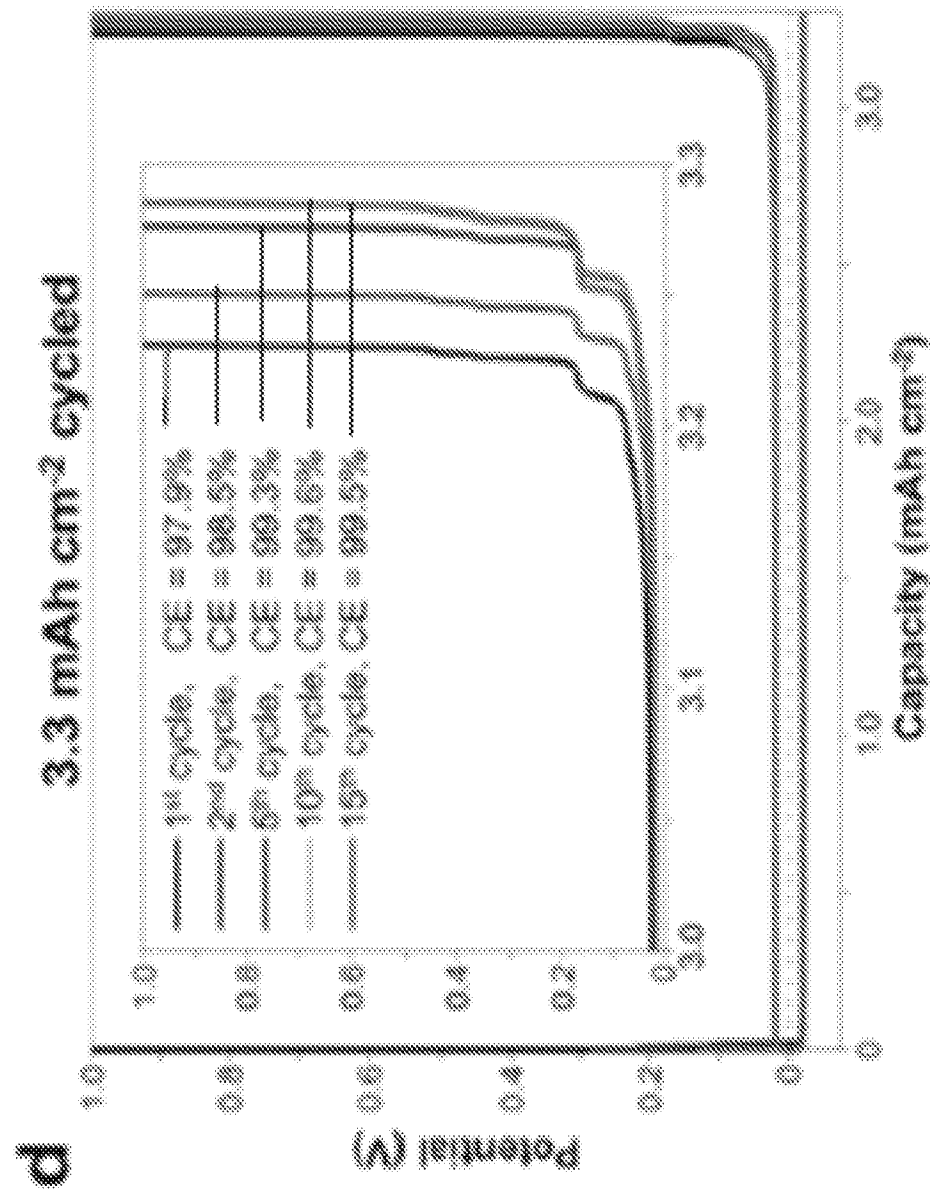


Figure 6 (continued)

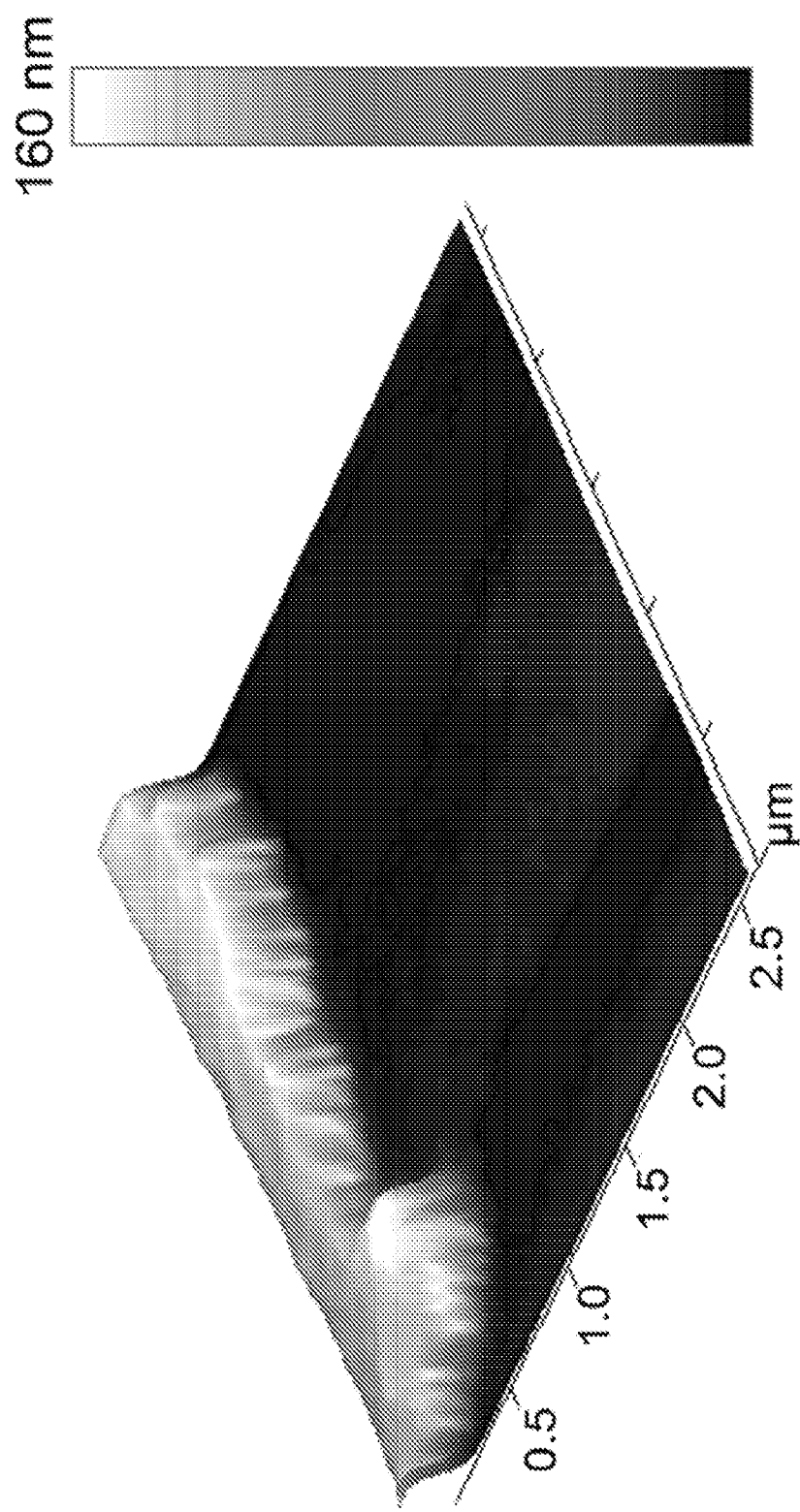


FIG. 7

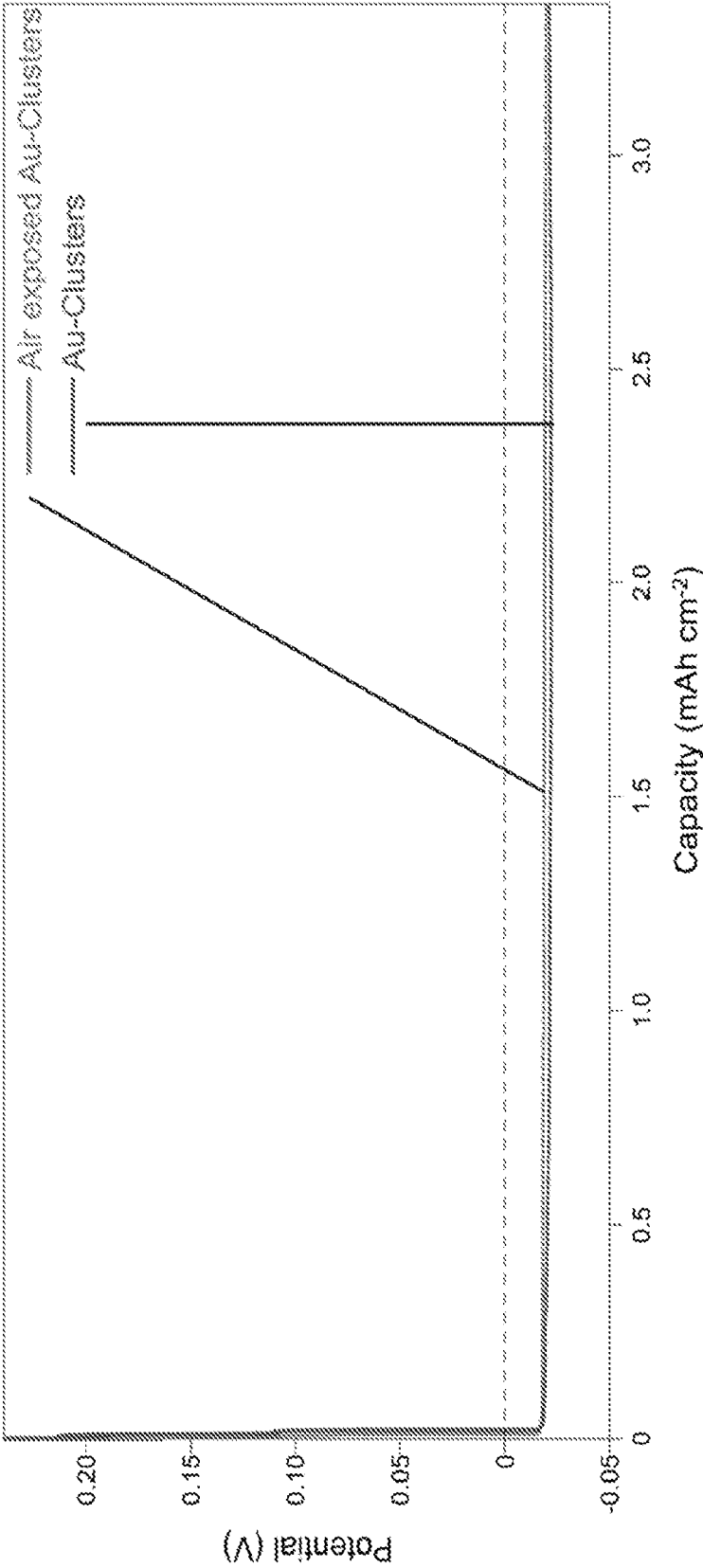


FIG. 8

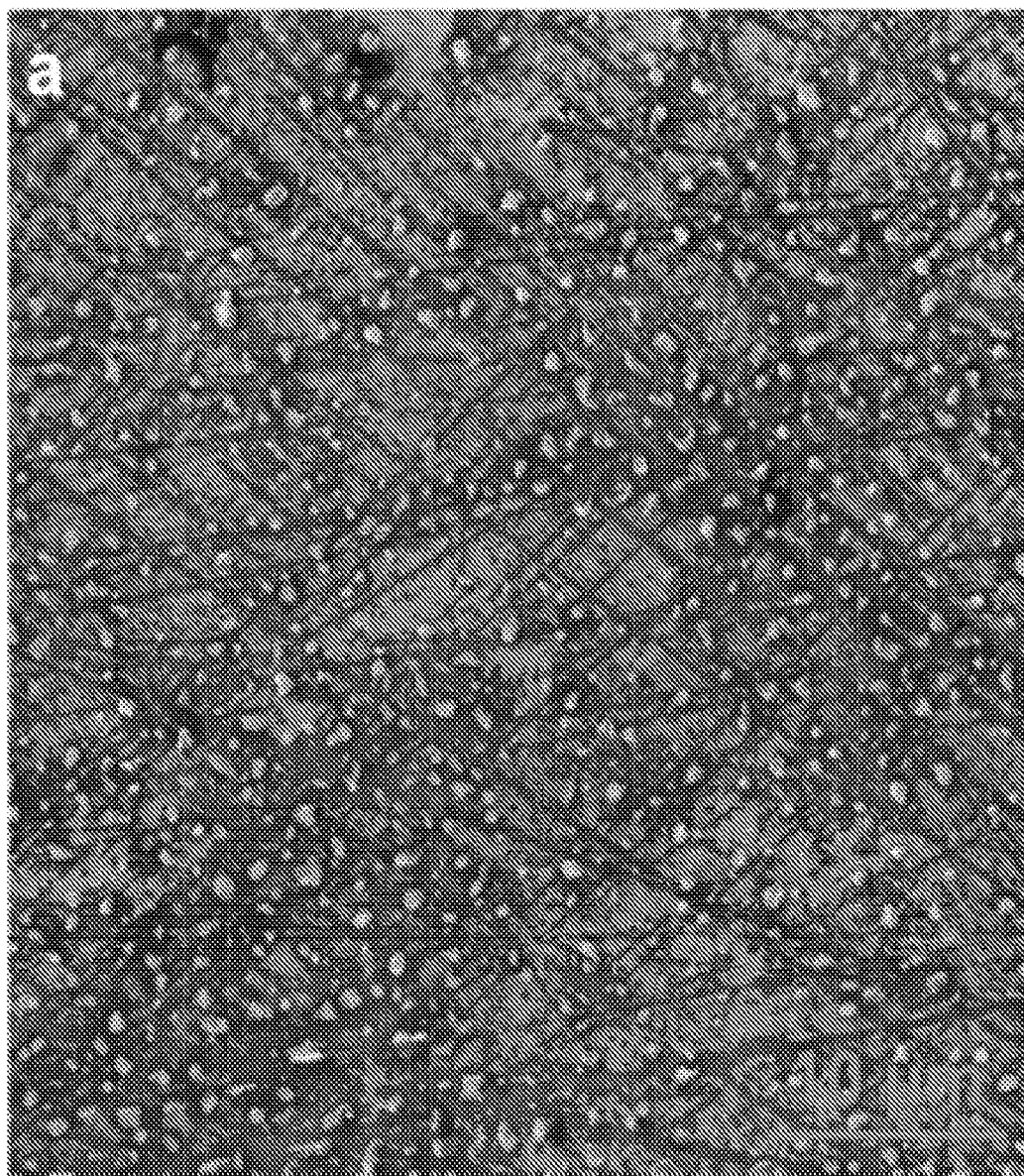


Figure 9

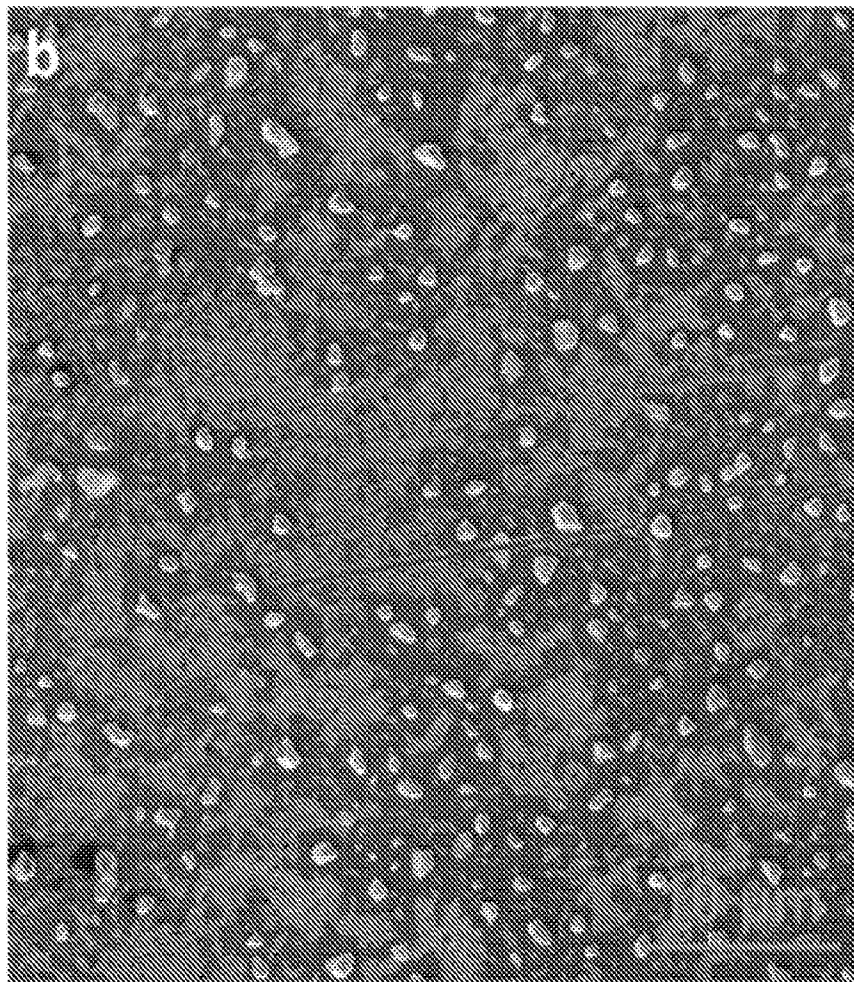


Figure 9 (continued)

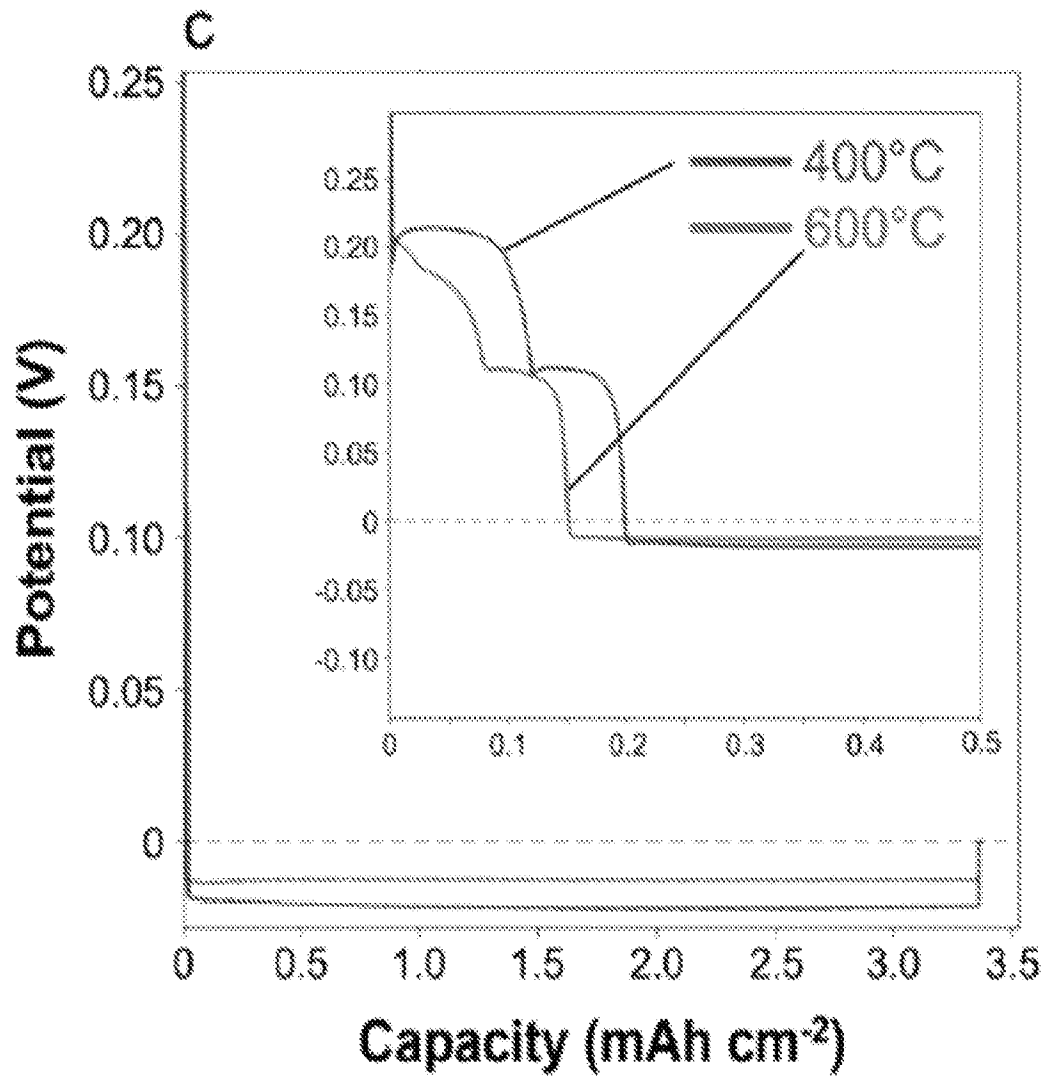


Figure 9 (continued)

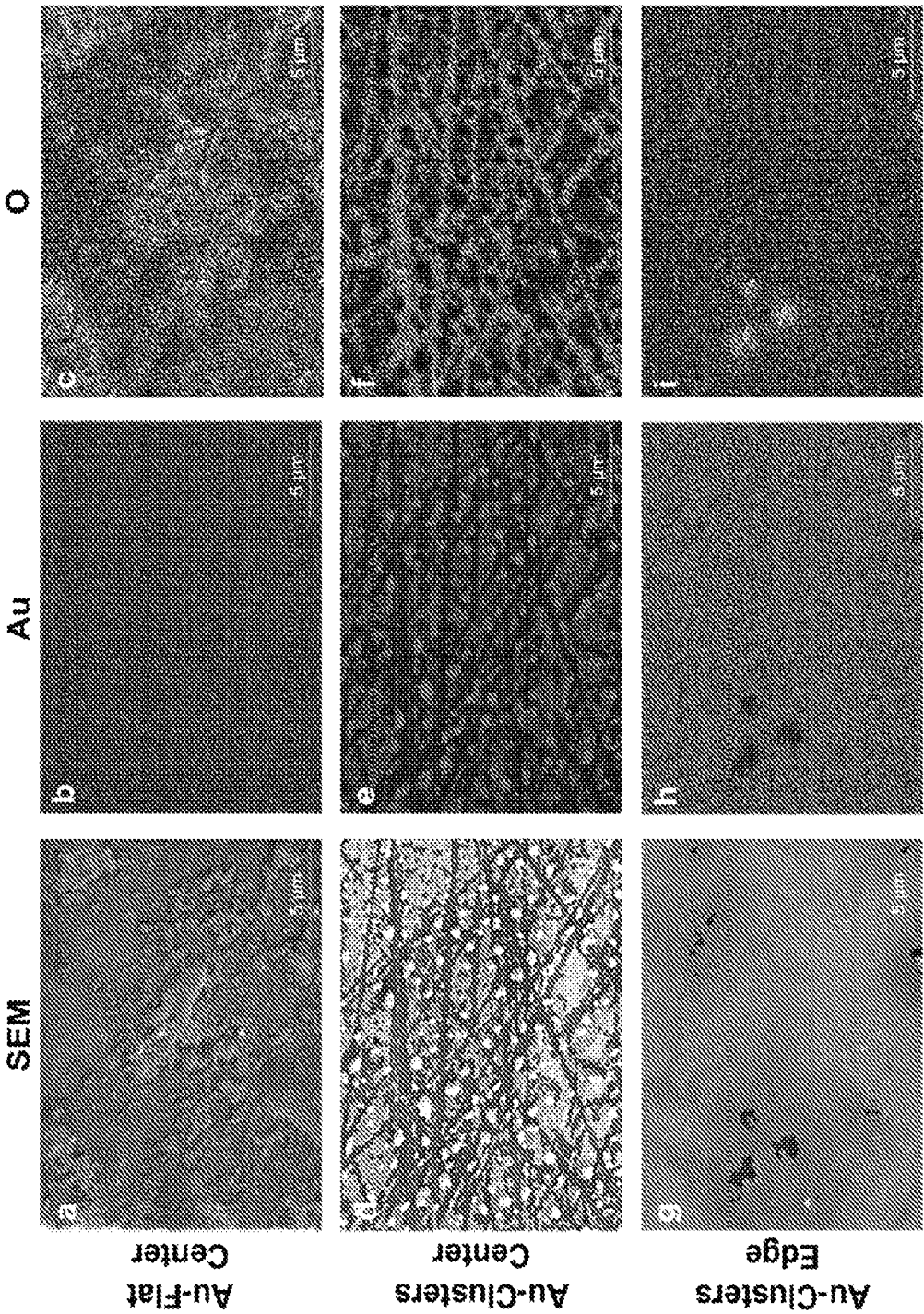


FIG. 10

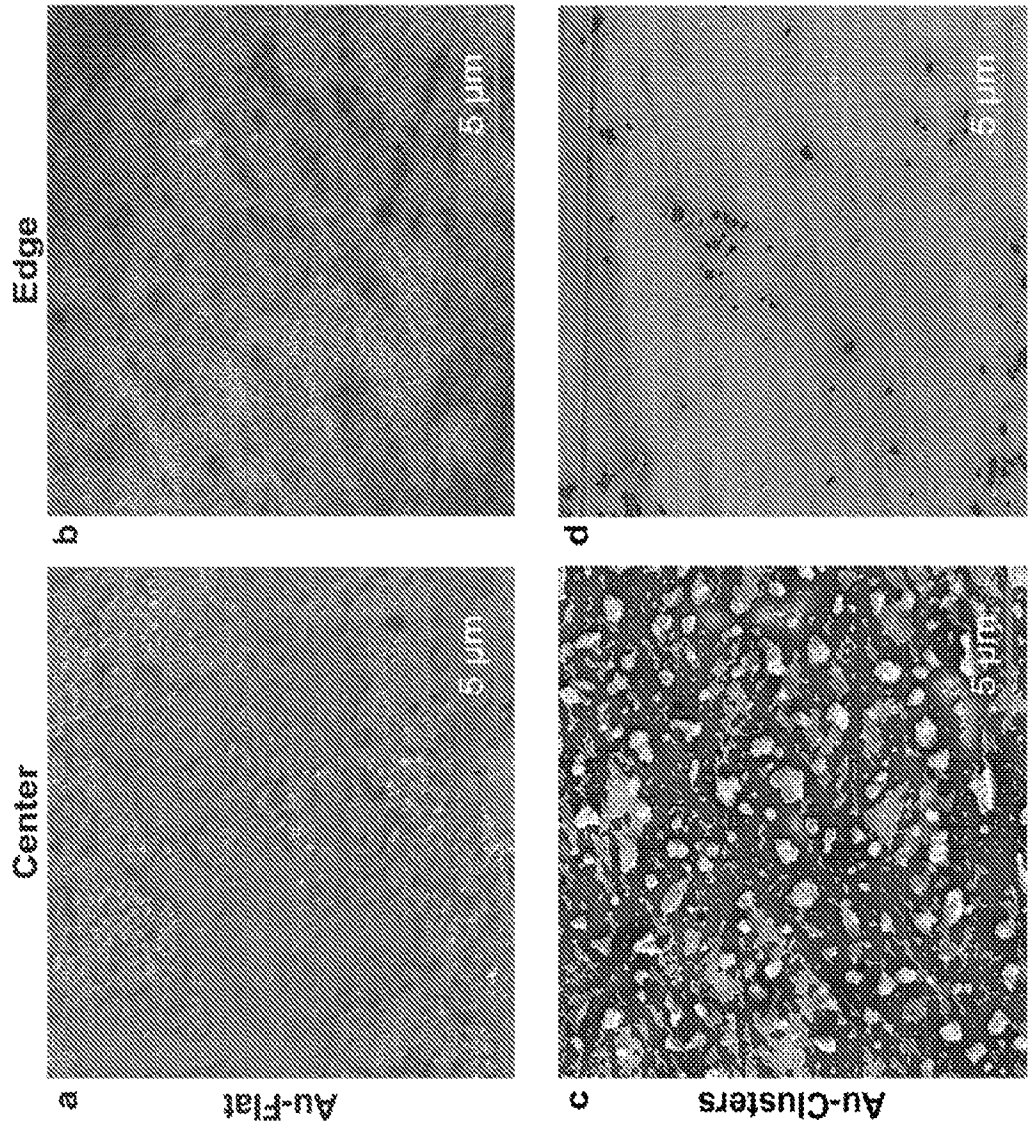


FIG. 11

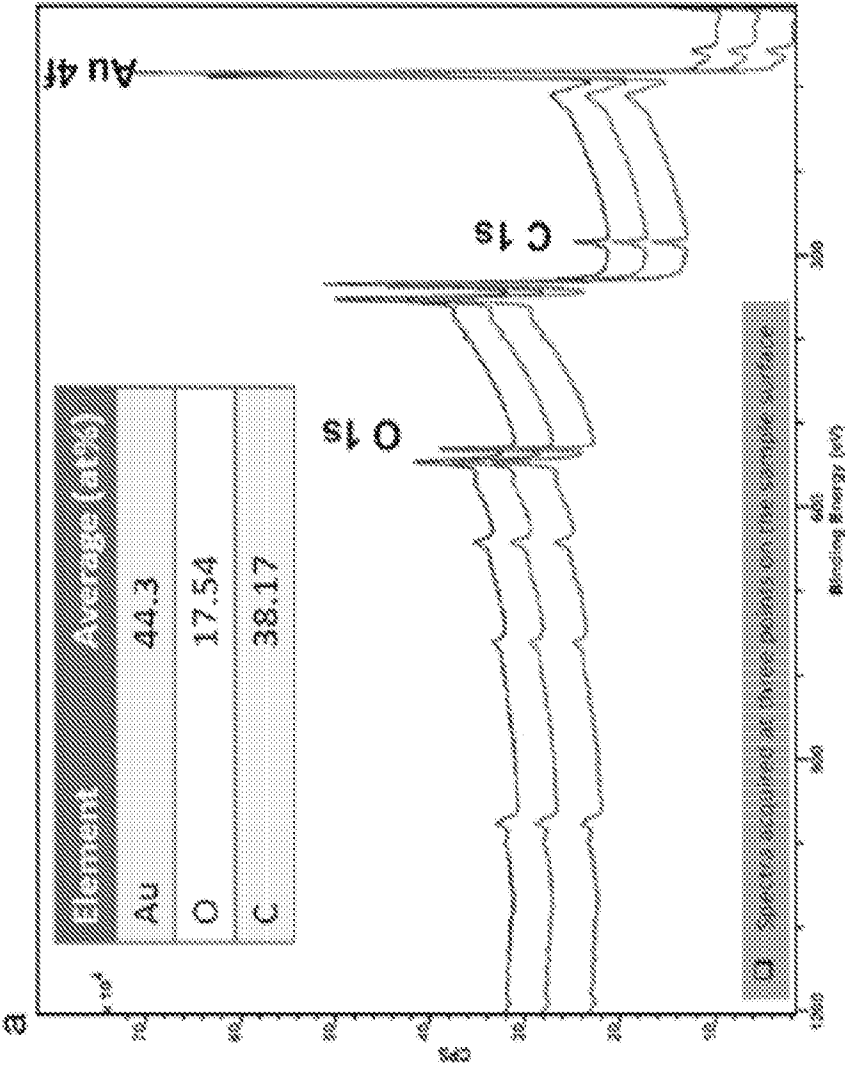


Figure 12

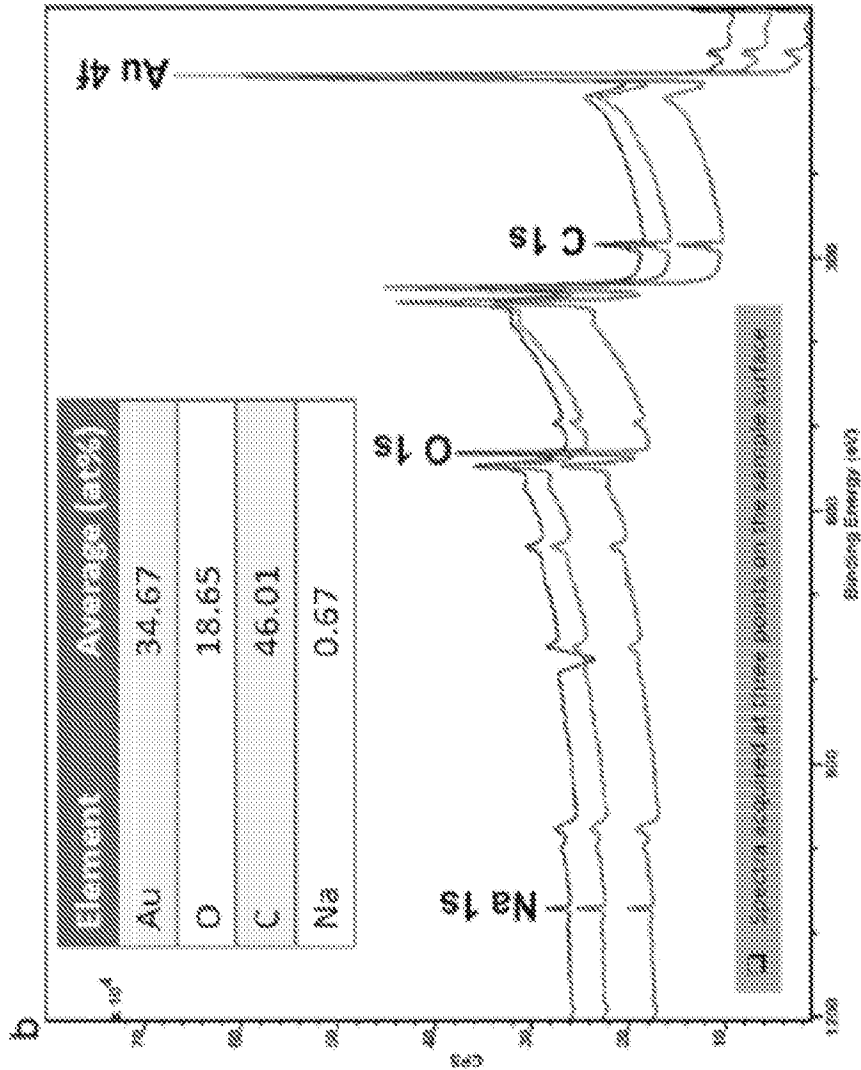


Figure 12 (continued)

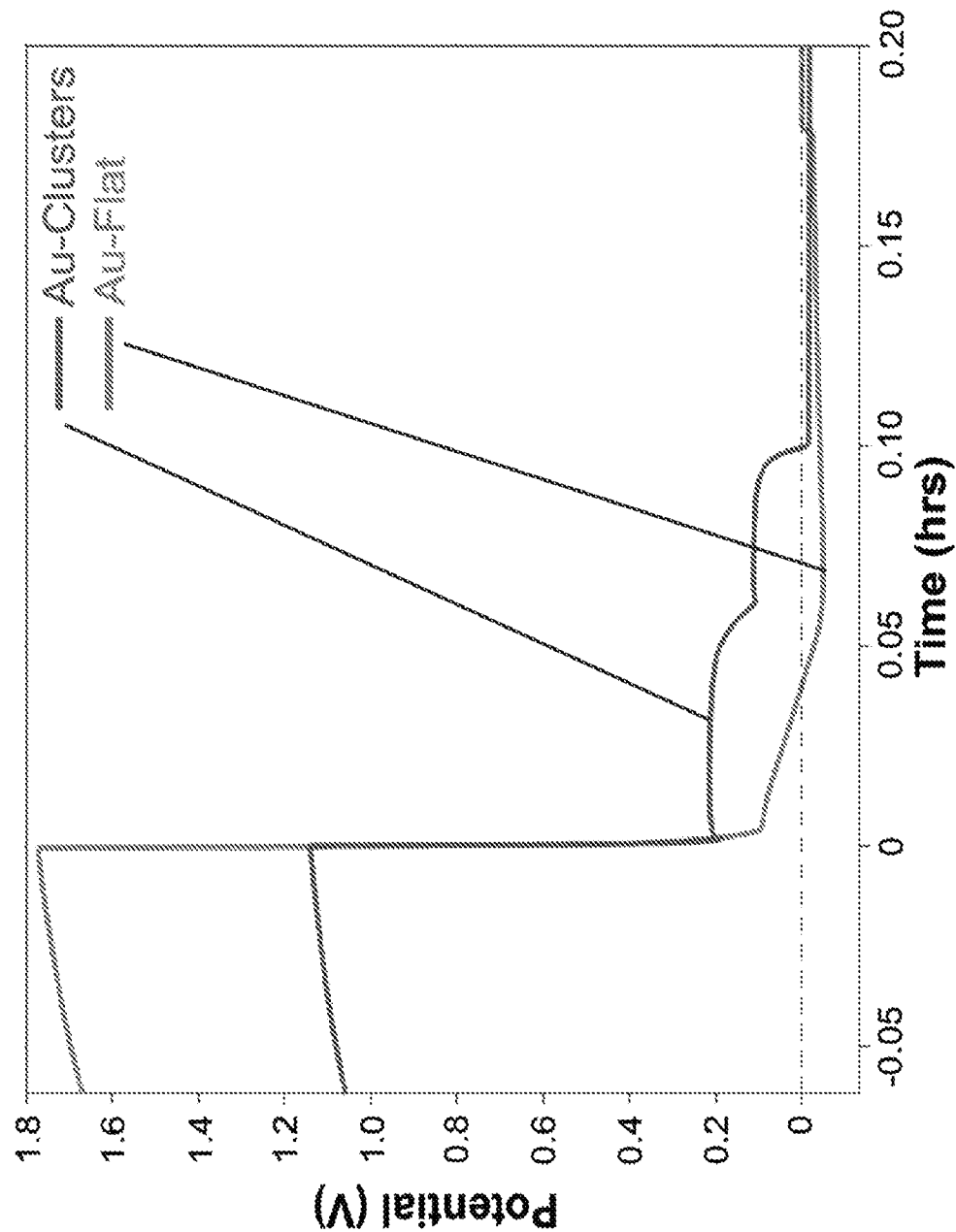


FIG. 13

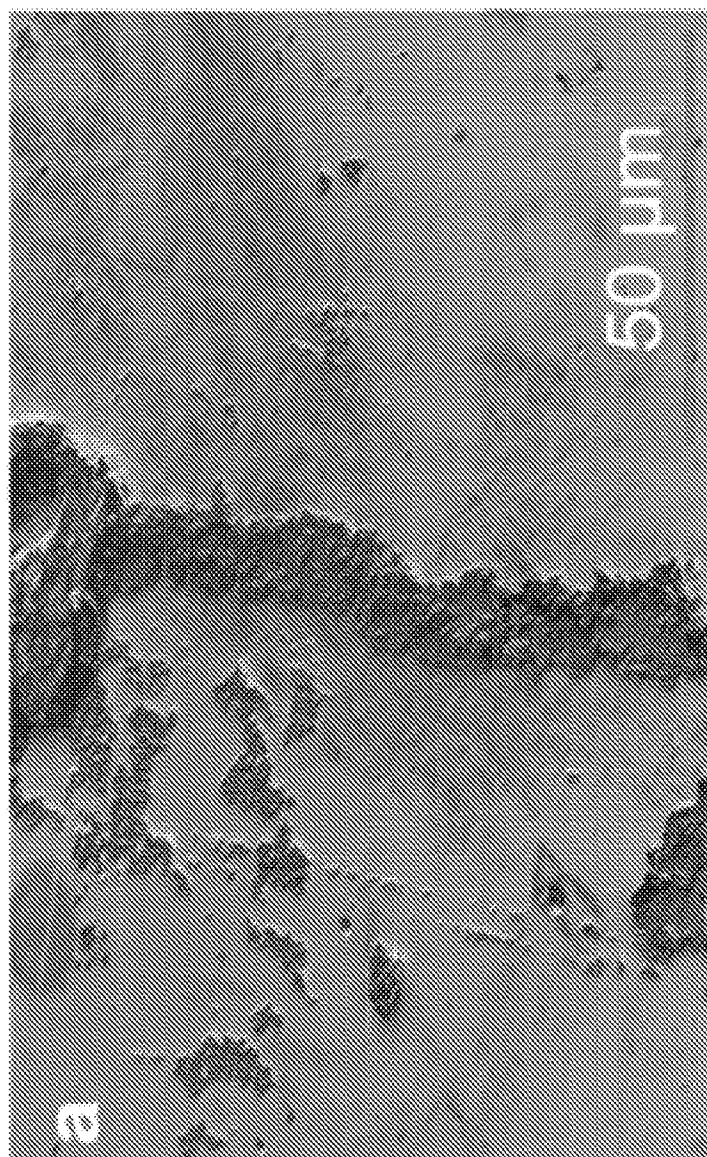


Figure 14

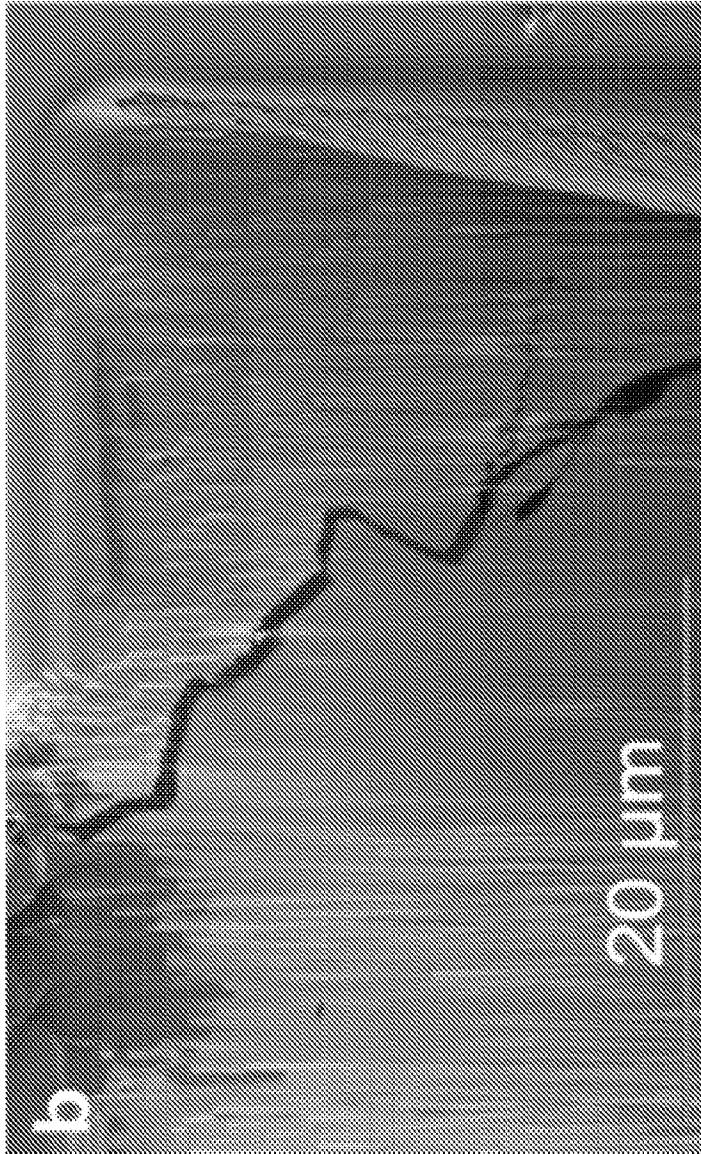


Figure 14 (continued)

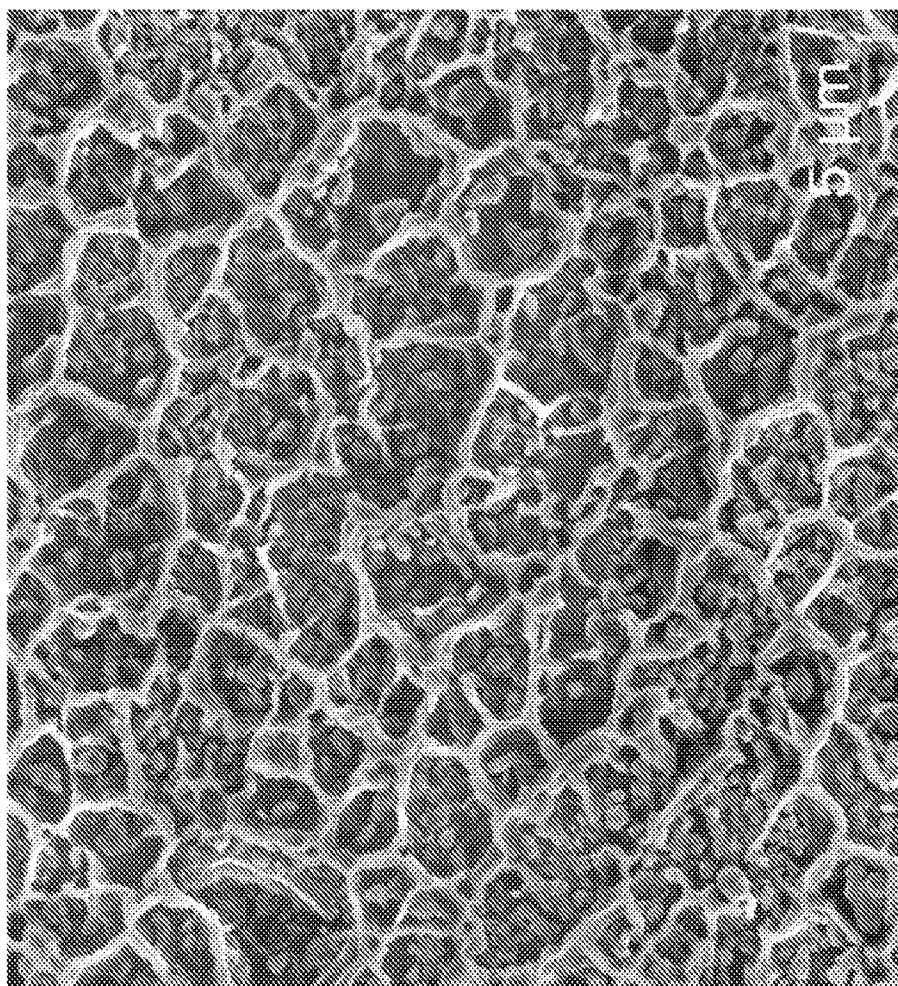


FIG. 15

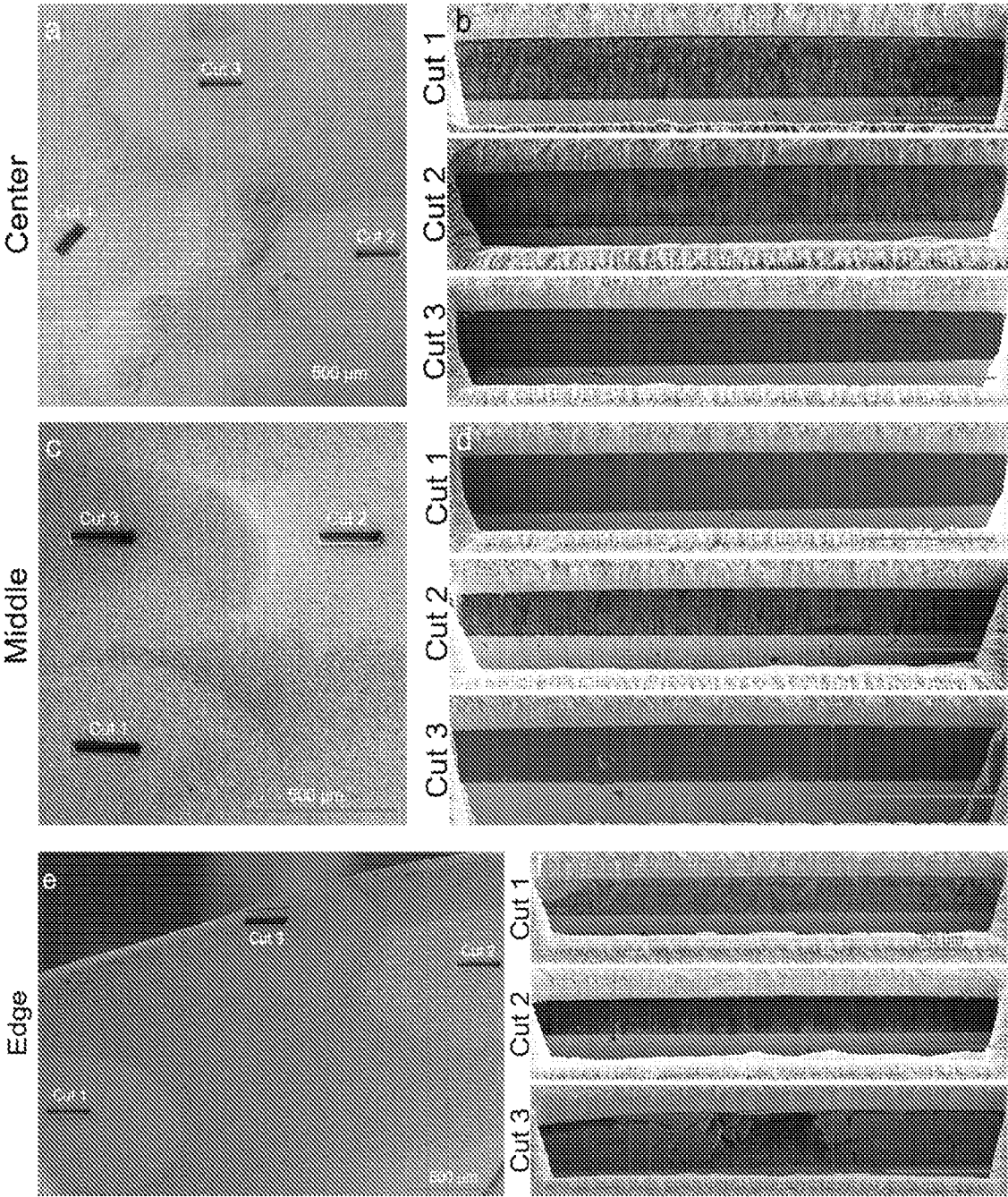


FIG. 16

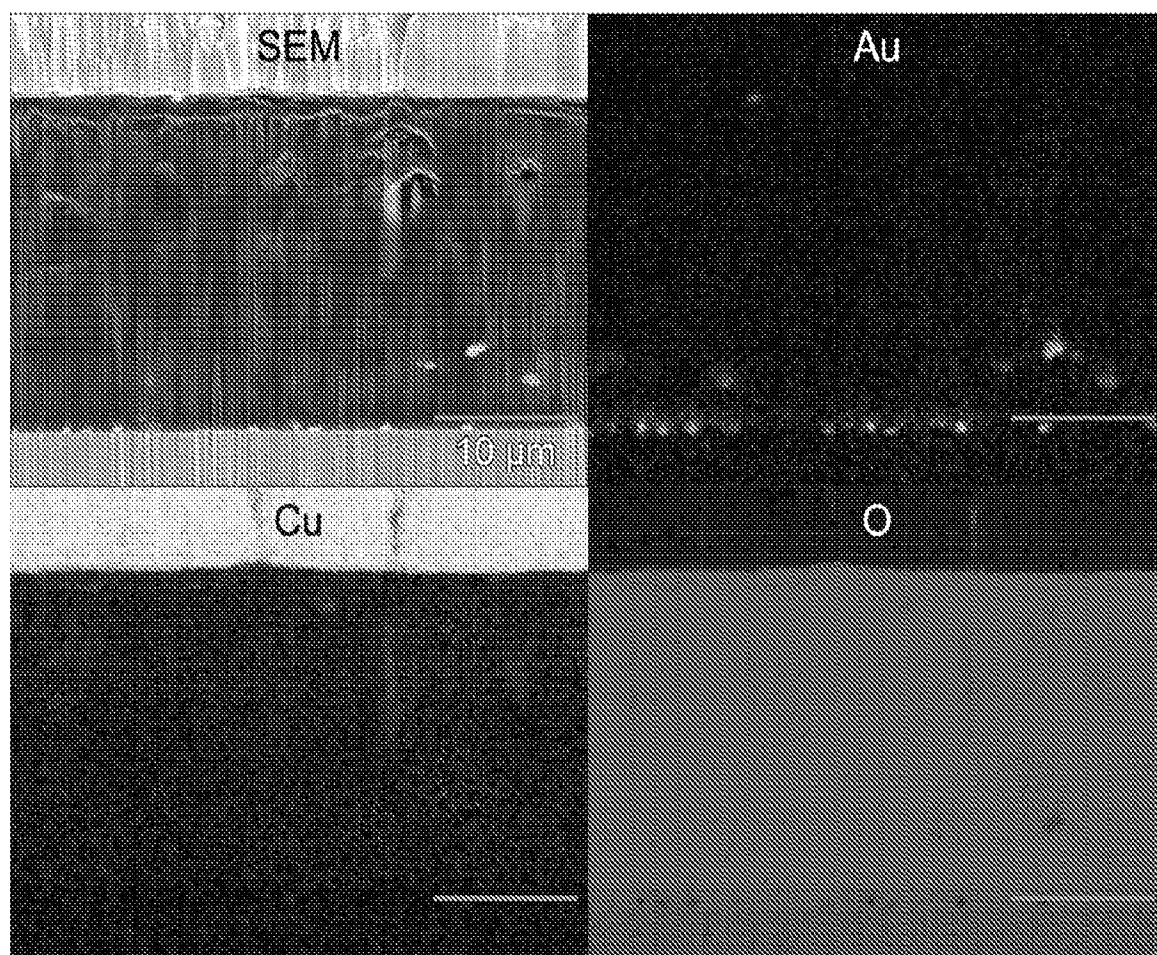


FIG. 17

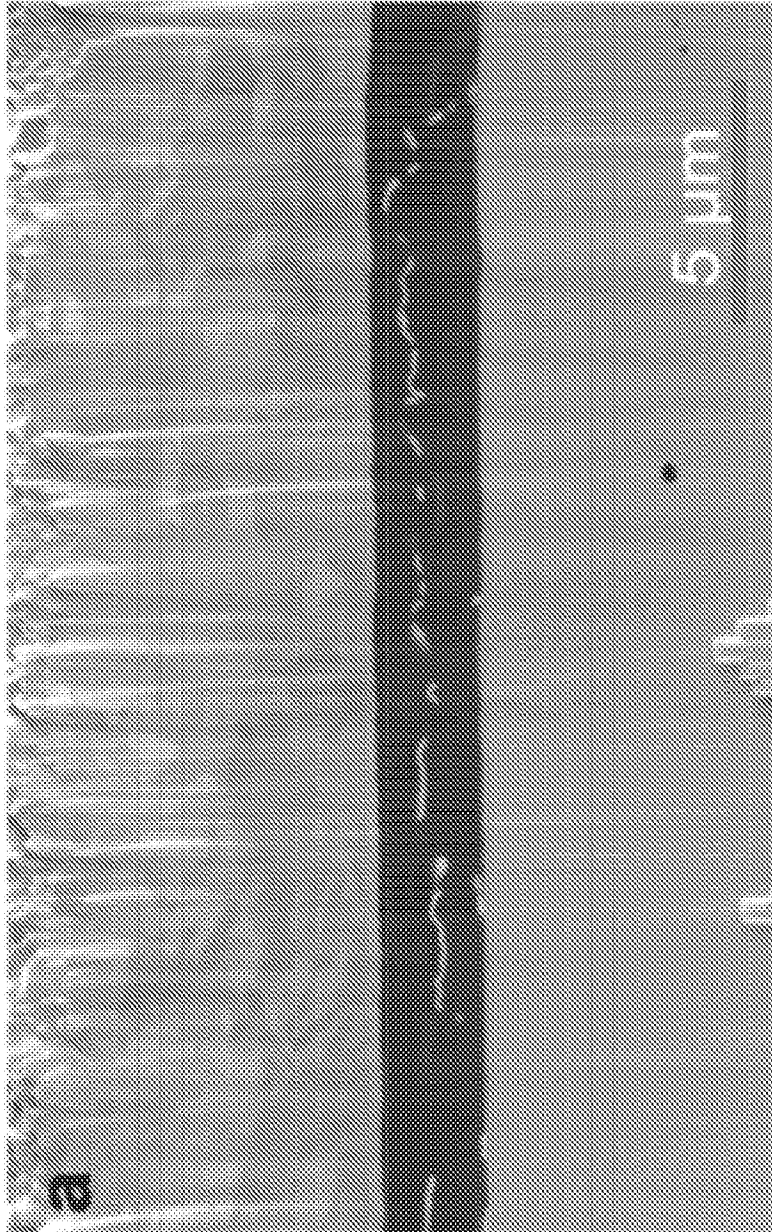


Figure 18

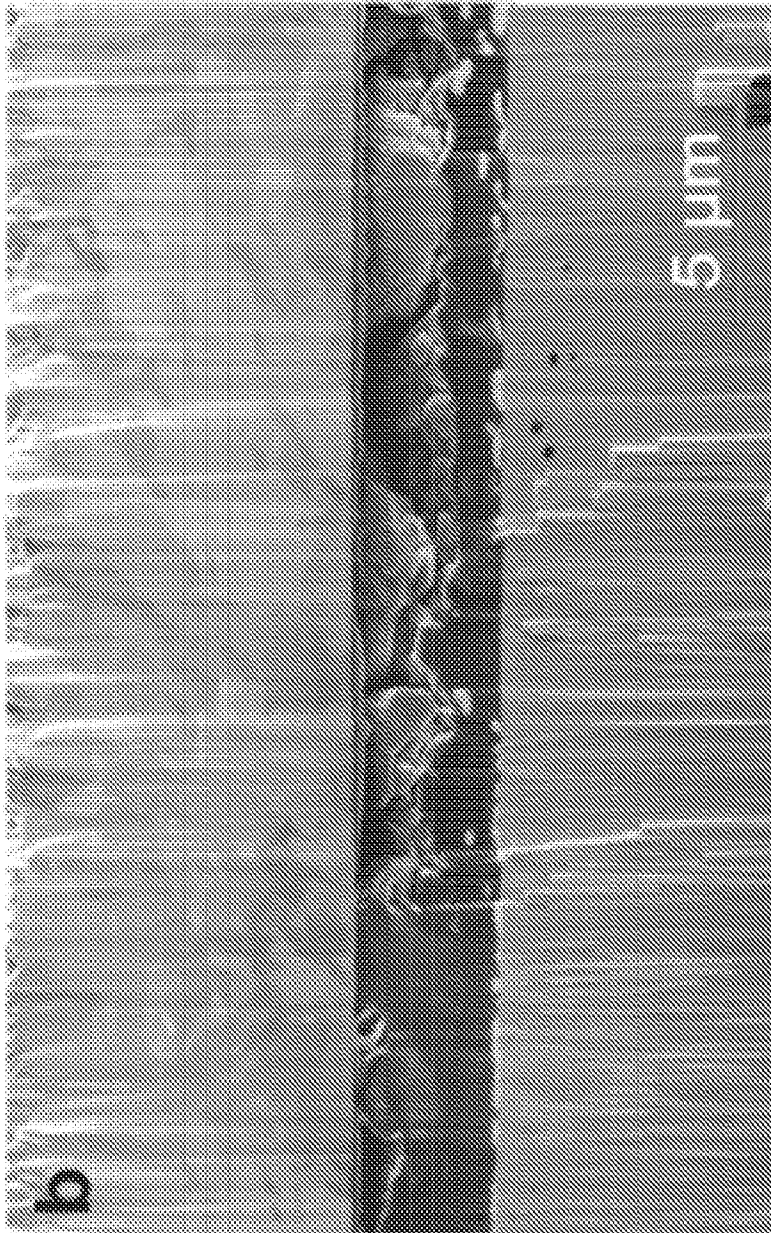


Figure 18 (continued)

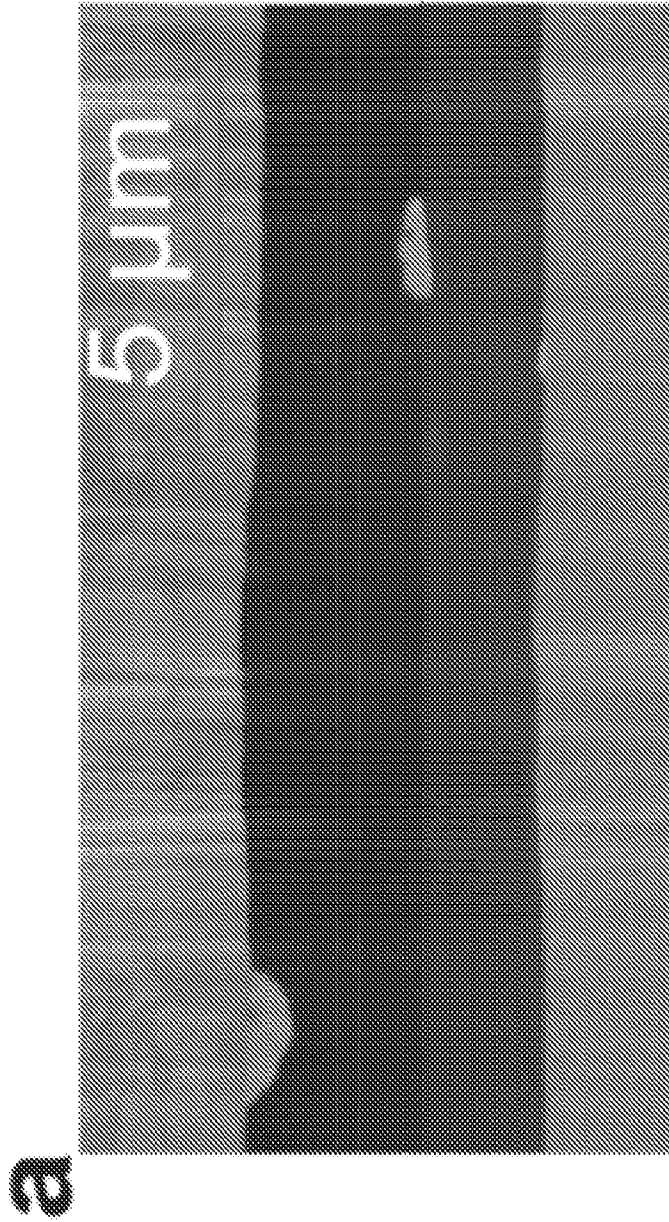


Figure 19

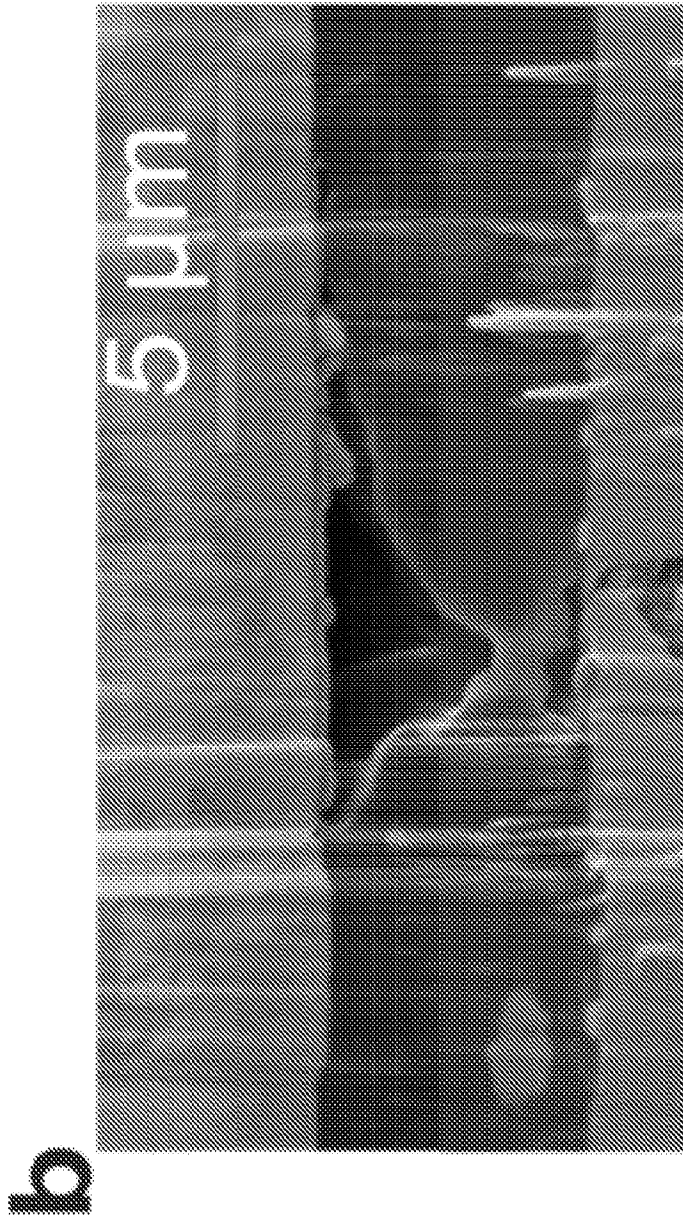


Figure 19 (continued)

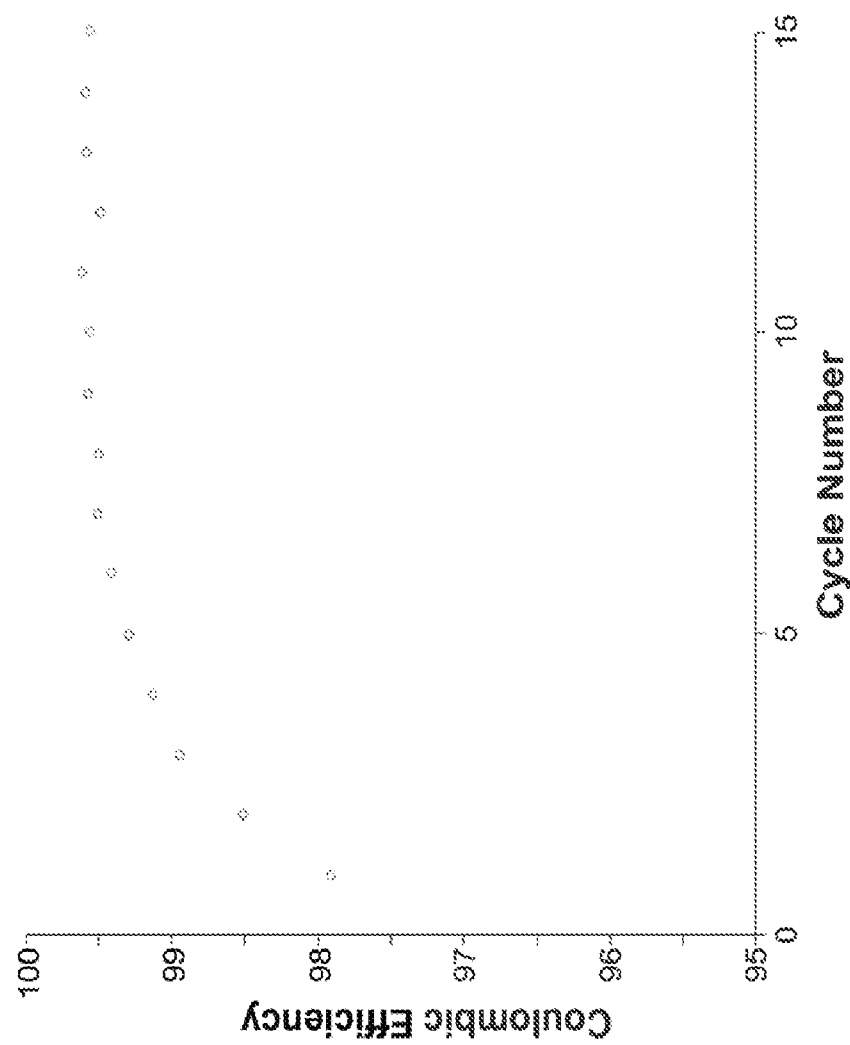


FIG. 20

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US23/80683

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. H01M 10/0562; H01M 4/134 (2023.01)

ADD.

CPC - INV. H01M 10/0562; H01M 4/134

ADD. C04B 2235/3215; C04B 2235/764; H01M 2300/0071

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0121354 A1 (FRYSZ, C. ET AL.) 08 June 2006; Paragraphs: [0004], [0009], and [0026-0029]	1-4, 6-9, 18
X --- A	US 2021/0091370 A1 (KABUSHIKI KAISHA TOSHIBA) 25 March 2021; Paragraphs: [0020], [007-0088], and [0167]; Claim 7	1-3, 10-12 --- 4-9, 13-66
X --- Y	US 2018/0301751 A1 (THE REGENTS OF THE UNIVERSITY OF MICHIGAN) 18 October 2018; see entire document	1-3, 13-16, 19-24, 28, 31, 33-43, 45-66 --- 4-12, 17-18, 25-27, 29-30, 32, 44
Y	US 2021/0257658 A1 (UNIVERSITY OF MARYLAND, COLLEGE PARK) 19 August 2021; Fig. 59; Paragraph: [0115]	5, 32
Y	US 2014/0170465 A1 (POLYPLUS BATTERY COMPANY) 19 June 2014; Paragraphs: [0095-0096]	17, 44
Y	US 2019/0051934 A1 (KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY) 14 February 2019; Paragraphs: [0026-0027] and [0076]	25-27, 29-30

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

12 March 2024 (12.03.2024)

Date of mailing of the international search report

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