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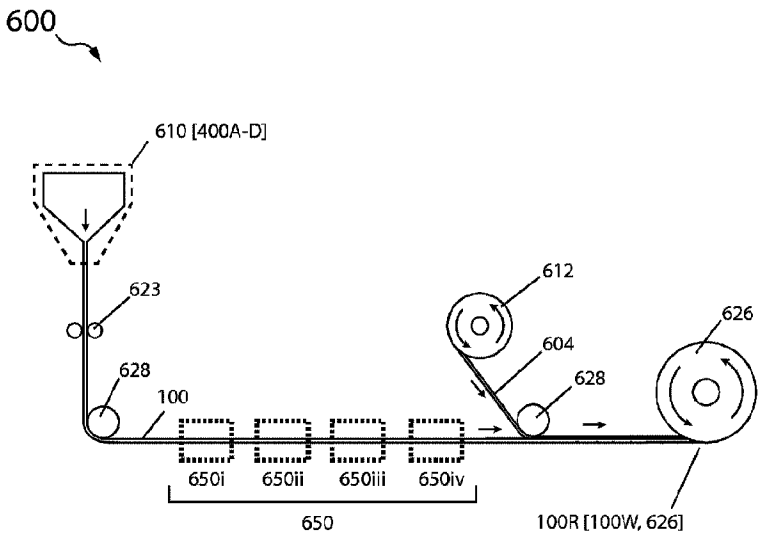
(54) Titre : ELECTROLYTE AUTONOME SOLIDE EN VERRE CONDUCTEUR D'IONS LITHIUM A BASE DE SULFURE ET STRUCTURES ASSOCIEES, CELLULES ASSOCIEES ET PROCEDES ASSOCIES

(54) Title: STANDALONE SULFIDE BASED LITHIUM ION-CONDUCTING GLASS SOLID ELECTROLYTE AND ASSOCIATED STRUCTURES, CELLS AND METHODS



(57) Abrégé/Abstract:
A standalone lithium ion-conductive solid electrolyte including a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass is capable of high performance in a lithium metal battery by providing a high degree of lithium ion conductivity while being highly resistant to the initiation and/or propagation of lithium dendrites. Such an electrolyte is also itself manufacturable, and readily adaptable for battery cell and cell component manufacture, in a cost-effective, scalable manner.

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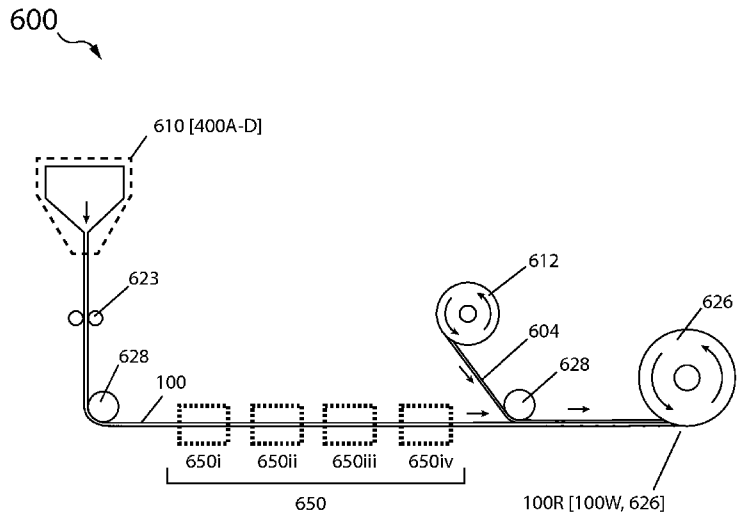

Figure 6

(57) Abstract: A standalone lithium ion-conductive solid electrolyte including a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass is capable of high performance in a lithium metal battery by providing a high degree of lithium ion conductivity while being highly resistant to the initiation and/or propagation of lithium dendrites. Such an electrolyte is also itself manufacturable, and readily adaptable for battery cell and cell component manufacture, in a cost-effective, scalable manner.

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STANDALONE SULFIDE BASED LITHIUM ION-CONDUCTING GLASS SOLID ELECTROLYTE AND ASSOCIATED STRUCTURES, CELLS AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application 62/086,641, filed December 2, 2014, titled LITHIUM ION CONDUCTING GLASS LAYERS AND ASSOCIATED PROTECTED LITHIUM METAL ELECTRODES AND BATTERY CELLS; and from U.S. Provisional Patent Application 62/111,048, filed February 2, 2015, titled LITHIUM ION CONDUCTING GLASS LAYERS AND ASSOCIATED PROTECTED LITHIUM METAL ELECTRODES AND BATTERY CELLS; and from U.S. Provisional Patent Application 62/146,809, filed April 13, 2015, titled FREESTANDING LITHIUM ION CONDUCTING ARTICLES AND ASSOCIATED ELECTRODE ASSEMBLIES AND BATTERY CELLS, and from U.S. Provisional Patent Application 62/149,250, filed April 17, 2015, titled FREESTANDING LITHIUM ION CONDUCTING ARTICLES AND ASSOCIATED ELECTRODE ASSEMBLIES AND BATTERY CELLS; and from U.S. Provisional Patent Application 62/165,791, filed May 22, 2015, titled LITHIUM ION CONDUCTING WALL STRUCTURES AND LITHIUM ELECTRODE ASSEMBLIES AND ASSOCIATED CONTINUOUS ROLLS AND LITHIUM BATTERY CELLS AND METHODS OF MAKING THEREOF; and from U.S. Provisional Patent Application 62/171,561, filed June 5, 2015, titled STANDALONE INORGANIC SOLID ELECTROLYTE SHEETS, AND STANDALONE LITHIUM ION CONDUCTIVE SOLID ELECTROLYTE SEPARATORS, CONTINUOUS INORGANIC SEPARATOR ROLLS, LITHIUM ELECTRODE ASSEMBLIES, AND BATTERY CELLS THEREOF, AS WELL AS METHODS OF MAKING THEREOF; and from U.S. Provisional Patent Application 62/196,247, filed July 23, 2015, titled STANDALONE INORGANIC SOLID ELECTROLYTE SHEETS, AND STANDALONE LITHIUM ION CONDUCTIVE SOLID ELECTROLYTE SEPARATORS, CONTINUOUS INORGANIC SEPARATOR ROLLS, LITHIUM ELECTRODE ASSEMBLIES, BATTERY CELLS THEREOF, AND METHODS OF MAKING; and from U.S. Provisional Patent Application 62/222,408, filed

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September 23, 2015, titled VITREOUS SOLID ELECTROLYTE SHEETS OF Li ION CONDUCTING SULFUR BASED GLASS AND ASSOCIATED STRUCTURES, CELLS AND METHODS; and from U.S. Patent Application 14/954,816 filed November 30, 2015.

FIELD OF THIS DISCLOSURE

[0002] This disclosure relates generally to the field of lithium electrochemical devices and components thereof, and in particular to lithium battery cells, lithium electrode assemblies, and Li ion-conducting solid electrolyte components (*e.g.,* separators and solid electrolyte sheets) for use in lithium battery cells, as well as methods for making said components, electrode assemblies and battery cells.

BACKGROUND OF THIS DISCLOSURE

[0003] There is a continuing need for high performance battery cells and their associated cell components, and particularly for high energy density secondary batteries.

SUMMARY

[0004] Provided herein is a standalone lithium ion-conductive solid electrolyte, methods of making and using the electrolyte, and battery cells and cell components incorporating the electrolyte. An electrolyte in accordance with this disclosure is capable of high performance in a lithium metal battery by providing a high degree of lithium ion conductivity while being highly resistant to the initiation and/or propagation of lithium dendrites. In addition, such an electrolyte is also itself manufacturable, and readily adaptable for battery cell and cell component manufacture, in a cost-effective, scalable manner.

[0005] In one aspect, provided is a standalone lithium ion-conductive solid electrolyte including a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass. The glass has a liquid-like surface, an area of at least $10cm^2$, a thickness of no more than 100μm, and a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm. The liquid-like surface lacks flaws sufficient to initiate lithium dendrite penetration. For example, the liquid-like surface lacks

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surface flaws having a depth dimension greater than 1% of the sheet thickness, preferably less than 0.1% of the sheet thickness, and generally no more than 5μm. Such a surface can be obtained through melt processing of a sulfide-based lithium ion conducting glass, such as by drawing molten glass or pulling/drawing a glass preform into a sheet. A sheet formed in this manner lacks powder particle, inter-particle boundaries, or contiguous void manifestations of a pressed powder compact extending between first and second principal surfaces that are sufficient to propagate a Li dendrite, and the liquid-like surface lacks flaw manifestations of a pressed powder compact that are sufficient to initiate Li dendrite penetration.

[0006] The electrolyte glass sheet can have physical dimensions and features suitable or particularly adapted for service as a separator in a battery cell. For example, the sheet can have a variety of areas such that it does not constrain battery cell format. It can have a substantially uniform thickness of no more than 100μm, either as formed or as subsequently processed. And it can have substantially parallel lengthwise edges, again either as formed or as subsequently processed. The electrolyte glass sheet can also be configured as a flexible roll to facilitate storage and processing, for example a continuous web at least 100cm in length.

[0007] In some embodiments, the sheet is characterized as an inorganic vitreous sulfide-based glass sheet. The vitreous sheet may be further characterized as having a threshold current for lithium dendrite initiation that is greater than $1mA/cm^2$.

[0008] Characterization of thermal, and associated viscosity, properties of a glass may be made with reference to the glass stability factor $\{T_x - T_g\}$, which is the separation of the onset of crystallization (T_x) and the glass transition temperature (T_g). Sulfur-based glass compositions that are less prone to crystallization and/or have higher melt viscosities, and therefore a higher glass stability factor, but still retain a requisite level of Li ion conductivity ($>10^{-5}$S/cm) have been developed. While apparently counterintuitive to decrease the lithium ion conductivity of a glass that is specifically intended for use in a battery cell as a lithium ion conductor, in various embodiments this approach is contemplated for making and improving properties of the vitreous glass solid electrolyte sheets. Accordingly, in various embodiments the composition of a suitable sulfide-based glass system is adjusted to enhance thermal properties, even at the sacrifice of reduced conductivity, so that an electrolyte glass sheet as

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described and claimed may be obtained where the glass has a stability factor $\{T_x - T_g\}$ < 100°C; or less than 50°C; or even less than 30°C.

[0009] In some embodiments, the sulfide-based glass is of a type Li_2S-YS_n; Li_2S-YS_n-YO_n and combinations thereof, wherein Y is selected from the group consisting of Ge, Si, As, B, or P, and n = 2, 3/2 or 5/2, and the glass is chemically and electrochemically compatible in contact with lithium metal. Suitable glass may comprise Li_2S and/or Li_2O as a glass modifier and one or more of a glass former selected from the group consisting of P_2S_5, P_2O_5, SiS_2, SiO_2, B_2S_3 and B_2O_3. In some embodiments, the glass may be devoid of phosphorous.

[0010] In another aspect, a method of making a standalone lithium ion conductive solid electrolyte is provided. The method involves drawing a molten sheet of lithium ion conducting sulfide glass into a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass.

[0011] In still another aspect, another method of making a standalone lithium-ion conductive solid electrolyte is provided, the method involving providing a lithium ion conducting sulfide glass pre-form, and pulling on the preform at a temperature sufficient to draw the pre-form to a ribbon having a thickness in the range of 5 to 100um.

[0012] In other aspects, the standalone sulfide based lithium ion-conductive glass solid electrolyte may be disposed in a battery cell component as a separator adjacent a negative lithium electroactive layer, or in a battery cell as a separator between a positive electrode and a negative lithium electroactive layer.

[0013] This and other aspects are described in further detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figs. 1A-D illustrate a freestanding Li ion conducting solid electrolyte sheet of this disclosure.

[0015] Figs. 1E-F illustrate a freestanding Li ion conducting solid electrolyte sheet of this disclosure and a mother-sheet from which it is cut-to-size.

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[0016] Fig. 2 illustrates surface defects at the interface between a sulfide-based glass and Li metal.

[0017] Fig. 3A illustrates a continuous roll of the instant solid electrolyte sheet wound on a spool.

[0018] Fig. 3B illustrates a continuous roll of a freestanding Li ion conducting solid electrolyte sheet in the form of a web from which individual discrete solid electrolyte sheets are excised and stacked.

[0019] Figs. 4A-D illustrate apparatus for making a freestanding Li ion conducting solid electrolyte sheet in accordance with various embodiments of this disclosure: Figs. 4A-B illustrate a fusion draw apparatus; Fig. 4C illustrates a slot draw apparatus; and Fig. 4D illustrates a preform draw apparatus.

[0020] Figs. 5A-C illustrate flowcharts for methods of making a continuous freestanding Li ion conducting solid electrolyte inorganic vitreous glass sheet of this disclosure.

[0021] Fig. 6 illustrates a fabrication system and method for making a continuous web of a freestanding Li ion conducting solid electrolyte sheet in accordance with this disclosure in the form of a continuous roll; the web configured using an inline sheet to roll process.

[0022] Figs. 7A-B illustrate electrode subassemblies in accordance with various embodiments of this disclosure.

[0023] Figs. 8A illustrates a cross sectional depiction of a lithium metal electrode assembly in accordance with this disclosure.

[0024] Figs. 8B illustrates a method of making a lithium metal electrode assembly in accordance with various embodiments of this disclosure.

[0025] Figs. 8C-G illustrate cross sectional depictions of lithium metal electrode assemblies, in accordance with various embodiments of this disclosure.

[0026] Fig. 9 illustrates a positive electrode assembly in accordance with this disclosure.

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[0027] Figs. 10A-E illustrate battery cells in accordance with various embodiments of this disclosure. In various embodiments the battery cell is a solid-state cell; a cell having a common liquid electrolyte; a hybrid cell having lithium metal electrode assembly of this disclosure; a constructed with a lithium metal free laminate; and a hybrid cell having a positive electrode assembly of this disclosure.

DETAILED DESCRIPTION

[0028] Reference will now be made in detail to specific embodiments of the disclosure. Examples of the specific embodiments are illustrated in the accompanying drawings. While the disclosure will be described in conjunction with these specific embodiments, it will be understood that it is not intended to limit the disclosure to such specific embodiments. On the contrary, it is intended to cover alternatives, modifications, and equivalents as may be included within the spirit and scope of the disclosure. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. The present disclosure may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail so as to not unnecessarily obscure the present disclosure.

[0029] A standalone lithium ion-conductive solid electrolyte in accordance with this disclosure can include a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass capable of high performance in a lithium metal battery by providing a high degree of lithium ion conductivity while being highly resistant to the initiation and/or propagation of lithium dendrites. Such an electrolyte is also itself manufacturable, and readily adaptable for battery cell and cell component manufacture, in a cost-effective, scalable manner.

[0030] With reference to **Figs. 1A-F** there are illustrated freestanding vitreous sheets of sulfide-based lithium ion conducting glass **100** in accordance with various embodiments of this disclosure, as described herein. The glass electrolyte sheets are highly conductive of Li ions, with intrinsic room temperature Li ion conductivity $\geq 10^{-5}$S/cm, preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm. Moreover, the sheets have physical dimensions and features suitable or particularly adapted for service as a separator in a battery cell, including substantially uniform thickness (t) of no more

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than 100 μm, scalability to long continuous lengths (*e.g.,* >50cm) and large areas (*e.g.,* >100cm^2), manufacturably adjustable area aspect ratios, and flexibility commensurate with winding.

[0031] By "substantially uniform thickness" it is generally meant that the thickness of the referenced article is sufficiently uniform for its intended purpose; for example the thickness of the solid electrolyte sheet is sufficiently uniform for its intended purpose as a solid electrolyte sheet in a battery cell. When using the term "uniform thickness" (e.g., with respect to the thickness of the solid electrolyte sheet or a fluid stream of glass) it is meant that the thickness variation is at most 20% of the average thickness (t), and more preferably less. In embodiments, wherein the average thickness is 250 μm ≤ t < 500 μm, the thickness variation is preferably ≤ 2%, and more preferably ≤ 1%; in embodiments wherein the average thickness is 100 μm ≤ t < 250 μm, the thickness variation is preferably ≤ 5%, and more preferably ≤ 2%; in embodiments wherein the average thickness is 50 μm ≤ t < 100 μm the thickness variation is preferably ≤ 10%, and more preferably ≤ 5%, and more preferably ≤ 2%; in embodiments wherein the average thickness is 10 μm ≤ t < 50 μm the thickness variation is preferably ≤ 20%, more preferably ≤ 10%, even more preferably ≤ 5%; and yet even more preferably ≤ 2%; and in embodiments wherein the average thickness is 5 μm ≤ t < 10 μm the thickness variation is preferably ≤ 20%, more preferably ≤ 10%, and even more preferably ≤ 5%.

[0032] In particular embodiments, glass sheet **100** is formed as a long flexible ribbon with substantially parallel lengthwise edges, and length (l) to width (w) area aspect ratio (l/w) ≥ 10, and therefore suitable as a continuous separator in a battery cell with a wound or folded construction. Preferably, the ribbon is sufficiently robust when flexed to have a bending radius ≤ 10 cm, preferably ≤ 5cm, more preferably ≤ 2.5cm, even more preferably ≤ 1cm, and yet even more preferably ≤ 0.5cm, and thus capable of being wound as such without fracture.

[0033] In various embodiments sheet **100** has substantially parallel lengthwise edges and an area footprint ≥ 10cm^2, ≥ 25cm^2, ≥ 50cm^2, ≥ 100cm^2, or ≥ 1000cm^2. In various embodiments, sheet **100** has length dimension ≥ 10cm, ≥ 20cm, ≥ 30cm, ≥50cm, or ≥ 100cm. In various embodiments, the width dimension of the sheet is

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between 1 to 5cm (*e.g.,* about 1cm, about 2cm, about 3cm, about 4cm, or about 5cm wide) or between 5 to 10cm (*e.g.,* about 5cm, or about 6cm, or about 7cm, or about 8cm or about 9cm, or about 10cm wide). In various embodiments the solid electrolyte sheet is in the shape of a thin ribbon having length (l) $\geq$ 10cm, width (w) between 1 to 10cm, and area aspect ratio (l/w) $\geq$ 10, or $\geq$ 20. The sheet may be cut into pieces of any suitable size for use, such as a separator in into a battery cell or component.

[0034] Continuing with reference to **Figs. 1A-D**, sheet **100** is embodied as a freestanding inorganic vitreous glass sheet that is not surrounded or supported by a substrate, and thus sheet **100** is substrate-less and capable of being stored, transported and integrated into battery cell manufacturing processes as a standalone solid electrolyte separator or cell component. By use of the term freestanding when referring to the sulfide glass sheet, it is meant that the sheet is a self-supporting layer of substantially uniform sulfide glass composition. Accordingly, in various embodiments a freestanding solid electrolyte sheet is substrate-less. By use of the term standalone (e.g., "standalone vitreous glass sheet" or "standalone lithium ion-conductive solid electrolyte") it is meant that the referenced material or article (e.g. sheet or electrolyte) is a discrete battery cell component, and thus is not, or has not yet been incorporated in a battery cell or an electrode assembly.

[0035] In various embodiments, sheet **100** is fabricated to ensure that it is substantially impervious to liquids that it may contact during operation of a device in which it is incorporated, such as a liquid electrolyte in a battery cell. Accordingly sheet **100** should be free (*i.e.,* devoid) of through porosity including pinholes or defects that would allow a liquid electrolyte to seep across the sheet. In other embodiments liquid impermeability is not a requisite property of the solid electrolyte sheet; for instance, sheet **100** incorporated as a separator in a fully solid-state Li-ion battery cell. In such cases the sheet **100** may nevertheless be substantially impenetrable, by which it is meant, as it pertains to lithium metal dendrites within the context of the described solid electrolytes configured in a lithium battery cell, that over the service life of the battery cell, lithium metal dendrites are unable to penetrate across the sheet, and preferably cannot extend deeply or at all into the bulk of the solid electrolyte sheet (*e.g.,* beyond 10% of the sheet thickness), and in this way the referenced battery cell is resistant to electrical shorting and fracture that might

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otherwise result from dendritic in-growth of lithium metal into pre-existing flaws or microstructural features on or nearby the sheet surface.

[0036] In various embodiments, sheet **100** is fabricated to be highly resistant against initiation and propagation of lithium dendrites. Without intending to be limited by theory it is believed that the ability of the solid electrolyte sheet to resist and preferably prevent dendritic through penetration in a lithium battery cell is based on its fabrication as a vitreous glass with liquid-like surfaces, by which it is meant a smooth amorphous surface, as resulting from the action of surface tension on a quiescent liquid. And by vitreous it is meant a glass derived from a continuous solidified glass melt (*e.g.,* as opposed to a powder compact), and therefore lacking powder particle, inter-particle boundary, and contiguous void manifestations of a pressed powder compact extending between the first and second principal surfaces of the glass sheet, and the liquid-like surface lacks flaw manifestations of a pressed powder compact that are sufficient to initiate Li dendrite penetration. Preferably the liquid-like surface of the vitreous sheet is essentially free of crystalline phases and of exceptionally smooth topography, having an average surface roughness $R_a < 0.1$um, preferably < 0.05um, more preferably $R_a < 0.01$um, and even more preferably $R_a < 0.005$um, and yet even more preferably $R_a < 0.001$um.

[0037] The vitreous solid electrolyte glass sheet of this disclosure addresses numerous shortcomings of pressed/hot-pressed sulfide glass powder compacts, polycrystalline ceramic membranes (*e.g.,* garnets), and solid polymer electrolyte films (*e.g.,* PEO-like).

[0038] For example, powder compaction is fraught with mechanical and electrochemical complications related to surface flaws, inter-particle boundaries and an undue density of void-like defects, which act as stress concentrators that limit strength, thwart flexibility and serve as Li dendrite initiators and facile pathways for dendritic shorting. And while simultaneous heating and pressing (*i.e.,* hot pressing) at high pressures for extended times can be useful for improving inter-particle cohesion, it adds a costly additional step that complicates processing and does not adequately address surface flaws related to dendrite initiation, as further described below. Moreover, powder compaction, while suitable for making small pressed pellets, is a

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batch process that is not scalable, and cannot be used to make long flexible sheets of glass.

[0039] Mechanical failure of any glass (*e.g.,* window glass) will occur when the stress and defect size reach a critical combination. The reliability is therefore statistical, but nonetheless related to the largest sized flaws on the surface. In contrast, small shallow flaws are perceived as less important, since the underlying mechanical strength of the sheet is largely unaffected by their existence. When shallow flaws are small in number density, or even singular, their very existence is generally considered insignificant from a practical perspective.

[0040] At practical current densities however, as described further herein, a shallow flaw at an otherwise liquid-like surface can be prohibitive for realizing a dendrite resistant solid electrolyte glass sheet, if the flaw depth is beyond a threshold size for dendrite initiation. With reference to **Fig. 2**, in a lithium metal battery cell, wherein a vitreous solid electrolyte sheet **100** is in contact with a solid Li metal layer **210**, a flaw extending beyond a threshold depth can create a highly localized hot spot for current focusing, which can lead to very high local current densities and dendritic penetration of Li metal into the sheet during cell charging, even for electrolytes with elastic moduli well above 20 GPa.

[0041] The threshold flaw depth is determined by several factors, including the detailed flaw geometry, the effective fracture toughness of the electrolyte, K_{1c}^{eff} which is typically less than the fracture toughness determined from a mechanical fracture test, K_{1c}, the sheet thickness (*t*), and the local current density, I_{local}, which in turn is proportional to the nominal lithium anode current density, $I_{nominal}$. The general functional relationship for the nominal lithium anode current densities, I_{thr}, may be expressed as

$$I_{thr}=f(K_{1c}^{eff},\ t/ (\Gamma, \nu, I_{local}))$$

where

K_{1c}^{eff} is the effective fracture toughness at the flaw tip where flaw extension most readily occurs

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Γ is the deepest flaw extension into the solid electrolyte

t is the sheet thickness

ν is the viscosity or the equivalent flow stress (both temperature dependent) of the solid lithium, and

I_{local} is the solid electrolyte/lithium metal anode interface current density in the immediate vicinity of the surface flaw. Typically $I_{local} > I_{nominal.}$

[0042] To mitigate dendrite propagation through a solid electrolyte sheet having a liquid-like surface in direct contact with a solid Li metal layer, the deepest flaw extension Γ into the sheet should be less than 1% of the sheet thickness, and preferably less than 0.1%, and generally no more than 5 μm. For example, the deepest flaw extension in a 100 μm thick sheet should be less than 1 μm, and preferably less than 0.1 μm; and for a 50 μm thick sheet it should be less than 0.5 μm, and preferably less than 0.05 μm.

[0043] Moreover, threshold current densities associated with dendrite initiation can be determined experimentally, or can be estimated from analytical approximations to the associated fracture mechanics-electrochemical problem. Typical experiments on *polycrystalline* solid electrolytes in direct contact with solid Li metal anodes have typically shown threshold charging current densities for dendrite initiation below $0.5mA/cm^2$. In contrast, vitreous sulfide solid electrolytes with smooth interfaces, such as prepared by the methods contemplated herein, have surprisingly sustained current densities in excess of 2 mA/cm^2 without dendrite penetration, when cycling 2 mAh/cm^2 of lithium metal for over 50 cycles. Subject to these principles, the inventors are now able to characterize the surface quality of the sheet based on experimentally determined values for I_{thr}, by cycling a solid Li metal layer against the solid electrolyte sheet at 1 mAh/cm^2 for at least 50 charge cycles without propagating a dendrite across the sheet. In various embodiments the solid electrolyte sheet is characterized as having a surface quality commensurate with an I_{thr} no less than $1mA/cm^2$, preferably no less than $2mA/cm^2$, more preferably I_{thr} is no less than 3 mA/cm^2, even more preferably I_{thr} is no less than 4 mA/cm^2, and yet even more preferably I_{thr} is no less than 5 mA/cm^2.

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[0044] Considering the sensitivity of dendrite initiation to the presence of shallow flaws, in order for the vitreous solid electrolyte sheet to retain its I_{thr} value during handling and downstream processing of cell components and cells, special care should be given to minimize contact damage.

Vitreous Web of Solid Electrolyte Sulfide Glass

[0045] With reference to **Fig. 3A**, in various embodiments the solid electrolyte sheet may be of sufficient flexibility, length and manufacturability to be fabricated as a continuous web of vitreous inorganic Li ion conducting sulfide glass **100W**, having a length typically greater than 50cm, and preferably greater than 100cm, and even more preferably greater than 1000cm long. In various embodiments, glass web **100W** serves a solid electrolyte substrate-sheet for the formation of downstream battery cell components, including electrode subassemblies, electrode assemblies, and battery cells of this disclosure.

[0046] As illustrated in **Fig. 3A**, in various embodiments web **100W** is sufficiently flexible that it may be formed into a continuous roll **100R** without fracture, and typically wound on a support spool **301** for storage and/or transportation. Preferably continuous web **100W** has bending radius $\leq$ 100 cm, and preferably $\leq$ 50 cm, more preferably $\leq$ 10 cm, even more preferably $\leq$ 5 cm, and yet even more preferably $\leq$ 2.5 cm, and thus capable of being wound as such without fracture. In various embodiments the spool or drum has a diameter in the range of 100cm – 200cm; or 50cm to 100cm; or 20 to 50cm; or 10cm to 20cm; or 5cm to 10cm; or 2.5cm to 5cm. In various embodiments continuous roll **100R** serves as a supply roll or a source roll for R_2R manufacture or roll-to-sheet processing of downstream battery cell components and battery cells.

[0047] As illustrated in **Fig. 3B**, in various embodiments, multiple discrete solid electrolyte sheets **100Z** (*e.g.,* a stack of solid electrolyte sheets) may be excised (*i.e.,* cut to size) from Li ion conducting glass web **100W**. The sheet may be cut into pieces of any suitable size for use, such as a separator in into a battery cell or component. In various embodiments, web **100W** yields at least 5 discrete solid electrolyte sheets having length of at least 10cm, preferably at least 10 such sheets,

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more preferably at least 50 such sheets, and even more preferably at least 100 such sheets.

[0048] In various embodiments, to facilitate winding, storage and/or use of a supporting spool, a protective material interleave (not shown) may be disposed between adjacent layers of the source roll in order to prevent the opposing web surfaces from contacting each other. Generally, the protective interleave is not a lithium ion conductor. In various embodiments the interleave may be a porous polymer layer (*e.g.,* micro-porous) or a dry swellable polymer layer (*i.e.,* a dry gellable polymer layer), suitable to serve as both interleave in the source roll and as a porous or gel battery separator component in a battery cell.

Thermal Parameters

[0049] Recognizing the benefit of perfecting the sulfide glass into a vitreous glass sheet, as opposed to a powder construct, methods and modified sulfur-containing glass compositions that are less prone to crystallization and/or have higher melt viscosities but still retain a requisite level of Li ion conductivity ($>10^{-5}$S/cm) have been developed. In particular, methods of increasing the glass stability factor and/or Hruby parameter, including increasing the amount of oxygen in the glass, increasing the oxygen to sulfur mole ratio, increasing the amount of oxide network former in the glass, increasing the ratio of oxide network former to sulfide network former, incorporating intermediate network formers, decreasing the amount of bond breaking lithium ions, tuning the composition of the base sulfide glass to have more than 4 main elemental constituents (*e.g.,* 5 main elemental constituents: S, Li, B, P, and O) or more than 5 main elemental constituents (*e.g.,* 6 main elemental constituents: S, Li, Si, B, P, and O) and combinations thereof are described. In addition, additives to the base glass are also contemplated for use herein as devitrifying agents and crystallization inhibitors.

[0050] Moreover, while apparently counterintuitive to decrease the Li ion conductivity of a glass that is specifically intended for use in a battery cell as a Li ion conductor, in various embodiments this is the approach contemplated herein for making and improving properties of the vitreous solid electrolyte glass sheets of this disclosure. Accordingly, in various embodiments the composition of the sulfide base

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glass system is adjusted to enhance thermal properties at the sacrifice of reduced conductivity.

[0051] A number of terms are used in the description for discussing the thermal properties of the glass. $\{T_x - T_g\}$ is the difference between the onset of crystallization (T_x) and the glass transition temperature (T_g), and is also referred to herein as the glass stability factor; $\{T_n - T_x\}$ is the difference between the temperature at which the glass is drawn (T_n) and the onset of crystallization. The liquidus temperature is (T_{liq}). The melting temperature of the glass is (T_m). The strain temperature is the temperature at which the viscosity of the glass is approximately $10^{14.6}$poise, and stresses may be relieved in hours. The annealing temperature is the temperature at which the viscosity is approximately $10^{13.4}$poise, and stresses in a glass may be relieved in less than 1 hour or minutes. And finally, the softening temperature is defined as the temperature at which the glass has viscosity of ~$10^{7.6}$poise. The glass is usually suitable for drawing at or above this temperature.

[0052] Several techniques exist for the measurement of these characteristic temperatures. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are the most common. Generally, a large separation between T_x and T_g (*i.e.*, a large glass stability factor) is desirable for drawing glass.

[0053] Another method of determining or estimating glass stability is through the Hruby parameter (H_r parameter), as given by the following equation:

$$Hr = \frac{Tx - Tg}{Tm - Tc}$$

[0054] A high value of H_r suggests high glass stability, and the larger, the more stable the glass against crystallization. For example, a glass having $H_r < 1$, is generally highly prone to crystallization and considered unstable.

Vitreous Sulfide Glass Composition

[0055] In accordance with the disclosure, the Li ion conducting vitreous glass has room temperature intrinsic Li ion conductivity $\geq 10^{-5}$S/cm, preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm. By use of the term intrinsic when referring to the ionic

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conductivity of a material it is meant the inherent conductivity of the material itself, in the absence of any other additional material agents, such as, for example, liquid solvents or organic molecules or organic material phases. To achieve this level of conductivity in an inorganic amorphous material phase, sulfide based Li ion conducting glasses are particularly suitable (*i.e.,* sulfur-containing glasses). Without intending to be limited by theory, compared to oxygen, sulfur is found to be a highly desirable element of the material phase. Sulfur is generally more polarizable than oxygen, and this tends to weaken the interaction between glass forming skeletal ions and mobile lithium ions, which in turn enhances lithium ion mobility and increases associated ionic conductivity. Accordingly, in various embodiments the material phase has a glass skeleton composed in part of sulfur and through which Li ions move. Without intending to be limited by theory, sulfur may serve several roles, including cross-linking sulfur that forms the glass structure and non-crosslinking sulfur that combines terminally with mobile Li ions.

[0056] Accordingly, in various embodiments the continuous amorphous material phase of solid electrolyte sheet **100** is an inorganic sulfide based glass comprising S (sulfur) as a main constituent element, Li (lithium) as a main constituent element and further comprising one or more M_1 main constituent elements selected from the group consisting of P (phosphorous), B (boron), Al (aluminum), Ge (germanium), Se (selenium), As (arsenic), O (oxygen) and Si (silicon).

[0057] In embodiments, the sulfide based solid electrolyte material further comprises O (oxygen) as a constituent element (*e.g.,* typically as a secondary constituent element). In other embodiments, the amorphous sulfide glass is a non-oxide, and thus substantially devoid of oxygen as a constituent element. Typically the mol% of Li in the glass is significant, and in particular embodiments the mole percent of Li in the glass is at least 10 mol%, and more typically at least 20 mol% or at least 30 mol%; in some embodiments it is contemplated that the mole percent of Li in the glass is greater than 40 mol% or greater than 50 mol% or even greater than 60 mol%. In various embodiments the glass is devoid of alkali metal ions other than Li.

[0058] In various embodiments as a main constituent element of the glass, sulfur (S) is present to at least 10mol%, and typically significantly higher; for instance, $\geq$ 20mol% of S, or $\geq$ 30mol% of S, or $\geq$ 40mol% of S. In various embodiments the

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concentration of sulfur as a main constituent element in the glass is between 20-60mol%, or between 30% - 50mol% (*e.g.,* about 25mol%, about 30mol%, about 35mol %, about 40mol%, about 45mol%, or about 50mol%). In various embodiments sulfur is the major elemental constituent of the glass, which is to mean the mol% of sulfur is greater than that of any other constituent element.

[0059] Various Li ion conducting sulfur based glasses (*i.e.,* sulfur-containing glasses) are contemplated for use herein. These include lithium phosphorous sulfide, lithium phosphorous oxysulfide, lithium boron sulfide, lithium boron oxysulfide, lithium boron phosphorous oxysulfide, lithium silicon sulfide, lithium silicon oxysulfide, lithium germanium sulfide, lithium germanium oxysulfide, lithium arsenic sulfide, lithium arsenic oxysulfide, lithium selenium sulfide, lithium selenium oxysulfide, lithium aluminum sulfide, lithium aluminum oxysulfide, and combinations thereof.

[0060] In various embodiments the sulfur glass, in addition to the main glass constituent elements, includes certain additives and compounds to enhance conductivity, such as halide salts (*e.g.,* LiCl, LiBr, LiI), aluminum (*e.g.,* aluminum oxide as an intermediate network former), Ga_2S_3, Al_2S_3, nitrogen (*e.g.,* thio-nitrides), as well as phosphate (*e.g.,* lithium phosphate (*e.g.,* Li_3PO_4, $LiPO_3$), sulfate (*e.g.,* Li_2SO_4), silicate (*e.g.,* Li_4SiO_4) and borate salts (*e.g.,* $LiBO_3$). In embodiments, various devitrifying agents may be added to the sulfide glass to enhance its stability against crystallization.

[0061] The sulfur-based glasses are sometimes described herein within the context of the glass system to which they belong, and roughly based on the stoichiometry of the materials incorporated in the glass as main and secondary elemental constituents, without reference to additives.

[0062] In various embodiments the sulfide glass system is of a type Li_2S-YS_n wherein Y is a glass former constituent element and may be Ge, Si, As, B, or P; and wherein n = 2, 3/2 or 5/2. For example, in various embodiments the glass system may be Li_2S-$PS_{5/2}$ or Li_2S-$BS_{3/2}$ or Li_2S-SiS_2. In various embodiments the glass system may be a combination of two or more such systems; for example, Li_2S-$PS_{5/2}$-$BS_{3/2}$ or Li_2S-$PS_{5/2}$-SiS_2 or Li_2S-$PS_{5/2}$-$BS_{3/2}$-SiS_2.

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[0063] In various embodiments the sulfide glass system is of a type Li_2S-YS_n-YO_n wherein Y is a glass former constituent element, and may be Ge, Si, As, B, or P; and wherein n = 2, 3/2 or 5/2. For example, in various embodiments the glass system may be Li_2S-$PS_{5/2}$-$PO_{5/2}$ or Li_2S-$BS_{3/2}$-$BO_{3/2}$ or Li_2S-SiS_2-SiO_2.

[0064] In various embodiments the sulfide glass system is of a type Li_2S-Y^1S_n-Y^2O_m wherein Y^1 and Y^2 are different glass former constituent elements, and may be Ge, Si, As, B, or P; and wherein n = 2, 3/2 or 5/2 and m = 2, 3/2 or 5/2, as appropriate based on the common standard valence of the constituent element. For example, in various embodiments the glass system may be Li_2S-$PS_{5/2}$-$BO_{3/2}$ or Li_2S-$BS_{3/2}$-$PO_{5/2}$ or Li_2S-$PS_{5/2}$-SiO_2.

[0065] In various embodiments the glass system may be a combination of two or more such systems of the type Li_2S-YS_n and Li_2S-Y^1S_n-Y^2O_m; wherein Y is a glass former constituent element, and may be Ge, Si, As, B, or P; Y^1 and Y^2 are different glass former constituent elements, and may be Ge, Si, As, B, or P; and wherein n = 2, 3/2 or 5/2 and m = 2, 3/2 or 5/2, as appropriate based on the common standard valence of the constituent element.

[0066] In various afore said embodiments, Li_2S may be wholly or partially substituted for by Li_2O.

[0067] Specific sulfur-based glass systems contemplated are of the type Li_2S-YS_n; Li_2S-YS_n-YO_n and combinations thereof; for which Y=Ge, Si, As, B, and P; and n = 2, 3/2, 5/2. Specific systems include Li_2S-P_2S_5; Li_2S-B_2S_3; Li_2S-SiS_2; Li_2S-P_2S_5-P_2O_5; Li_2S-P_2S_5-P_2O_3; Li_2S-B_2S_3-B_2O_3; Li_2S-P_2S_5-B_2S_3; Li_2S-P_2S_5-B_2S_3-B_2O_3; Li_2S-B_2S_3-P_2O_5; Li_2S-B_2S_s-P_2O_3; Li_2S-SiS_2-P_2O_5; Li_2S-P_2S_5-SiO_2; Li_2S-P_2S_5-P_2O_5-B_2S_3-B_2O_3 and combinations thereof.

[0068] The continuous Li ion conducting inorganic glass may be described as having a glass network former that brings about the skeletal lattice and a glass network modifier, such as a lithium compound, that introduces ionic bonds and thereby serves as a disrupter of the lattice and provides mobile lithium ions for conduction. In various embodiments additional network formers may be incorporated in the glass. For instance, in various embodiments the glass system may have the general formula:

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xNET(major former): yNET(minor former): zNET(modifier)

$$wherein\ z = 1 - (x + y)$$

[0069] NET(major former) is the major glass network former and its mole fraction, x, is the largest of all the network formers used to make the glass. Net(minor former) represents one or more minor glass network formers that is present in the glass with mole fraction, y. In all instances the mole fraction of the major glass former is larger than that of any minor glass former. However, the combined mole fraction of the minor glass formers may be greater than that of the major glass former. NET(modifier) is generally Li_2S or Li_2O or some combination thereof.

[0070] The network former (major or minor) may be a compound of the type A_aR_b, or a combination of two or more different compounds of this type. For instance, A may be Silicon, Germanium, Phosphorous, Arsenic, Boron, Sulfur and R may be Oxygen, Sulfur, or Selenium; and the network modifier may be of the type N_mR_c, with N being Lithium and R being Oxygen, Sulfur, or Selenium; and a,b, m, and c represent the indices corresponding to the stoichiometry of the constituents.

[0071] In various embodiment the major network former is B_2S_3, P_2S_5 or SiS_2, and the minor network former is one or more of B_2O_3, P_2O_5, P_2O_3, SiO_2, B_2S_3, P_2S_5, SiS_2, Al_2S_3, Li_3PO_4, $LiPO_3$ Li_2SO_4 $LiBO_3$. Specific examples include: i) Li_2S as the network modifier, B_2S_3 as the major former, and one or more minor formers selected from the group consisting of B_2O_3, P_2O_5, P_2O_3, SiO_2, P_2S_5, SiS_2, Al_2S_3, Li_3PO_4, $LiPO_3$ Li_2SO_4 $LiBO_3$; ii) i) Li_2S as the network modifier, P_2S_5 as the major former, and one or more minor formers selected from the group consisting of B_2O_3, P_2O_5, P_2O_3, SiO_2, B_2S_3, SiS_2, Al_2S_3, Li_3PO_4, $LiPO_3$ Li_2SO_4 $LiBO_3$; iii) Li_2S as the network modifier, SiS_2 as the major former, and one or more minor formers selected from the group consisting of B_2O_3, P_2O_5, P_2O_3, SiO_2, P_2S_5, B_2S_3, Al_2S_3, Li_3PO_4, $LiPO_3$ Li_2SO_4 $LiBO_3$. In various embodiments, the network modifier is Li_2S or Li_2O, or some combination thereof.

[0072] Selecting the appropriate sulfide glass composition depends on the end of use of the solid electrolyte sheet, and ultimately on the type and application of the battery cell in which it is intended to operate. Among the many potential considerations are

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form factor, cell construction, cost, power requirements, and service life. Accordingly, the glass composition may be adjusted to enhance one or more of i) chemical and electrochemical compatibility of the glass in direct contact with Li metal and/or a liquid electrolyte; ii) flexibility, shape and size; iii) glass formability (especially as it relates to thermal properties); and iv) Li ion conductivity. Optimizing one or more of these parameters generally requires a tradeoff.

[0073] In various embodiments the sulfide glass system is selected for its chemical and electrochemical compatibility in direct contact with lithium metal.

[0074] Chemical compatibility to Li metal is an attribute that relates to the kinetic stability of the interface between glass sheet **100** and a lithium metal layer, and electrochemical compatibility generally assesses the ability of that interface to function in a battery cell. Both properties require the formation of a solid electrolyte interphase (SEI) that stops reacting with the glass surface once formed (*i.e.,* chemical compatibility) and is sufficiently dense and conductive that its interface resistance is acceptable for its use in a battery cell.

[0075] Incorporating certain constituent elements into glass sheet **100** is desirable for creating an SEI commensurate with both chemical and electrochemical compatibility. In various embodiments, phosphorous is incorporated as a main constituent element for producing an effective SEI, as phosphorous in direct contact with lithium metal reacts to form lithium phosphide (*e.g.,* Li_3P), a compound highly conductive of Li ions and fully reduced. To form an acceptable SEI, phosphorous may be present in small amount (*e.g.,* as a secondary constituent of the glass). Adding phosphorous as a secondary constituent element provides an effective method for reducing resistance at the interface, and may be used to effect compatibility in a glass system, which, in the absence of phosphorous does not form a stable SEI, such as silicon sulfide glass systems with SiS_2 or SiO_2 as a primary network former. In other embodiments, however, Si may be intentionally excluded as a constituent element of sulfide glass sheet **100**.

[0076] Notably, it has been discovered that phosphorous sulfide glass systems are not the only glasses chemically and electrochemically compatibility in direct contact with Li metal. Surprisingly, boron sulfide glasses, even in the absence of phosphorous,

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have shown remarkable chemical and electrochemical compatibility against metallic lithium. Accordingly, in various embodiments phosphorous may be excluded from the glass as a constituent element, mitigating potential issues associated with high vapor pressure of the melt and chemical reactivity. However, in small amount, adding phosphorous as a secondary constituent element to the boron sulfide glasses should not impart processing issues, and may be used, as described below, as a method for reducing resistance at the Li metal solid electrolyte interface.

[0077] In various embodiments adding oxygen and silicon provides a method for improving thermal properties, especially for enhancing glass formability, including glass stability (*e.g.,* increasing the glass stability factor and/or Hruby parameter) and/or viscosity at the liquidus temperature (T_{liq}). For instance, adding silicon as a secondary constituent to a phosphorous sulfide or boron sulfide glass provides a method for increasing glass stability and/or viscosity at T_{liq}, while retaining compatibility to Li metal. The addition of oxygen as a constituent element may also afford benefit in these regards. In various embodiments oxygen may be incorporated as a main or secondary constituent element in lithium phosphorous sulfide and lithium boron sulfide glass systems as a method for increasing the glass stability factor and/or Hruby parameter. For instance, xLi_2S-yP_2S_5-$zSiS_2$, xLi_2S-yB_2S_3-$zSiS_2$, xLi_2S-yP_2S_5-$zSiO_2$, xLi_2S-yB_2S_3-$zSiO_2$, xLi_2S-yB_2S_3-zB_2O_3, xLi_2S-yP_2S_5-zP_2O_5; wherein with $x+y+z = 1$ and x=0.4-0.8, y=0.2-0.6, and z ranging from 0 to 0.2 (*e.g.,* about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.2).

[0078] Solid electrolyte sheets of silicon sulfide based glasses are particularly advantageous for use as a separator sheet in battery cells which employ a common liquid electrolyte or wherein the separator sheet does not contact electroactive material. For instance, xLi_2S-$ySiS_2$; xLi_2S-$ySiS_2$-$zSiO_2$; xLi_2S-$ySiS_2$-yB_2S_3; xLi_2S-$ySiS_2$-yB_2O_3; xLi_2S-y B_2S_3-$zSiO_2$; wherein with $x+y+z = 1$ and x=0.4-0.8, y=0.2-0.6, and z ranging from 0 to 0.2 (*e.g.,* about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.2).

[0079] With consideration of the above discussion, it is clear that in limited amount certain elements can have a beneficial role for enhancing performance of sheet 100 and/or improving glass stability for processing. The addition of phosphorous can

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reduce interfacial resistance with Li metal and the addition of oxygen can improve glass stability. In a boron sulfide glass, the addition of phosphorous, as a secondary constituent element, can be made via the incorporation of P_2S_5 and the addition of oxygen via B_2O_3; yielding the glass system: Li_2S-B_2S_3-P_2S_5-B_2O_3; wherein B_2S_3 is the primary network former, P_2S_5 and B_2O_3 are secondary network formers, and Li_2S is the network modifier. As such, the oxygen to phosphorous mole ratio can be varied. In another embodiment the phosphorous and oxygen mole ratio may be constrained by incorporating P_2O_5 as a single ingredient, giving rise to the glass system Li_2S-B_2S_3-P_2O_5; wherein B_2S_3 is the primary network former, P_2O_5 is a secondary former, and Li_2S is the network modifier.

[0080] Specific examples include, $0.7Li_2S$-$0.29P_2S_5$-$0.01P_2O_5$; $0.7Li_2S$-$0.28P_2S_5$-$0.02P_2O_5$; $0.7Li_2S$-$0.27P_2S_5$-$0.03P_2O_5$; $0.7Li_2S$-$0.26P_2S_5$-$0.04P_2O_5$; $0.7Li_2S$-$0.25P_2S_5$-$0.05P_2O_5$; $0.7Li_2S$-$0.24P_2S_5$-$0.06P_2O_5$; $0.7Li_2S$-$0.23P_2S_5$-$0.07P_2O_5$; $0.7Li_2S$-$0.22P_2S_5$-$0.08P_2O_5$; $0.7Li_2S$-$0.21P_2S_5$-$0.09P_2O_5$; $0.7Li_2S$-$0.2P_2S_5$-$0.1P_2O_5$; $0.7Li_2S$-$0.29B_2S_3$-$0.01B_2O_3$; $0.7Li_2S$-$0.28B_2S_3$-$0.02B_2O_3$; $0.7Li_2S$-$0.27B_2S_3$-$0.03B_2O_3$; $0.7Li_2S$-$0.26B_2S_3$-$0.04B_2O_3$; $0.7Li_2S$-$0.25B_2S_3$-$0.05B_2O_3$; $0.7Li_2S$-$0.24B_2S_3$-$0.06B_2O_3$; $0.7Li_2S$-$0.23B_2S_3$-$0.07B_2O_3$; $0.7Li_2S$-$0.22B_2S_3$-$0.08B_2O_3$; $0.7Li_2S$-$0.21B_2S_3$-$0.09B_2O_3$; $0.7Li_2S$-$0.20B_2S_3$-$0.1B_2O_3$; $0.7Li_2S$-$0.29B_2S_3$-$0.01P_2O_5$; $0.7Li_2S$-$0.28B_2S_3$-$0.02P_2O_5$; $0.7Li_2S$-$0.27B_2S_3$-$0.03P_2O_5$; $0.7Li_2S$-$0.26B_2S_3$-$0.04P_2O_5$; $0.7Li_2S$-$0.25B_2S_3$-$0.05P_2O_5$; $0.7Li_2S$-$0.24B_2S_3$-$0.06P_2O_5$; $0.7Li_2S$-$0.23B_2S_3$-$0.07P_2O_5$; $0.7Li_2S$-$0.22B_2S_3$-$0.08P_2O_5$; $0.7Li_2S$-$0.21B_2S_3$-$0.09P_2O_5$; $0.7Li_2S$-$0.20B_2S_3$-$0.1P_2O_5$.

Methods of Making

[0081] Vitreous sulfide-based glass sheet **100** may be fabricated using an overflow technique such as fusion draw, which uses a drawing tank and takes advantage of gravity to allow molten glass to flow down the outside surfaces of the tank, and in this way yield two flowing glass surfaces which are joined to form a single flowing sheet.

[0082] With reference to the fusion draw apparatus **400A** in **Figs. 4A-B**, a material batch of Li ion conducting sulfide glass powder, which may be formed by mechanical milling, is heated in a melting vessel wherefrom it is caused to flow (via flow pipes **405**) into a trough-like container **407** in an amount sufficient to cause overflow of the melt **409** from both sides of the trough. The opposing flows are then combined by

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fusion to form a single liquid stream of unbroken continuity **100**, which may be fed to drawing equipment (*e.g.,* via edge rollers or glass pulling rods), for controlling the thickness of the sheet, depending upon the rate at which the solidified portion of the sheet is pulled away. Accordingly, the major surfaces of the as-solidified glass sheet, or at least its high quality center portion, are pristine, as they have not contacted any part of the apparatus (*e.g.,* the trough walls or flow pipes), and therefore have superior surface quality. In various embodiments, the fusion draw process may be modified to allow for the drawing of two dissimilar glasses, one optimized for contact with lithium metal and the other optimized for a different purpose(s) or utility such as contact with a positive electrode battery cell component (*e.g.,* a lithium positive electroactive material) or a liquid phase electrolyte, or ease of processing or high conductivity. For instance, a first sulfide glass stream of unbroken continuity (*e.g.,* having as main constituent elements: lithium, sulfur, and silicon) fused to a second sulfide glass stream (*e.g.,* having as main constituent elements: lithium, sulfur, and one or more of boron or phosphorous).

[0083] In an alternative process, freestanding solid electrolyte sheet **100** may be formed by slot draw to yield a substantially amorphous vitreous solid electrolyte sheet of Li ion conducting sulfur-containing glass. With reference to **Fig. 4C**, an apparatus **400** for making the freestanding sheet using a slot drawing process is illustrated. The apparatus includes melting vessel **460**, for heating and holding a material batch, typically in powder form (*e.g.,* a powder batch of sulfide glass or a batch of raw precursor powders in proper stoichiometry for making the glass), above the batch melting temperature, and an open slot **470** near the bottom of the tank and through which the batch of molten glass flows by drawing to form continuous glass sheet **100** which may be optionally pulled through rollers **480** for shaping, and optionally traversed into furnace **490** for an annealing heat treatment, and thereafter optionally placed through a second set of rollers **485** and/or subjected to an edge removal process (as described above) to yield the solid electrolyte sheet in its final or near final form.

[0084] Additional processing steps may be used to enhance the cooling rate, such as flowing a non-reactive inert fluid (*e.g.,* ultra dry nitrogen or argon) over one or both

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surfaces, typically a gas (*e.g.,* helium or argon). The cooling gas should have a very low moisture and oxygen content, preferably less than 10ppm.

[0085] In various embodiments vitreous solid electrolyte glass sheet **100** is formed by preform drawing, wherein a preform of the sulfide based solid electrolyte glass is drawn (*e.g.,* pulled) in length at a temperature above the glass transition temperature, to the desired shape and size. Typically, the preform is heated to a temperature at which it has low enough viscosity to deform under its own weight, which is usually at around the softening temperature of the glass. Upon drawing, the heated portion starts to flow, and becomes a highly viscous fluid stream, typically in the range of 10^4 - 10^6 poise.

[0086] With reference to **Fig. 4D** there is shown an apparatus **400D** suitable for preform draw of a sulfide based solid electrolyte sheet of the instant disclosure, and sometimes referred to as a redraw process. In operation, the vitreous preform **410D** is heated in a deformation zone **420D** and then drawn using mechanized rollers **430D**. Within the deformation zone the preform is exposed to heat sufficient to raise its temperature above T_g but below T_m and preferably below T_x, and then drawn to a sheet of desired length and thickness. In some embodiments it is contemplated that the drawing apparatus includes a flow system for flowing an inert gas nearby the drawn sheet in order to speed up cooling of the drawn sheet section, the gas preferably having a very low moisture and oxygen content, as described above.

[0087] The resulting cross sectional shape of the formed sheet is usually similar to that of the preform from which it has been drawn. Preferably, the preform has a smooth flat surface with minimal surface roughness and waviness. In various embodiments the preform is, itself, a vitreous glass construct. For instance, the preform may be made by molding molten glass into a rectangular bar-like shape of substantial width and thickness typically 10 times that desired for the sheet. For example, to a draw a thin vitreous solid electrolyte ribbon in the range of 10 to 500 μm thick, in various embodiments the preform is rectangular with a thickness in the range of 200 μm to 1000 μm, a width of 5 to 20 cm, and a length of about 30cm to 100cm (*e.g.,* a rectangular shaped bar, about 5 cm wide, about 30cm long and about 400um thick). Methods and apparatus' for drawing a glass preform to form a

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substrate for semiconductor devices and flat panel displays are described in US Pat. Pub. No.: US20070271957, US20090100874; 20150068251.

[0088] With reference to **Figs. 5A-C** there is illustrated flowcharts representative of various methods **500A-C** of making vitreous solid electrolyte sheet **100** using draw processes as described above. Methods **500A-C** include a first step of selecting a glass composition **505**. For example, the composition may be selected for suitability to the particular draw process of making sheet **100** (*e.g.,* preform draw and/or melt draw).

[0089] In various methods, the step of selecting the sulfur containing glass composition is based on glass stability factor and conductivity; *e.g.,* selecting a glass composition having a glass stability factor >20°C, or >30°C, or >40°C, or >50°C, or >60°C, or >70°C, or >80°C or >90°C or >100°C and a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm.

[0090] In various methods, the step of selecting the sulfur containing glass composition is based on Hruby parameter and conductivity; *e.g.,* selecting a glass composition having Hruby parameter >0.4, or >0.5, or >0.6, or >0.7, or >0.8, or >0.9, or >1 and a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm.

[0091] In various methods the step of selecting the sulfur containing glass composition involves adjusting the mole percent of Li and/or S (sulfur) and/or O (oxygen) and/or Si (silicon) in the glass to achieve a Hruby parameter of >0.5, or >0.6, or >0.7, or >0.8, or >0.9, or >1 and a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm.

[0092] In various methods the step of selecting the sulfur containing glass composition involves adjusting the mole percent of Li and/or S (sulfur) and/or O (oxygen) and/or Si (silicon) in the glass to achieve a glass stability factor of >50°C, or >60°C, or >70°C, or >100°C and a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm.

[0093] In various methods the step of selecting the sulfur containing glass composition involves adjusting the mole percent of O (oxygen) to within a value of 1

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– 20mol% to achieve a glass stability factor >50°C, or >60°C, or >70°C, or >80°C or >90°C or >100°C while still retaining an interface resistance with a Li metal layer that is no more than 200 Ω-cm^2 and preferably no more than 100 Ω-cm^2, and more preferably no more than 50 Ω-cm^2, and even more preferably no more 25 Ω-cm^2, or no more than 10 Ω-cm^2.

[0094] In various methods the step of selecting the sulfur containing glass composition involves adjusting the mole percent of Si (silicon) to within a value of 1 – 20mol% to achieve a glass stability factor >50°C, or >60°C, or >70°C, or >80°C or >90°C or >100°C while still retaining an interface resistance with a Li metal layer that is no more than 200 Ω-cm^2 and preferably no more than 100 Ω-cm^2, and more preferably no more than 50 Ω-cm^2, and even more preferably no more 25 Ω-cm^2, or no more than 10 Ω-cm^2.

[0095] In various methods the step of selecting the sulfur containing glass composition involves adjusting the mole percent of P (phosphorous) in the glass within a value of 1 – 20mol% to achieve an interface resistance with a Li metal layer that is no more than 200 Ω-cm^2, and preferably no more than 100 Ω-cm^2, and more preferably no more than 50 Ω-cm^2, and even more preferably no more 25 Ω-cm^2, or no more than 10 Ω-cm^2.

[0096] In various methods, the step of selecting the glass composition includes replacing a certain amount of sulfur in the glass with oxygen, or a certain amount of boron in the glass with silicon, the amount sufficient to increase the glass stability factor by at least 10°C or the Hruby parameter by at least 0.1, while maintaining a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm. In various embodiments the glass stability factor is increased by at least 20°C, 30°C, 40°C, 50°C, 60°C, or 70°C by the oxygen replacement for sulfur, while maintaining the requisite Li ion conductivity of $\geq 10^{-5}$S/cm. In various embodiments the Hruby parameter is increased by at least 0.2, 0.3, 0.4, 0.5, 0.6, or 0.7 by the oxygen replacement for sulfur or the silicon replacement for boron, while maintaining the requisite Li ion conductivity.

[0097] In various methods, the step of selecting the glass composition includes decreasing the amount of Li by an amount sufficient to increase the glass stability

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factor by at least 10°C or the Hruby parameter by at least 0.1, while maintaining a Li ion conductivity $\geq 10^{-5}$S/cm, and preferably $\geq 10^{-4}$S/cm, and more preferably $\geq 10^{-3}$S/cm. In various embodiments the glass stability factor is increased by at least 20°C, 30°C, 40°C, 50°C, 60°C, or 70°C by the decrease in Li content, while maintaining at least the requisite Li ion conductivity of $\geq 10^{-5}$S/cm. In various embodiments the Hruby parameter is increased by at least 0.2, 0.3, 0.4, 0.5, 0.6, or 0.7 by the decrease in Li content, while maintaining the aforesaid Li ion conductivity values.

[0098] In various methods, the step of selecting the glass composition includes: i) selecting a sulfide base glass system composed of at least one glass former and glass modifier; ii) determining a high conductivity composition within the selected glass system (*e.g.,* the highest Li ion conductivity, or within 50% of that value); and iii) adjusting the high conductivity composition to increase the glass stability factor and/or Hruby parameter by at least 10°C and/or 10% relative to that of the high conductivity composition, or enhancing the glass stability factor and/or Hruby parameter by at least 20°C or 20%, or at least 30°C or 30%, or at least 40°C or 40%, or at least 50°C or 50%; and further wherein the Li ion conductivity of the selected composition is lower than that of the high conductivity composition by as much as 2 fold, 5 fold, 10 fold or even 100 fold lower (*e.g.,* between a 2 fold to 10 fold reduction in conductivity, or between a 10 fold to 100 fold reduction).

[0099] In various methods, the step of selecting the glass composition includes: i) selecting a sulfide based glass system composed of at least one glass former and glass modifier; ii) determining a high conductivity composition within the selected system which has the highest Li ion conductivity (or within 50% of that value); and iii) adjusting the high conductivity composition to increase the glass viscosity at the liquidus temperature by at least 10% relative to the high conductivity composition (and preferably by at least 20%, or at least 30%, or at least 40%, or at least 50%); and further wherein the Li ion conductivity of the selected composition is lower than that of the high conductivity composition by as much as 2 fold, 5 fold, 10 fold or even 100 fold (*e.g.,* between 2 fold to 10 fold reduction or between a 10 fold to 100 fold reduction in Li ion conductivity).

[0100] Continuing with reference to **Figs. 5A-C**, once the Li ion conducting sulfur containing glass composition is selected **505**, the raw precursor materials (*e.g.,* Li_2S,

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SiS_2, and P_2S_5 powders) **510** are processed. With reference to methods **500A-B**, as illustrated in **Figs. 5A-B**, the processing steps involve forming **530A** a vitreous preform **540A** from the raw precursor materials, followed by drawing the preform **550A** to make the vitreous glass ribbon **560A** or melting the raw precursor materials **530B** to form molten glass **540B** for making the vitreous solid electrolyte sheet **560B** by melt drawing **550B**. In method **500C** the process involves the extra step of making a glass batch **520C** from the raw precursor materials, and then processing the glass preform or drawing a sheet from the twice-melted glass. In various embodiments, the batch glass formed in step **520C** may be processed by melt/quenching the raw material precursors or by mechanical milling. The re-melting or formation of a vitreous preform from a batch glass, regardless of how it (the batch glass) is formed, allows better control of processing variables, including minimizing loss of volatile constituents.

[0101] In various embodiments vitreous solid electrolyte sheet **100** is sufficiently flexible and long to be configured as a continuous web of Li ion conducting glass, typically wound on a spool, and thus suitable as a source roll for downstream (R_2R) or roll-to-sheet processing of electrode subassemblies, electrode assemblies and battery cells. Preferably the continuous web has bending radius $\leq$ 100 cm, and preferably $\leq$ 50 cm, more preferably $\leq$ 30 cm, even more preferably $\leq$ 10 cm, and yet even more preferably $\leq$ 5 cm, or $\leq$ 2.5 cm, or $\leq$ 1 cm, and thus can be wound as such without fracture.

[0102] In various embodiments the spool or drum has a diameter >100 cm and $\leq$ 200cm; or >50 cm and $\leq$ 100cm; or >25 cm and $\leq$ 50cm; or >10 cm and $\leq$ 25; or >5 cm and $\leq$ 10 cm; or >1 cm and $\leq$ 5 cm; or >0.5 cm and $\leq$ 1 cm. In various embodiments the freestanding and flexible vitreous sulfur-based glass strip is ultimately wound about a spindle for incorporation into a battery cell, the spindle having a diameter of about 1cm or less (*e.g.,* a spindle of diameter 5mm, 4mm, 3mm, 2mm, 1mm, and 0.5mm).

[0103] The instant web of vitreous solid electrolyte glass sheet is typically of sufficient length for cutting to size solid electrolyte ribbons for at least two individual solid electrolyte separator components or electrode assembly components. Typically, the length of the web is sufficient for making many multiples of such said components

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(*e.g.,* at least 5, at least 10, or at least 20 of such said components). For example, at least 5, 10 or at least 20 discrete solid electrolyte ribbons. For instance, in various embodiments the length of the solid electrolyte web of vitreous Li ion conducting sulfide glass is more than 20cm, 50cm, 100cm, 500cm or more than 1000cm long.

[0104] Preferably, the vitreous web of solid electrolyte glass is flexible, and formed as a continuous roll on a spool for storage, transportation and component manufacture, such as, in various embodiments, roll to roll (R_2R) manufacturing of downstream battery cell components, including electrode subassemblies, electrode assemblies, and battery cells thereof. Preferably, the solid electrolyte web has sufficiently high surface quality and thickness uniformity that it requires no post solidification grinding and/or polishing. In making a solid electrolyte separator component from the web, discrete solid electrolyte glass sheets of predetermined length and width are cut to size (*e.g.,* preferably a laser cutting).

[0105] In various embodiments, the continuous web of vitreous Li ion conducting glass serves as a downstream substrate onto which a lithium electroactive material layer (*e.g.,* lithium metal) or a tie-layer and/or a current collecting layer (*e.g.,* Cu or Ni metal) is deposited or placed with adherence (*i.e.,* adhered to the vitreous glass web). When making individual lithium electrode assemblies from a continuous web, in various embodiments the lithium metal layer may be deposited or adhered onto the web in an intermittent fashion, and typically in periodic sections, thus creating lithium coated sections separated by uncoated regions (*e.g.,* by using masking techniques). In other embodiments, individual glass sheets may be cut to size from the vitreous web prior to depositing the lithium metal layer or tie-layer and/or current collecting layer.

[0106] In various embodiments roll processing of the web is inline with the solid electrolyte vitreous glass sheet drawing process. With reference to **Fig. 6**, there is illustrated a sheet to roll fabrication system **600** for processing a vitreous web of solid electrolyte glass **100W** in the form of a continuous roll. Sheet to roll fabrication system **600** includes solid electrolyte sheet drawing apparatus **610** (*e.g.,* melt draw or preform draw apparatus **400** or **400D** respectively, such as a fusion draw apparatus, a slot draw apparatus, or a redraw/preform draw apparatus) configured inline with roll processing apparatus that includes one or more drive mechanisms **623** (*e.g.,* a pair of opposing counter rotating rollers), guide rollers **628**, and take-up spool **626** for

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winding the inorganic vitreous solid electrolyte glass sheet into continuous roll **100R**. Preferably, the counter rollers, which are generally motor-driven, are positioned to contact a peripheral edge region of the as-drawn solid electrolyte sheet, and in this way the major area portion of the solid electrolyte sheet (*e.g.,* the high quality center portion) is maintained in a pristine surface state condition (*i.e.,* untouched). Driven by the rotating rollers, solid electrolyte ribbon (long sheet) **100W** is typically conveyed along one or more guide rollers (*e.g.,* roller **628**) before engaging with take-up roll **626**. The web of solid electrolyte glass **100W** may be conveyed in an unsupported fashion, or the apparatus may include a support mechanism for supporting the moving vitreous glass ribbon as it is conveyed toward the take-up roll, and/or into one or more processing stages **650** (**650i, 650ii, 650iii, 650iv**). Typically, solid electrolyte web **100W** is caused to traverse through a furnace or hot zone stage **650i** for annealing the glass sheet prior to engaging with the take-up roll for winding. The processing stages may include a slitting stage **650ii** with a cutting device (*e.g.,* a wire saw) configured to remove edge portions from the high quality center portion of the as-drawn glass. Other stages are contemplated, including a stage for configuring a protector element along the lengthwise edges of the solid electrolyte sheet **650iii** and/or material layer coating stages **650iv** for coating the surface of solid electrolyte glass web **100W** with a tie-layer coating and/or a current collector coating and/or a lithium metal layer, as described in more detail herein below with respect to making a web of electrode sub-assemblies and/or a web of lithium electrode assemblies.

[0107] Optionally, to keep the solid electrolyte sheet surfaces from directly contacting each other, interleave **604** (a protective web material layer) may be wound together with the inorganic web of solid electrolyte glass via interleave supply roll/take off-roll **612**. The interleaf interposed between layers of the glass sheet roll. Care should be taken in the proper selection of the interleaf, and in particular embodiments the major opposing surfaces of interleave material layer **604** are composed of vitreous carbon (*e.g.,* the interleave may be an organic polymer layer (*e.g.,* a polyolefin or polyester layer) or thin inorganic glass having a vitreous carbon surface coating). Also contemplated is the use of edge protector elements, which, as described above, protect the edges of the solid electrolyte sheet against physical damage, and may also serve as a spacer between sheet layers when the web is wound on a spool, and in this way, the

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high quality center portion of the solid electrolyte sheet is kept in a pristine surface state (*i.e.,* untouched by a foreign solid surface).

Electrode Sub-Assembly

[0108] With reference to **Figs. 7A-B**, there is illustrated electrode subassembly **700A-B**, which, in accordance with the present disclosure, generally serves as a standalone component for making a lithium metal electrode assembly, and in some embodiments may be incorporated directly into a battery cell, also of the present disclosure. As illustrated, subassembly **700A-B** is a freestanding substrate laminate composed of a solid electrolyte sheet **100** covered in direct contact by material layer **701**, which provides a surface for creating an electrochemically efficient interface with a lithium metal layer during the making of a standalone lithium metal electrode assembly or during the course of charging in a battery cell.

[0109] Material layer **701** may be characterized as having interior surface **701i** adjacent to and in direct contact with surface **101A** of solid electrolyte sheet **100,** and exposed surface **701ii** opposing the exterior environment about the subassembly. Typically, material layer **701** is significantly thinner than solid electrolyte sheet **100** on which it is coated, formed on or adhered to. In various embodiments material layer **701** or a layer portion thereof is a transient layer that effectively disappears (*e.g.,* by alloying) once a lithium metal layer is applied or deposited onto it.

[0110] As mentioned above, electrode subassembly **700A-B** is a standalone component useful for making a lithium metal electrode assembly or battery cell of the present disclosure. However, the electrode subassembly by itself is not a capacity-bearing electrode, and thus does not contain electroactive material (*e.g.,* Li metal) for providing ampere-hour capacity to a battery cell. Accordingly, electrode subassembly **700A-B** has exceptional component shelf life and handle-ability for manufacturing.

[0111] With reference to **Fig. 7A**, in various embodiments electrode subassembly **700A** is a bi-layer laminate of material layer **701** (a single layer, typically of uniform composition) coated, adhered or placed onto solid electrolyte sheet **100**. With reference to **Fig. 7B**, in various embodiments, subassembly **700B** is composed of more than two layers; for instance, material layer **701** may itself be a multilayer of

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two or more material layers disposed on surface **101A** of sheet **100** (*e.g.,* **701a** a tie-layer in direct contact with solid electrolyte sheet **100,** and second layer **710b** a current collector layer in direct contact with the tie-layer).

[0112] In various embodiments material layer **701** is a chemically functional tie-layer coating for creating an electrochemically efficient interface between sheet **100** and a lithium metal layer, and may also provide some protection against damage during storage and handling. Accordingly, the tie layer is of suitable composition and thickness to enhance bonding. In particular embodiments the tie-layer reactively alloys with Li metal on contact to form an electrochemically operable interface. The tie-layer is preferably a transient layer, which transforms and essentially disappears upon the formation or deposition of lithium metal on its surface. In various embodiments the tie-layer is thin enough and/or the lithium layer is of sufficient mass (*i.e.,* thickness) to completely dissolve the tie layer (*e.g.,* via an alloying reaction), and preferably the elements of the tie-layer are in such small amount and fully dispersed throughout the lithium metal layer to be insignificant.

[0113] In various embodiments protective tie-layer **701** is a coating of a metal or semi-metal suitable for forming an electrochemically operable interface between a lithium metal layer and solid electrolyte sheet **100**, and, in particular, an electrochemically efficient interface for plating and striping lithium metal in a battery cell. In various embodiments, the tie-layer is a metal or semi-metal such as Al, Ag, In, Au, Sn, Si, or the like, or an alloy or inter-metallic combination of metals or semi-metals capable of alloying or being alloyed by lithium metal on contact.

[0114] In various embodiments the tie-layer **701** is a metal or semi-metal coating deposited by physical vapor deposition (*e.g.,* by evaporation) onto first principal side surface **101A** of sheet **100**. Tie-layer **701** is a transient film that on contact with Li metal atomically disperses throughout the lithium metal layer. In various embodiments tie-layer **701** is of a composition and thickness to fully alloy with lithium metal on contact at room temperature, and in some embodiments heat may be applied to facilitate alloying and atomic diffusion. In various embodiments the tie-layer thickness is in the range of 0.05 to 5μm and more typically between 0.05 to 1μm (*e.g.,* about 0.05μm, or 0.1μm, 0.2μm, 0.3μm, 0.4μm, 0.5μm, 0.6μm, 0.7μm, 0.8μm, 0.9μm, or about 1.0μm, or 2.0μm, 3.0μm, 4.0μm or about 5.0μm).

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[0115] The tie-layer provides a subassembly surface for mating the solid electrolyte sheet to a lithium metal layer (*e.g.,* extruded lithium film), when forming a lithium electrode assembly or battery cell of the present disclosure. In particular, by reactively alloying with Li metal, the tie layer facilitates formation of an electrochemically operable interface. Moreover, the tie-layer is a transient material layer in that once the lithium metal layer is applied or formed, the tie-layer effectively disappears as it alloys with Li.

[0116] With reference to **Fig. 7A**, in various embodiments the lithium metal layer is applied onto exterior tie-layer surface **701ii** during fabrication of a lithium electrode assembly (*e.g.,* a Li foil hot rolled onto the tie-layer). In other embodiments the lithium metal layer is formed by electrochemically plating Li metal adjacent to interior tie-layer surface **701i** during initial charging of a battery cell in which the electrode subassembly is incorporated. Whether formed electrochemically in a battery cell or applied or coated to form a lithium metal electrode assembly, lithium metal interacts with the tie-layer to form an intimate electrochemically operable interface between the as-formed or applied lithium metal layer and first principal side surface **101A** of solid electrolyte sheet **100**.

[0117] With reference to subassembly **700B** in **Fig.7B,** in various embodiments material layer **701** is a multilayer (*e.g.,* a bi-layer) devoid of Li metal. In various embodiments bi-layer **701** is composed of tie-layer **701a** in direct contact with first principal side surface **101A** of sheet **100**, and current collecting layer **701b** in direct contact with the tie-layer. The tie-layer sandwiched between sheet **100** and current collecting layer **701b**. In various embodiments the tie-layer may be evaporated onto the solid electrolyte sheet **100** followed by applying a current collecting layer **701b** directly onto the tie-layer **701a**. In other embodiments it is contemplated that the tie-layer may be evaporated onto the current collector layer, and the multi-layer, so formed, applied onto the sheet. Multiple tie-layer coatings are also contemplated herein, such as one or more additional tie-layer coatings disposed between tie-layer **701a** and current collecting layer **701b**. For instance, an additional tie-layer may be utilized to enhance and improve the Li metal interface in direct contact with current collecting layer **701b**.

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[0118] In alternative embodiments it is contemplated that the current collecting layer may be applied directly onto sheet surface **101A**, in the absence of a tie-layer.

[0119] The current collector layer may be a thin metal foil, or a thin metal film on a polymer substrate, or a coating applied directly onto sheet surface 101A, or indirectly via a tie-layer. For example a thin Cu or Ni foil, or a laminate of a Cu film on a polyethylene terephthalate (PET) substrate. The current collector should be a material layer that is substantially unreactive in contact with Li metal and of sufficient electronic conductivity to provide effective current collection, typically a metal (*e.g.,* Cu or Ni).

[0120] In various embodiments, the current collecting layer is preferably significantly thinner than solid electrolyte sheet **100** (*e.g.,* $\leq$ 1/5 or $\leq$ 1/10 the thickness of sheet **100**), and preferably no thicker than 10μm. In various embodiments the current collecting material layer is < 20μm thick, and typically < 15μm, and more preferably ≤10um, and even more preferably ≤5μm thick (*e.g.,* between 10 to 5μm thick; for example about 5μm, or 4μm, or 3μm, or 2μm, or 1μm thick).

[0121] In various embodiments, electrode subassembly **700A** serves as a substrate component for making a standalone lithium metal electrode assembly of the present disclosure. In other embodiments electrode subassembly **700A** may be directly incorporated into a lithium battery cell as a lithium free negative electrode, completely devoid of Li metal, as described in more detail below.

Electrode Assembly

[0122] With reference to **Fig. 8A**, standalone electrode assembly **800** is a lithium metal electrode assembly composed of solid electrolyte sheet **100** serving as a substrate for lithium metal component layer **820**, which is composed of lithium metal layer **810** and optional current collecting layer **812**. By use of the term standalone with respect to the lithium metal electrode assembly it is meant that the electrode assembly is a discrete component absent of a positive electrode and that it exists as a freestanding component outside of a battery cell.

[0123] In various embodiments, standalone lithium metal electrode assembly **800** contains sufficient amount of Li metal to support the rated capacity of the cell in

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which it is disposed, and in particular matches or exceeds the rated area ampere-hour capacity of the positive electrode. For example, the positive electrode having an area capacity of 1mAh/cm^2 and the Li metal layer thickness is at least 5μm; or 1.5mAh/cm^2 and the Li metal layer thickness is at least 7.5μm; or 2mAh/cm^2 and the Li metal layer thickness is at least 10μm; or 2.5mAh/cm^2 and the Li metal layer thickness is at least 12.5μm; or 3mAh/cm^2 and the Li metal layer thickness is at least 15μm; or 3.5mAh/cm^2 and the Li metal layer thickness is at least 17.5μm; or 4mAh/cm^2 and the Li metal layer thickness is at least 20μm; or 4.5mAh/cm^2 and the Li metal layer thickness is at least 22.5μm; or 5mAh/cm^2 and the Li metal layer thickness is at least 25μm.

[0124] In other embodiments, the amount of lithium metal in standalone electrode assembly **800**, prior to incorporation into a battery cell, is insufficient to support the rated capacity of the cell. For instance, the rated capacity of the cell is about 50% greater than the Li metal capacity of the standalone electrode assembly, or about 100% greater, or about 150% greater, or about 200% greater, or about 250% greater, or about 300% greater, or about 350% greater, or about 400% greater, or about 450% greater, or about 500% greater. For example, the positive electrode having an area capacity of 1mAh/cm^2 and the Li metal layer thickness is < 5μm; or the positive electrode having an area capacity of 2mAh/cm^2 or about 3mAh/cm^2 or about 4mAh/cm^2 or about 5mAh/cm^2 and the Li metal layer thickness is < 10μm (*e.g.,* about 5μm).

[0125] In some embodiments electrode assembly **800** is fabricated by depositing lithium metal layer **810** (*e.g.,* by evaporation or sputter deposition) directly onto sheet surface **101A** or indirectly via a tie-layer (*e.g.,* the lithium deposited onto exterior surface **701ii** of subassembly **700A**, as illustrated in **Fig. 7A**). When evaporated, lithium metal layer **810** typically has thickness in the range of 5 to 30μm (*e.g.,* about 5μm, about 10μm, about 15μm, about 20μm, about 25μm, or about 30μm.

[0126] In other embodiments, the Li metal layer may be an extruded Li foil, or Li film on a current collecting substrate, with the thickness of the lithium metal layer being about 5μm, 10μm, 15μm, 20μm, 25μm, 30μm, 35μm, 40μm, 45μm, or 50 μm thick). Electrode assembly **800** formed by adhering the Li foil or Li film directly onto

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surface **101A** of solid electrolyte sheet **100** (*e.g.,* by laminating with heat) or by laminating the Li foil/film to a subassembly of a tie-layer coated sheet, as described above. To enhance bonding and improve the interface, the Li foil/film is treated or processed to expose fresh Li surfaces just prior to lamination. For example, in various embodiments the Li foil is freshly extruded and then immediately laminated to sheet **100**, or the Li foil/film may be treated to expose fresh surfaces (*e.g.,* by bristle scrubbing the surface). The freshly extruded or treated foil is then immediately mated to sheet **100** (*e.g.,* directly onto sulfide glass surface **101A** or a tie layer if a subassembly is employed). Exposure of the fresh Li surfaces to the ambient environment should be minimized to the maximum possible extent, and the ambient environment should have a very low moisture and oxygen content of preferably less than 10ppm.

[0127] By use of the term "fresh" when referring to an extruded Li foil or a freshly scrubbed lithium metal surface it is meant that the ambient exposure time between extruding/scrubbing and laminating is limited to avoid forming a prohibitively thick resistive film on the lithium surface. To be considered fresh, ambient exposure should be limited to minutes, typically < 10 minutes, and preferably < 1 minute and more preferably < 30 seconds. In embodiments, ambient exposure is between 1– 3 minutes, or less than 60 seconds, or less than 30 seconds, or less than 20 seconds, or less than 10 seconds (*e.g.,* within about 10 or 5 seconds).

[0128] With reference to **Fig. 8B**, in other embodiments standalone lithium metal electrode assembly **800** may be formed by laminating current collecting layer **812** directly onto solid electrolyte sheet **100** by evaporating Li metal or by spraying molten lithium as a bonding layer between it (**812**) and sheet **100**, followed by optional roller pressing. Notably, prior to the laminating step, current collector **812** (*e.g.,* Cu foil) is devoid of Li metal, and thus the technique provides a method for bonding sheet **100** to a discrete self-supporting Cu foil in the absence of a pre-existing lithium metal layer. Moreover, the thickness of the Li metal bonding layer can be adjusted. In various embodiments it is advantageous to have an exceptionally thin bonding layer, of thickness sufficient to effect bonding but otherwise scant as it pertains to the amount of capacity it provides to a battery cell. For example, a scant Li metal bonding layer may have thickness of no more than about 5μm (*e.g.,* about 1 -

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2μm), and is highly advantageous when combining the electrode assembly with a Li ion positive electrode in a battery cell, wherein almost all of the Li cell capacity is derived from the fully lithiated intercalation compound of the positive electrode (*e.g.*, LCO, NCA, NMC). In operation, the thin Li metal bonding layer serves as a seed layer for enhancing uniformity of Li metal deposition onto current collector 812 during initial charging of the battery cell, without burdening the cell with an overcapacity of Li metal because it (the bonding layer) is scant relative to the area capacity of the positive electrode.

[0129] In an alternative embodiment, not shown, it is contemplated that current collector layer **812** may have a pre-existing lithium metal layer already present on its surface prior to laminating to the solid electrolyte in the presence of a lithium metal vapor.

[0130] With reference to **Fig. 8C** there is illustrated what is termed herein an encapsulated standalone lithium metal electrode assembly **800C**. In various embodiments encapsulated assembly **800C** is composed of lithium metal component layer **820** encapsulated between a first solid electrolyte sheet **100** and an opposing backplane component **830** impermeable to liquids it comes into contact with, and preferably non-reactive. Lithium metal component layer **820** comprises a lithium metal layer in direct contact with sheet **100**, and one or more optional layers, as described in more detail below, which are adjacent to backplane **830**. Solid electrolyte sheet **100** and backplane component **830** respectively define the major exterior opposing surfaces of the lithium metal electrode assembly. By use of the term encapsulate when referring to the lithium metal component layer of the assembly it is meant that the solid electrolyte sheet and backplane component are in contiguous mechanical force contact with the lithium metal component layer. Accordingly, as a result of the encapsulation, lithium metal component layer **820**, and in particular the lithium metal layer, may be subjected to stacking pressure when incorporated in a battery cell.

[0131] In some embodiments the encapsulated lithium metal electrode assembly is double-sided and the backplane component is a second solid electrolyte sheet (*e.g.*, substantially identical to the first solid electrolyte sheet). In other embodiments, backplane component is not a Li ion conductor, and the encapsulated lithium metal

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electrode assembly is referred to herein as single-sided; for instance, the backplane may be a substantially inert material layer or an electronically conductive material layer with current collector functionality. By use of the term single-sided or double-sided it is meant with respect to whether one or both sides of the electrode assembly supports Li ion through transport (via electrical migration).

[0132] With reference to **Fig. 8D**, in some embodiments encapsulated electrode assembly **800D** is double-sided, and the backplane component is a second solid electrolyte sheet (designated as **100-2**). When double-sided, lithium metal component layer **820** is typically a tri-layer composed of current collecting layer **812** disposed between first and second lithium metal layers, **810-1** and **810-2** respectively.

[0133] In various embodiments, the encapsulated double-sided lithium metal electrode assembly is fabricated by providing a first and a second lithium metal electrode assembly as described above with reference to **Fig. 8A**, and combining the two assemblies between a single current collecting layer **812**, or when the two assemblies are provided each with their own current collecting layer, they may be combined by placing one on the other (*i.e.,* current collector to current collector).

[0134] With reference to **Fig. 8E**, in other embodiments, the backplane component is not a Li ion conductor, and assembly **800E**, encapsulated, is single-sided. In various embodiments, when single-sided, backplane component **830** may be an inert material component layer, or electronically conductive with current collector functionality. For instance, inert backplane component **830** may be a polymeric layer (rigid or flexible) or when electronically conductive, the backplane may be a multi-layer of at least one polymer layer providing an exterior surface of the assembly and an electronically conductive metal layer in electronic communication with the lithium metal layer (*e.g.,* in direct contact with the lithium metal layer or in direct contact with a Cu current collecting layer).

[0135] In various embodiments the encapsulated assembly may be edge sealed along the lengthwise and/or widthwise dimensions. When entirely sealed along its edges, the assembly is fully sealed and preferably hermetic, and the lithium metal layer(s) are isolated from the external environment.

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[0136] With reference to **Fig. 8F**, in various embodiments the edge seals (*e.g.*, lengthwise edges as shown) may be effected by fusion or pinch sealing the peripheral edges of solid electrolyte sheet **100-1** to that of solid electrolyte sheet **100-2**. The direct bonding between sheets **100-1** and **100-2** may be performed with heat and/or pressure. For instance by heating the periphery of one or both sheets above T_g (*e.g.*, using a laser to heat the edges), and more typically above the softening temperature, and pressing/compressing (*i.e.*, pinching) to effect the seal, or heating above T_m and allowing the sheets to fusion seal to each other.

[0137] In other embodiments, as shown in **Fig. 8G**, the edge seal(s) may include a discrete sidewall component **835** interfacing with solid electrolyte sheet **100-1** and backplane component **830**. The discrete sidewall component may be an inert polymer or a glass wire placed along the lengthwise edge and then heat/fusion sealed to sheet **100** and the backplane component **830** (*e.g.*, a second solid electrolyte sheet). When the edge seal is made with a fusion sealable glass, it is generally not a Li ion conductor (*e.g.*, a non-conducting sulfide glass). In other embodiments the discrete sidewall component may be an epoxy seal; *e.g.*, the epoxy applied as a viscous fluid along the lengthwise edge(s), and then cured (*e.g.*, with heat).

Positive Electrode Assembly

[0138] With reference to **Fig. 9**, in various embodiments the electrode assembly is a standalone positive electrode assembly, wherein a positive electroactive component layer is encapsulated between a pair of vitreous solid electrolyte sheets of the present disclosure. Specifically, positive electrode assembly **900** is double-sided and composed of first and second solid electrolyte sheets **100-1** and **100-2** edge sealed via discrete sidewall component **835** (*e.g.*, as described above in various embodiments for the lithium metal electrode assemblies). Positive electroactive material component layer **960** is typically a tri-layer of current collecting layer **964** (*e.g.*, aluminum or stainless foil) coated on both sides by an electroactive material layer **962-1** and **962-2**, which, in various embodiments has a lithium ion intercalation compound as its electroactive material (*e.g.*, an oxide such as *e.g.*, $LiCoO_2$, $LiMn_2O_4$, LiNiO, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$). In various embodiments, positive electrode assembly **900** includes liquid electrolyte in contact with electroactive layer **962**, and present in its pores. In various embodiments, as shown, the assembly

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includes a first and second porous separator layer or gel electrolyte layer (designated as **970-1** and **970-2**, respectively), which, impregnated with liquid electrolyte, provide positive separation between the electroactive layers and their opposing solid electrolyte sheets. Preferably the assembly is well sealed around its edges, and the liquid electrolyte is prevented from seeping out (*e.g.,* hermetically sealed). In alternative embodiments the positive electrode assembly may be single-sided and second solid electrolyte sheet **100-2** replaced with a backplane component impermeable to the liquid electrolyte and preferably non-reactive (*e.g.,* a polymer or metal layer). When double-sided, it is contemplated that positive electrode assembly **900** may be edge sealed with a fusion or pinch seal as described above, rather than using a discrete sidewall component. In some embodiments, a solid polymer electrolyte may be used to effect positive separation between the electroactive layers and the opposing solid electrolyte sheets. In this way, the positive electrode assembly may be devoid of a liquid electrolyte.

Battery Cells

[0139] With reference to **Fig. 10A** there is illustrated a lithium battery cell **1000A** in accordance with the present disclosure, the battery cell comprising a cell laminate **1001** including solid electrolyte sheet **100** disposed between positive electrode **1060** and negative lithium electroactive layer **1010**, for example a lithium metal layer such as those described above with reference to layer **810** in **Figs. 8A-I**.

[0140] In various embodiments the combination of lithium electroactive layer **1010** (*e.g.,* an evaporated or extruded lithium metal layer) and solid electrolyte sheet **100** (*e.g.,* a vitreous sulfide glass) is incorporated in the battery cell as standalone solid-state lithium metal electrode assembly **800**, as described above with reference to **Figs. 8A-I**.

[0141] Cell laminate **1001** is generally disposed in a cell housing (not shown). In various embodiments the cell laminate is sufficiently flexible to be foldable and more preferably windable, and thereby cell **1000A** may be of a wound prismatic or wound cylindrical construction, or a foldable construct disposed in a rigid or pouch-like housing (*e.g.,* a multilayer laminate material). Battery cell **1000A** may be made by: i) combining layers: **1010**, **100**, and **1060**, to form laminate **1001**; ii) winding or folding

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the laminate into a shaped construct (*e.g.,* cylindrical or prismatic); iii) placing the shaped construct into a rigid or flexible housing such as a multilayer laminate pouch or rigid container; and then sealing the pouch or container. When a liquid electrolyte is employed in the cell, it is typically dispensed after the laminate is disposed in the cell housing.

[0142] In various embodiments, laminate **1001** is wound or folded with radius of curvature $\leq$ 3cm, or $\leq$ 2cm, or $\leq$ 1cm, or $\leq$ 0.5cm, or $\leq$ 0.25cm, without fracturing solid electrolyte sheet **100**. In various embodiments cell **1000A** includes a spindle about which laminate **1001** is wound, the spindle typically having diameter $\leq$ 6cm, $\leq$ 4cm, $\leq$ 2cm, $\leq$ 1cm, or $\leq$ 0.5cm.

[0143] In various embodiments, positive electrode **1060** includes positive electroactive layer **1062** disposed on current collecting layer **1064C** (*e.g.,* a metal foil, such as aluminum, nickel, stainless steel or the like). In various embodiments positive electrode **1060** may be solid-state (*i.e.,* devoid of a liquid electrolyte) or it may contain a liquid electrolyte, typically impregnated in the pores of electroactive layer **1062**. In various embodiments positive electroactive layer **1062** is a lithium ion intercalation layer composed of a lithium ion intercalation compound as the electroactive material. When combined with a liquid electrolyte, positive electroactive layer **1062** is typically porous, and when solid-state the layer is preferably dense (*e.g.,* a highly compacted particle composite). Particularly suitable lithium ion intercalation compounds include, for example, intercalating transition metal oxides such as lithium cobalt oxides, lithium manganese oxides, lithium nickel oxides, lithium nickel manganese cobalt oxides, lithium nickel cobalt aluminum oxides (*e.g.,* $LiCoO_2$, $LiMn_2O_4$, LiNiO, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and the like) or intercalating transition metal phosphates and sulfates (*e.g.,* $LiFePO_4$, $Li_3V_2(PO_4)_3$, LiCoPO4, $LiMnPO_4$, and $LiFeSO_4$) or others (*e.g.,* $LiFeSO_4F$ and $LiVPO_4F$), as well as high voltage intercalating materials capable of achieving cell voltages versus lithium metal in excess of 4.5 Volts.

[0144] In various embodiments the electroactive material of layer **1062** is of the conversion reaction type including transition metal oxides, transition metal fluorides, transition metal sulfides, transition metal nitrides and combinations thereof (*e.g.,*

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MnO_2, Mn_2O_3, MnO, Fe_2O_3, Fe_3O_4, FeO, Co_3O_4, CoO, NiO, CuO, Cu_2O, MoO_3, MoO_2, and RuO_2)).

[0145] In various embodiments the electroactive material of layer **1062** is elemental sulfur and/or lithium polysulfide species, typically dissolved in a non-aqueous liquid electrolyte. In such said embodiments, the battery cell may be considered a lithium sulfur battery. Generally, when making use of dissolved electroactive species (polysulfides or otherwise), electroactive layer **1062** is an electron transfer medium that facilitates electrochemical redox during discharge and charge, and, as such, is typically a porous metal or porous carbonaceous layer.

[0146] In various embodiments battery cell **1000A** is of the hybrid cell type, having a fully solid-state negative electrode (*e.g.,* a fully solid-state lithium metal electrode assembly) and a positive electrode impregnated with a liquid electrolyte, and thus the positive electrode not solid-state. In other embodiments cell **1000A** is fully solid-state, and thus entirely devoid of liquid phase electrolyte. In various fully solid state cell embodiments, solid electrolyte sheet **100** serves as the sole solid electrolyte separator layer between negative lithium electroactive layer **1010** (*e.g.,* a lithium metal layer) and positive electrode **1060**.

[0147] In various embodiments cell **1000A** is not fully solid state, and thus includes a liquid phase electrolyte. In some embodiments the liquid phase electrolyte is a common electrolyte present throughout the cell and contacts both the positive electrode (*e.g.,* positive electroactive layer **1062**) and negative lithium electroactive layer **1010** (*e.g.,* lithium metal layer). By use of the term "common electrolyte" it is meant that the liquid electrolyte contacts both the negative electroactive layer and the positive electroactive layer, and thus the "common liquid electrolyte" is continuous throughout cell laminate **1001**. A common liquid electrolyte yields a rather unusual and counterintuitive cell construction, in that it employs both a solid-state separator composed of solid electrolyte sheet **100** (preferably devoid of through porosity) and a continuous liquid phase electrolyte that contacts both positive electroactive layer **1062** and negative electroactive layer **1010**. In fact, solid electrolyte sheet **100** may be used as a Li ion conducting solid electrolyte separator layer in an otherwise conventional lithium ion cell, with the solid electrolyte sheet providing through conduction for Li ions while preventing short circuiting by lithium dendrites and providing protection

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against thermal runaway. In some embodiments, sheet **100** serves as a direct replacement for the micro-porous polymeric separator layer commonly employed in conventional lithium ion cells (*e.g.,* Celgard® or the like), and in such embodiments battery cell **1000A** includes a common liquid electrolyte but is explicitly devoid of a porous separator layer. For example, battery cell **1000A** may be embodied by positive electrode **1060** having porous positive electroactive layer **1062** comprising a lithium ion intercalation compound (*e.g.,* $LiCoO_2$) and porous negative electroactive layer **1010** having as its electroactive material a lithium ion intercalation material or alloying material (*e.g.,* intercalatable carbon or silicon or some combination thereof). Moreover, while this disclosure contemplates that the common liquid electrolyte may exist primarily in the pores of the positive and negative electroactive layers, it is not limited as such, and in some embodiments the cell may include one or more porous separator layers (*e.g.,* a micro-porous polymer layer such as a porous polyolefin or the like) or gel electrolyte layer positioned between solid electrolyte sheet **100** and electroactive layer(s) **1010** and/or **1062**. When incorporated in a cell having a common liquid electrolyte, solid electrolyte sheet **100** is preferably substantially impervious to the common liquid electrolyte, but the invention is not necessarily so limited.

[0148] In various embodiments the battery cell of the present disclosure is of a hybrid cell type: composed of a solid-state and sealed negative electrode assembly, as described above, and a positive electrode impregnated with a liquid electrolyte. When referring to an electrode assembly as solid-state it is meant that the assembly does not contain liquid, and in particular that the electroactive material of the assembly does not contact liquid phase electrolyte.

[0149] With reference to **Fig. 10B**, in various embodiments battery cell **1000B** is of the hybrid type, and solid-state negative electrode assembly **1040** is an edge sealed lithium metal electrode assembly, such as **800F**, illustrated in **Fig. 8F**. In particular embodiments the liquid electrolyte is present in the pores of positive electroactive material layer **1062**, and is chemically compatible in direct contact with second side surface **101B** of sheet **100**. To prevent the liquid electrolyte from contacting lithium metal layer **810**, solid electrolyte sheet **100** should be free of through porosity and impermeable to the liquid electrolyte, and therefore substantially impervious.

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[0150] In various embodiments, and in particular when the solid electrolyte sheet is a sulfide based glass, the liquid phase electrolyte is non-aqueous, and exceptionally dry, meaning that it is has very low moisture content, preferably less than 20 ppm, more preferably less than 10 ppm, and even more preferably less than 5 ppm. Non-aqueous liquid electrolytes suitable for use herein include solutions of organic solvent(s), such as carbonates (*e.g.,* DMC, DEC, PC, EC), and a lithium salt dissolved therein (*e.g.,* $LiBF_4$, $LiClO_4$, $LiPF_6$, LiTf and LiTFSI; where Tf = trifluormethansulfonate; TFSI = bis(trifluoromethanesulfonyl)imide), as well as liquid electrolytes based on ionic liquids, as are known in the battery field arts.

[0151] In various embodiments, cell laminate **1001B** includes separator layer **1070** disposed between negative electrode **1040** and positive electrode **1060B**; the separator layer typically a porous material layer or gel electrolyte layer impregnated with the non-aqueous liquid electrolyte. For instance, separator layer **1070** a porous organic polymer, such as a porous polyolefin layer (*e.g.,* microporous). Separator layer **1070** provides positive separation between second principal side surface **101B** of solid electrolyte sheet **100** and positive electroactive material layer **1062**. The separator layer may provide various benefits. In particular embodiments, layer **1070** enables the combination of a solid electrolyte sheet and a positive electroactive material layer that are chemically incompatible in direct contact with each other. In other hybrid cell embodiments, the composition of solid electrolyte sheet **100** is chemically compatible in direct contact with the positive electroactive material of layer **1062**, and laminate **1001B** may be absent layer **1070**, and sheet **100** and layer **1062** disposed in direct contact. Cell laminate **1001B** may be wound or folded and incorporated into a cell housing. Thereafter, the liquid phase electrolyte dispensed into the cell, wherein it contacts positive electrode **1020B** but does not contact lithium metal layer **810**, as it is isolated inside the sealed electrode assembly.

[0152] In particular embodiments cell **1000B** is composed of: i) electroactive layer **810** - a lithium metal layer; ii) solid electrolyte sheet **100** - a substantially impervious vitreous Li ion conducting sulfide based glass sheet; iii) positive electroactive material layer **1062** - composed of a lithium intercalation material, such as an oxide (*e.g.,* $LiCoO_2$, $LiMn_2O_4$, LiNiO, $LiNiMnCoO_2$ or the like) or phosphate (*e.g.,* $LiFePO_4$); iv) optional separator layer **1070**- a porous polymer or gel, impregnated

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with a liquid phase electrolyte; v) a non-aqueous liquid phase electrolyte present in the pores of layers **1062** and **1070**, and chemically compatible with second principal side surface **101B** of sulfide based solid electrolyte glass sheet **100**. For instance, lithium metal layer **810** and solid electrolyte sheet **100** incorporated into cell **1000B** as an edge sealed solid-state lithium metal electrode assembly.

[0153] With reference to **Fig. 10C** there is illustrated a fully solid-state battery cell **1000C** in accordance with various embodiments of this disclosure. The cell includes solid-state positive electrode **1060C**; solid-state negative electrode **1040C**; and Li ion-conducting solid electrolyte sheet **100** serving as separator. In some embodiments, components **1060C/1040C/100** are incorporated into the cell as discrete material layers. In other embodiments, separator sheet **100** and negative/positive electrodes **1040C/1060C** are incorporated in the cell as standalone components (*e.g.,* standalone lithium negative electrode assembly or as a standalone lithium positive electrode assembly.

[0154] Solid-state positive electrode **1040C** includes positive electroactive layer **1062C** and current collector layer **1024C**. In various embodiments electroactive layer **1062C** is a composite of positive electroactive material combined with solid electrolyte material of composition similar to, or the same as, that of vitreous sulfide glass sheet **100**. Without limitation, particle composite layer **1062** may be fabricated by compaction or tape casting of positive electroactive particles, Li ion conducting sulfide glass or sulfide glass-ceramic particles, and optionally electronically conductive particles for enhancing electronic conductivity, such as a carbonaceous material, (*e.g.,* carbon black particles). In particular embodiments the positive electroactive particles are Li ion intercalating compounds, as described above (*e.g.,* metal oxides).

[0155] Solid-state negative electrode **1040C** is composed of electroactive material layer **1010C**, which may be a lithium metal layer as described above, with optional current collecting layer **1012C**. In various embodiments, lithium metal layer **1010C** and solid electrolyte sheet **100** are incorporated into cell **1000C** as a standalone lithium metal electrode assembly in accordance with various embodiments of the present disclosure. In alternative embodiments, negative electroactive layer **1010C** is not a lithium metal layer, but rather a layer comprising lithium electroactive material

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having a potential near that of lithium metal, such as, but not limited to, intercalatable carbon, silicon or a combination thereof. In such said embodiments, electroactive layer **1010C** may be a particle compact or tape cast layer of negative electroactive material particles (*e.g.,* intercalatable carbon) combined with solid electrolyte particles of composition similar to, or the same as, that which constitutes sheet **100**. Negative electroactive layer **1010C** may further contain electronically conductive diluents (such as high surface area carbons) as well as binder materials for enhancing mechanical integrity of the layer.

[0156] In various embodiments fully solid-state battery cell **1000C** is composed of positive and negative electrodes that are each composite powder compacts or tape cast layers, separated by a solid electrolyte sheet of the present disclosure (*e.g.,* a vitreous sheet of a Li ion conducting sulfide based glass).

[0157] With reference to **Fig. 10D** there is illustrated a process for making a lithium metal battery cell **1000D** that, in its as-fabricated state, is devoid of lithium metal. The cell is composed of cell laminate **1001D** comprising: i) electrode subassembly **700B** having current collecting layer **701b** and optional tie layer **701a**, as described above with reference to **Fig. 7B**; and ii) positive electrode **1060** comprising electroactive layer **1062** and current collecting layer **1064**. In some embodiments cell **1000D** is a hybrid cell with a liquid electrolyte impregnated as described above with reference to **Fig 10B**. In other embodiments cell **1000D** may be a solid-state battery cell, and therefore absent liquid electrolyte and its associated separator layer **1070**. Continuing with reference to **Fig. 10D**, electroactive layer **1062** is a fully lithiated lithium intercalation material layer, and is the sole source of Li in the as-fabricated cell. Lithium metal **810** is formed as a result of the initial cell charge, as Li from layer **1062** is plated onto electrode subassembly **700B**, and in particular onto current collecting layer **701b**, thereby producing lithium metal component layer **1020**.

[0158] Finally, with reference to **Fig. 10E** there is illustrated a lithium metal battery cell **1000E** in accordance with the present disclosure; the cell is composed of positive electrode assembly **900** (shown in detail in **Fig. 9**) and lithium metal layer **810-1** and **810-2** disposed in direct contact with first surface **101A** of respective solid electrolyte sheets **100-1** and **100-2**.

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[0159] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art. Although various details have been omitted for clarity's sake, various design alternatives may be implemented. Therefore, the present examples are to be considered as illustrative and not restrictive, and the disclosure is not to be limited to the details given herein, but may be modified within the scope of the appended claims.

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What is claimed is:

1. A standalone lithium ion-conductive solid electrolyte, comprising:
a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass having,
a liquid-like surface;
an area of at least 10 cm^2;
a thickness of no more than 100 μm; and
a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm,
wherein the electrolyte is disposed in a battery cell component as a separator adjacent a negative lithium electroactive layer.

2. The electrolyte of claim 1, wherein the electrolyte is disposed in a battery cell between a positive electrode and a negative lithium electroactive layer.

3. A method of making a standalone Li-ion conductive solid electrolyte, the method comprising drawing a molten sheet of Li ion conducting sulfide glass into a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass, wherein the drawing occurs at or above the softening temperature of the glass.

4. The method of claim 3, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} <$ 100°C.

5. The method of claim 3, wherein the drawn freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass has,
a liquid-like surface;
an area of at least 10 cm^2;
a thickness of no more than 100 μm; and
a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm.

6. A method of making a standalone Li-ion conductive solid electrolyte, the method comprising:
providing a Li ion conducting sulfide glass pre-form; and
pulling on the preform at a temperature sufficient to draw the pre-form to a vitreous glass ribbon having a thickness in the range of 5 to 100 μm.

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7. The method of claim 6, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} <$ 100°C.

8. The method of claim 6, wherein the ribbon is a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass having,

a liquid-like surface;

an area of at least 10 cm^2;

a thickness of no more than 100 μm; and

a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm.

9. A battery cell comprising:

a positive electrode;

a negative electrode comprising a lithium electroactive layer; and

a lithium ion-conductive solid electrolyte in lithium ion communication with the positive electrode and the negative electrode, the

lithium ion-conductive solid electrolyte, comprising:

a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass having,

a liquid-like surface;

an area of at least 10 cm^2;

a thickness of no more than 100 μm; and

a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm.

10. The battery cell of claim 9, wherein the glass sheet has a substantially uniform thickness of no more than 100 μm.

11. The battery cell of claim 9, wherein the glass sheet further comprises parallel lengthwise edges.

12. The battery cell of claim 9, wherein the glass sheet is a continuous web at least 100 cm in length.

13. The battery cell of claim 9, wherein the glass sheet is a continuous web at least 1000 cm in length.

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14. The battery cell of claim 9, wherein the vitreous sulfide-based glass sheet is characterized as having a threshold current for Li dendrite initiation that is greater than 1 mA/cm^2.

15. The battery cell of claim 9, wherein the liquid-like surface lacks surface flaws having a depth dimension greater than 1% of the sheet thickness.

16. The battery cell of claim 9, wherein the sheet lacks of powder particles, inter-particle boundaries, or contiguous voids extending between first and second principal surfaces that are sufficient to propagate a Li dendrite, and the liquid-like surface lacks flaw manifestations of a pressed powder compact that are sufficient to initiate Li dendrite penetration.

17. The battery cell of claim 9, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} <$ 100°C.

18. The battery cell of claim 9, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} <$ 50°C.

19. The battery cell of claim 9, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} <$ 30°C.

20. The battery cell of claim 9, wherein the sulfide-based glass is of a type Li_2S-YS_n; Li_2S-YS_n-YO_n and combinations thereof, wherein Y is selected from the group consisting of Ge, Si, As, B, or P, and n = 2, 3/2 or 5/2.

21. The battery cell of claim 20, wherein the glass is chemically and electrochemically compatible in contact with lithium metal.

22. The battery cell of claim 20, wherein the glass is devoid of phosphorous.

23. The battery cell of claim 9, wherein the glass comprises Li_2S and/or Li_2O as a glass modifier and one or more of a glass former selected from the group consisting of P_2S_5, P_2O_5, SiS_2, SiO_2, B_2S_3 and B_2O_3.

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24. An electrode assembly, comprising:

a lithium ion-conductive solid electrolyte, comprising:

a freestanding inorganic vitreous sheet of sulfide-based lithium ion conducting glass having,

a liquid-like surface;

an area of at least 10 cm^2;

a thickness of no more than 100 μm; and

a room temperature intrinsic lithium ion conductivity of at least 10^{-5} S/cm; and

a lithium metal layer in direct contact with the liquid-like surface of the sheet.

25. The electrode assembly of claim 24, wherein the glass sheet further comprises parallel lengthwise edges.

26. The electrode assembly of claim 24, wherein the glass sheet is a continuous web at least 1000 cm in length.

27. The electrode assembly of claim 24, wherein the liquid-like surface lacks surface flaws having a depth dimension greater than 1% of the sheet thickness.

28. The electrode assembly of claim 24, wherein the sulfide glass has a glass stability factor $\{T_x-T_g\} < 30°C$.

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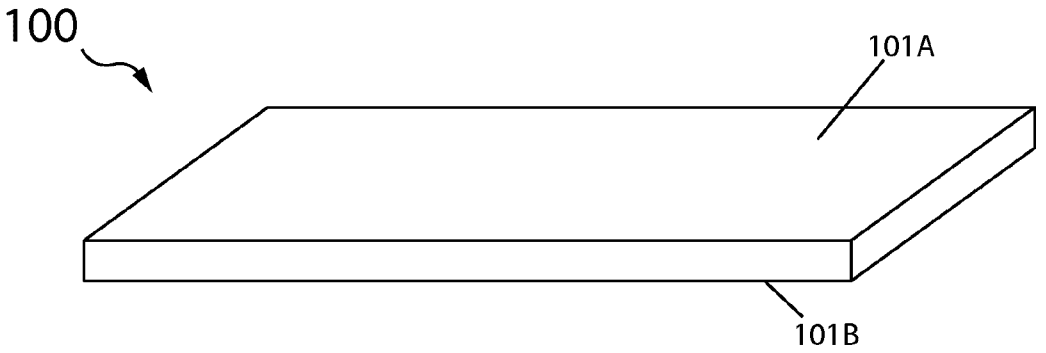


Figure 1A

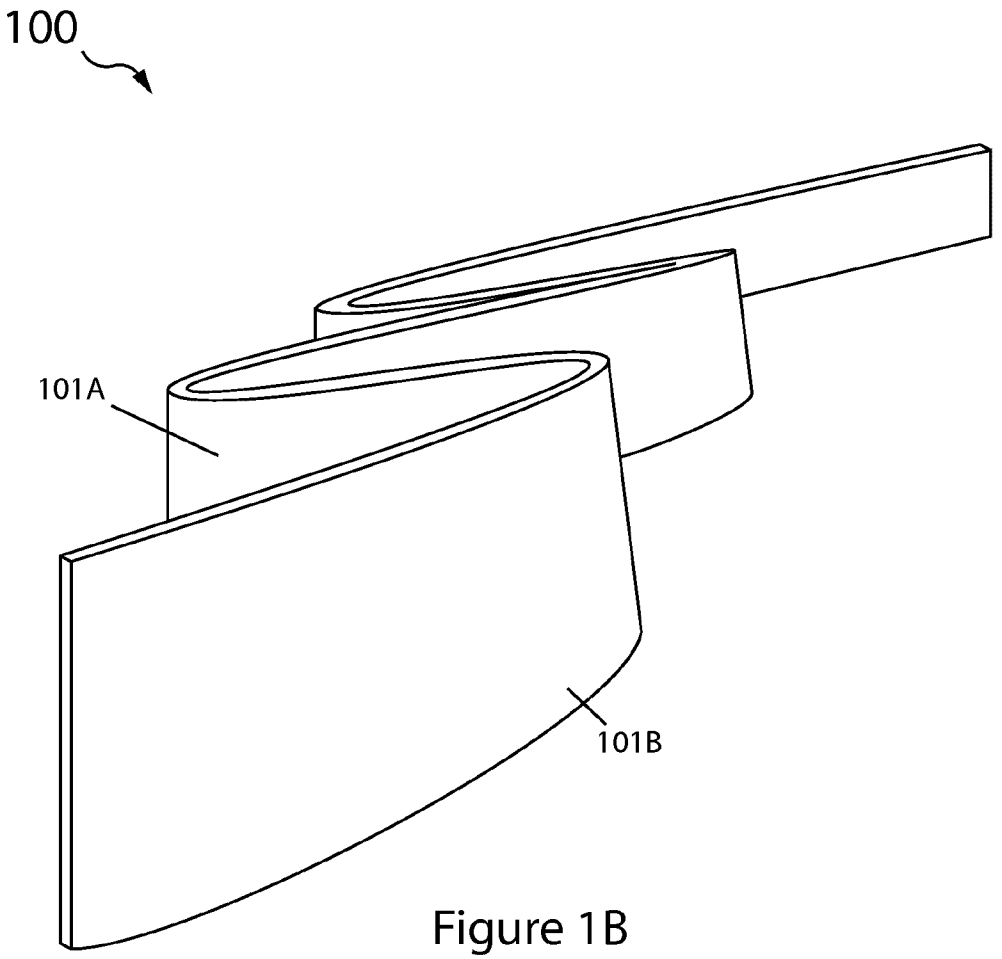


Figure 1B

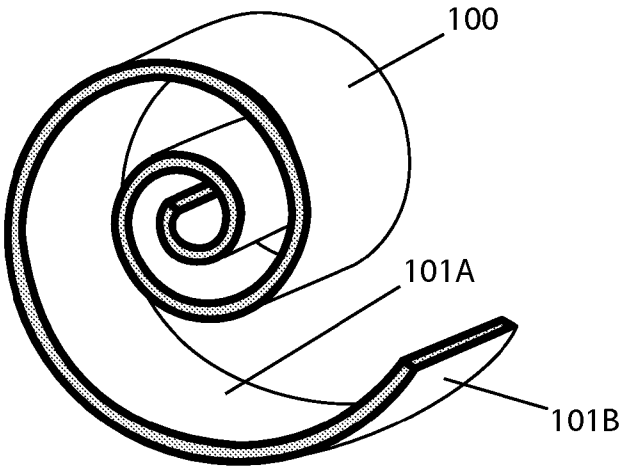


Figure 1C

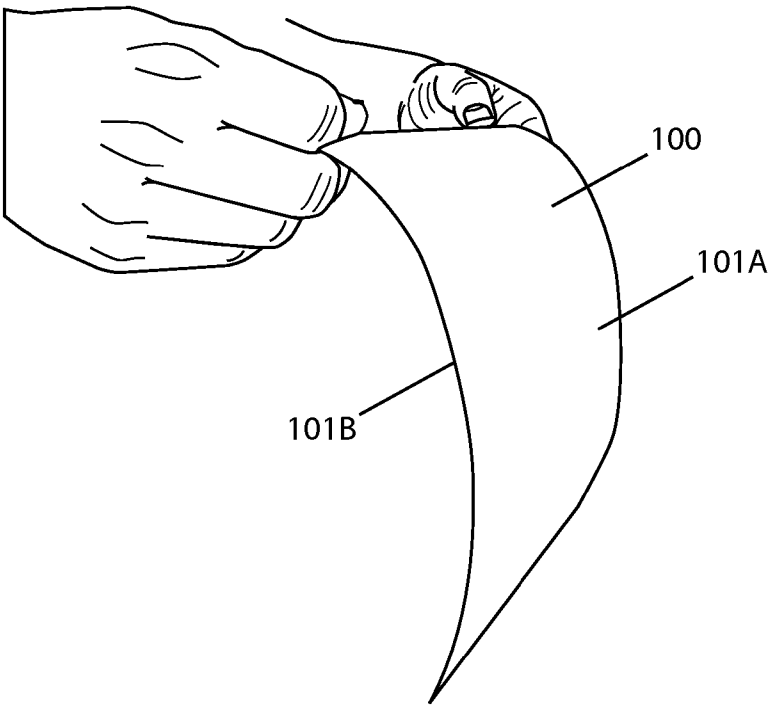


Figure 1D

Date Reçue/Date Received 2022-04-14

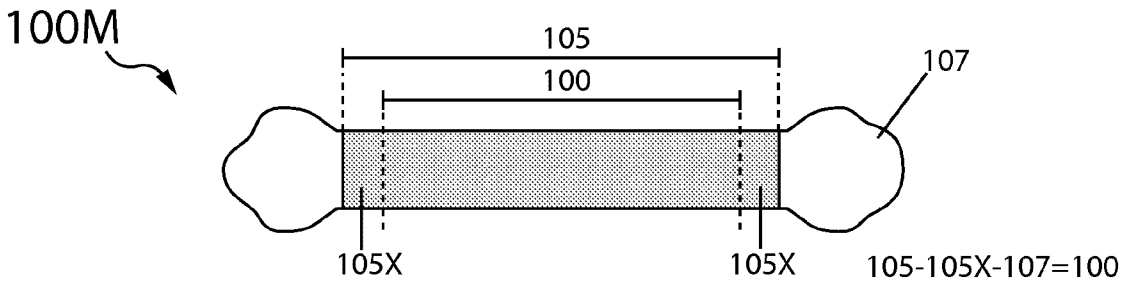


Figure 1E

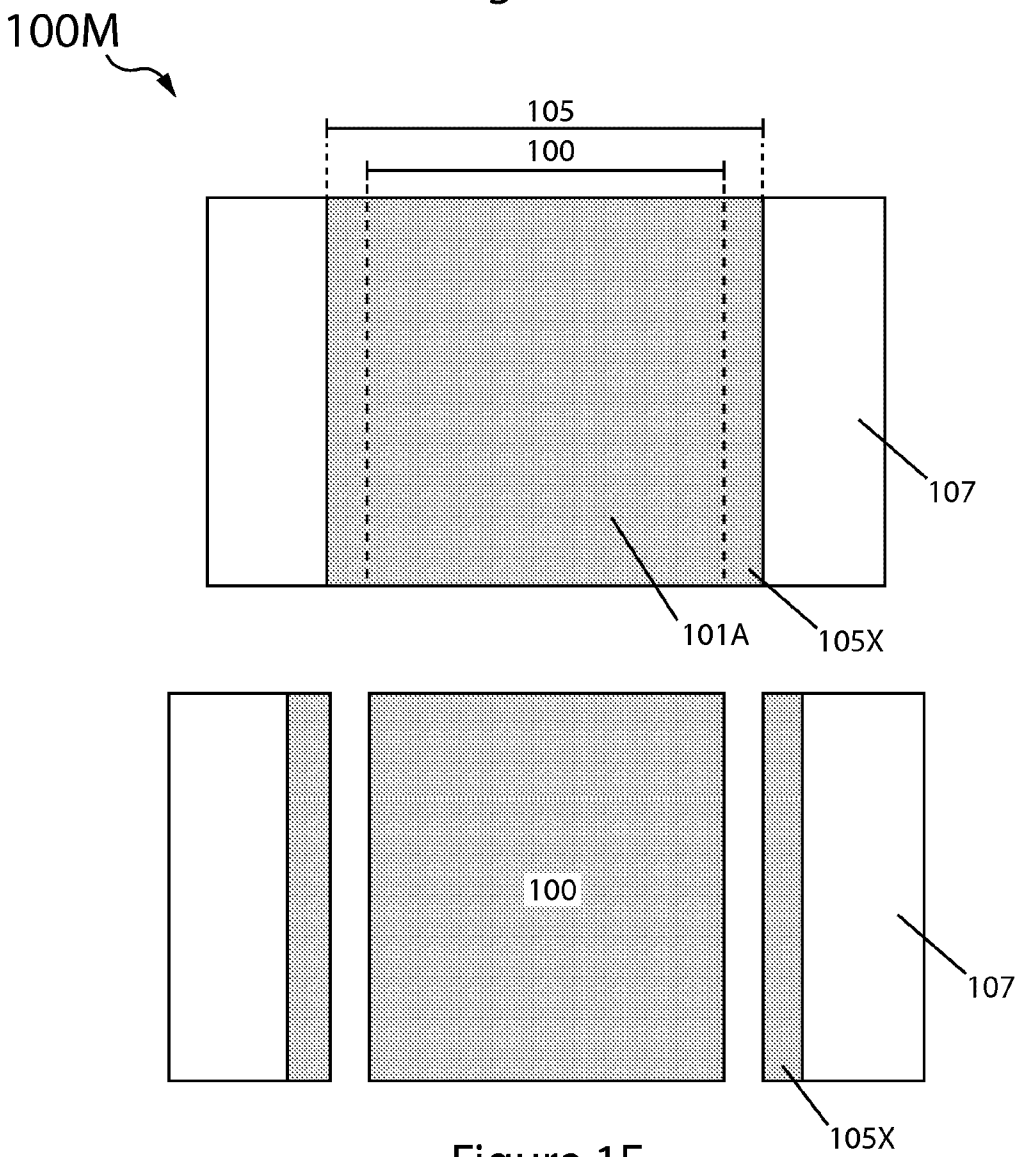


Figure 1F

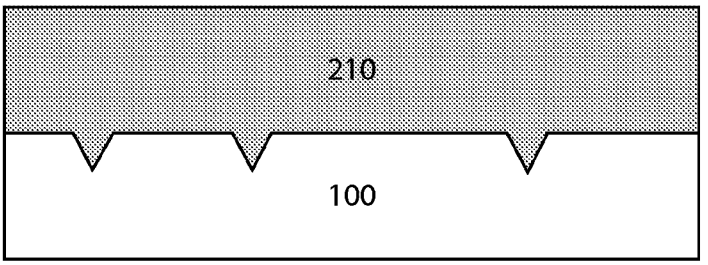


Figure 2

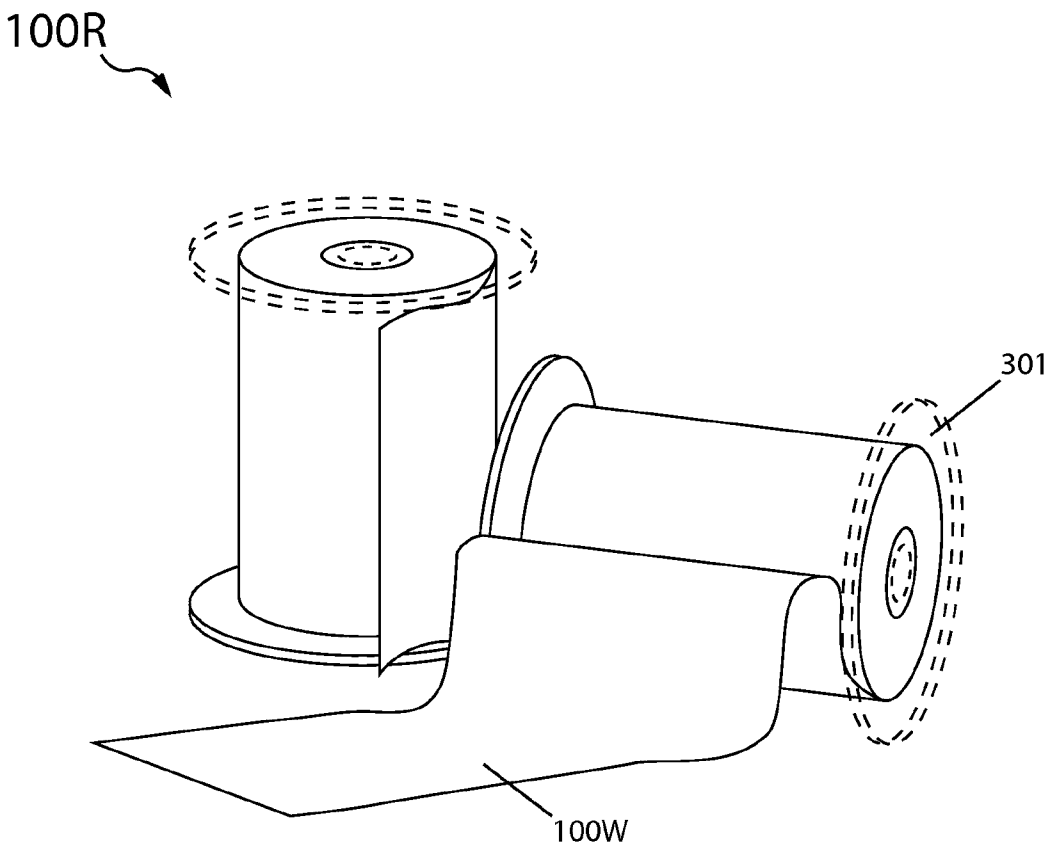


Figure 3A

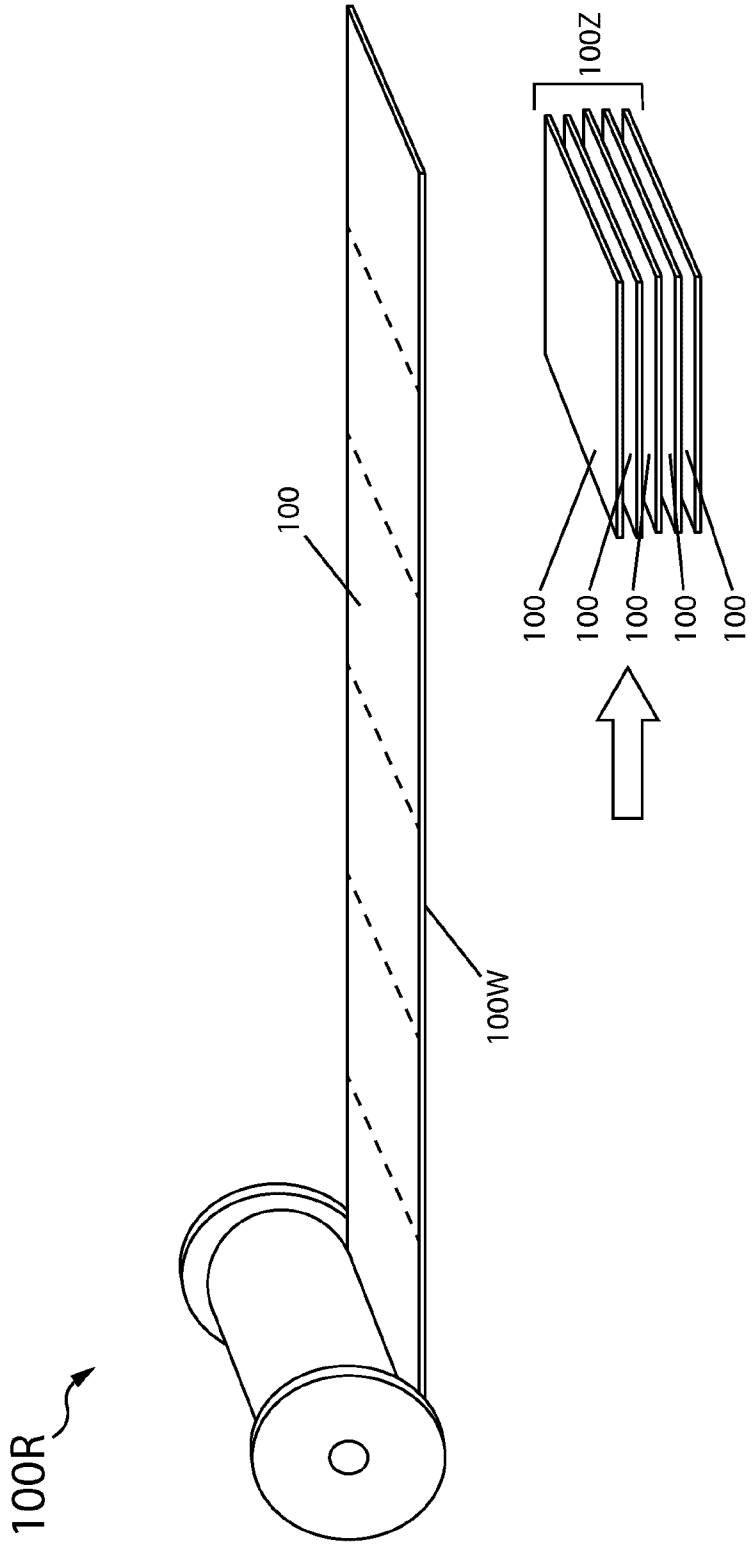


Figure 3B

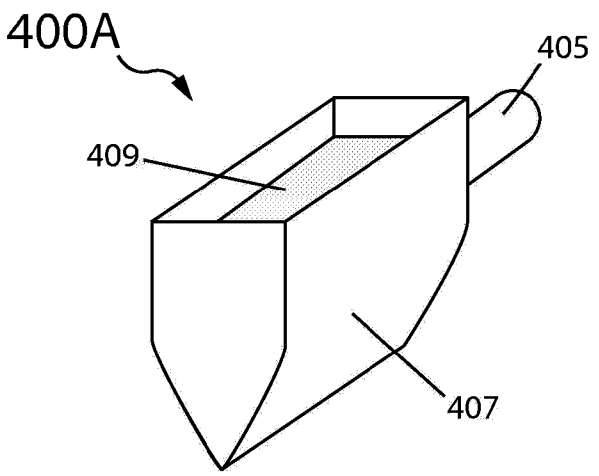


Figure 4A

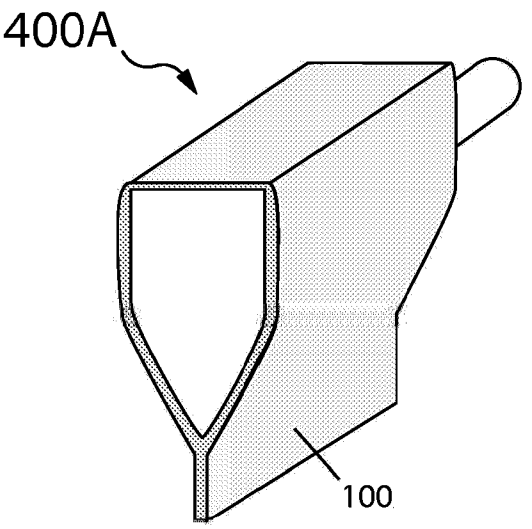


Figure 4B

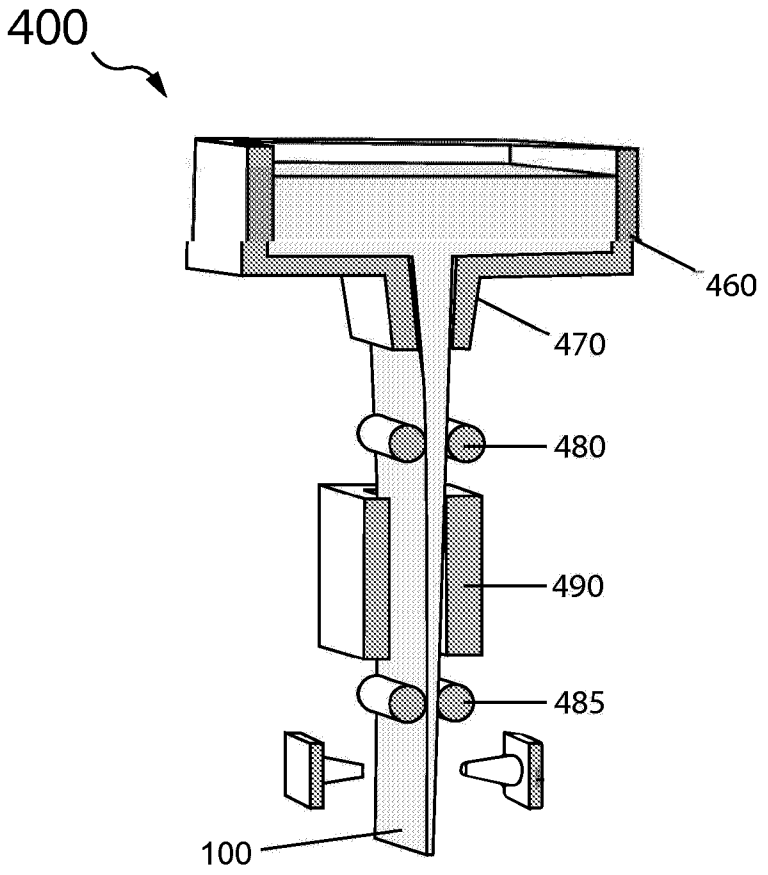


Figure 4C

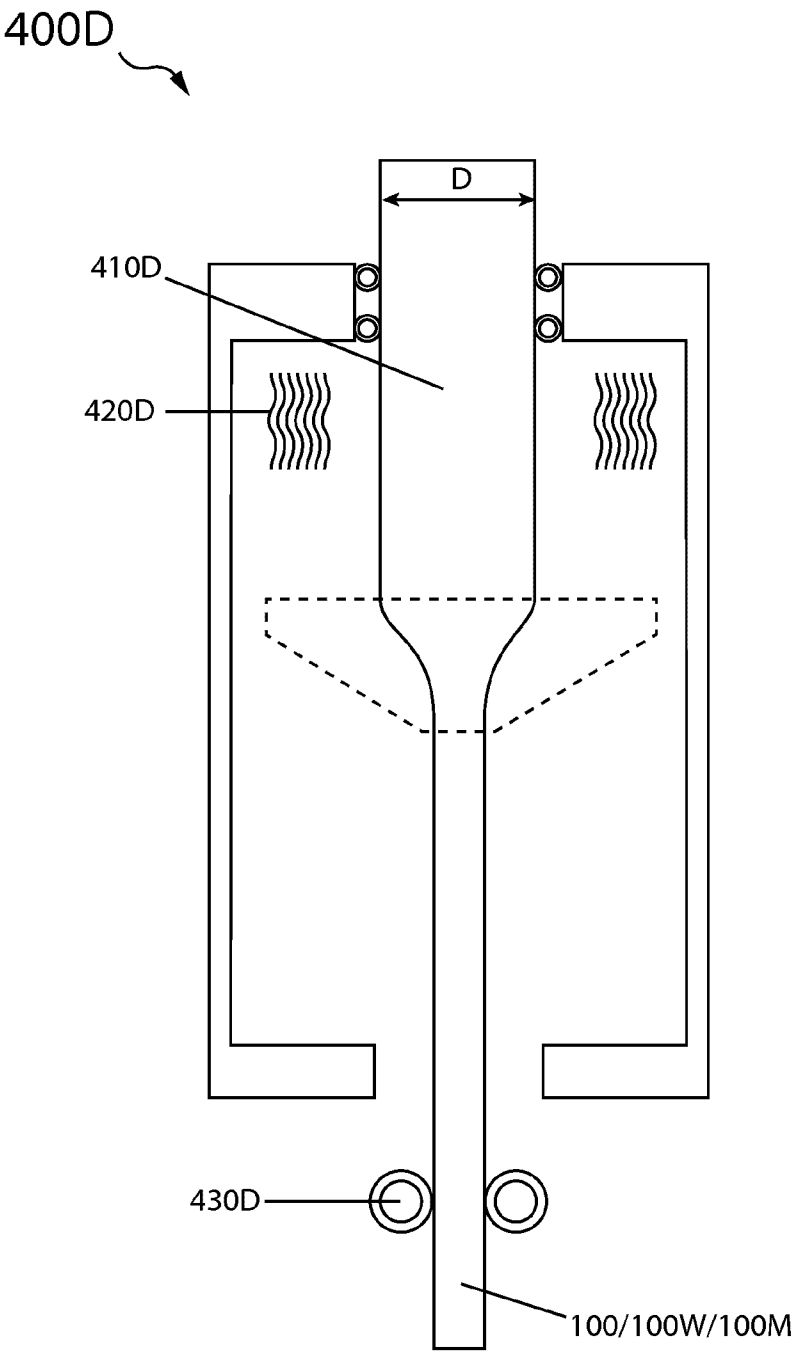


Figure 4D

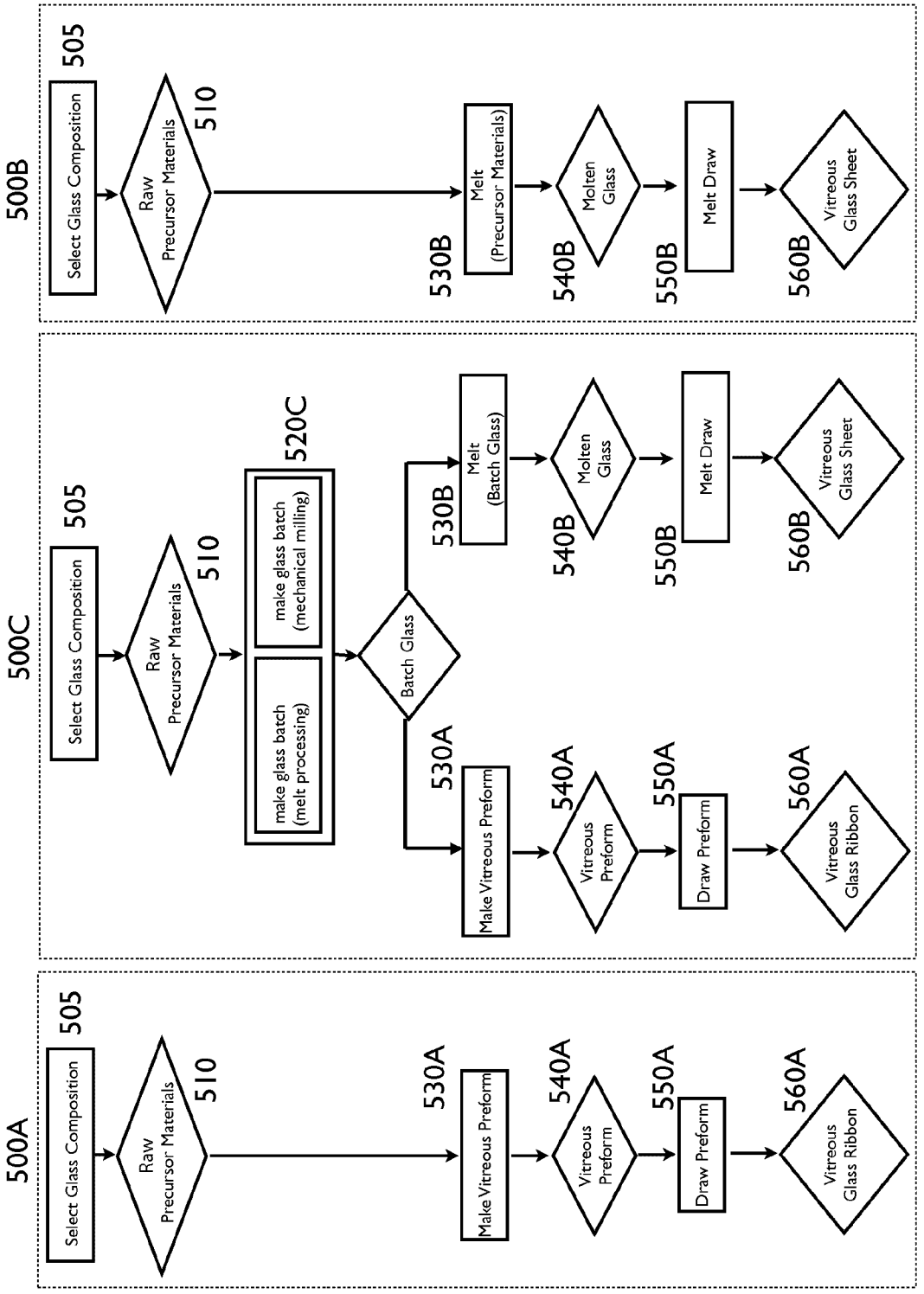


Fig. 5A

Fig. 5B

Fig. 5C

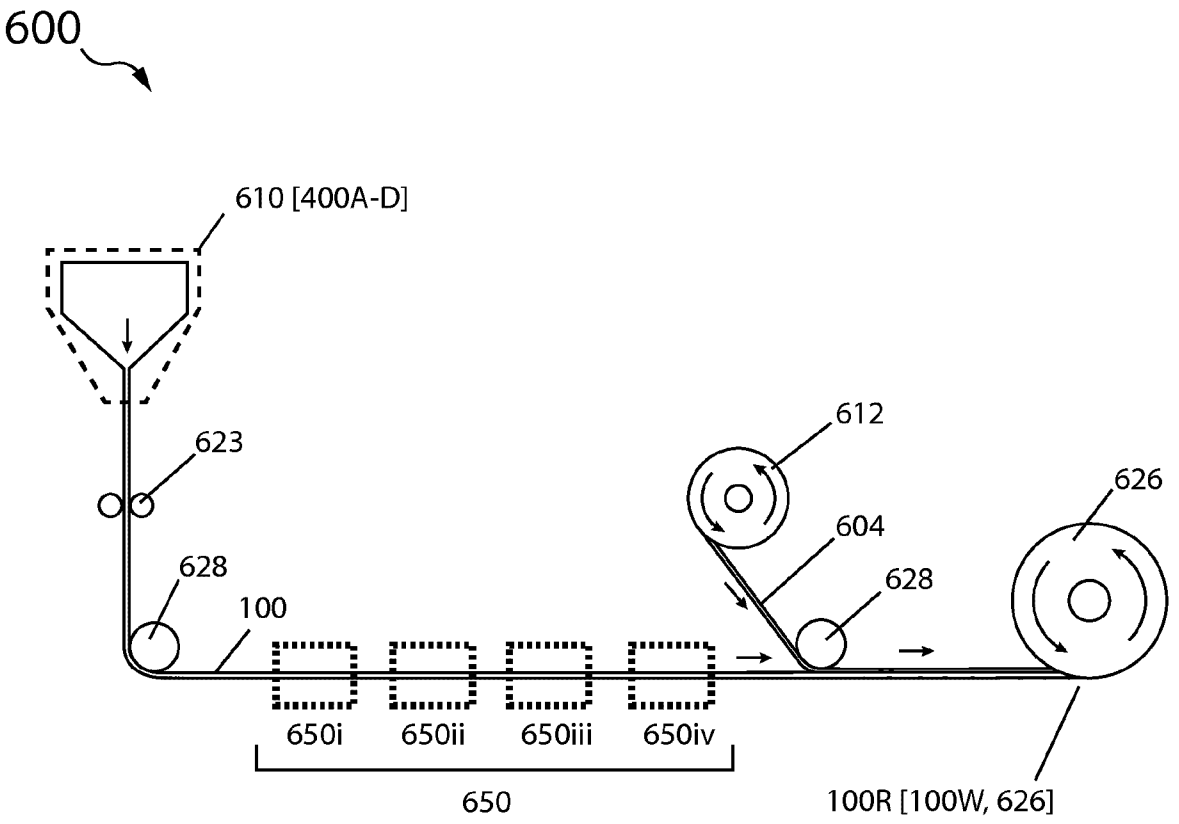

600
610 [400A-D]
623
628
100
612
604
628
626
650i
650ii
650iii
650iv
650
100R [100W, 626]

Figure 6

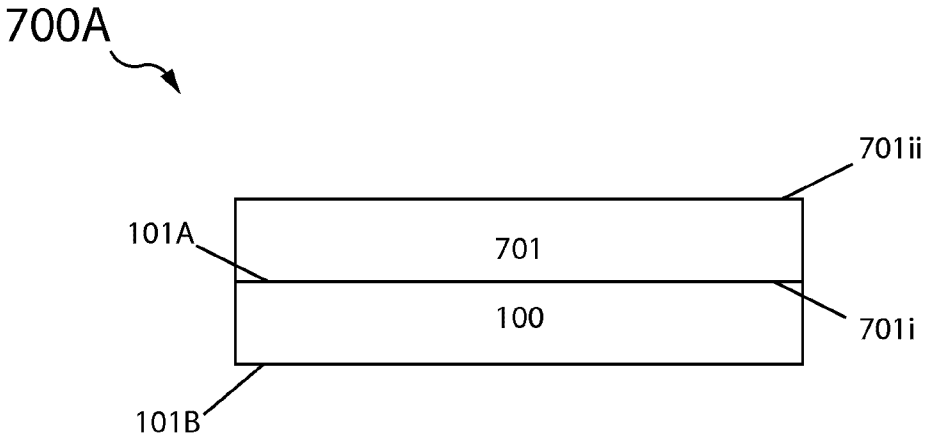


Figure 7A

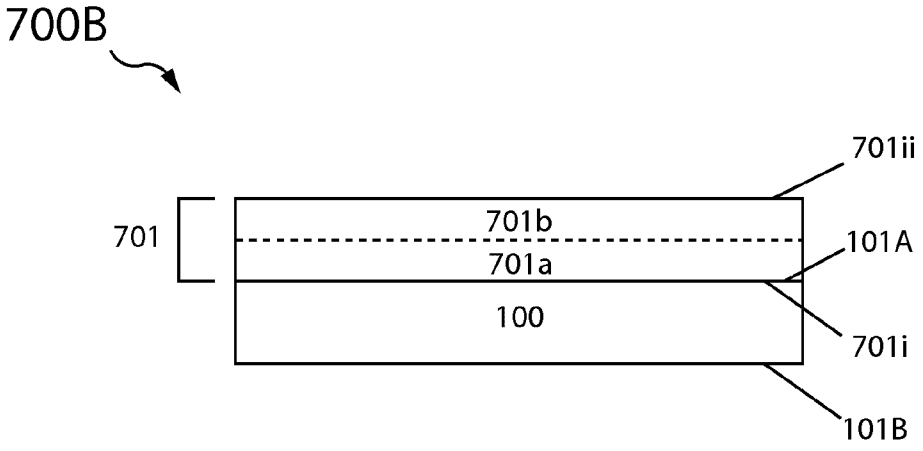


Figure 7B

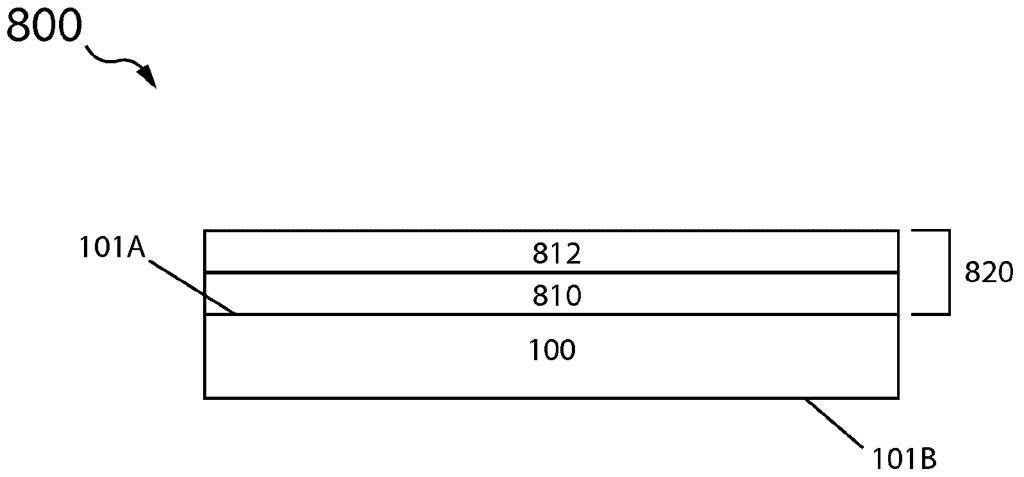


Figure 8A

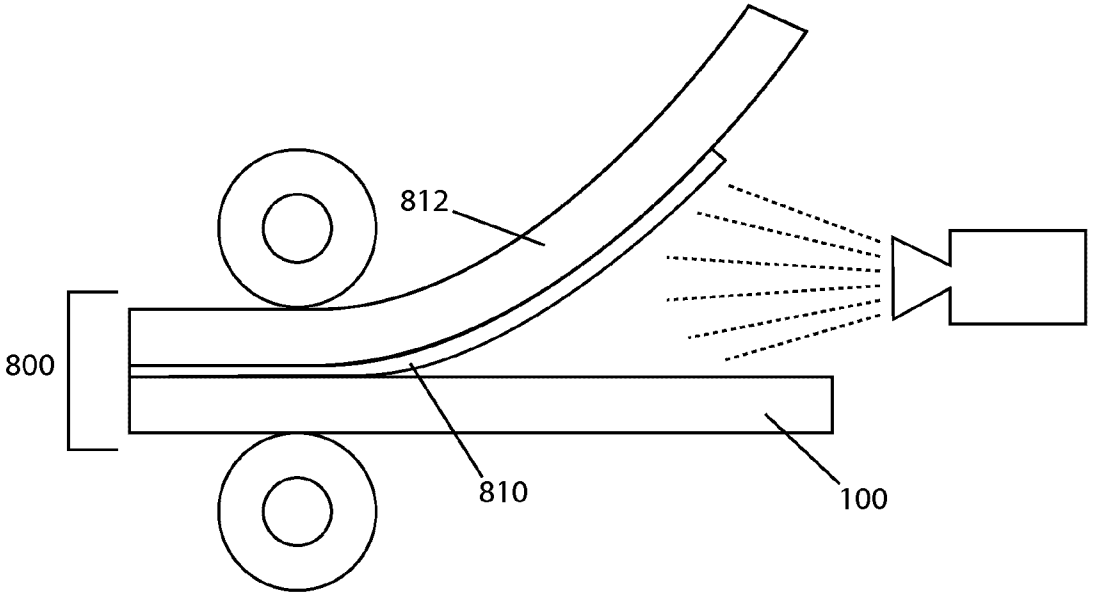


Figure 8B

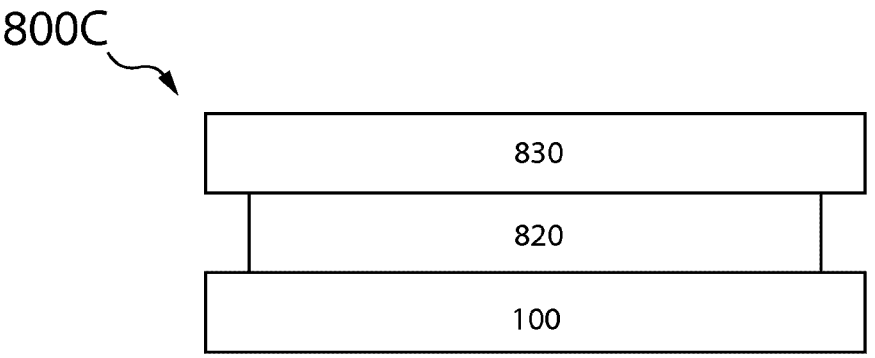


Figure 8C

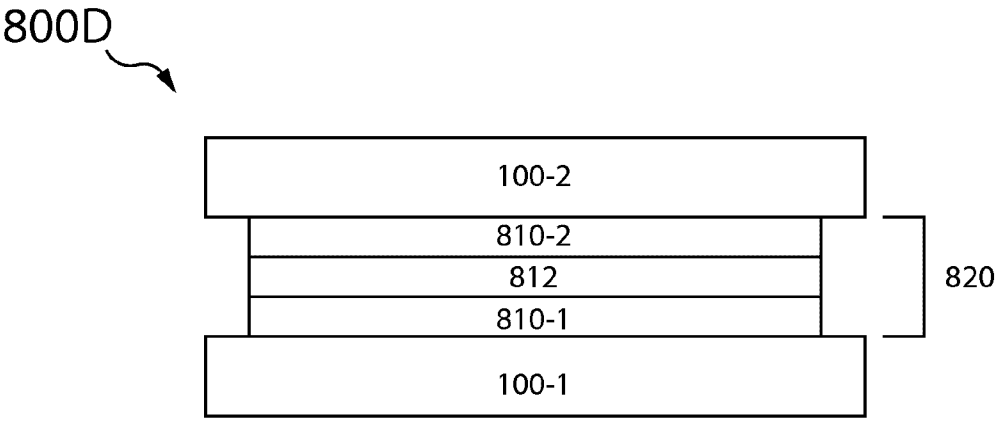


Figure 8D

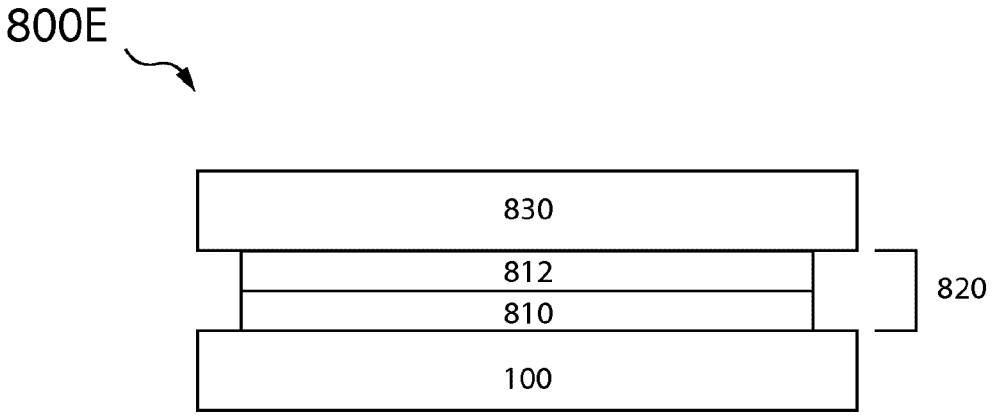


Figure 8E

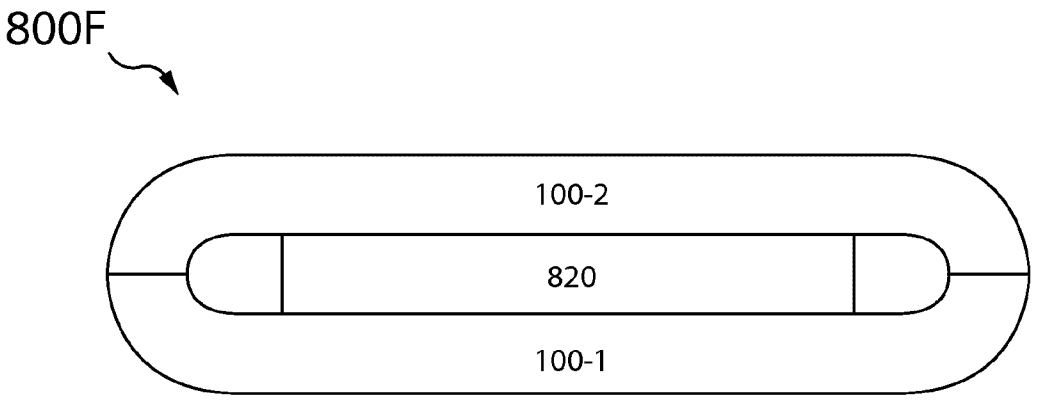


Figure 8F

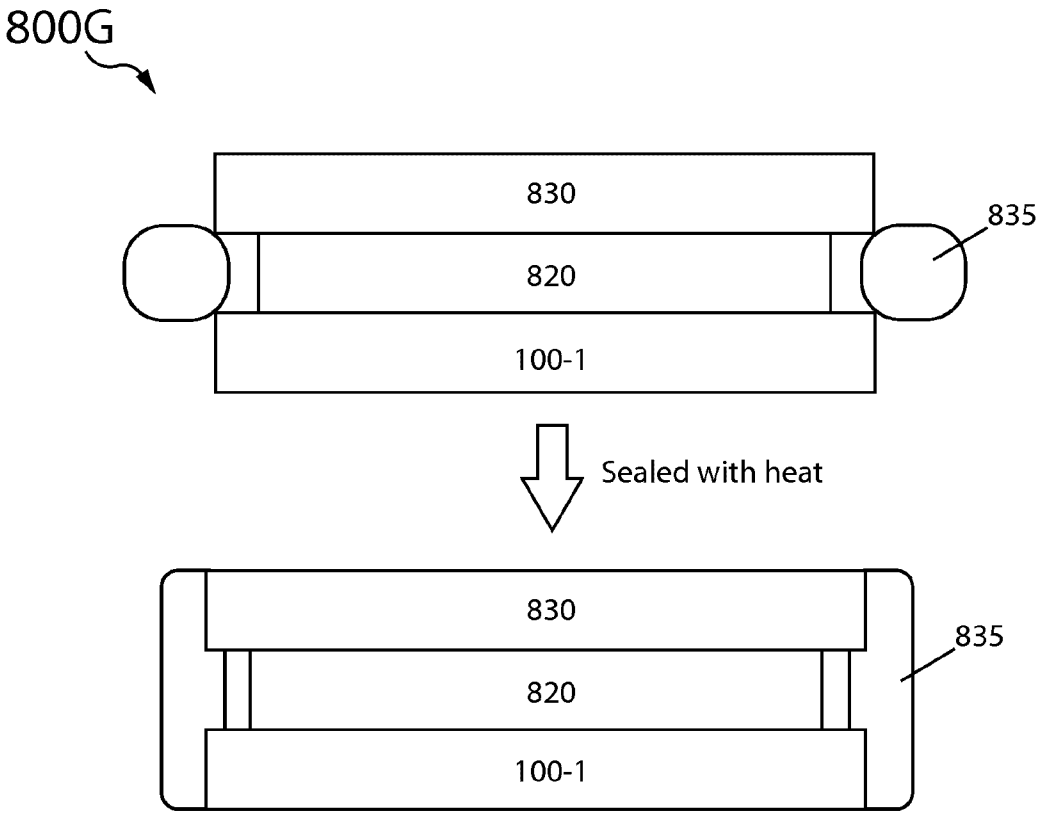


Figure 8G

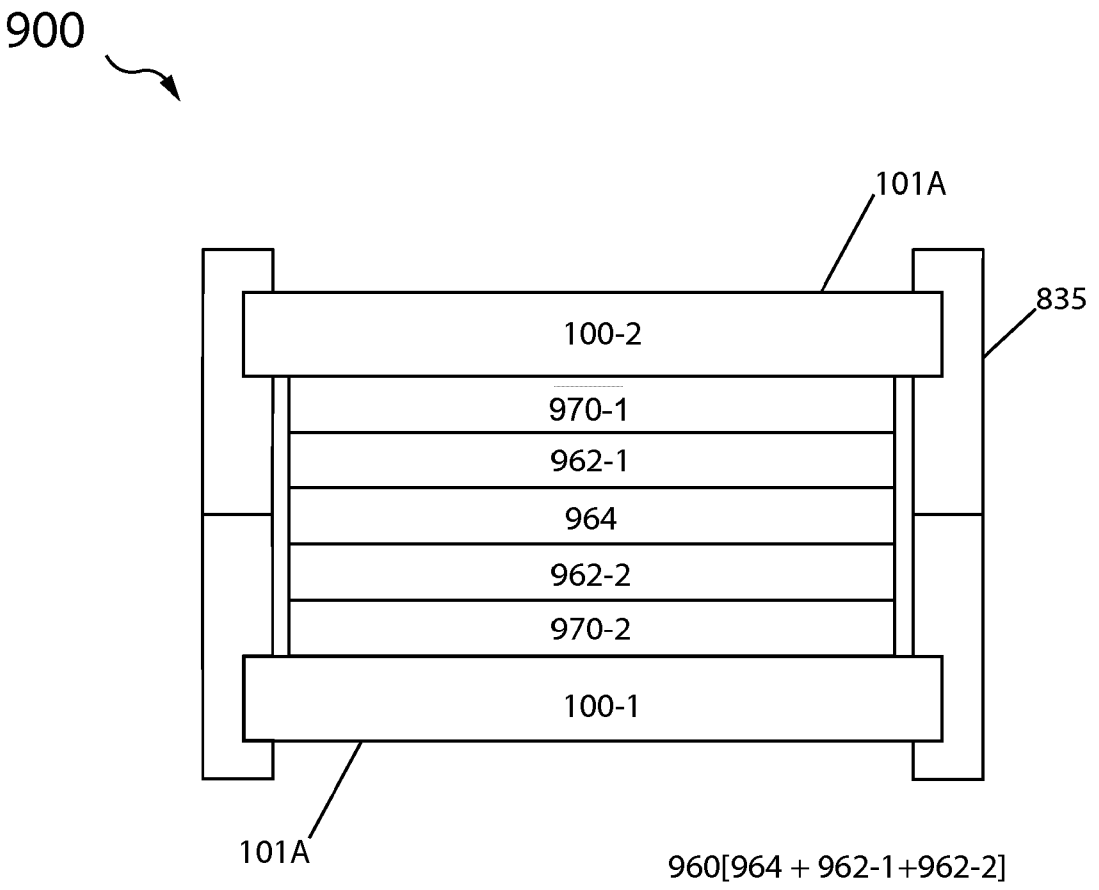

900
101A
835
100-2
970-1
962-1
964
962-2
970-2
100-1
101A
960[964 + 962-1+962-2]

Figure 9

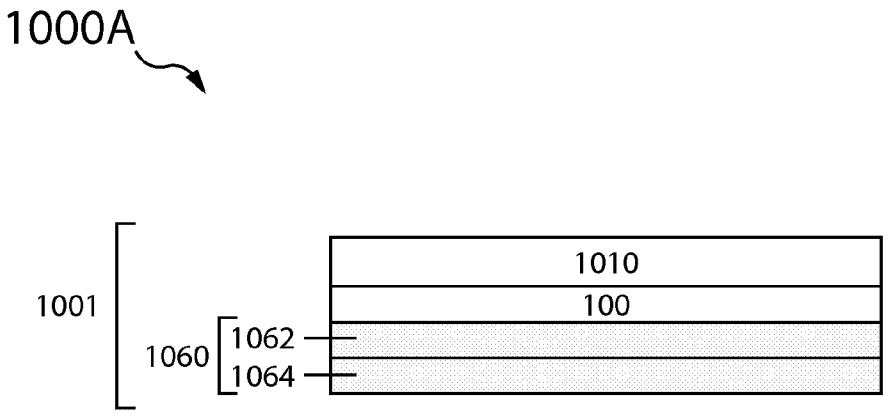


Figure 10A

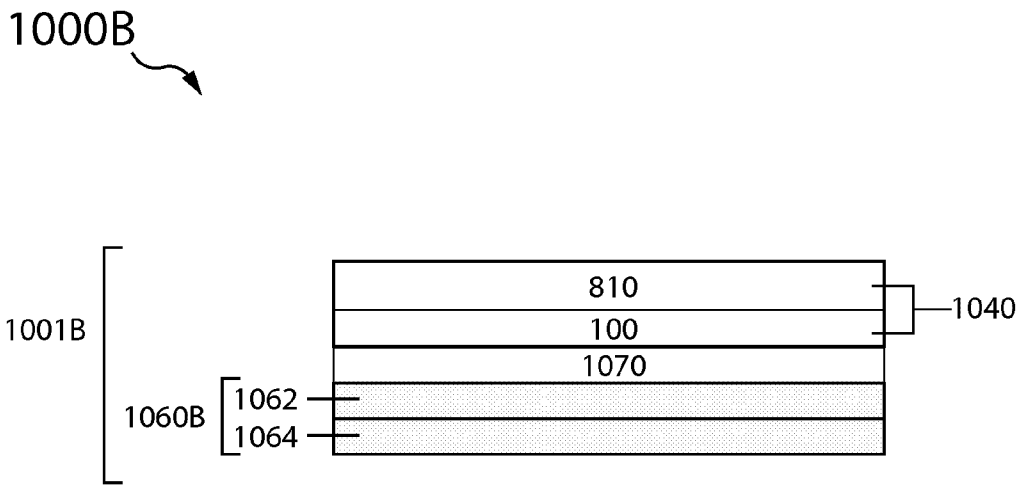


Figure 10B

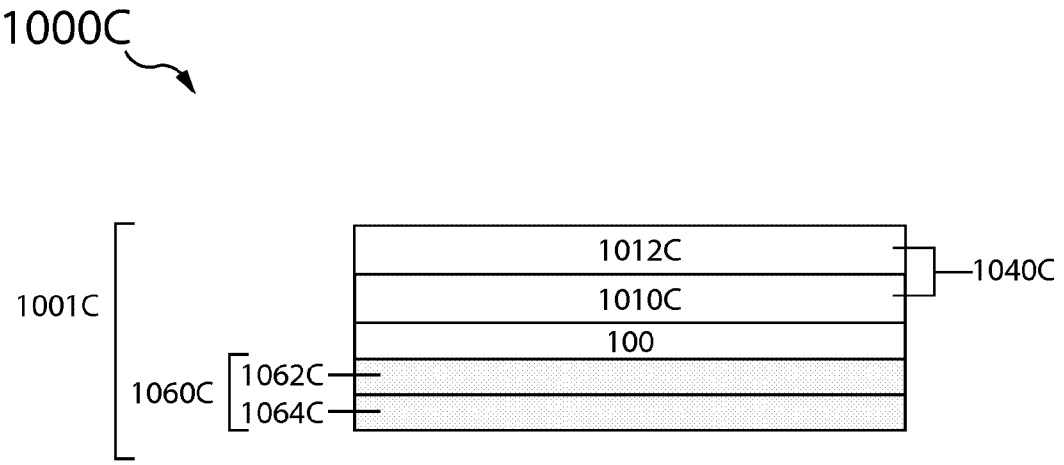
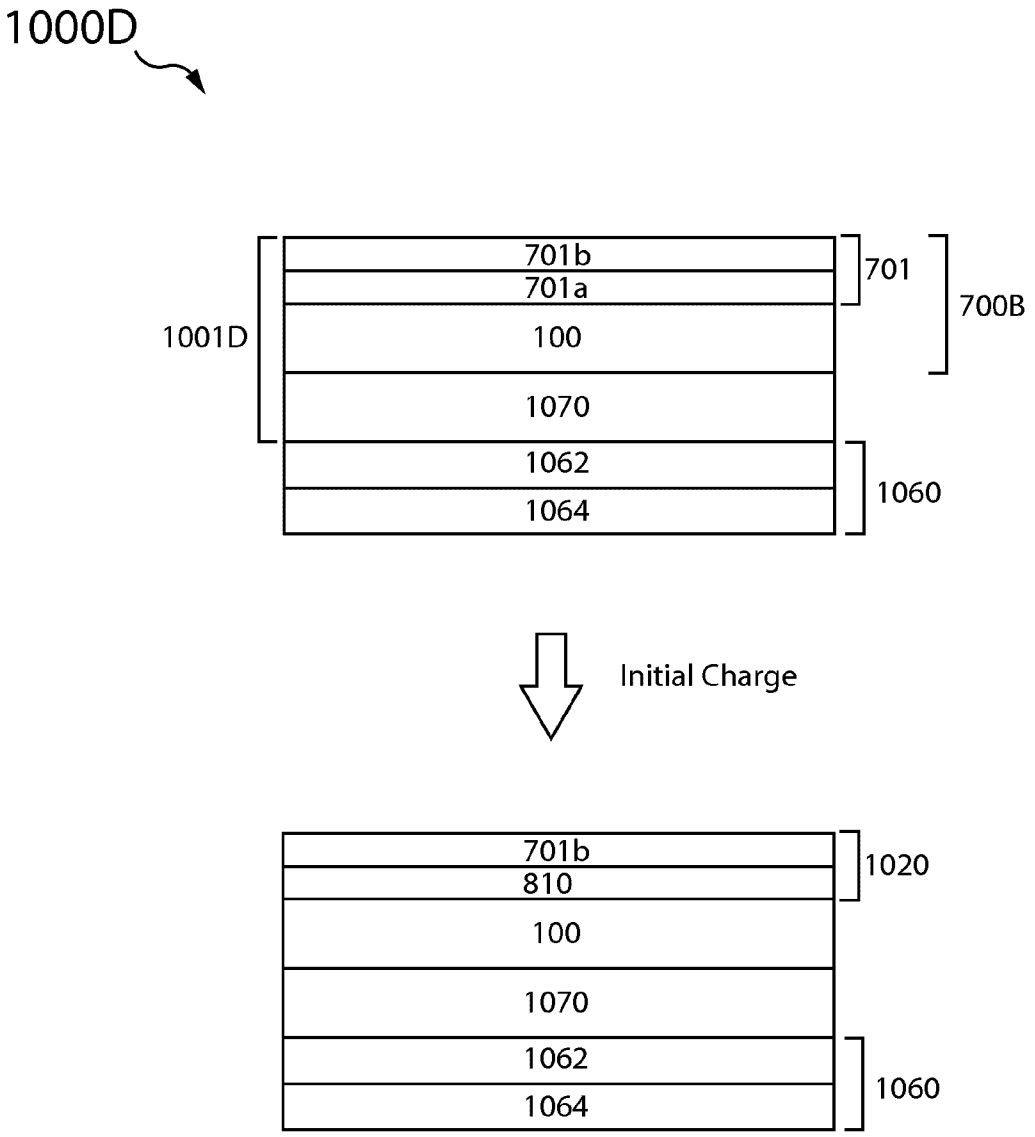


Figure 10C


1000D
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701a
100
1070
1062
1064
701
700B
1001D
1060
Initial Charge
701b
810
100
1070
1062
1064
1020
1060

Figure 10D

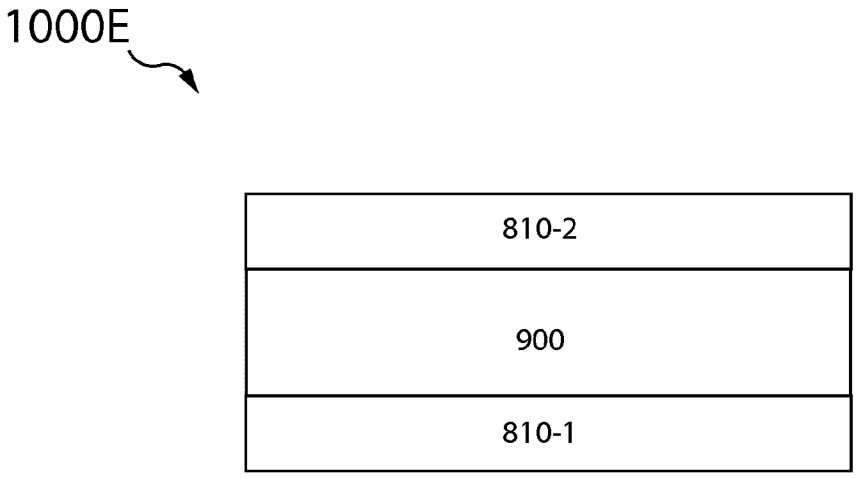
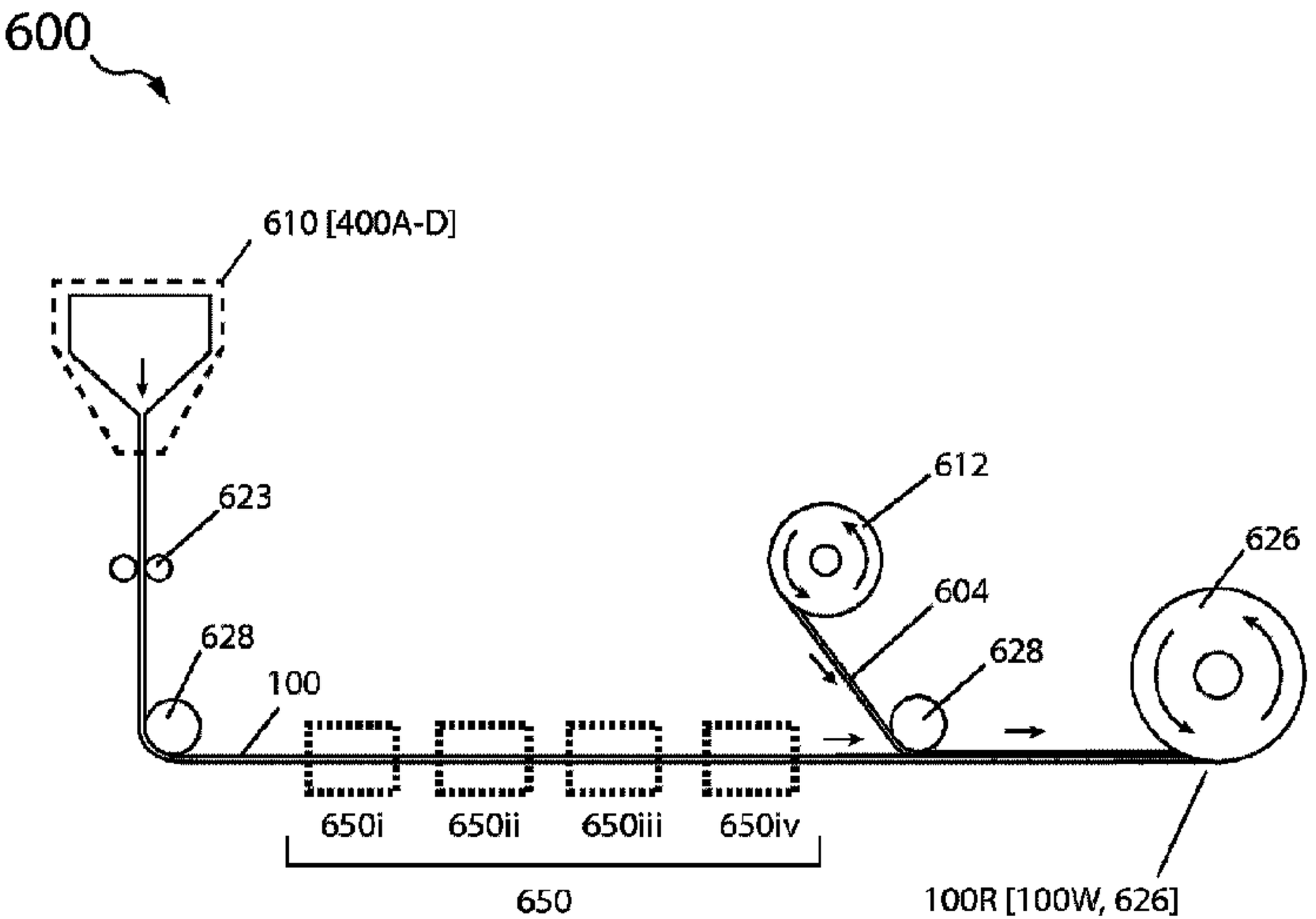


Figure 10E


600
610 [400A-D]
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628
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650iii
650iv
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100R [100W, 626]