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(54) Title: CURRENT COLLECTOR INDEPENDENT ALKALI-METAL ANODE STACK MANUFACTURING AND TRANSFER

(57) Abstract: A method and apparatus for forming a lithium metal anode device stack is provided. The lithium metal manufactured using a plastic-containing substrate with a release layer formed thereon. A solid electrolyte is deposited onto the release layer using non-vacuum coating technology. The remainder of the device stack is deposited in a vacuum chamber and lamination transferred onto a current collector to form an anode stack.

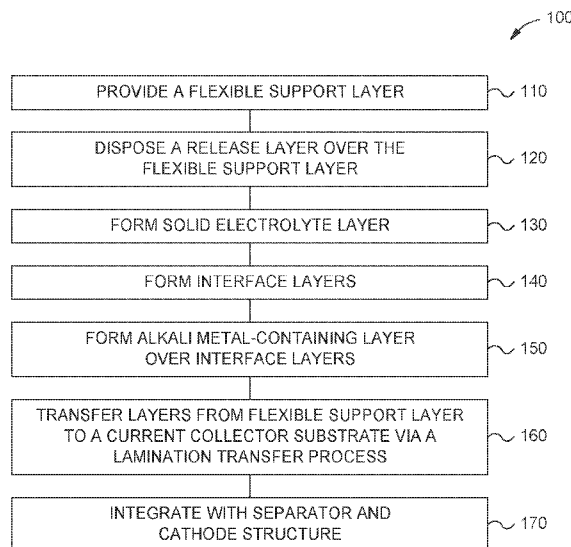


FIG. 1



## **CURRENT COLLECTOR INDEPENDENT ALKALI-METAL ANODE STACK MANUFACTURING AND TRANSFER**

### **TECHNICAL FIELD**

[0001] The disclosure generally relates to lithium metal containing devices and methods for manufacturing lithium metal containing devices. More particularly, the disclosure relates to lithium metal anode device stacks for energy storage devices and a methods for manufacturing the same.

### **BACKGROUND**

[0002] Rechargeable electrochemical storage systems are currently becoming increasingly essential for many fields of everyday life. High-capacity electrochemical energy storage devices, such as lithium-ion (Li-ion) batteries, are used in a growing number of applications, including portable electronics, medical, transportation, grid-connected large energy storage, renewable energy storage, and uninterruptible power supply (UPS). Traditional lead/sulfuric acid batteries often lack the capacitance and are often inadequately cyclable for these growing applications. Lithium-ion batteries, however, are thought to have the best chance.

[0003] Lithium is an alkali metal. Like the heavy element homologs of the first main group, lithium is characterized by a strong reactivity with a variety of substances. Lithium reacts violently with water, alcohols and other substances that contain protic hydrogen, often resulting in ignition. Lithium is unstable in air and reacts with oxygen, nitrogen and carbon dioxide. Lithium is normally handled under an inert gas atmosphere (noble gases such as argon) and the strong reactivity of lithium entails that other processing operations also be performed in an inert gas atmosphere. As a result, lithium provides several challenges when it comes to processing, storage, and transportation.

[0004] Protective surface treatments have been developed for lithium metal. One method of protective surface treatment of lithium metal consists of coating the lithium

metal with a wax layer, for example, polyethylene wax. However, a large amount of coating agent is generally applied which interferes with subsequent processing of the lithium metal layer.

[0005] Therefore, there is a need for methods and systems for the deposition and processing of lithium metals used in energy storage devices.

## SUMMARY

[0006] The disclosure generally relates to lithium metal containing devices and methods for manufacturing lithium metal containing devices. More particularly, the disclosure relates to lithium metal anode device stacks for energy storage devices and a methods for manufacturing the same.

[0007] In one aspect, a method of making an energy storage device is provided. The method includes forming an electrolyte containing layer over a release layer disposed over a flexible support layer. The method further includes forming one or more interface layers over the solid electrolyte containing layer. The method further includes evaporating an alkali metal onto the one or more interface layers. The method further includes transferring the release layer, the electrolyte containing layer, the one or more interface layers, and the alkali metal to a substrate to form an anode film stack.

[0008] Implementations may include one or more of the following. The flexible support layer comprises a material selected from the group consisting of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), metallized plastic, paper, or a combination thereof. The solid electrolyte containing layer is deposited over the release layer using non-vacuum coating. The one or more interface layers and the alkali metal are deposited in a vacuum environment. The method further includes transferring the flexible support layer, the release layer, and the solid electrolyte containing layer into a vacuum environment prior to forming the one or more interface layers. The one or more interface layers comprises an interface dielectric material. The interface dielectric material is selected from  $\text{AlOx}$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates  $\text{RENiO}_3$ , or a combination thereof. RE can be a trivalent rare-earth. RE can be lanthanide. RE

can be selected from La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu, or a combination thereof. The one or more interface layers further comprises a plating and stripping enhancement layer. The plating and stripping enhancement layers may be selected from alloys of metals or chalcogenides. The plating and stripping enhancement layers comprise Ag, Bi, Sn, Si, Ga, In, alloys of Ag, Bi, Sn, Si, chalcogenides of Ag, Bi, Sn, Si, Ga, In, or a combination thereof. The electrolyte containing layer is formed in a first processing chamber and the one or more interface layers and the alkali metal are formed in a second processing chamber. The alkali metal is lithium. Transferring the release layer, the electrolyte containing layer, the one or more interface layers, and the alkali metal to a substrate to form an anode film stack comprises a lamination process.

[0009] In yet another aspect, an alkali metal-containing film stack for energy storage device is provided. The alkali metal-containing film stack includes a flexible support layer, a release layer disposed over the flexible support layer capable of separating from the flexible support layer, an electrolyte containing layer formed over the release layer, one or more interface layers over the solid electrolyte containing layer, and an alkali metal-containing layer formed over the one or more interface layers.

[0010] Implementations can include one or more of the following. The flexible support layer includes a material selected from polyethylene terephthalate (PET), paper, and a combination thereof. The one or more interface layers include an interface dielectric material is selected from  $\text{AlOx}$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates  $\text{RENiO}_3$ , or a combination thereof. The one or more interface layers further include a plating and stripping enhancement layer. The plating and stripping enhancement layers are selected from alloys of metals or chalcogenides. The plating and stripping enhancement layers include Ag, Bi, Sn, Si, alloys of Ag, Bi, Sn, Si, chalcogenides of Ag, Bi, Sn, Si, or combination thereof.

[0011] In yet another aspect, a lamination transfer system is provided. The lamination transfer system includes a lamination transfer chamber and a system controller. The system is configured to cause the lamination transfer chamber to

perform a process. The process includes conveying a film stack from a supply hub toward a pickup hub, contacting the film stack with a current collector, laminating the film stack to the current collector, and removing a support layer from the film stack, wherein the film stack comprises the flexible support layer, a release layer disposed over the flexible support layer capable of separating from the flexible support layer, an electrolyte containing layer formed over the release layer, one or more interface layers over the solid electrolyte containing layer, and an alkali metal-containing layer formed over the one or more interface layers.

[0012] Implementations can include one or more of the following. The flexible support layer includes a material selected from polyethylene terephthalate (PET), paper, and a combination thereof. The one or more interface layers include an interface dielectric material is selected from  $\text{AlOx}$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates  $\text{RENiO}_3$ , or a combination thereof. The one or more interface layers further include a plating and stripping enhancement layer. The plating and stripping enhancement layers are selected from alloys of metals or chalcogenides. The plating and stripping enhancement layers include Ag, Bi, Sn, Si, alloys of Ag, Bi, Sn, Si, chalcogenides of Ag, Bi, Sn, Si, or combination thereof.

[0013] In yet another aspect, a non-transitory computer readable medium has stored thereon instructions, which, when executed by a processor, causes the process to perform operations of the above apparatus and/or method.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0014] So that the manner in which the above-recited features of the present disclosure can be understood in detail, a more particular description of the aspects, briefly summarized above, may be had by reference to implementations, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical implementations of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective implementations.

[0015] FIG. 1 illustrates a flowchart showing selected operations of a method of forming an energy storage device in accordance with one or more implementations of the present disclosure.

[0016] FIGS. 2A-2G illustrates views of various stages of manufacturing an energy storage device according to the method of FIG. 1 in accordance with one or more implementations of the present disclosure.

[0017] FIG. 3 illustrates a flowchart showing selected operations of another method of forming an energy storage device in accordance with one or more implementations of the present disclosure.

[0018] FIGS. 4A-4E illustrate views of various stages of manufacturing an energy storage device according to the method of FIG. 3 in accordance with one or more implementations of the present disclosure.

[0019] FIG. 5 illustrates a flowchart showing selected operations of yet another method of forming an energy storage device in accordance with one or more implementations of the present disclosure.

[0020] FIGS. 6A-6E illustrate views of various stages of manufacturing an energy storage device according to the method of FIG. 5 in accordance with one or more implementations of the present disclosure.

[0021] FIG. 7 illustrates a flowchart showing selected operations of yet another method of forming an energy storage device in accordance with one or more implementations of the present disclosure.

[0022] FIGS. 8A-8E illustrate views of various stages of manufacturing an energy storage device according to the method of FIG. 7 in accordance with one or more implementations of the present disclosure.

[0023] FIG. 9 illustrates a schematic view of a flexible substrate coating apparatus in accordance with one or more implementations of the present disclosure.

[0024] FIG. 10 illustrates a schematic view of a lamination transfer apparatus in accordance with one or more implementations of the present disclosure.

[0025] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one implementation may be beneficially incorporated in other implementations without further recitation.

## DETAILED DESCRIPTION

[0026] The disclosure generally relates to lithium metal containing devices and methods for manufacturing lithium metal containing devices. More particularly, the disclosure relates to lithium metal anode device stacks for energy storage devices and a methods for manufacturing the same.

[0027] Substrate independent direct transfer (SIDT) is a method for forming anode device stacks by transferring one or more layers including an alkali metal layer, for example, a lithium containing layer, to a current collector in implementations where lithium metal functions as an anode or for pre-lithiating an anode material which is already formed on the current collector. The already formed anode material can include or be, but is not limited to, graphite, silicon, silicon graphite, silicon oxide graphite, silicon, metalized plastic, and copper. In SIDT processes, lithium is formed over a support layer composed of one or more materials such as polyethylene terephthalate (PET), paper, or combinations thereof. The materials on the flexible support layer are directly transferred to either a current collector or an anode, if already present, for pre-lithiation. A release layer formed between the alkali metal layer and the flexible substrate enables transferring lithium and other materials off of the support layer and onto the current collector or anode if already present.

[0028] In one or more implementations, which can be combined with other implementations, a lithium metal anode device stack is manufactured using a plastic-containing substrate with a release layer formed thereon. A solid electrolyte is deposited onto the release layer using non-vacuum coating technology. The remainder of the device stack is deposited in a vacuum chamber and lamination transferred onto a current collector to form an anode film stack.

[0029] Lithium metal anodes may be manufactured by laminating extruded/rolled lithium onto a current collector, for example, a copper current collector. Lithium is a

very reactive element and quality control is challenging. Moreover, lithium is not stable with most electrolyte systems and also melts at low temperatures. Advanced thin film interface layers are needed and existing vacuum roll-to-roll technology could be used to build an anode film stack by combining non-vacuum and vacuum processes where lithium or alloys are deposited on a first substrate and then laminated onto a current collector.

[0030] In order to improve lithium metal/alloy anode performance, anode film stacks need improved interface control. Current lithium anode manufacturing does not utilize vacuum roll-to-roll manufacturing. In one or more implementations, which can be combined with other implementations, an anode device stack is built on a carrier substrate, which is independent of the anode device stack. This anode device stack enables an anode with good edge quality, engineered control, and also provides an engineering opportunity for development of high quality pristine interface layers without breaking vacuum.

[0031] One or more implementations of the present disclosure provide for improved interface control using vacuum deposition without breaking vacuum. Roll-to-roll manufacturing of interface layers provides a high volume manufacturing solution, which includes substrate independent deposition and transfer (SIDT) of a lithium anode device stack. High quality lithium alloys can be deposited on a first substrate just before lamination transfer to preserve the highest quality materials in the device stack.

[0032] In one or more implementations, which can be combined with other implementations, a plastic containing substrate, for example, polyethylene terephthalate (PET) substrate with a release layer, for example, silicone or other deposited release layers, is provided. A solid electrolyte is deposited over the release layer using conventional non-vacuum coating, for example, slot-die coating. A roll of the plastic substrate with solid electrolyte is mounted into a vacuum deposition system. An alkali metal and optionally an alloy compatible interface layer can be deposited in vacuum environment. To decrease cell impedance, an enhanced lithium stripping and depositing behavior metal or alloy thin film is deposited. In some implementations, lithiophilic materials that promote lateral growth instead of island type of growth are

deposited for uniform plating/stripping behavior. Lithium metal or alloys thereof is then deposited. The process from the alkali metal deposition can be performed in a single chamber without breaking vacuum. The web may be slit as per electrode dimension requirements. The lithium or lithium alloy surface is then laminated with a current collector. A cathode structure and/or separator can be integrated with the formed anode device stack to form the energy storage device.

[0033] Implementations can include one or more of the following. The substrate includes PET material. The solid electrolyte layer includes a polymer electrolyte material. The interface layers include at least one of an interface dielectric material, plating and stripping enhancement layers, and lithiophilic layers. The interface layers are deposited under vacuum. The interface layers are deposited under vacuum in a roll-to-roll deposition system. The interface dielectric layer may be selected from  $\text{AlOx}$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates  $\text{RENiO}_3$ , or a combination thereof. RE can be a trivalent rare-earth. RE can be lanthanide. RE can be selected from La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu, or a combination thereof. The plating and stripping enhancement layers may be selected from metals, alloys of metals, or chalcogenides of the metals. The plating and stripping enhancement layers may be selected from Ag, Bi, Sn, Si, Ga, In, alloys of metals or chalcogenides of Ag, Bi, Sn, Si, Ga, In, or a combination thereof. Deposition of alkali metal or alloys thereof, for example, lithium metal or its alloys. The interface layers and the alkali metal layers or alloys thereof may be deposited without breaking vacuum. The anode device stack may be cut as per electrode dimension requirements followed by lamination transfer onto the current collector. The anode device stack is transferred from the substrate to a current collector via a substrate independent deposition and transfer (SIDT) process. The anode device stack is laminated onto the current collector. The current collector can include or be, but is not limited to copper, metallized plastic, paper, stainless steel, metal mesh, or a combination thereof. The anode device stack and anode current collector are integrated with a cathode structure and/or separator to form an energy storage device. The cathode structure may contain a cathode material and a cathode current collector. The cathode structure may be formed by a lithium-ion coating line.

[0034] It is noted that while the particular substrate on which some implementations described herein can be practiced is not limited, it is particularly beneficial to practice the implementations on flexible substrates, including for example, web-based substrates, panels and discrete sheets. The flexible substrate can also be in the form of a foil, a film, or a thin plate.

[0035] It is also noted here that a flexible substrate or web as used within the implementations described herein can typically be characterized in that it is bendable. The term “web” can be synonymously used to the term “strip,” the term “flexible substrate,” or the term “flexible conductive substrate.” For example, the web as described in implementations herein can be a polymer material.

[0036] FIG. 1 illustrates a flow chart of a method 100 for manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. FIGS. 2A-2G illustrate views of various stages of manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. Although FIGS. 2A-2G are described in relation to the method 100, it will be appreciated that the structures disclosed in FIGS. 2A-2G are not limited to the method 100, but instead may stand alone as structures independent of the method 100. Similarly, although the method 100 is described in relation to FIGS. 2A-2G, it will be appreciated that the method 100 is not limited to the structures disclosed in FIGS. 2A-2G but instead may stand alone independent of the structures disclosed in FIGS. 2A-2G. It should be understood that FIGS. 2A-2G illustrate only partial schematic views of the energy storage device structure 200, and the energy storage device structure 200 may contain any number of additional layer and/or additional materials common to energy storage devices, which are not shown for the sake of brevity. It should also be noted that although the method 100 illustrated in FIG. 1 is described sequentially, other process sequences that include one or more operations that have been omitted and/or added, and/or have been rearranged in another desirable order, fall within the scope of the implementations of the disclosure provided herein.

[0037] Referring to FIG. 2A, at operation 110 a flexible support layer 210 is provided. The flexible support layer 210 has a frontside 210f (also referred to as a front surface) and a backside 210b (also referred to as a back surface) opposite the

frontside 210f. The flexible support layer 210 may comprise any suitable material that is compatible with the targeted processing conditions. In some implementations, the flexible support layer 210 includes a plurality of sub-layers. In one or more implementations, which can be combined with other implementations, the flexible support layer 210 can be or include, one or more layers selected from plastic, polymer materials, metallized plastic, metals, paper, multilayers thereof, or a combination thereof. Example of suitable polymer materials include polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), poly(methyl methacrylate) (PMMA), cellulose tri-acetate (TAC), polypropylene (PP), polyethylene (PE), polycarbonates (PC), multilayers thereof, or a combination thereof.

[0038] In one or more implementations, which can be combined with other implementations, the flexible support layer 210 has a thickness in a range from about 1 micron to about 100 microns, or in a range from about 1 micron to about 100 microns, or in a range from about 10 microns to about 50 microns, or in a range from about 25 microns to about 50 microns.

[0039] Referring to FIG. 2B, at operation 120 a release layer 220 is formed on the frontside 210f of the flexible support layer 210. In one or more implementations, which may be combined with other implementations, the release layer 220 and the flexible support layer 210 are pre-fabricated. The release layer 220 has a frontside 220f (also referred to as a front surface) and a backside 220b (also referred to as a back surface) opposite the frontside 220f. In one or more implementations, the release layer 220 is deposited on the frontside 210f of the flexible support layer 210 such that the backside 220b of the release layer 220 contacts the frontside 210f of the flexible support layer 210. Any suitable process may be used to form the release layer 220 on the frontside of the flexible support layer 210. The release layer 220 may be deposited using non-vacuum coating techniques, for example, coating techniques performed in atmosphere.

[0040] The release layer 220 may be or include any material suitable for releasing the anode device stack during the SIDT process. The release layer 220 may be or include polymer release layers (for example, plastics, silicone, polymethylacrylate (PMA), polyethylene terephthalate (PET), fluorocarbons, polyvinylidene fluoride

(PVDF), polytetrafluoroethylene (PTFE), etc.), poly(olefin sulfones), organic materials, inorganic materials, among other materials. In some implementations, which can be combined with other implementations, the release layer 220 includes one or more nanosheets, such as one or more two-dimensional (2D) materials. In one or more implementations, which can be combined with other implementations, the release layer has a thickness of about 1 nm to about 500 nm, such as about 10 nm to about 300 nm, such as about 50 to about 200 nm. In some implementations, the release layer includes a plurality of sub-layers, each layer having a thickness of about 5 nm or less.

[0041] Organic or polymer based release layers can be deposited using wet-chemistry coating processes, for example, slot die coating techniques, comma bar coating techniques, or gravure coating techniques, or vacuum deposition techniques as described.

[0042] The release layer 220 may be or include inorganic materials, for example, BN, AlO<sub>x</sub>, AlOOH, Al, or a combination thereof. In particular implementations, the release layer 220 includes a multi-layer structure, for example, a multilayer structure of Al/AlO<sub>x</sub>/AlOOH. Inorganic based release layers can be deposited using vapor deposition techniques, for example, PVD techniques such as sputter deposition and electron beam deposition techniques.

[0043] In one or more implementations, the polymer material of the release layer 220 is selected so that the SIDT stack can be debonded from flexible support layer 210 by photo-initiated lift-off wherein the polymer material interacts with photons entering from the flexible support layer 210.

[0044] In one or more implementations, the release layer 220 can be or include a polymer material that is capable of photoinduced depolymerization. In one or more implementations, the polymer material can be or include a poly(olefin sulfone) material capable of photoinduced depolymerization. The poly(olefin sulfone) may be combined with photobase generators (PBGs). The poly(olefin sulfone) can be doped with a photosensitizer, for example, pyridine N-oxide. The depolymerization process can be induced by, for example, X-rays, electron-beam irradiation, or low-energy irradiation.

Suitable poly(olefin sulfone) materials include poly(1-butene sulfone) (PBS), poly(1-pentane sulfone) (PPS), poly(1-hexane sulfone) (PHS), poly(1-octene sulfone) (POS), poly(cyclopentene sulfone), poly(2-methyl-1-butene sulfone) (PMBS), poly(2-methyl-1-pentene sulfone) (PMPS), poly(2-methyl 1-hexene sulfone) (PMHS), poly(2-methyl-1-nonene sulfone) (PMNS), poly(cyclohexene sulfone), or a combination thereof.

[0045] As used herein, a “2D material,” is an atomically thin crystalline solid having a single or few layered structure. In some implementations, the 2D materials herein have intra-layer covalent bonding and interlayer van der Waals bonding. In some implementations, the 2D material can have a property selected from the group consisting of high carrier mobility, superconductivity, mechanical flexibility, high thermal conductivity, high optic and UV adsorption, a peel strength on silicone of about 3 to about 100 gram-force/in, weak interlayer bonding, and combinations thereof. The peel strength can be measured using TESA 7475 test tape having a width of 25 mm, and using a peeling angle of 180° and a peeling speed of 300 mm/min (3M method). Without being bound by theory, it is believed that selecting a 2D material having weak interlayer bonding enables ease of subsequently peeling the release layer from the support layer. In some implementations, each of the layers of the SIDT stack 100 can have a melting temperature that is higher than a melting temperature of the alkali metal-containing layer.

[0046] In some implementations, each layer can have melting points that are equal and/or decrease with each added layer such that the flexible support layer 210 has the highest melting point, the release layer 220 has a melting point lower than the support layer and the alkali metal-containing layer has the lowest melting point. In some implementations, the two-dimensional material includes one or more of titanium disulfide (TiS<sub>2</sub>), tungsten disulfide (WS<sub>2</sub>), molybdenum disulfide (MoS<sub>2</sub>), boron nitride (BN), aluminum hydroxide oxide (AlHO<sub>2</sub>), MoO<sub>3</sub>, graphene, carbon nitride, layered double hydroxide, derivatives thereof, and combinations thereof. In some implementations, the 2D material includes a metal nitride, a metal sulfide, a metal hydroxide oxide, a carbon-containing material, derivatives thereof, or combinations thereof.

[0047] Referring to FIG. 2C, optionally at operation 130, a solid electrolyte interface (SEI) layer 230 is formed over the release layer 220. The solid electrolyte interface layer 230 has a frontside 230f (also referred to as a front surface) and a backside 230b (also referred to as a back surface) opposite the frontside 230f. In one or more implementations, the solid electrolyte interface layer 230 is deposited on the frontside 220f of the release layer 220 such that the backside 230b of the solid electrolyte interface layer 230 contacts the frontside 220f of the release layer 220. Any suitable process may be used to form the solid electrolyte interface layer 230 on the frontside 220f of the release layer 220. The solid electrolyte interface layer 230 may be deposited using non-vacuum coating techniques.

[0048] The solid electrolyte interface layer 230 may comprise any suitable material that is compatible with the targeted ion conducting. In some implementations, the solid electrolyte interface layer 230 can include or be a metal salt, such as lithium salt. The lithium salt can be one or more of  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_3)_3$ ,  $\text{LiBF}_6$ ,  $\text{LiClO}_4$ BETTE electrolyte, or combinations thereof. The electrolyte can be in a gel or polymer matrix medium.

[0049] In one or more implementations, the solid electrolyte interface layer 230 can be or include materials selected from fluorocarbons (PTFE, PVDF),  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{MgO}$ ,  $\text{AlO}_x$ ,  $\text{AlHO}_2$ ,  $\text{RENiO}_3$  (RE=rare earth),  $\text{BN}$ ,  $\text{BaTiO}_3$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , silicon doped lithium tantalum phosphates, for example,  $\text{Li}_{(1+x)}\text{Ta}_2\text{P}_{(1-x)}\text{Si}_x\text{O}_8$ ,  $\text{Li}_{1.5}\text{Ta}_2\text{P}_{0.5}\text{Si}_{0.5}\text{O}_8$ , lithium tantalum phosphates, for example,  $\text{LiTa}_2\text{PO}_8$  (LTPO),  $\text{Li}_2\text{Ta}_2\text{SiO}_8$  (LTSO),  $\text{Li}_{0.34}\text{La}_{0.56}\text{TiO}_3$ , lithium aluminum titanium phosphates, for example,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LATP), lithium aluminum germanium phosphates, for example,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ge}_{1.7}(\text{PO}_4)_3$  (LAGP), garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO), or a combination thereof.

[0050] In one or more implementations, the solid electrolyte interface layer 230 may be formed using non-vacuum coating techniques. Suitable coating techniques include, but are not limited to, a slot-die coating process, a doctor-blade coating process, a three-dimensional (3D) printing process, or a combination thereof. In one or more alternative implementations, the solid electrolyte interface layer 230 may be formed using vacuum coating techniques.

[0051] After operation 130 and prior to operation 140, the partially formed device structure 200 may be transferred into a vacuum coating system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9.

[0052] Referring to FIG. 2D, optionally at operation 140, one or more interface layers 240 are formed over the solid electrolyte interface layer 230. The interface layers 240 are disposed between the release layer 220 and the alkali metal-containing layer 250. The interface layers 240 can include or be at least one of an interface dielectric material, a plating and stripping enhancement layer, and a lithiophilic layer. The interface layers 240 may be deposited under vacuum. The interface layers 240 may be deposited under vacuum in a roll-to-roll deposition system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9. The interface dielectric layer may be selected from  $\text{AlOx}$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates ( $\text{RENiO}_3$ ), or a combination thereof. RE can be a trivalent rare-earth. RE can be lanthanide. RE can be selected from La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu, or a combination thereof. RE can be selected from Sm, Nd, and Eu. The RE nickelates can be doped with ions. Suitable ions for doping include lithium ions, sodium ions, magnesium ions, potassium ions, hydrogen ions, and aluminum ions. In one example, the RE nickelate is  $\text{SmNiO}_3$  doped with lithium ions. The plating and stripping enhancement layers may be or include alloys of metals or chalcogenides. The plating and stripping enhancement layers may be or include Ag, Bi, Sn, Si, Cu, alloys of metals or chalcogenides of Ag, Bi, Sn, Si, Cu, or a combination thereof. The lithiophilic layer may be or include at least one of: a metal including Al, Au, Ag, Bi, Pt, Zn, Si, Sn, Mg, In, Ga, or Cu, alloys thereof, or a metal oxide including  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{RENiO}_3$ ,  $\text{AlOx}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{CoO}$ , or  $\text{MnO}$ . The interface layers 240 may be deposited by vapor deposition techniques, for example, chemical vapor deposition (CVD), atomic layer deposition (ALD), physical vapor deposition (PVD), such as thermal evaporation or sputtering.

[0053] In one or more implementations, which can be combined with other implementations, the one or more interface layers 240 include a dielectric layer. The dielectric layer can be lithium fluoride, aluminum oxide, aluminum hydroxide oxide, boron nitride, carbon nitride, titanium oxide, lithium titanium oxide, zirconium oxide,

tantalum oxide, barium titanate, lithium zirconium oxide, molybdenum oxide, silicon oxide, lithium silicon oxide, or a combination thereof.

[0054] In one or more implementations, which can be combined with other implementations, the one or more interface layers 240 include a plating and stripping enhancement layer(s). The plating and stripping enhancement layer(s) can include a metallic layer. The metallic layer can be or include silver, bismuth, tin, copper, aluminum, silicon, or a combination thereof. The plating and stripping enhancement layer(s) can include a metallic layer. The metallic layer can be or include silver, bismuth, tin, copper, aluminum, silicon, indium, gallium, or a combination thereof. The plating and stripping enhancement layers may be selected from Ag, Bi, Sn, Si, Cu, Al, alloys of metals or chalcogenides of Ag, Bi, Sn, Si, or a combination thereof.

[0055] In one or more implementations, which can be combined with other implementations, the one or more interface layers 240 include a lithiophilic layer. The one lithiophilic layer may enable lateral growth of the subsequently deposited alkali metal-containing layer 250. The lithiophilic layer may be or include a metal or a metal oxide. The lithiophilic layer may be or include at least one of: a metal including Al, Au, Ag, Bi, Pt, Zn, Si, Sn, Mg, In, Ga, or Cu, alloys thereof, or a metal oxide including  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{RENiO}_3$ ,  $\text{AlO}_x$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{CoO}$ , or  $\text{MnO}$ . The lithiophilic layer may be deposited by at least one process selected from the group of immersing, spin coating, dip coating, spray coating, doctor blade coating, solution casting, drop coating, PVD, and CVD.

[0056] Referring to FIG. 2E, at operation 150, an alkali metal-containing layer 250 is formed over the frontside 220f of the release layer 220. The alkali metal-containing layer 250 includes a frontside 250f (also referred to as a front surface) and a backside 250b (also referred to as a back surface) opposite the frontside 250f. In some implementations, where any of the solid electrolyte interface layer 230 and the one or more interface layers 240 are present, the alkali metal-containing layer 250 may be formed directly on the underlying layers, for example, any of the solid electrolyte interface layer 230 and the one or more interface layers 240. In some implementations, where the solid electrolyte interface layer 230 and the one or more interface layers 240 are not present, the alkali metal-containing layer 250 is formed

directly on the frontside 220f of the release layer 220. The alkali metal-containing layer 250 may be or include lithium. The alkali metal-containing layer 250 may be deposited under vacuum. The alkali metal-containing layer 250 may be deposited under vacuum in a roll-to-roll deposition system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9. The alkali metal-containing layer 250 may be deposited via a physical vapor deposition process, for example, an evaporation process or a sputtering process. The evaporation process may be an electron beam evaporation process or a thermal evaporation process.

[0057] Referring to FIG. 2E, the SEI layer 230, the one or more interface layers 240, and the alkali metal-containing layer 250 form a SIDT film stack 255. Although the SIDT film stack 255 is shown as including the release layer 220, the SIDT film stack 255 may or may not contain the release layer 220.

[0058] The SIDT film stacks described herein are formed such that the alkali metal-containing layer 250, e.g., the lithium layer, is deposited last on the SIDT film stack. Depositing the lithium layer last enables forming the film stack without damaging the lithium layer, which typically has a lower melting point relative to other materials that are formed in energy storage device. Conventional methods of forming energy storage devices include direct deposition of molten lithium onto the current collector in lithium metal anode formation or onto the anode material in pre-lithiation implementations. These methods further include maintaining the underlying substrate as the lithium layer is formed to prevent damage to the lithium. In contrast, the SIDT film stack 255 and methods described herein, enable forming the alkali metal-containing layer 250 last prior to transferring the SIDT film stack 255 to the current collector during operation 160.

[0059] In some implementations, which can be combined with other implementations, a passivation layer can optionally be included in the SIDT film stack 255. In some implementations, the passivation layer includes a carbonate of the alkali metal in the alkali metal-containing layer 250. In some implementations, which can be combined with other implementations, the alkali metal-containing layer 250 is a lithium layer and the passivation layer comprises lithium carbonate. The passivation layer can be formed by exposure of the alkali metal-containing layer 250 to carbon dioxide.

In some implementations, the alkali metal-containing layer 250 is exposed to carbon dioxide in the presence of heat. Without wishing to be bound by theory, it is believed that the carbon dioxide reacts with the alkali metal to form a thin layer of alkali metal carbonate on the exposed surface of the alkali metal-containing layer 250. In some implementations, the carbonated alkali metal passivation layer, for example, the lithium carbonate passivation layer, can have a thickness ranging from about 50 nm to about 100 nm. The carbonated alkali metal passivation layer can serve as a protective layer for the alkali metal-containing layer 250. For example, the carbonated alkali metal passivation layer can protect the alkali metal-containing layer 250 from oxidation and damage during storage and shipping.

[0060] After operation 150 and prior to operation 160, the device structure 200 including the SIDT film stack 255 may be transferred from a vacuum coating system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9 to a lamination transfer apparatus, for example, the lamination transfer system 1000 shown in FIG. 10. The lamination transfer process may include applying the flexible substrate 260 to the frontside 250f of the alkali metal-containing layer 250 and removing the flexible support layer 210 and optionally the release layer 220 from the SEI layer 230 to form the anode film stack 265.

[0061] Referring to FIG. 2F, at operation 160, the SIDT film stack 255 is transferred from the flexible support layer 210 to a flexible substrate 260 to form an anode film stack 265. Operation 160 may include lamination transfer onto a current collector to form an anode stack. In some implementations, where pre-lithiation is involved, an anode material may already be formed over the flexible substrate 260 and the alkali metal-containing layer 250 contacts the anode material formed over the flexible substrate 260. The flexible substrate 260 may be or include flexible film, such as a CPP film (i.e., a casting polypropylene film), an OPP film (i.e., an oriented polypropylene film), or a PET film (i.e., a polyethylene terephthalate film). Alternatively, the flexible substrate may be a pre-coated paper, a polypropylene (PP) film, a PEN film, a polylactic acid (PLA) film, or a PVC film. The flexible substrate 260 can be or include one or more current collectors, the current collector can include aluminum (Al), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co), manganese (Mn), chromium (Cr), stainless steel, clad materials, alloys thereof, and a combination

thereof. In particular implementations, the flexible substrate 260 can be or includes copper.

[0062] In one or more implementations, which can be combined with other implementations, during operation 160 the release layer 220 is transferred or partially transferred with the SIDT film stack as is shown in FIG. 2F. Alternatively, in other implementations, the release layer 220 remains or partially remains on the flexible support layer 210 after operation 160.

[0063] Referring to FIG. 2G, at operation 170 the anode film stack 265 may be combined with a separator 290, a cathode stack 285, or both the separator 290 and the cathode stack 285 to form the energy storage device structure 400. The separator 290 may include, a microporous polymeric separator including a polyolefin, by way of non-limiting example. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), which may be either linear or branched. If a heteropolymer is derived from two monomer constituents, the polyolefin may assume any copolymer chain arrangement, including those of a block copolymer or a random copolymer. Similarly, if the polyolefin is a heteropolymer derived from more than two monomer constituents, it may likewise be a block copolymer or a random copolymer. In certain implementations, the polyolefin may be polyethylene (PE), polypropylene (PP), or a blend of PE and PP, or multi-layered structured porous films of PE and/or PP. Commercially available polyolefin porous membranes include CELGARD® 2500 (a monolayer polypropylene separator) and CELGARD® 2320 (a tri-layer polypropylene/polyethylene/polypropylene separator) available from Celgard LLC.

[0064] In one or more implementations, which can be combined with other implementations the cathode stack 285 includes a cathode current collector 280 and cathode material 270. The cathode current collector 280 may be or include any of the flexible films described and aluminum (Al), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co), tin (Sn), silicon (Si), manganese (Mn), magnesium (Mg), alloys thereof, and combinations thereof. The cathode current collector 280 may be or include any of aluminum (Al), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co), tin (Sn), silicon (Si), manganese (Mn), magnesium (Mg), alloys thereof, and combinations thereof. In

particular implementations, the cathode current collector 280 may be or include aluminum.

[0065] The cathode material 270 may be or include any suitable cathode material. The cathode material 270 or cathode may be or include any material compatible with the anode and may include an intercalation compound, an insertion compound, or an electrochemically active polymer. Suitable intercalation materials include, for example, sulfur, lithium-containing metal oxides,  $\text{MoS}_2$ ,  $\text{FeS}_2$ ,  $\text{MnO}_2$ ,  $\text{TiS}_2$ ,  $\text{NbSe}_3$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{V}_6\text{O}_{13}$  and  $\text{V}_2\text{O}_5$ . Suitable polymers include, for example, polyacetylene, polypyrrole, polyaniline, and polythiophene. In some implementations the cathode material 270 includes a polymer binder material as described herein. The cathode material 270 or cathode may be or include a layered oxide, such as lithium cobalt oxide, an olivine, such as lithium iron phosphate, or a spinel, such as lithium manganese oxide. Examples of lithium-containing oxides may be layered, such as lithium cobalt oxide ( $\text{LiCoO}_2$ ), or mixed metal oxides, such as  $\text{LiNi}_x\text{Co}_{1-2x}\text{MnO}_2$ ,  $\text{LiNiMnCoO}_2$  ("NMC"),  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ,  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and doped lithium rich layered-layered materials, wherein x is zero or a non-zero number. Examples of phosphates may be or include iron olivine ( $\text{LiFePO}_4$ ) and its variants (such as  $\text{LiFe}_{(1-x)}\text{Mg}_x\text{PO}_4$ ),  $\text{LiMoPO}_4$ ,  $\text{LiCoPO}_4$ ,  $\text{LiNiPO}_4$ ,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ,  $\text{LiVOPO}_4$ ,  $\text{LiMP}_2\text{O}_7$ , or  $\text{LiFe}_{1.5}\text{P}_2\text{O}_7$ , wherein x is zero or a non-zero number. Examples of fluorophosphates may be or include  $\text{LiVPO}_4\text{F}$ ,  $\text{LiAlPO}_4\text{F}$ ,  $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ ,  $\text{Li}_5\text{Cr}(\text{PO}_4)_2\text{F}_2$ ,  $\text{Li}_2\text{CoPO}_4\text{F}$ , or  $\text{Li}_2\text{NiPO}_4\text{F}$ . Example of silicates may be or include  $\text{Li}_2\text{FeSiO}_4$ ,  $\text{Li}_2\text{MnSiO}_4$ , or  $\text{Li}_2\text{VOSiO}_4$ . Examples of non-lithium compounds may be or include  $\text{Na}_5\text{V}_2(\text{PO}_4)_2\text{F}_3$ .

[0066] FIG. 3 illustrates a flow chart of a method 300 for manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. FIGS. 4A-4E illustrate views of various stages of manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. Although FIGS. 4A-4E are described in relation to the method 300, it will be appreciated that the structures disclosed in FIGS. 4A-4E are not limited to the method 300, but instead may stand alone as structures independent of the method 300. Similarly, although the method 300 is described in relation to FIGS. 4A-4E, it will

be appreciated that the method 300 is not limited to the structures disclosed in FIGS. 4A-4E but instead may stand alone independent of the structures disclosed in FIGS. 4A-4E. It should be understood that FIGS. 4A-4E illustrate only partial schematic views of the energy storage device structure 400, and the energy storage device structure 400 may contain any number of additional layer and/or additional materials common to energy storage devices, which are not shown for the sake of brevity. It should also be noted that although the method 300 illustrated in FIG. 3 is described sequentially, other process sequences that include one or more operations that have been omitted and/or added, and/or have been rearranged in another desirable order, fall within the scope of the implementations of the disclosure provided herein.

[0067] At operation 310 a flexible support layer is provided. Referring to FIG. 4A, the flexible support layer may be the flexible support layer 210 as described. At operation 320, a release layer is formed on the frontside 210f of the flexible support layer 210. The release layer may be the release layer 220 as described. In one or more implementations, which may be combined with other implementations, the release layer 220 and the flexible support layer 210 are pre-fabricated.

[0068] At operation 330, one or more fluoropolymer containing layers are formed on or over the release layer 220. Referring to FIG. 4A, one or more fluoropolymer containing layers 430a-b (referred to collectively as 430) are formed on or over the release layer 220. Although a variety of fluoropolymers may be used, in certain implementations, the polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), perfluoroalkoxy alkane (PFA), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), perfluoroelastomer (FFPM), or combinations thereof. In one implementation, which can be combined with other implementations, the first fluoropolymer containing layer 430a is or includes PVDF and the second fluoropolymer containing layer 430b is or includes PTFE. In one or more implementations, the one or more fluoropolymer containing layers 430 further include photosensitive materials, which are activated during the pattern lift-off process.

[0069] Any suitable deposition process may be used to deposit the one or more fluoropolymer containing layers 430. The deposition process may be selected from

the group of physical vapor deposition (PVD), chemical vapor deposition (CVD), and wet chemistry polymerization. By way of non-limiting example, physical vapor deposition (PVD) processes may include thermal evaporation, sputtering, and the like. By way of non-limiting example, the chemical vapor deposition (CVD) may include low pressure chemical vapor deposition (LPCVD), thermal CVD, and the like. The wet-chemistry may include monomer to polymerization processes. After deposition, the one or more fluoropolymer containing layers 430 may be subjected to a secondary heat treatment, for example, exposed to 120 degrees Celsius for about 30 minutes in inert atmosphere.

[0070] In one or more implementations, which can be combined with other implementations, a temperature in a reaction chamber during the deposition process is less than or equal to about 180 degree Celsius. Pressure in the reaction chamber where the deposition process occurs may be from ambient down to high vacuum ( $10^{-6}$  torr). In one or more implementations, an atmosphere within the reaction chamber is inert, for example, an argon atmosphere.

[0071] Referring to FIG. 4B, at operation 340, an alkali metal-containing layer is formed over or on the one or more fluoropolymer containing layers 430. The alkali metal-containing layer may be the alkali metal-containing layer 250 as described. In some implementations, where any of the one or more fluoropolymer containing layers 430 are present, the alkali metal-containing layer 250 may be formed directly on the underlying layers, for example, any of the one or more fluoropolymer containing layers 430. In one implementation, the process conditions of the operation 340 are selected such that the alkali metal-containing layer 250 interacts with the underlying fluoropolymer layer to form an interface layer, for example, the interface layer 450 depicted in FIG. 4C.

[0072] At operation 350, optionally, the energy storage device structure 400 is exposed to a post-treatment process. The post-treatment process may be a thermal treatment process. Examples of thermal treatment processes include induction heating, infrared lamp heating, and laser treatment. Referring to FIG. 4C, the thermal treatment process forms the interface layer 450 from the lithium metal of the alkali metal-containing layer 250 and the underlying fluoropolymer layer, for example, the

second fluoropolymer containing layer 430b. The interface layer 450 may be a lithium fluoride (LiF) layer. The alkali metal-containing layer 250, the interface layer 450 (if present), and the one or more fluoropolymer containing layers 430 form a SIDT film stack 455. The SIDT film stack 455 may or may not contain the release layer 220 or a portion of the release layer 220.

[0073] In one or more implementations, the post-treatment process is a laser treatment process where the laser is directed through the PET/PTFE/Li stack to activate the interface of alkali metal-containing layer 250 and the second fluoropolymer containing layer 430b, for example, the Li-PTFE interface, from the PET side and enhance reaction with Li/PTFE to form the LiF layer. In addition, exposure to the laser can help induce Li transfer process (dense LiF formation from lower density polymer-Li interface creating a void volume). This void volume can make removal of the flexible support layer 210 easier during the lamination transfer process of operation 360.

[0074] Laser post treatment or UV post treatment can also be utilized for local interface debonding by selective heating, and this could be used for pattern transfer. Alkali metal/alloy film on plastic substrate with an interface layer sensitive to Laser or UV light is sandwiched onto a current collector (e.g., Cu, Ni, SS, metallized plastic etc.) and the layers stack is passed through rollers first for mechanical contact before selective area shining of laser or UV light to transfer alkali metal/alloy pattern onto the current collector. In addition, the current collector can also be patterned such that areas that do not need Alkali-metal/alloy are covered with ink printed pattern using, for example, Teflon with black carbon pigment. The ink pattern can be easily removed post SIDT with, for example, laser scribing.

[0075] Referring to FIG. 3, although operation 350 is shown as occurring prior to the transfer process of operation 360, in one or more implementations, operation 350 occurs after or during the lamination transfer process of operation 360.

[0076] After operation 350 and prior to operation 360, the device structure 400 including the SIDT film stack 455 may be transferred from a vacuum coating system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9 to a

lamination transfer apparatus, for example, the lamination transfer apparatus shown in FIG. 10.

[0077] In some implementations, which can be combined with other implementations, a passivation layer can optionally be included in the SIDT film stack 455 as described.

[0078] Referring to FIG. 4D, at operation 360, the SIDT film stack 455 is transferred from the flexible support layer 210 to a flexible substrate 260 to form an anode film stack 465. Operation 360 may include lamination transfer onto a current collector to form an anode stack. The lamination transfer process may be performed in a lamination transfer apparatus, for example, the lamination transfer system 1000 shown in FIG. 10. The lamination transfer process may include applying the flexible substrate 260 to the frontside 250f of the alkali metal-containing layer 250 and removing the flexible support layer 210 and optionally the release layer 220 from the one or more fluoropolymer containing layers 430 to form the anode film stack 465.

[0079] In one or more implementations, which can be combined with other implementations, the release layer 220 is transferred or partially transferred with the SIDT film stack 455. Alternatively, in other implementations, the release layer 220 remains or partially remains on the flexible support layer 210 after operation 160.

[0080] Referring to FIG. 4E, at operation 370 the anode film stack 465 may be combined with a separator 290, a cathode stack 285, or both a separator 290 and a cathode stack 285 to form the energy storage device structure 400.

[0081] FIG. 5 illustrates a flow chart of a method 500 for manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. FIGS. 6A-6E illustrate views of various stages of manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. Although FIGS. 6A-6E are described in relation to the method 500, it will be appreciated that the structures disclosed in FIGS. 6A-6E are not limited to the method 500, but instead may stand alone as structures independent of the method 500. Similarly, although the method 500 is described in relation to FIGS. 6A-6E, it will be appreciated that the method 500 is not limited to the structures disclosed in FIGS.

6A-6E but instead may stand alone independent of the structures disclosed in FIGS. 6A-6E. It should be understood that FIGS. 6A-6E illustrate only partial schematic views of the energy storage device structure 600, and the energy storage device structure 600 may contain any number of additional layers and/or additional materials common to energy storage devices, which are not shown for the sake of brevity. It should also be noted that although the method 500 illustrated in FIG. 5 is described sequentially, other process sequences that include one or more operations that have been omitted and/or added, and/or have been rearranged in another desirable order, fall within the scope of the implementations of the disclosure provided herein.

[0082] At operation 510 a flexible support layer is provided. Referring to FIG. 6A, the flexible support layer may be the flexible support layer 210 as described. At operation 520, a release layer is formed on the frontside 210f of the flexible support layer 210. The release layer may be the release layer 220 as described. In one or more implementations, which may be combined with other implementations, the release layer 220 and the flexible support layer 210 are pre-fabricated.

[0083] At operation 530, one or more fluoropolymer containing layers are formed on or over the release layer 220. Referring to FIG. 6A, one or more fluoropolymer containing layers 430 are formed on or over the release layer 220. In one implementation, which can be combined with other implementations, the one or more fluoropolymer containing layer 430 is or includes PVDF.

[0084] At operation 540, one or more interface layers 610 are formed over or on the one or more fluoropolymer containing layers 430. The one or more interface layers 610 are disposed between the one or more fluoropolymer containing layers 430 and the alkali metal-containing layer 250. The one or more interface layers 610 may be similar to the interface layers 240. The one or more interface layers 610 may include or be at least one of an interface dielectric material, a plating and stripping enhancement layer, and a lithiophilic layer as described. The one or more interface layers 610 may decrease impedance in the energy storage device structure 600. The one or more interface layers 610 may be deposited under vacuum. The one or more interface layers 610 may be deposited by vapor deposition methods, for example, chemical vapor deposition (CVD), atomic layer deposition (ALD), physical vapor

deposition (PVD), such as thermal evaporation or sputtering. The one or more interface layers 610 may be deposited under vacuum in a roll-to-roll deposition system, for example, the flexible substrate coating apparatus 900 shown in FIG. 9. In one implementation, which can be combined with other implementations, the one or more interface layers 610 include a first interface layer 610a and a second interface layer 610b as is shown in FIG. 6B. The first interface layer 610a may be or include an interface dielectric material. The first interface layer 610a may be or includes lithium fluoride. The lithium fluoride can be directly deposited on the underlying layer, for example, the one or more fluoropolymer containing layers 430. The lithium fluoride may be deposited via a physical vapor deposition process, for example, a sputtering process or an evaporation process. The sputtering process may include sputtering using a lithium fluoride (LiF) target. The evaporation process may include evaporating lithium fluoride (LiF) into gas phase

[0085] The second interface layer 610b may be or include a lithiophilic material. The lithiophilic material may enable lateral growth of the subsequently deposited alkali metal-containing layer 250. The lithiophilic material may be or include a metal or a metal oxide. The lithiophilic material may be at least one of: a metal including Al, Au, Ag, Bi, Pt, Zn, Si, Sn, Mg, or Cu, alloys thereof, or a metal oxide including CuO, ZnO, CoO, or MnO. The lithiophilic material may be deposited by at least one process selected from the group of immersing, spin coating, dip coating, spray coating, doctor blade coating, solution casting, drop coating, vapor deposition processes such as ALD, PVD, and CVD.

[0086] Referring to FIG. 6C, at operation 550, an alkali metal-containing layer is formed over or on the one or more interface layers 610. The alkali metal-containing layer may be the alkali metal-containing layer 250 as described. In some implementations, where the second interface layer 610b is present, the alkali metal-containing layer 250 may be formed directly on the second interface layer 610b.

[0087] As shown in FIG. 6C, the one or more fluoropolymer containing layers 430, the interface layers 610a, 610b, and the alkali metal-containing layer 250 form a SIDT film stack 655. The SIDT film stack 655 may or may not include the release layer 220 or portions of the release layer 220 as described.

[0088] After operation 550 and prior to operation 560, the device structure 600 including the SIDT film stack 655 may be transferred into a lamination transfer system, for example, the lamination transfer system 1000 shown in FIG. 10. In some implementations, which can be combined with other implementations, a passivation layer can optionally be included in the SIDT film stack 655 as described.

[0089] Referring to FIG. 6D, at operation 560, the SIDT film stack 655 is transferred from the flexible support layer 210 to a flexible substrate 260 to form an anode film stack 665. Operation 560 may include lamination transfer onto a current collector to form an anode stack. The lamination transfer process may be performed in a lamination transfer apparatus, for example, the lamination transfer system 1000 shown in FIG. 10. The lamination transfer process may include applying the flexible substrate 260 to the frontside 250f of the alkali metal-containing layer 250 and removing the flexible support layer 210 and optionally the release layer 220 from the one or more fluoropolymer containing layers 430 to form the anode film stack 665.

[0090] In one or more implementations, which can be combined with other implementations, the release layer 220 is transferred or partially transferred with the SIDT film stack 655. Alternatively, in other implementations, the release layer 220 remains or partially remains on the flexible support layer 210 after operation 560.

[0091] Referring to FIG. 6E, at operation 570 the anode film stack 665 may be combined with a separator 290, a cathode stack 285, or both a separator 290 and a cathode stack 285 to form the energy storage device structure 600 as described.

[0092] FIG. 7 illustrates a flow chart of a method 700 for manufacturing an energy storage device in accordance with one or more implementations of the present disclosure. FIGS. 8A-8E illustrate views of various stages of manufacturing an energy storage device structure 800 in accordance with one or more implementations of the present disclosure. Although FIGS. 8A-8E are described in relation to the method 700, it will be appreciated that the structures disclosed in FIGS. 8A-8E are not limited to the method 700, but instead may stand alone as structures independent of the method 700. Similarly, although the method 700 is described in relation to FIGS. 8A-8E, it will be appreciated that the method 700 is not limited to the structures disclosed

in FIGS. 8A-8E but instead may stand alone independent of the structures disclosed in FIGS. 8A-8E. It should be understood that FIGS. 8A-8E illustrate only partial schematic views of the energy storage device structure 800, and the energy storage device structure 800 may contain any number of additional layers and/or additional materials common to energy storage devices, which are not shown for the sake of brevity. It should also be noted that although the method 700 illustrated in FIG. 7 is described sequentially, other process sequences that include one or more operations that have been omitted and/or added, and/or have been rearranged in another desirable order, fall within the scope of the implementations of the disclosure provided herein.

[0093] At operation 710 a flexible support layer is provided. Referring to FIG. 8A, the flexible support layer may be the flexible support layer 210 as described. At operation 720, a release layer is formed on the frontside 210f of the flexible support layer 210. The release layer may be the release layer 220 as described. In one or more implementations, which may be combined with other implementations, the release layer 220 and the flexible support layer 210 are pre-fabricated. Optionally, at operation 730, one or more fluoropolymer containing layers (not shown) are formed on or over the release layer 220. The one or more fluoropolymer layers may be or include the one or more fluoropolymer containing layers 430.

[0094] At operation 740, a carbon monofluoride (CF<sub>x</sub>) layer 830 is formed. Referring to FIG. 8A, the carbon monofluoride (CF<sub>x</sub>) layer 830 is formed on or over the release layer 220. The carbon monofluoride (CF<sub>x</sub>) layer may be formed on or over the one or more fluoropolymer layers (if present).

[0095] The carbon monofluoride layer (CF<sub>x</sub>) may serve to enhance the cycling stability of the formed cell. In one or more implementations, which can be combined with other implementations, the carbon monofluoride (CF<sub>x</sub>) layer 830 may decompose to carbon and LiF by reacting with lithium during the first discharge process according to the following reaction (CF<sub>x</sub> + xLi<sup>+</sup> + xe<sup>-</sup> = C + xLiF). Not to be bound by theory, but it is believed that the carbon and LiF formed after the first discharge process contribute to the stabilization of the lithium metal battery.

[0096] In another implementation, which can be combined with other implementations, at least a portion of the carbon monofluoride (CF<sub>x</sub>) layer 830 is converted to LiF via a post deposition treatment process prior to the first discharge process. For example, the post deposition treatment process may be a post-treatment process as described in operation 350.

[0097] The carbon monofluoride (CF<sub>x</sub>) layer 830 may be deposited by at least one deposition process selected from the group of immersing, spin coating, dip coating, spray coating, doctor blade coating, solution casting, drop coating, PVD, plasma-enhanced chemical vapor deposition (PECVD), and CVD.

[0098] In one or more implementations, which can be combined with other implementations, the carbon monofluoride (CF<sub>x</sub>) layer 830 is formed by a vapor deposition process. In one or more implementations, the vapor deposition process is a fluorocarbon plasma deposition process. The fluorocarbon plasma deposition process may be an atmospheric plasma deposition process. The fluorocarbon plasma deposition process can be performed at atmospheric conditions or near atmospheric conditions. The plasma can be generated using an RF frequency power. The frequency of the RF power source is typically about 13.56 MHz or about 27 MHz or about 54 MHz. The frequency of the RF power source is another variable in generating a very high energy density plasma source, without plasma arcing, at atmospheric pressure. The plasma can be formed in-situ or be a remote plasma. The plasma can be an inductively coupled plasma or a capacitively coupled plasma. One skilled in the art may select a different frequency depending on the particular processing apparatus used and the plasma source gas used, in view of the present disclosure.

[0099] The plasma deposition process includes generating a fluorocarbon plasma. The fluorocarbon plasma can be generated from a fluorocarbon containing gas, for example, one or more perfluorocarbon containing gases (C<sub>x</sub>F<sub>y</sub>). Examples of suitable perfluorocarbon gases include carbon tetrafluoride (CF<sub>4</sub>), hexafluoroethane (C<sub>2</sub>F<sub>6</sub>), hexafluoropropylene (C<sub>3</sub>F<sub>6</sub>), perfluorocyclobutane (C<sub>4</sub>F<sub>8</sub>), perfluorocyclopentene (C<sub>5</sub>F<sub>8</sub>), or a combination thereof.

[00100] The plasma deposition process may further include introducing one or more inert gases, such as nitrogen, helium or argon. The plasma deposition process may further include introducing one or more reducing gases. The reducing gases can be selected from ammonia ( $\text{NH}_3$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), hydrogen ( $\text{H}_2$ ),  $\text{NF}_3$ , atomic hydrogen, radicals thereof, derivatives thereof, or a combination thereof. In one example, the one or more reducing gases includes hydrogen. In one or more implementations, which can be combined with other implementations, the carbon monofluoride ( $\text{CF}_x$ ) layer 830 is formed via a capacitively coupled fluorocarbon plasma generated by a 13.56 MHz RF power source. In one or more implementations, which can be combined with other implementations, the carbon monofluoride ( $\text{CF}_x$ ) layer 830 is formed via an atmospheric RF plasma using  $\text{CF}_4$ ,  $\text{H}_2$ , and He.

[00101] Referring to FIG. 8B, at operation 740, optionally one or more interface layers 610 are formed over or on the carbon monofluoride ( $\text{CF}_x$ ) layer 830. The one or more interface layers 610 may include a first interface layer 610a and a second interface layer 610b as described.

[00102] Referring to FIG. 8C, at operation 750, an alkali metal-containing layer is formed over or on the interface layers 610. The alkali metal-containing layer may be the alkali metal-containing layer 250 as described. In some implementations, where the second interface layer 610b is present, the alkali metal-containing layer 250 may be formed directly on the second interface layer 610b. If the interface layers 610a, 610b are not present, the alkali metal-containing layer 250 may be formed directly on the carbon monofluoride ( $\text{CF}_x$ ) layer 830.

[00103] In one or more implementations, which may be combined with other implementations, optionally, the energy storage device structure 800 is exposed to a post-treatment process. The post-treatment process may be used to convert at least a portion of the carbon monofluoride ( $\text{CF}_x$ ) layer 830 to LiF. The post-treatment process may be a thermal treatment process. The thermal treatment process forms the lithium fluoride layer from the lithium metal of the alkali metal-containing layer 250 and the underlying carbon monofluoride ( $\text{CF}_x$ ) layer, for example, the carbon monofluoride ( $\text{CF}_x$ ) layer 830. The alkali metal-containing layer 250, the interface

layers 610a, 610b (if present), and the carbon monofluoride (CF<sub>x</sub>) layer 830 (or LiF layer) form a SIDT film stack 855.

[00104] After operation 760 and prior to operation 770, the device structure 800 including the SIDT film stack 855 may be transferred into a lamination transfer system, for example, the lamination transfer system 1000 shown in FIG. 10. In some implementations, which can be combined with other implementations, a passivation layer can optionally be included in the SIDT film stack 855 as described.

[00105] Referring to FIG. 8D, at operation 770, the SIDT film stack 855 is transferred from the flexible support layer 210 to a flexible substrate 260 to form an anode film stack 865. Operation 770 may include lamination transfer onto a current collector to form the anode film stack 865. The lamination transfer process may be performed in a lamination transfer apparatus, for example, the lamination transfer system 1000 shown in FIG. 10. The lamination transfer process may include applying the flexible substrate 260 to the frontside 250f of the alkali metal-containing layer 250 and removing the flexible support layer 210 and optionally the release layer 220 from the and the carbon monofluoride (CF<sub>x</sub>) layer 830 to form the anode film stack 865.

[00106] In one or more implementations, which can be combined with other implementations, the release layer 220 is transferred or partially transferred with the SIDT film stack 855. Alternatively, in other implementations, the release layer 220 remains or partially remains on the flexible support layer 210 after operation 770.

[00107] Referring to FIG. 8E, at operation 780 the anode film stack 865 may be combined with a separator 290, a cathode stack 285, or both a separator 290 and a cathode stack 285 to form the energy storage device structure 800 as described.

[00108] FIG. 9 illustrates a schematic view of a flexible substrate coating apparatus 900 for forming at least a portion of the SIDT film stack described in accordance with one or more implementations of the present disclosure. The flexible substrate coating apparatus 900 may be a roll-to-roll coating system. The flexible substrate coating apparatus 900 may be used to perform portions of the method 100, for example, the portions of the method that are performed using vacuum deposition.

[00109] The flexible substrate coating apparatus 900 may be a SMARTWEB®, manufactured by Applied Materials, adapted for manufacturing lithium anode devices according to the implementations described herein. According to typical implementations, the flexible substrate coating apparatus 900 can be used for manufacturing lithium anodes, and particularly for portions of SIDT film stacks containing lithium anodes. The flexible substrate coating apparatus 900 is constituted as a roll-to-roll system including an unwinding module 902, a processing module 904 and a winding module 906. In one or more implementations, the processing module 904 comprises a plurality of processing modules or chambers 910, 920, 930 and 940 arranged in sequence, each configured to perform one processing operation to the continuous sheet of material 950 or web of material, for example, the flexible support layer 210. In one or more implementations, as depicted in FIG. 9, the processing chambers 910-940 are radially disposed about a coating drum 955. Arrangements other than radial are contemplated. For example, in another implementation, the processing chambers may be positioned in a linear configuration.

[00110] In one implementation, the processing chambers 910-940 are stand-alone modular processing chambers wherein each modular processing chamber is structurally separated from the other modular processing chambers. Therefore, each of the stand-alone modular processing chambers, can be arranged, rearranged, replaced, or maintained independently without affecting each other. Although four processing chambers 910-940 are shown, it should be understood that any number of processing chambers may be included in the flexible substrate coating apparatus 900.

[00111] The processing chambers 910-940 may include any suitable structure, configuration, arrangement, and/or components that enable the flexible substrate coating apparatus 900 to deposit portions of the SIDT film stack according to implementations of the present disclosure. For example, but not limited to, the processing chambers may include suitable deposition systems including coating sources, power sources, individual pressure controls, deposition control systems, and temperature control. According to typical implementations, the chambers are provided with individual gas supplies. The chambers are typically separated from each other for providing a good gas separation. The flexible substrate coating apparatus 900 according to implementations described herein is not limited in the number of

deposition chambers. For example, but not limited to, flexible substrate coating apparatus 900 may include 3, 6, or 12 processing chambers.

[00112] The processing chambers 910-940 typically include one or more deposition units 912, 922, 932, and 942. Generally, the one or more deposition units as described herein can be selected from the group of a CVD source, an ALD source, a PECVD source, and a PVD source. The one or more deposition units can include an evaporation source, a sputter source, such as, a magnetron sputter source, a DC sputter source, an AC sputter source, a pulsed sputter source, a radio frequency (RF) sputtering source, or a middle frequency (MF) sputtering source. The one or more deposition units can include an evaporation source. In one implementation, the evaporation source is a thermal evaporation source or an electron beam evaporation source. In one implementation, the evaporation source is a lithium (Li) source. Further, the evaporation source may also be an alloy of two or more metals. The material to be deposited (e.g., lithium) can be provided in a crucible. The lithium can, for example, be evaporated by thermal evaporation techniques or by electron beam evaporation techniques.

[00113] In some implementations, one or some of the chambers may be configured for performing deposition by other methods, such as, but not limited to, chemical vapor deposition, atomic laser deposition or pulsed laser deposition. In some implementations, one or some of the chambers may be configured for performing a plasma treatment process, such as a plasma oxidation or plasma nitridation process.

[00114] In one or more implementations, the processing chambers 910-940 are configured to process both sides of the continuous sheet of material 950. Although the flexible substrate coating apparatus 900 is configured to process the continuous sheet of material 950, which is horizontally oriented, the flexible substrate coating apparatus 900 may be configured to process substrates positioned in different orientations, for example, the continuous sheet of material 950 may be vertically oriented. In one or more implementations, the continuous sheet of material 950 is a flexible support layer as described. In one or more implementations, the continuous sheet of material 950 includes a PET substrate.

[00115] In one or more implementations, the flexible substrate coating apparatus 900 comprises a transfer mechanism 952. The transfer mechanism 952 may comprise any transfer mechanism capable of moving the continuous sheet of material 950 through the processing region of the processing chambers 910-940. The transfer mechanism 952 may comprise a common transport architecture. The common transport architecture may comprise a reel-to-reel system with a common take-up reel 954 positioned in the winding module 906, the coating drum 955 positioned in the processing module 904, and a feed reel 956 positioned in the unwinding module 902. The take-up reel 954, the coating drum 955, and the feed reel 956 may be individually heated. The take-up reel 954, the coating drum 955 and the feed reel 956 may be individually heated using an internal heat source positioned within each reel or an external heat source. The common transport architecture may further comprise one or more auxiliary transfer reels 953a, 953b positioned between the take-up reel 954, the coating drum 955, and the feed reel 956. Although the flexible substrate coating apparatus 900 is depicted as having a single processing region, in one or more implementations, it may be advantageous to have separated or discrete processing regions for each individual processing chamber 910-940. For implementations having discrete processing regions, modules, or chambers, the common transport architecture may be a reel-to-reel system where each chamber or processing region has an individual take-up-reel and feed reel and one or more optional intermediate transfer reels positioned between the take-up reel and the feed reel.

[00116] The flexible substrate coating apparatus 900 may comprise the feed reel 956 and the take-up reel 954 for moving the continuous sheet of material 950 through the different processing chambers 910-940. In one implementation, the first processing chamber 910 and the second processing chamber 920 are each configured to deposit one or more of the interface layers 240 of operation 140. The third processing chamber 930 and the fourth processing chamber 940 are configured to deposit a portion of an alkali metal-containing film, for example, the alkali metal-containing layer 250. In another implementation where the continuous sheet of material 950 is a polymer material, the first processing chamber 910 is configured to deposit a copper film on the polymer material. In one or more implementations, the finished negative electrode will not be collected on the take-up reel 954 as shown in the figures, but may

go directly for integration with the anode current collector and/or the cathode structure to form the anode device stack or energy storage device.

[00117] In one implementation, processing chambers 930 and 940 are configured for depositing a thin film of lithium metal on the continuous sheet of material 950. Any suitable lithium deposition process for depositing thin films of lithium metal may be used to deposit the thin film of lithium metal. Deposition of the thin film of lithium metal may be by PVD processes, such as evaporation. The chambers for depositing the thin film of lithium metal may include a PVD system, such as an electron-beam evaporator, a thermal evaporator, or a lamination system.

[00118] In one implementation, the first processing chamber 910 is configured for depositing a chalcogenide film on the lithium metal film. The chalcogenide film may be deposited using a PVD sputtering technique. In one implementation, the fourth processing chamber 940 is configured for forming a lithium oxide film or a lithium fluoride film on the chalcogenide film. Any suitable lithium deposition process for depositing thin films of lithium metal may be used to deposit the thin film of lithium metal. In one implementation, the evaporation chamber has a processing region that is shown to comprise an evaporation source that may be placed in a crucible, which may be a thermal evaporator or an electron beam evaporator (cold) in a vacuum environment, for example.

[00119] In operation, the continuous sheet of material 950 is unwound from the feed reel 956 as indicated by the substrate movement direction shown by arrow 908. The continuous sheet of material 950 may be guided via one or more auxiliary transfer reels 953a, 953b. It is also possible that the continuous sheet of material 950 is guided by one or more substrate guide control units (not shown) that shall control the proper run of the flexible substrate, for instance, by fine adjusting the orientation of the flexible substrate.

[00120] After uncoiling from the feed reel 956 and running over the auxiliary transfer reel 953a, the continuous sheet of material 950 is then moved through the deposition areas provided at the coating drum 955 and corresponding to positions of the deposition units 912, 922, 932, and 942. During operation, the coating drum 955

rotates around axis 951 such that the flexible substrate moves in the direction of arrow 908.

[00121] FIG. 10 illustrates a schematic side view of a lamination transfer system 1000 in accordance with one or more implementations of the present disclosure. The lamination transfer system 1000 includes equipment for transferring SIDT film stacks, for example, the SIDT film stacks 255, 455, 655, 855, including lithium films on a first flexible carrier 1010, for example, the flexible support layer 210, and a second flexible carrier 1020, for example the flexible support layer 210, to each side of a flexible substrate 1030, for example, the flexible substrate 260, so that the flexible substrate 1030 with the lithium films can be used as an electrode (e.g., anode) in a lithium-ion battery. The lamination transfer system 1000 includes a calendaring unit 1040 to transfer the SIDT film stacks on the flexible carriers 1010, 1020 to the flexible substrate 1030.

[00122] The lamination transfer system 1000 includes a first flexible carrier supply hub 1015. A supply roll 1011 of the first flexible carrier 1010 is positioned on the first flexible carrier supply hub 1015. In some embodiments, the first flexible carrier 1010 can be formed of a polymer material, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), metallized plastic, or combinations thereof. A SIDT film stack including a lithium film (not shown in FIG. 10) is positioned on the lower side 1010L of the first flexible carrier 1010, so that this lithium film faces an upper surface 1030U of the flexible substrate 1030 as the first flexible carrier 1010 and the flexible substrate 1030 are conveyed through the calendaring unit 1040. This lithium film may be the alkali metal-containing layer 250 in after being transferred to the flexible substrate 1030. The upper surface 1030U of the flexible substrate 1030 is on an opposite side relative to a lower surface 1030L of the flexible substrate 1030. The upper surface 1030U is also referred to as the first surface or the first side of the flexible substrate 1030 while the lower surface is also referred to as the second surface or the second side of the flexible substrate 1030.

[00123] The lamination transfer system 1000 includes a second flexible carrier supply hub 1025. A supply roll 1021 of the second flexible carrier 1020 is positioned on the second flexible carrier supply hub 1025. In some embodiments, the second

flexible carrier 1020 can be formed of a same material (e.g., PET) as the first flexible carrier 1010. A SIDT film stack including a lithium film (not shown in FIG. 10), for example, any of the SIDT film stacks 255, 455, 655, 855, is positioned on the upper side 1020U of the second flexible carrier 1020, so that this lithium film faces the lower surface 1030L of the flexible substrate 1030 as the second flexible carrier 1020 and the flexible substrate 1030 are conveyed through the calendaring unit 1040.

[00124] The lamination transfer system 1000 includes a flexible substrate supply hub 1035. A supply roll 1031 of the flexible substrate 1030 is positioned on the flexible substrate supply hub 1035. In some embodiments, the flexible substrate 1030 can be formed of one or more of copper, graphite, silicon, silicon graphite, silicon oxide graphite, silicon, metalized plastic, or other materials.

[00125] The lamination transfer system 1000 further includes the calendaring unit 1040. The calendaring unit 1040 includes a first calender roller 1041 and a second calender roller 1042. The first flexible carrier 1010, the second flexible carrier 1020, and the flexible substrate 1030 are arranged to be conveyed along a path that extends between the first calender roller 1041 and the second calender roller 1042. The flexible substrate 1030 is positioned between the first flexible carrier 1010 and the second flexible carrier 1020 when the first flexible carrier 1010, the second flexible carrier 1020, and the flexible substrate 1030 are conveyed between the first calender roller 1041 and the second calender roller 1042. The calender rollers 1041, 1042 exert a high amount of pressure on the flexible carriers 1010, 1020 and the flexible substrate 1030 that causes the SIDT film stack on each of the flexible carriers 1010, 1020 to be transferred to the flexible substrate 1030. In some embodiments, a release layer, for example, the release layer 220, is disposed on each of the flexible carriers 1010, 1020 between the corresponding flexible carrier 1010, 1020 and the SIDT film stack on that flexible carrier.

[00126] The lamination transfer system 1000 includes a first flexible carrier pickup hub 1016. A pickup roll 1012 of the first flexible carrier 1010 is positioned on the first flexible carrier pickup hub 1016. The SIDT film stack is no longer on the first flexible carrier 1010 when the first flexible carrier 1010 is wound onto the first flexible carrier

pickup hub 1016 because the SIDT film stack previously on the first flexible carrier 1010 is transferred onto the flexible substrate 1030 by the calendering unit 1040.

[00127] The lamination transfer system 1000 includes a second flexible carrier pickup hub 1026. A pickup roll 1022 of the second flexible carrier 1020 is positioned on the second flexible carrier pickup hub 1026. The SIDT film stack is no longer on the second flexible carrier 1020 when the second flexible carrier 1020 is wound onto the second flexible carrier pickup hub 1026 because the SIDT film stack previously on the second flexible carrier 1020 is transferred onto the flexible substrate 1030 by the calendering unit 1040.

[00128] The lamination transfer system 1000 includes a flexible substrate pickup hub 1036. A pickup roll 1032 of the flexible substrate 1030 is positioned on the flexible substrate pickup hub 1036. The flexible substrate 1030 includes a SIDT film stack on each of the upper surface 1030U and the lower surface 1030L of the flexible substrate 1030. The SIDT film stacks are transferred from the respective flexible carriers 1010, 1020 onto the flexible substrate 1030 by the calendering unit 1040.

[00129] The lamination transfer system 1000 further includes a plurality of rollers 1081-1088. In some embodiments, each of the rollers 1081-1088 can be passive rollers. The rollers 1081-1088 can assist in applying proper tension to and assist in changing the direction of the flexible carriers 1010, 1020 and the flexible substrate 1030 during the movement of each of the flexible carriers 1010, 1020 and the flexible substrate 1030 through the different portions of the lamination transfer system 1000. Some of the rollers 1081-1088 can also assist in moving the flexible carriers 1010, 1020 closer to or further away from the flexible substrate 1030. For example, the second and third rollers 1082, 1083 assist in bringing the flexible carriers 1010, 1020 into contact with the flexible substrate 1030 before the flexible carriers 1010, 1020 and the flexible substrate 1030 are conveyed through the calendering unit 1040. Additionally, the fourth and fifth rollers 1084, 1085 provide a location at which tension can be applied to the flexible carriers 1010, 1020 to peel the flexible carriers 1010, 1020 away from the flexible substrate 1030. In some embodiments, one or more of the rollers 1081-1088 can instead be a bar, such as metal bar, that can apply tension

to the carrier or flexible substrate during the movement of the carrier or flexible substrate.

[00130] The lamination transfer system 1000 can further include actuators (not shown) configured to rotate each of the hubs 1015, 1016, 1025, 1026, 1035, 1036, so that the flexible carriers 1010, 1020 and the flexible substrate 1030 can be conveyed from the corresponding supply hub 1015, 1025, 1035, through the calendering unit 1040, and to the corresponding pick hub 1016, 1026, 1036. The lamination transfer system 1000 can further include one or more actuators (not shown) to rotate the calender rollers 1041, 1042 of the calendering unit 1040. The rotational speed of the actuators can be adjusted to control the speed at which the flexible substrate 1030 and flexible carriers 1010, 1020 are conveyed through the lamination transfer system 1000.

[00131] In the lamination transfer system 1000, the flexible substrate 1030 is conveyed along a path from the supply roll 1031 that is supported by the supply hub 1035, past the first roller 1081, between the second and third rollers 1082, 1083, between the calender rollers 1041, 1042, between the fourth and fifth rollers 1084, 1085, past the eighth roller 1088, and to the pickup roll 1032 around the pickup hub 1036. The pickup hub 1036 is configured to rotate and assist in conveying the flexible substrate along the path after the flexible substrate 1030 passes between the first calender roller 1041 and the second calender roller 1042. Similarly, the pickup hubs 1016, 1026 are configured to rotate and assist in conveying the flexible carriers along paths between the supply hubs 1015, 1025 and the pickup hubs 1016, 1026.

[00132] The lamination transfer system 1000 can also include a controller 1005 for controlling processes performed by the lamination transfer system 1000. The controller 1005 can be any type of controller used in an industrial setting, such as a programmable logic controller (PLC). The controller 1005 includes a processor 1007, a memory 1006, and input/output (I/O) circuits 1008. The controller 1005 can further include one or more of the following components (not shown), such as one or more power supplies, clocks, communication components (e.g., network interface card), and user interfaces typically found in controllers for semiconductor equipment.

[00133] The memory 1006 can include non-transitory memory. The non-transitory memory can be used to store the programs and settings described below. The memory 1006 can include one or more readily available types of memory, such as read only memory (ROM) (e.g., electrically erasable programmable read-only memory (EEPROM), flash memory, floppy disk, hard disk, or random access memory (RAM) (e.g., non-volatile random access memory (NVRAM)).

[00134] The processor 1007 is configured to execute various programs stored in the memory 1006, such as a program configured to execute the methods 100, 300, 500, 700 described. During execution of these programs, the controller 1005 can communicate to I/O devices through the I/O circuits 1008. For example, during execution of these programs and communication through the I/O circuits 1008, the controller 1005 can control outputs (e.g., the actuators connected to the different hubs and the calendaring unit 1040). The memory 1006 can further include various operational settings used to control the lamination transfer system 1000. For example, the settings can include speed settings for the actuators connected to the hubs.

[00135] In the Summary and in the Detailed Description, and the Claims, and in the accompanying drawings, reference is made to particular features (including method operations) of the present disclosure. It is to be understood that the disclosure in this specification includes all possible combinations of such particular features. For example, where a particular feature is disclosed in the context of a particular aspect, implementation, or example of the present disclosure, or a particular claim, that feature can also be used, to the extent possible in combination with and/or in the context of other particular aspects and implementations of the present disclosure, and in the present disclosure generally.

[00136] Implementations described may be performed in a roll-to-roll coating system, such as a TopMet® roll-to-roll web coating system, a SMARTWEB® roll-to-roll web coating system, a TOPBEAM® roll-to-roll web coating system, all of which are available from Applied Materials, Inc. of Santa Clara, California. Other tools capable of performing high rate deposition processes may also be adapted to benefit from the implementations described. In addition, any system enabling the deposition processes described can be used to advantage. The apparatus description described

is illustrative and should not be construed or interpreted as limiting the scope of the implementations described. It should also be understood that although described as a roll-to-roll process, the implementations described may also be performed on discrete substrates.

[00137] Implementations and all of the functional operations described in this specification can be implemented in digital electronic circuitry, or in computer software, firmware, or hardware, including the structural means disclosed in this specification and structural equivalents thereof, or in combinations of them. Implementations described herein can be implemented as one or more non-transitory computer program products, i.e., one or more computer programs tangibly embodied in a machine readable storage device, for execution by, or to control the operation of, data processing apparatus, e.g., a programmable processor, a computer, or multiple processors or computers.

[00138] The processes and logic flows described in this specification can be performed by one or more programmable processors executing one or more computer programs to perform functions by operating on input data and generating output. The processes and logic flows can also be performed by, and apparatus can also be implemented as, special purpose logic circuitry, e.g., an FPGA (field programmable gate array) or an ASIC (application specific integrated circuit).

[00139] The term “data processing apparatus” encompasses all apparatus, devices, and machines for processing data, including by way of example a programmable processor, a computer, or multiple processors or computers. The apparatus can include, in addition to hardware, code that creates an execution environment for the computer program in question, e.g., code that constitutes processor firmware, a protocol stack, a database management system, an operating system, or a combination of one or more of them. Processors suitable for the execution of a computer program include, by way of example, both general and special purpose microprocessors, and any one or more processors of any kind of digital computer.

[00140] Computer readable media suitable for storing computer program instructions and data include all forms of nonvolatile memory, media and memory

devices, including by way of example semiconductor memory devices, e.g., EPROM, EEPROM, and flash memory devices; magnetic disks, e.g., internal hard disks or removable disks; magneto optical disks; and CD ROM and DVD-ROM disks. The processor and the memory can be supplemented by, or incorporated in, special purpose logic circuitry.

[00141] The term “comprises” and grammatical equivalents thereof are used herein to mean that other components, ingredients, operations, etc. are optionally present. For example, an article “comprising” (or “which comprises”) components A, B, and C can consist of (i.e., contain only) components A, B, and C, or can contain not only components A, B, and C but also one or more other components. In addition, whenever a composition, an element or a group of elements is preceded with the transitional phrase “comprising” or grammatical equivalents thereof, it is understood that it is contemplated that the same composition or group of elements may be preceded with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

[00142] Where reference is made herein to a method comprising two or more defined operations, the defined operations can be carried out in any order or simultaneously (except where the context excludes that possibility), and the method can include one or more other operations which are carried out before any of the defined operations, between two of the defined operations, or after all of the defined operations (except where the context excludes that possibility).

[00143] While the foregoing is directed to implementations of the present disclosure, other and further implementations of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

## Claims:

1. A method of making a storage device, comprising:  
forming an electrolyte containing layer over a release layer disposed over a flexible support layer;  
forming one or more interface layers over the solid electrolyte containing layer;  
evaporating an alkali metal onto the one or more interface layers; and  
transferring the release layer, the electrolyte containing layer, the one or more interface layers, and the alkali metal to a substrate to form an anode film stack.
2. The method of claim 1, wherein the flexible support layer comprises a material selected from polyethylene terephthalate (PET), paper, and a combination thereof.
3. The method of claim 1, wherein the solid electrolyte containing layer is deposited over the release layer using non-vacuum coating.
4. The method of claim 3, wherein the one or more interface layers and the alkali metal are deposited in a vacuum environment.
5. The method of claim 1, further comprising transferring the flexible support layer, the release layer, and the solid electrolyte containing layer into a vacuum environment prior to forming the one or more interface layers.
6. The method of claim 1, wherein the one or more interface layers comprises an interface dielectric material.
7. The method of claim 6, wherein the interface dielectric material is selected from  $\text{AlO}_x$ ,  $\text{AlOOH}$ ,  $\text{LiF}$ ,  $\text{BaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{LiAlO}_2$ ,  $\text{AlF}_3$ ,  $\text{BiF}_3$ ,  $\text{AgFx}$ , rare earth (RE) nickelates  $\text{RENiO}_3$ , or a combination thereof.
8. The method of claim 6, wherein the one or more interface layers further comprises a plating and stripping enhancement layer.

9. The method of claim 8, plating and stripping enhancement layers are selected from alloys of metals or chalcogenides.
10. The method of claim 9, wherein the plating and stripping enhancement layers comprise Ag, Bi, Sn, Si, alloys of Ag, Bi, Sn, Si, chalcogenides of Ag, Bi, Sn, Si, or combination thereof.
11. The method of claim 10, wherein the electrolyte containing layer is formed in a first processing chamber and the one or more interface layers and the alkali metal are formed in a second processing chamber.
12. The method of claim 1, wherein the alkali metal is lithium.
13. The method of claim 1, wherein transferring the release layer, the electrolyte containing layer, the one or more interface layers, and the alkali metal to a substrate to form an anode film stack comprises a lamination process.
14. An alkali metal-containing film stack for energy storage devices, comprising:  
a flexible support layer;  
a release layer disposed over the flexible support layer capable of separating from the flexible support layer;  
an electrolyte containing layer formed over the release layer;  
one or more interface layers over the solid electrolyte containing layer; and  
an alkali metal-containing layer formed over the one or more interface layers.
15. The alkali metal-containing film stack of claim 14, wherein the flexible support layer comprises a material selected from polyethylene terephthalate (PET), paper, and a combination thereof.
16. The alkali metal-containing film stack of claim 15, wherein the one or more interface layers comprises an interface dielectric material is selected from AlOx, AlOOH, LiF, BaTiO<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiAlO<sub>2</sub>, AlF<sub>3</sub>, BiF<sub>3</sub>, AgFx, rare earth (RE) nickelates RENiO<sub>3</sub>, or a combination thereof.

17. The alkali metal-containing film stack of claim 16, wherein the one or more interface layers further comprises a plating and stripping enhancement layer.
18. The alkali metal-containing film stack of claim 17, wherein the plating and stripping enhancement layers are selected from alloys of metals or chalcogenides.
19. The alkali metal-containing film stack of claim 18, wherein the plating and stripping enhancement layers comprise Ag, Bi, Sn, Si, alloys of Ag, Bi, Sn, Si, chalcogenides of Ag, Bi, Sn, Si, or combination thereof.
20. A lamination transfer system, comprising:  
a lamination transfer chamber; and  
a system controller configured to cause the lamination transfer chamber to perform a process, comprising:  
conveying a film stack from a supply hub toward a pickup hub;  
contacting the film stack with a current collector;  
laminating the film stack to the current collector; and  
removing a support layer from the film stack, wherein the film stack comprises the flexible support layer, a release layer disposed over the flexible support layer capable of separating from the flexible support layer, an electrolyte containing layer formed over the release layer, one or more interface layers over the solid electrolyte containing layer, and an alkali metal-containing layer formed over the one or more interface layers.

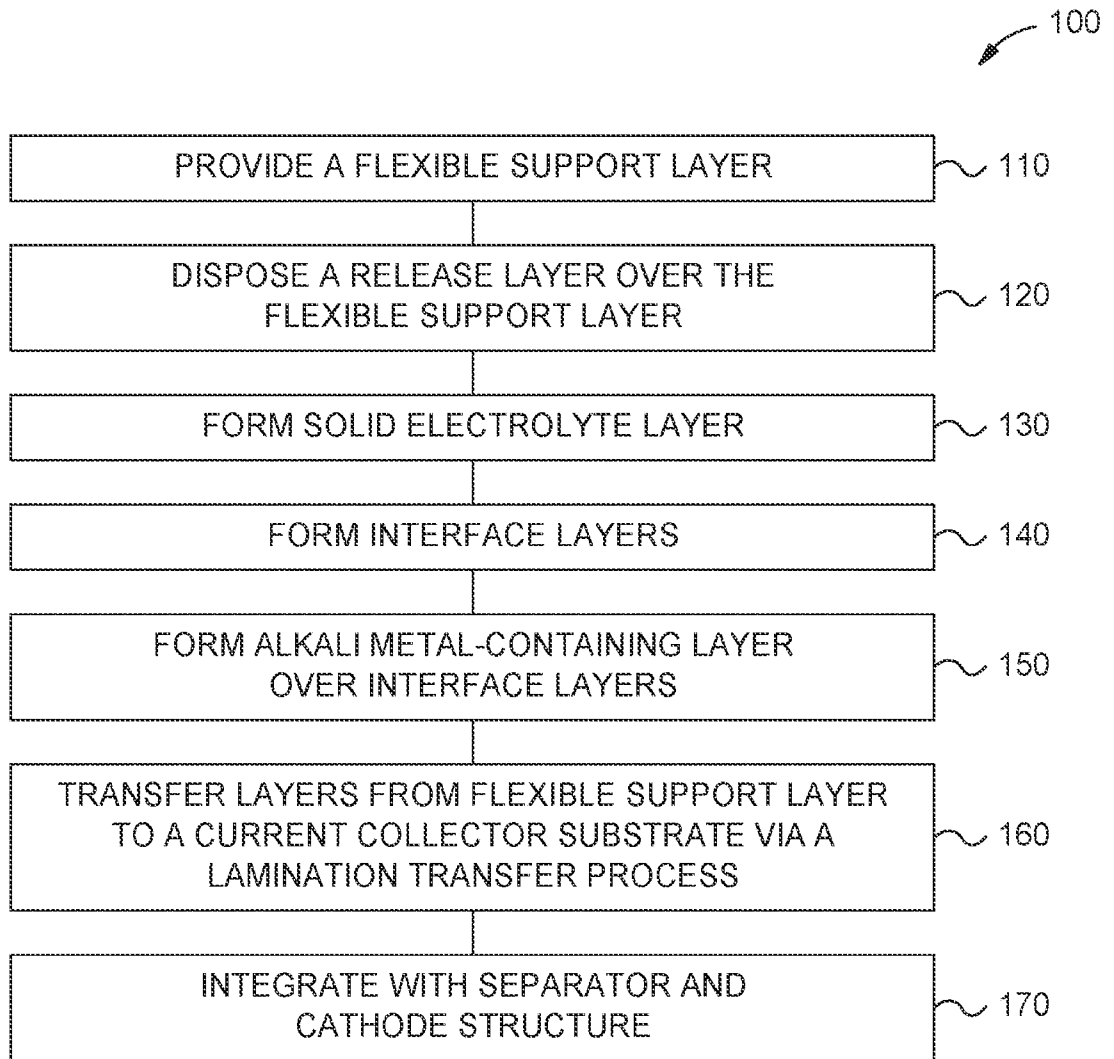
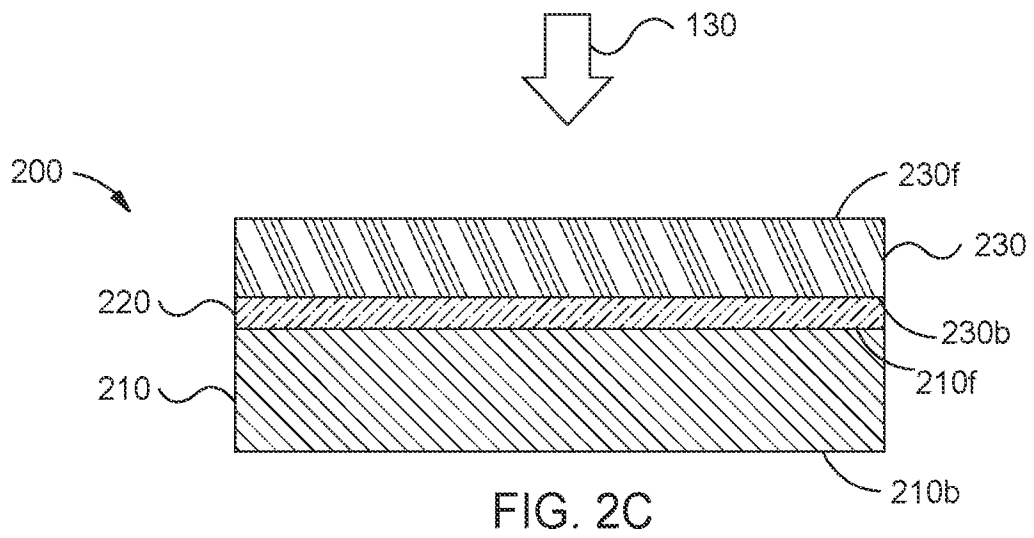
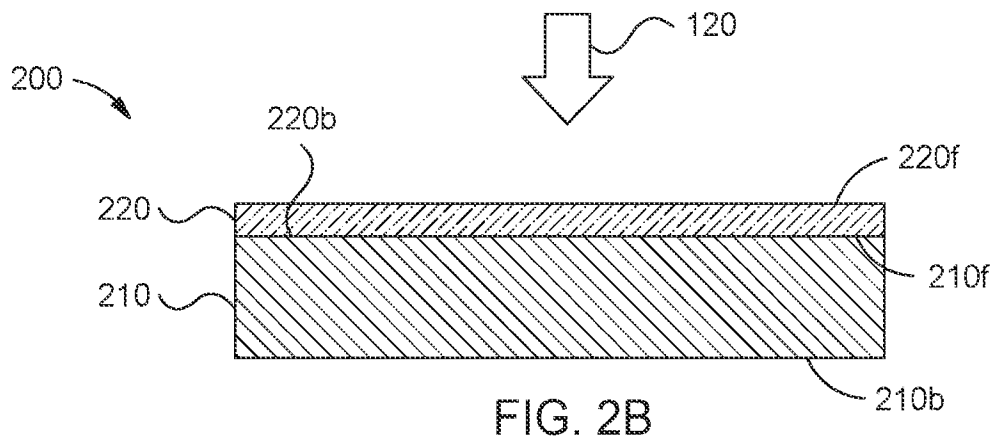
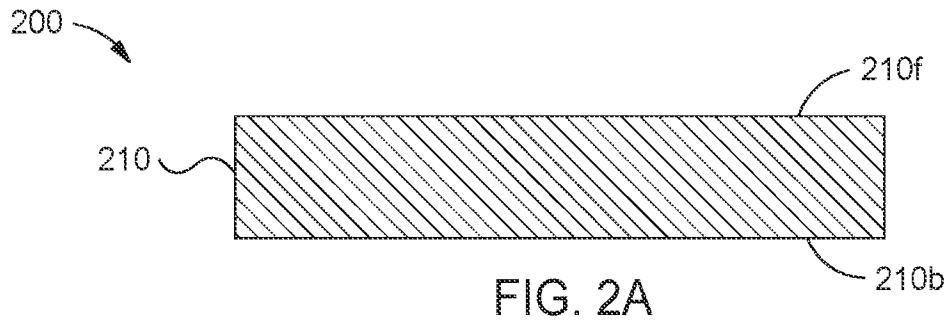


FIG. 1



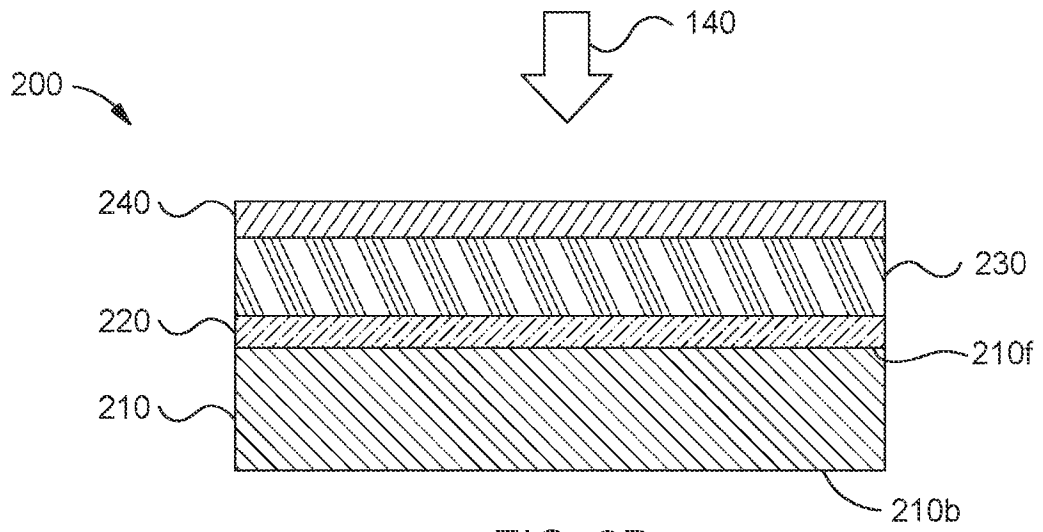


FIG. 2D

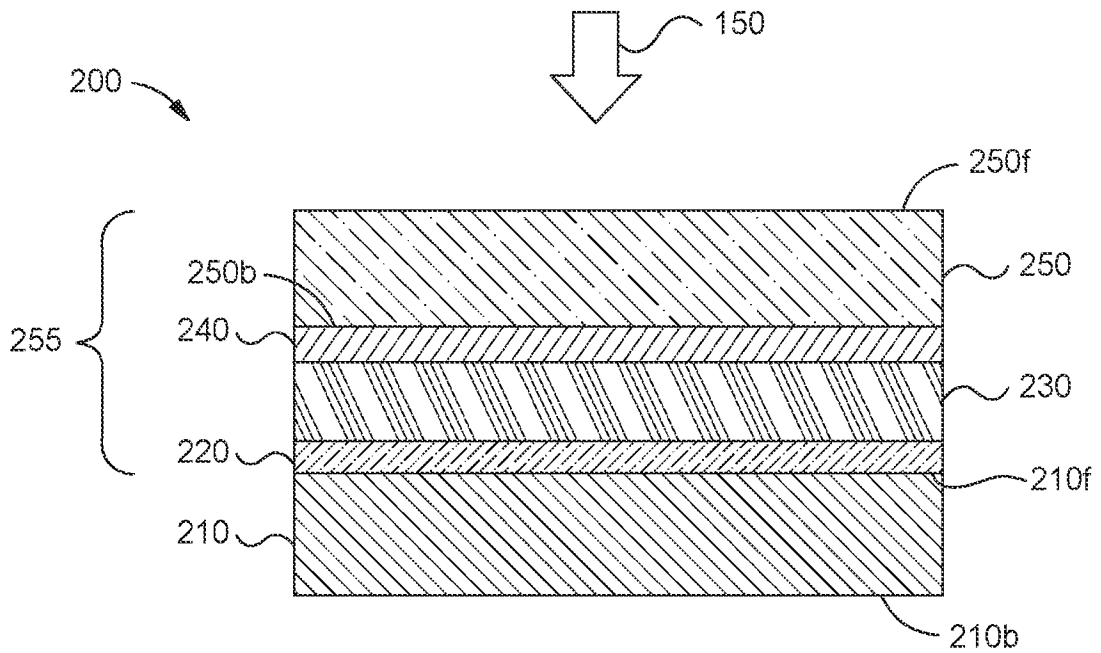


FIG. 2E

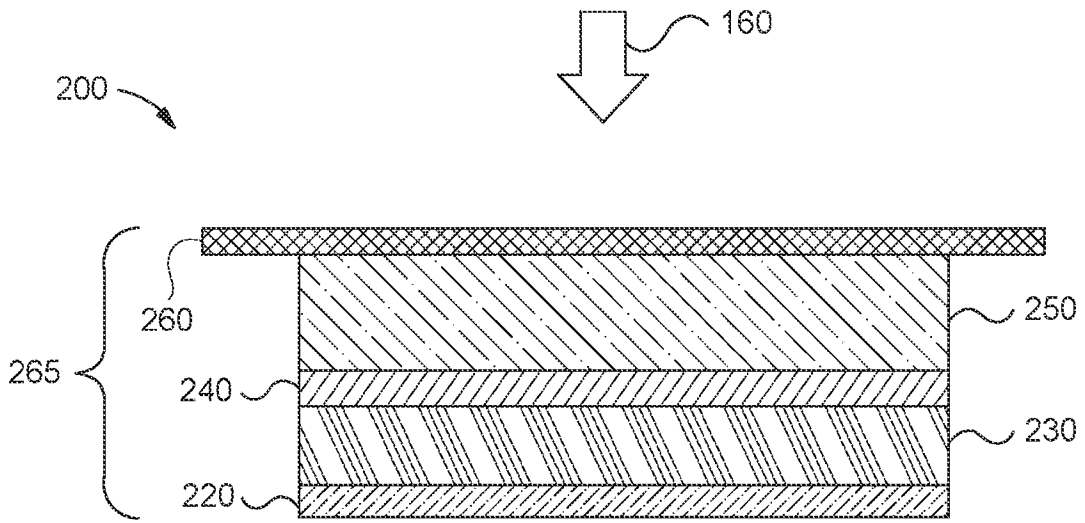


FIG. 2F

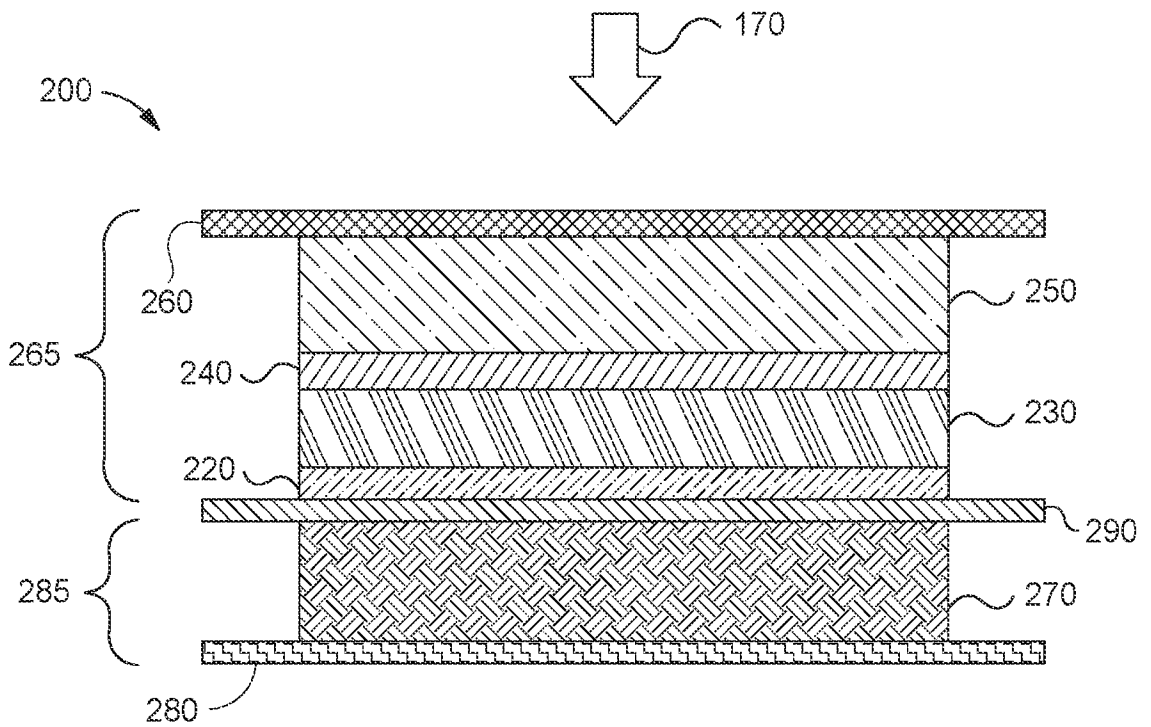


FIG. 2G

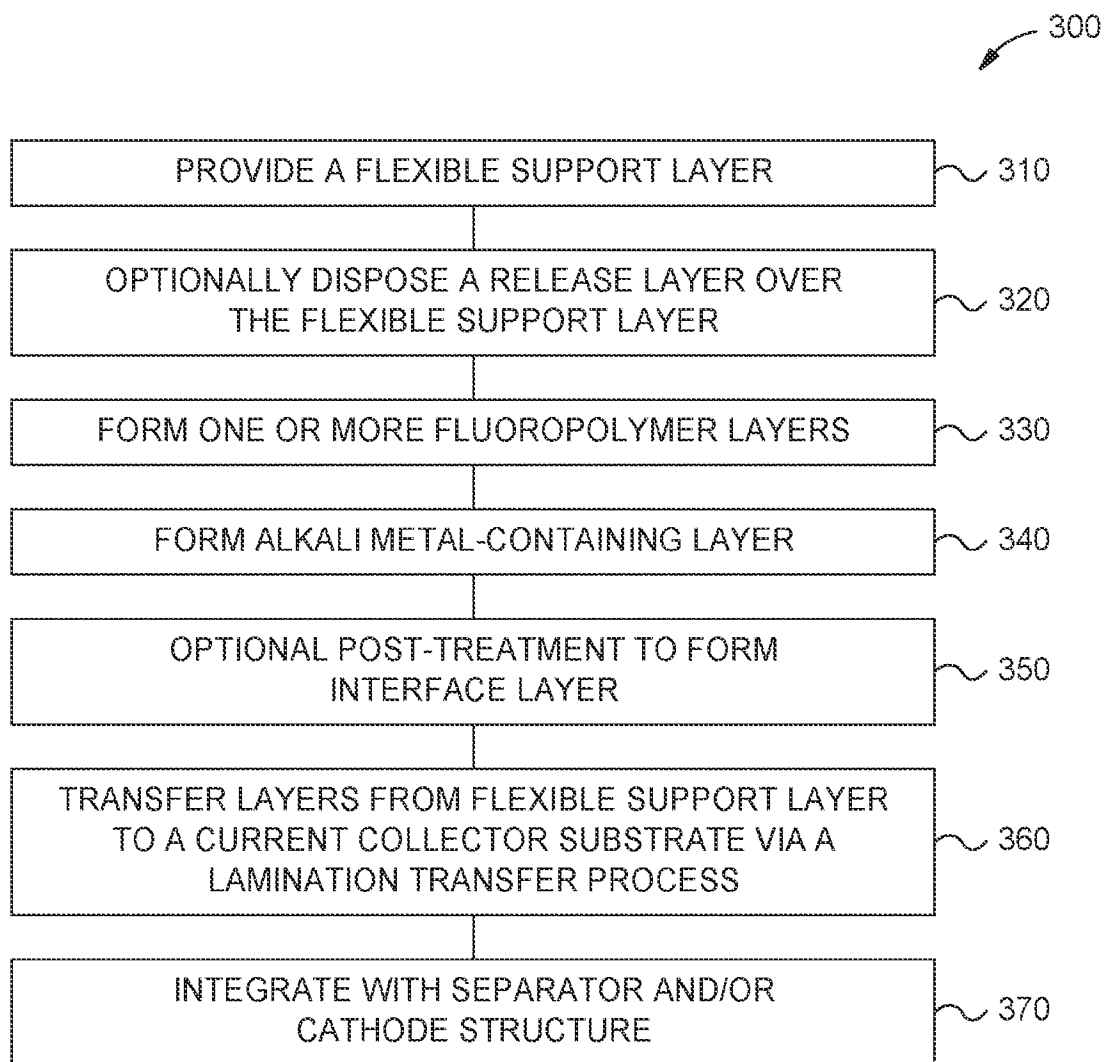


FIG. 3

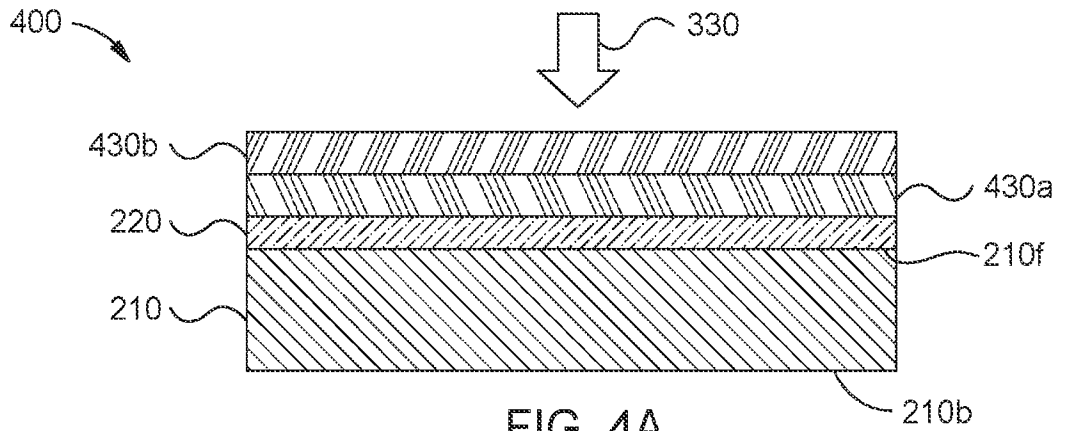


FIG. 4A

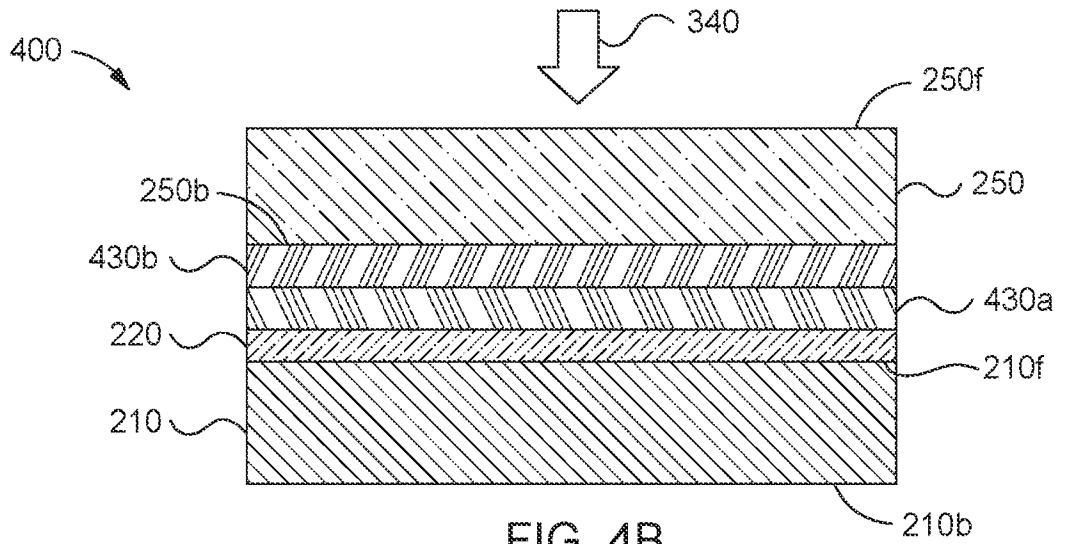


FIG. 4B

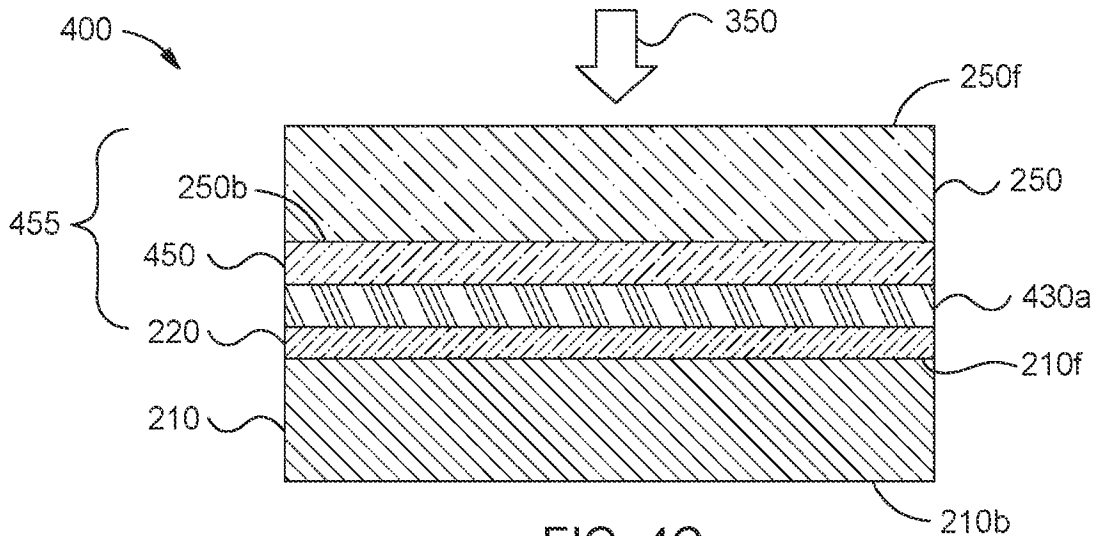


FIG. 4C

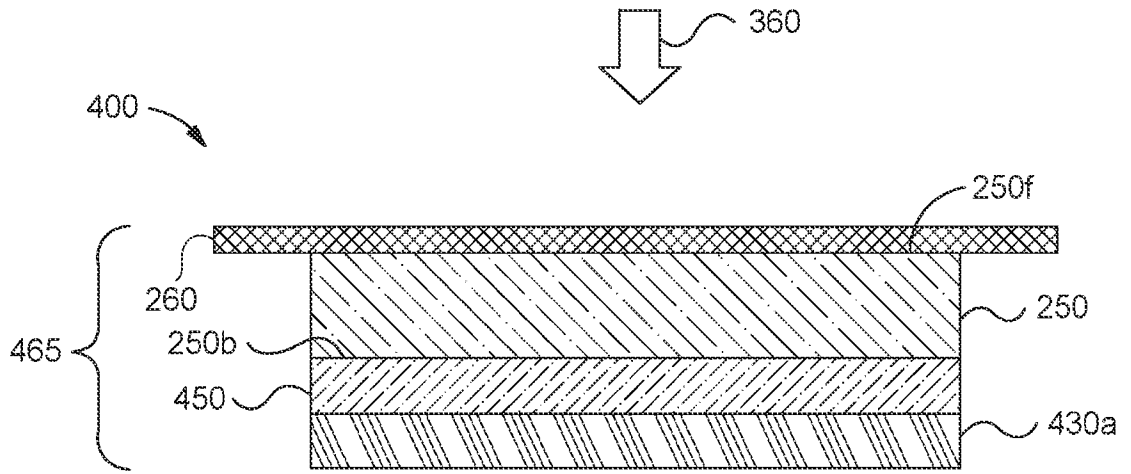


FIG. 4D

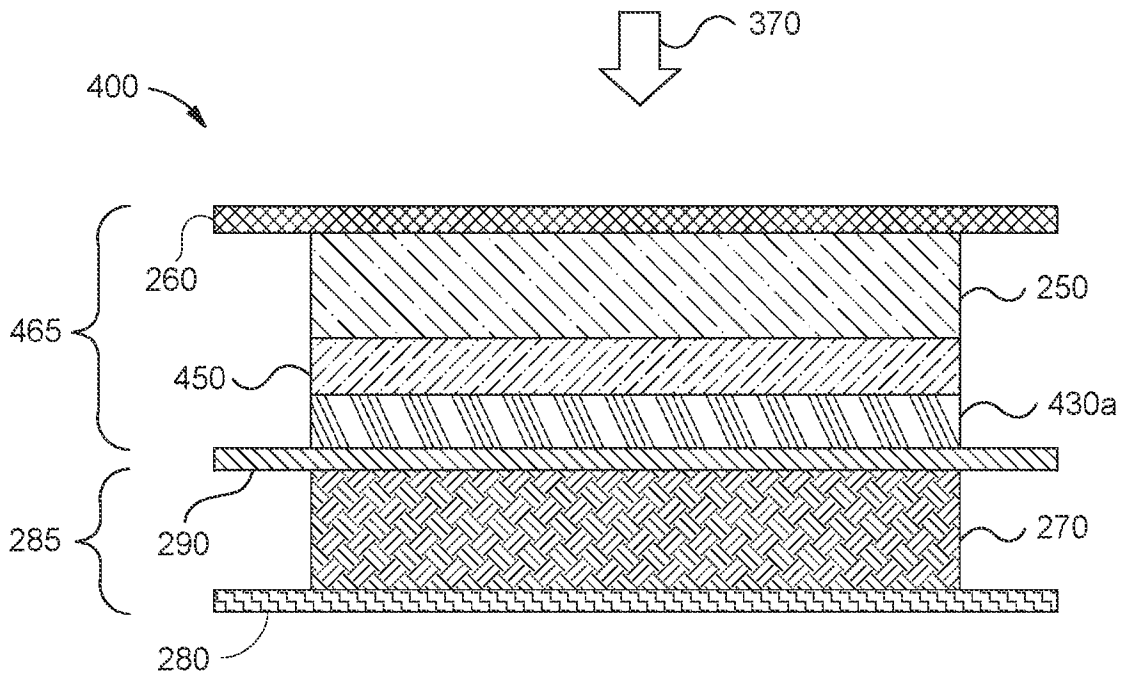


FIG. 4E

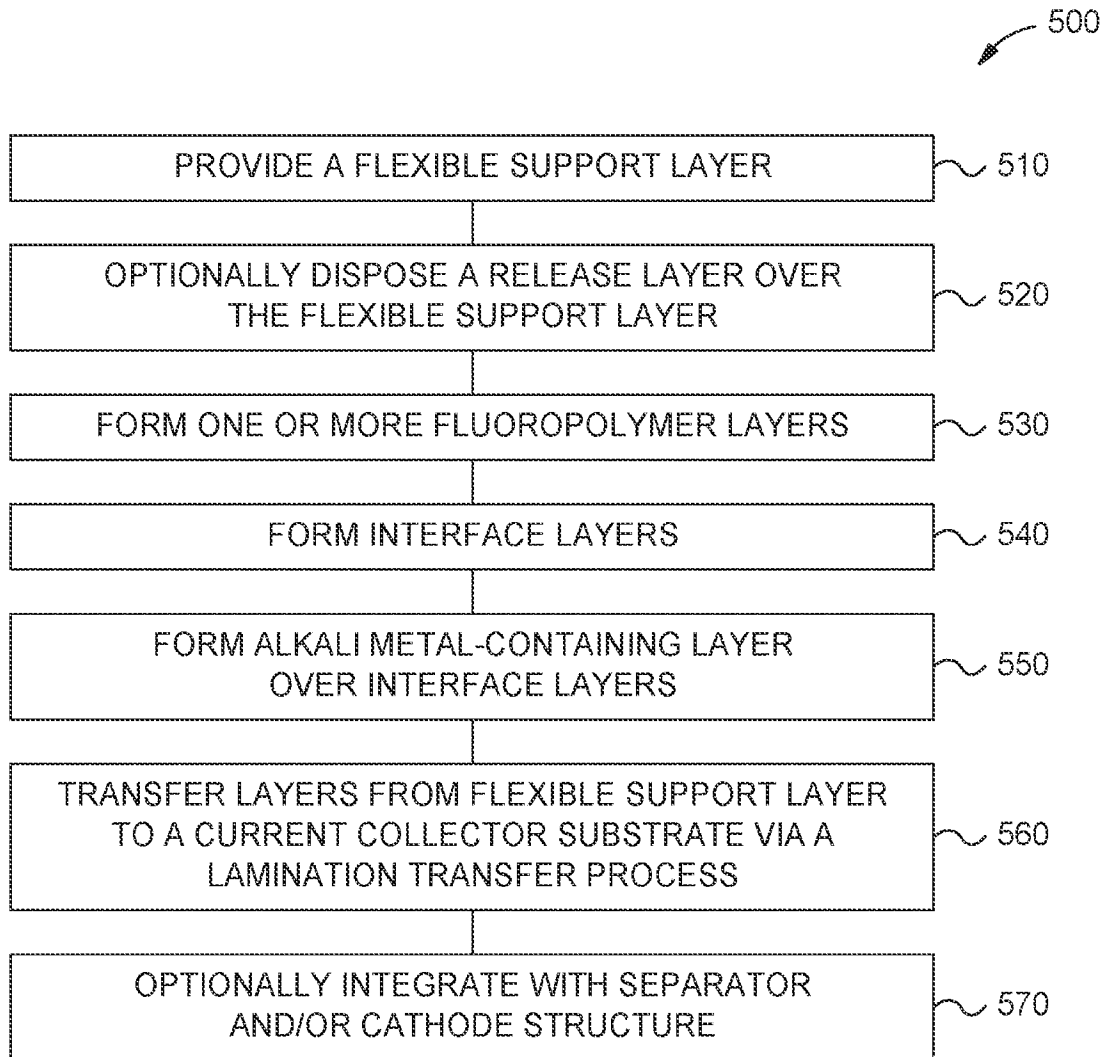


FIG. 5

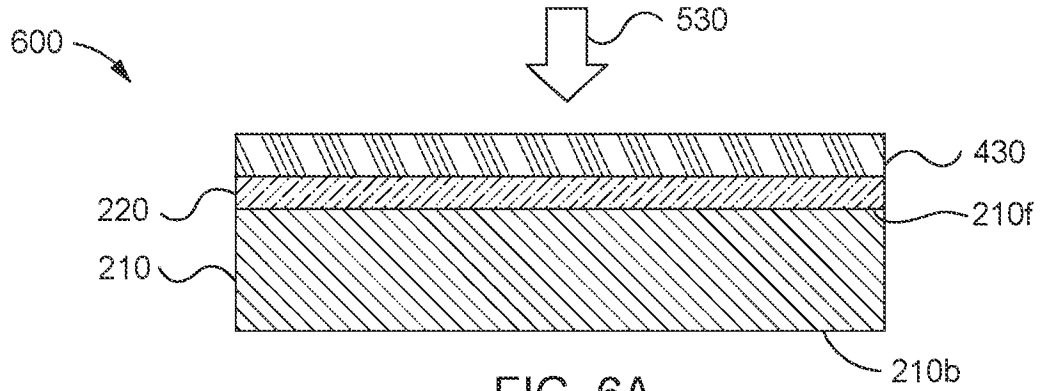


FIG. 6A

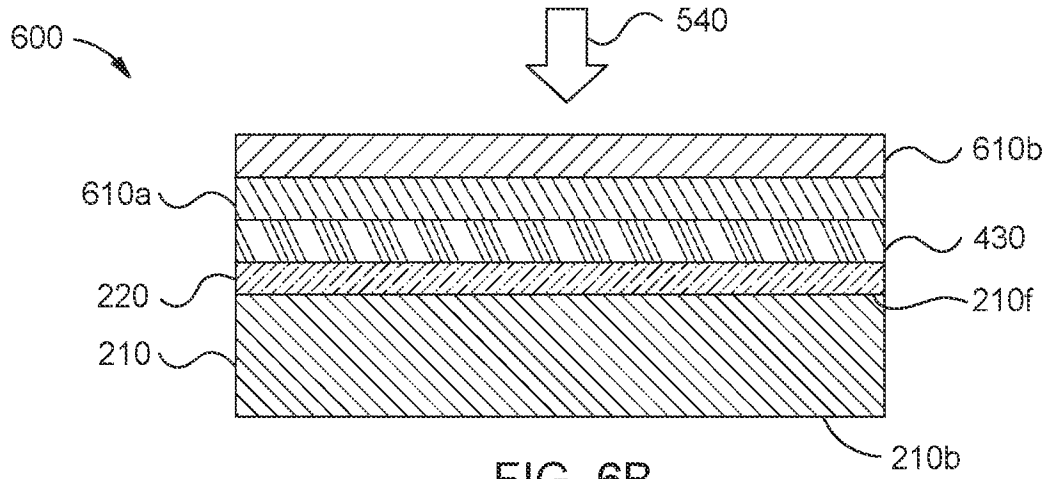


FIG. 6B

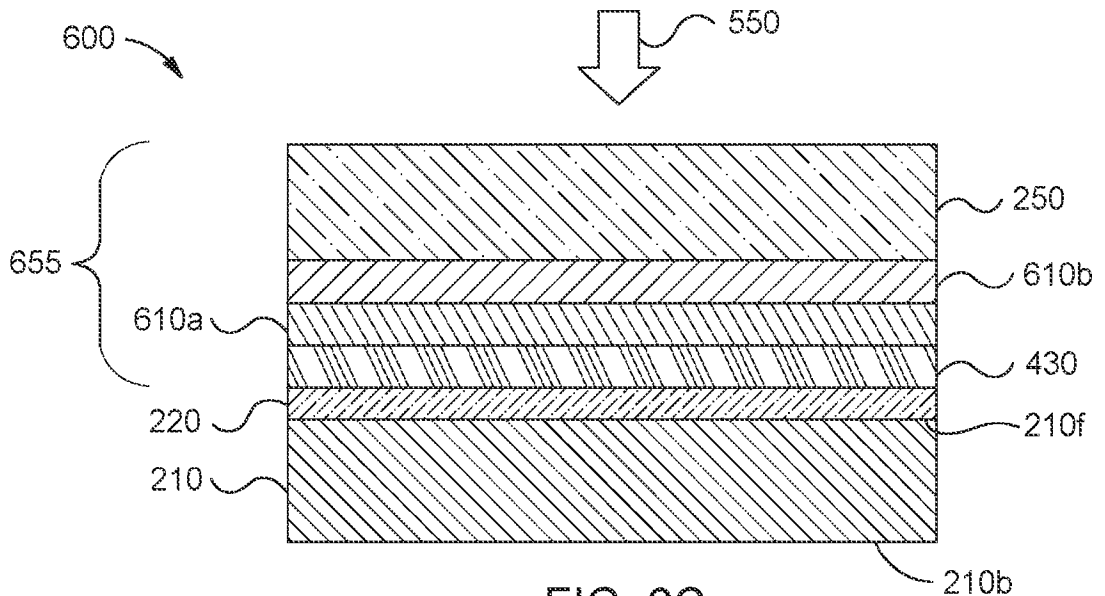


FIG. 6C

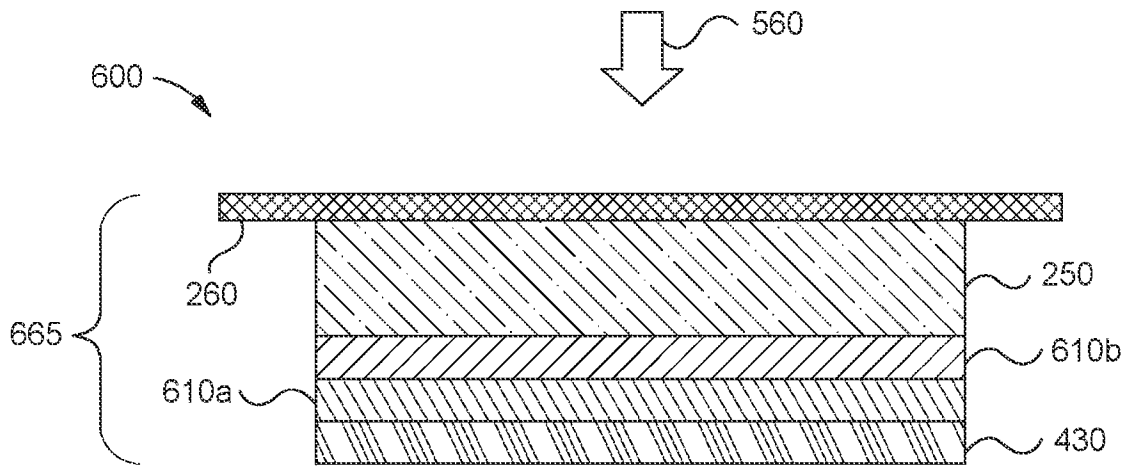


FIG. 6D

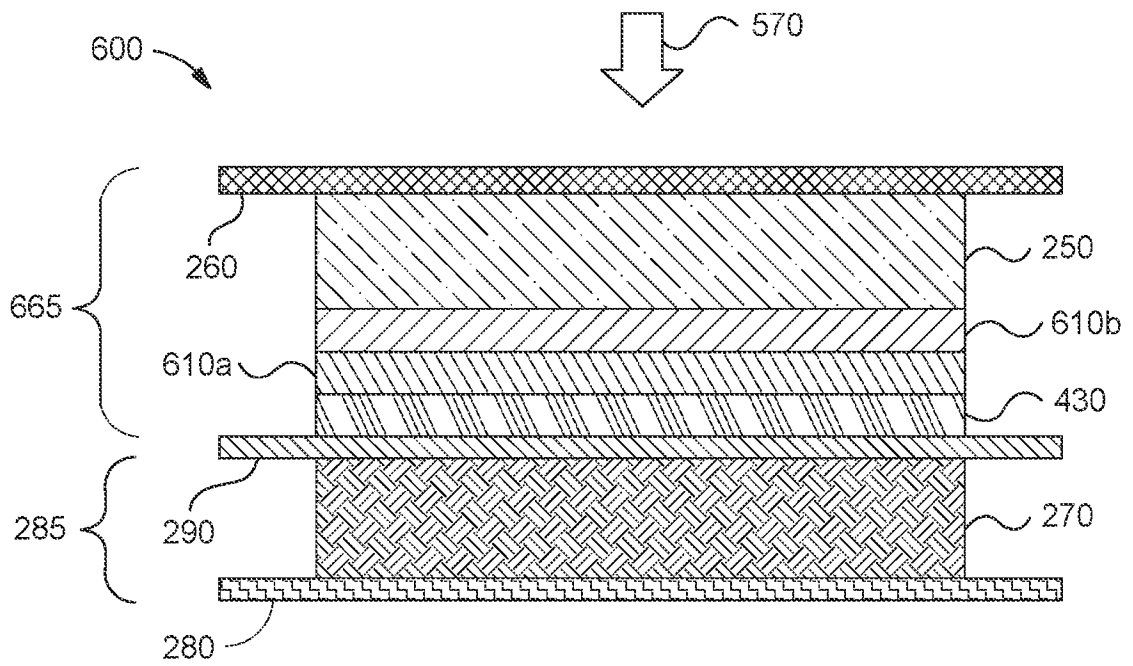


FIG. 6E

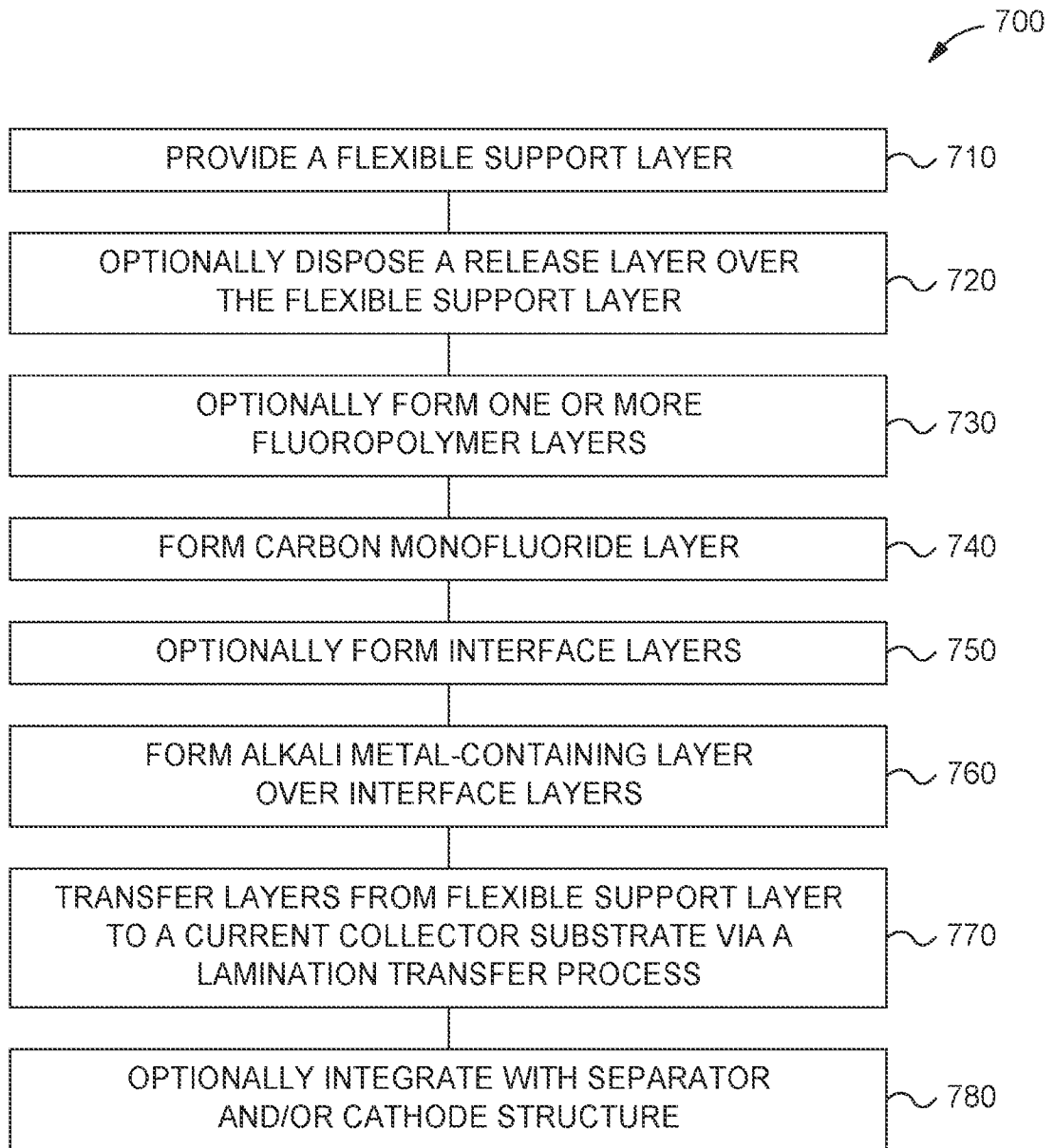


FIG. 7

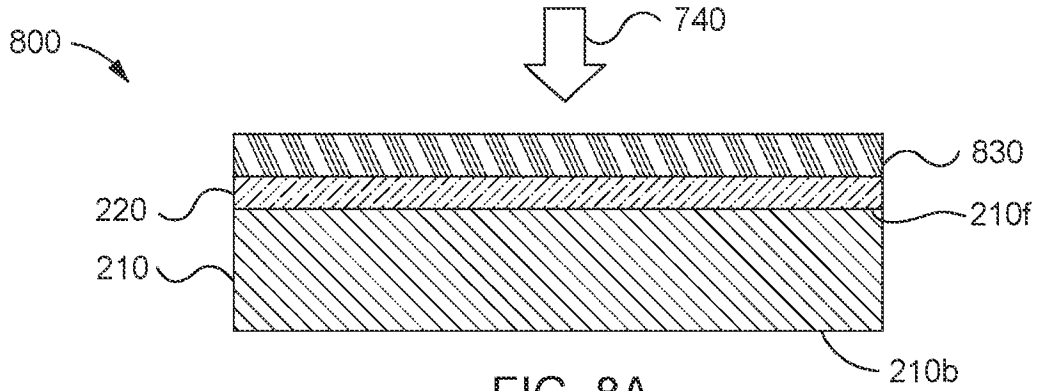


FIG. 8A

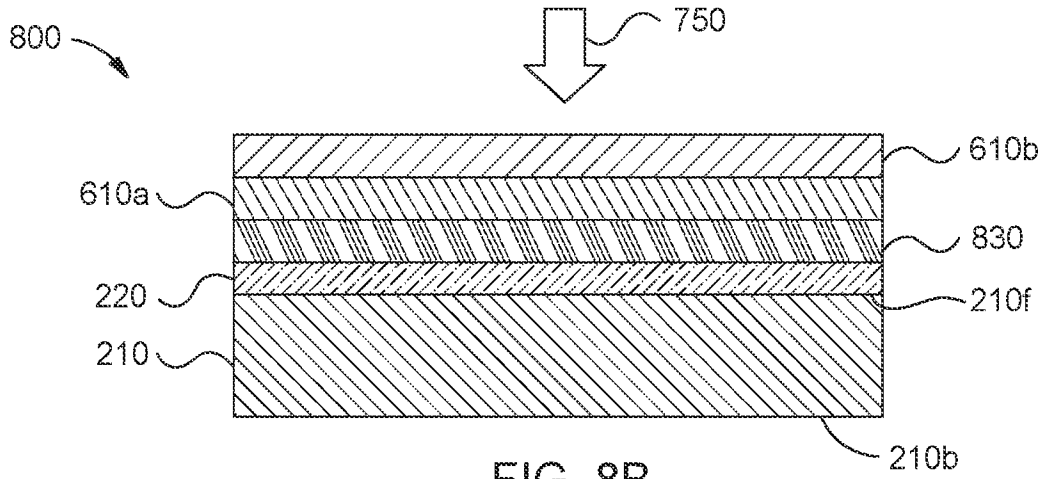


FIG. 8B

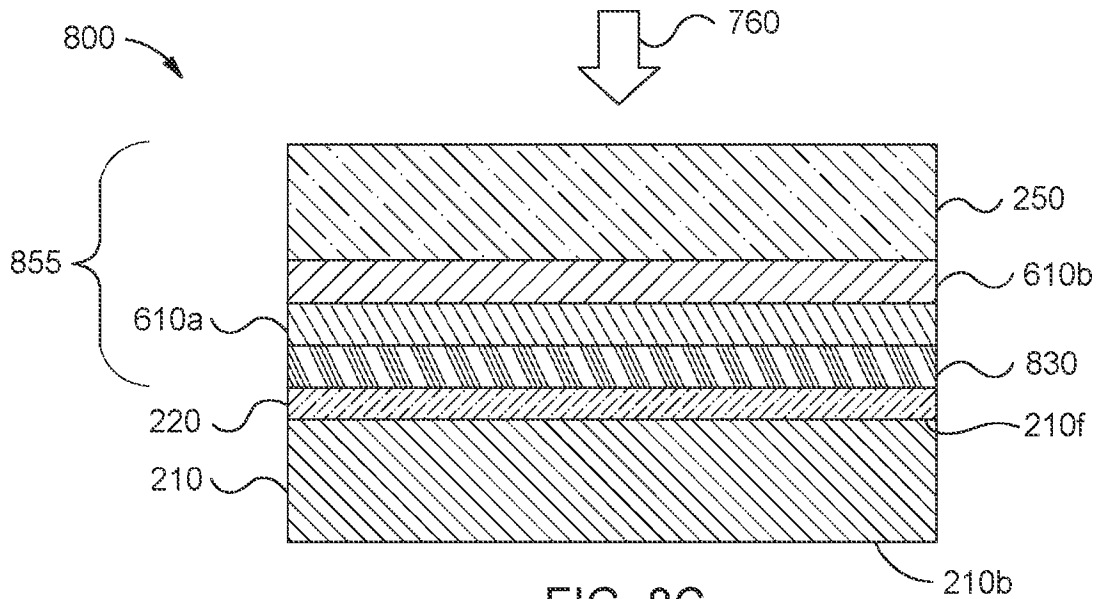


FIG. 8C

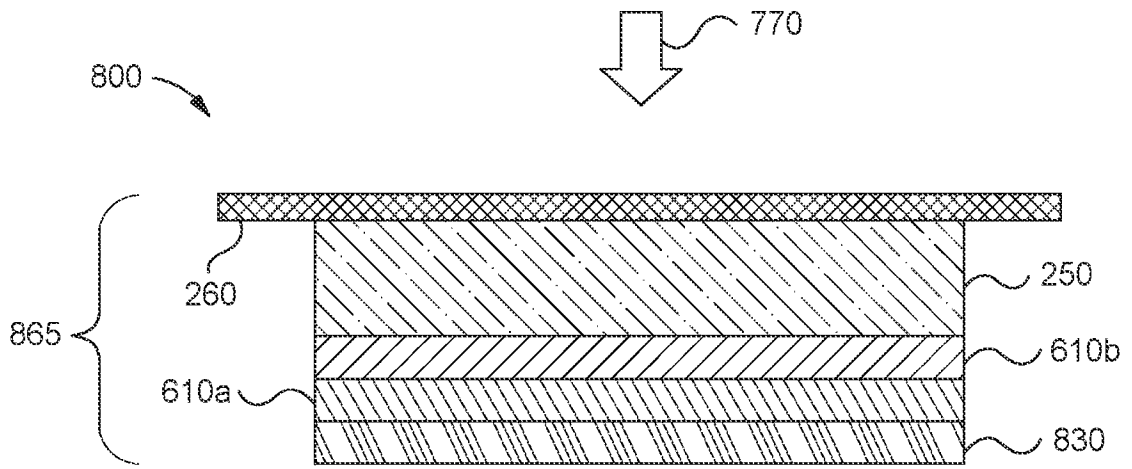


FIG. 8D

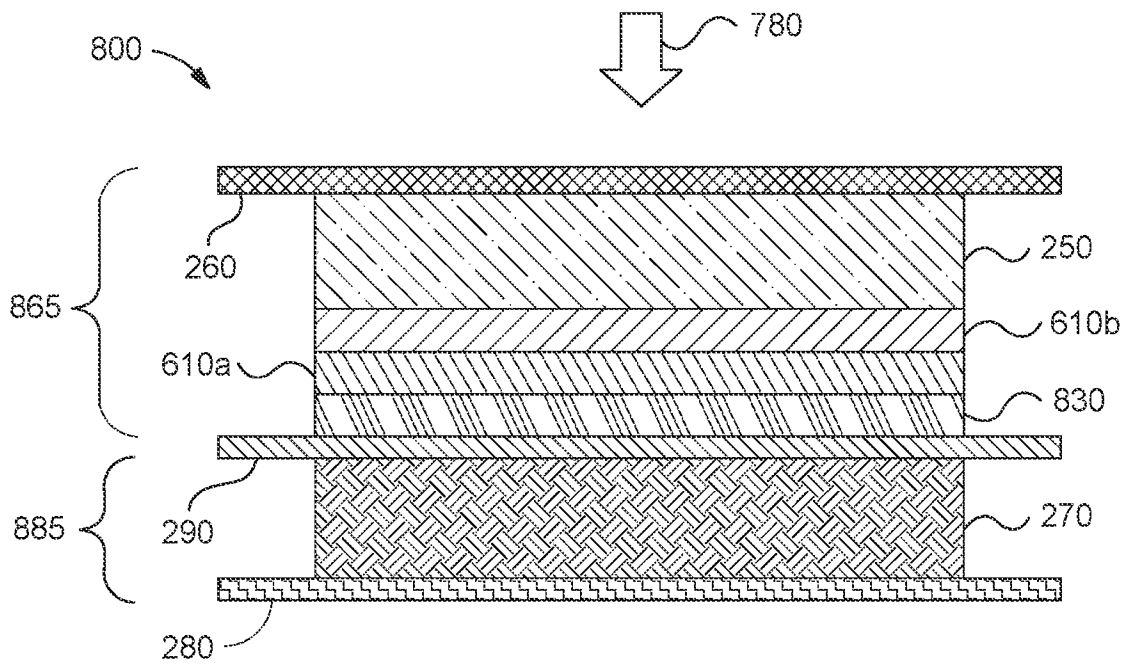


FIG. 8E

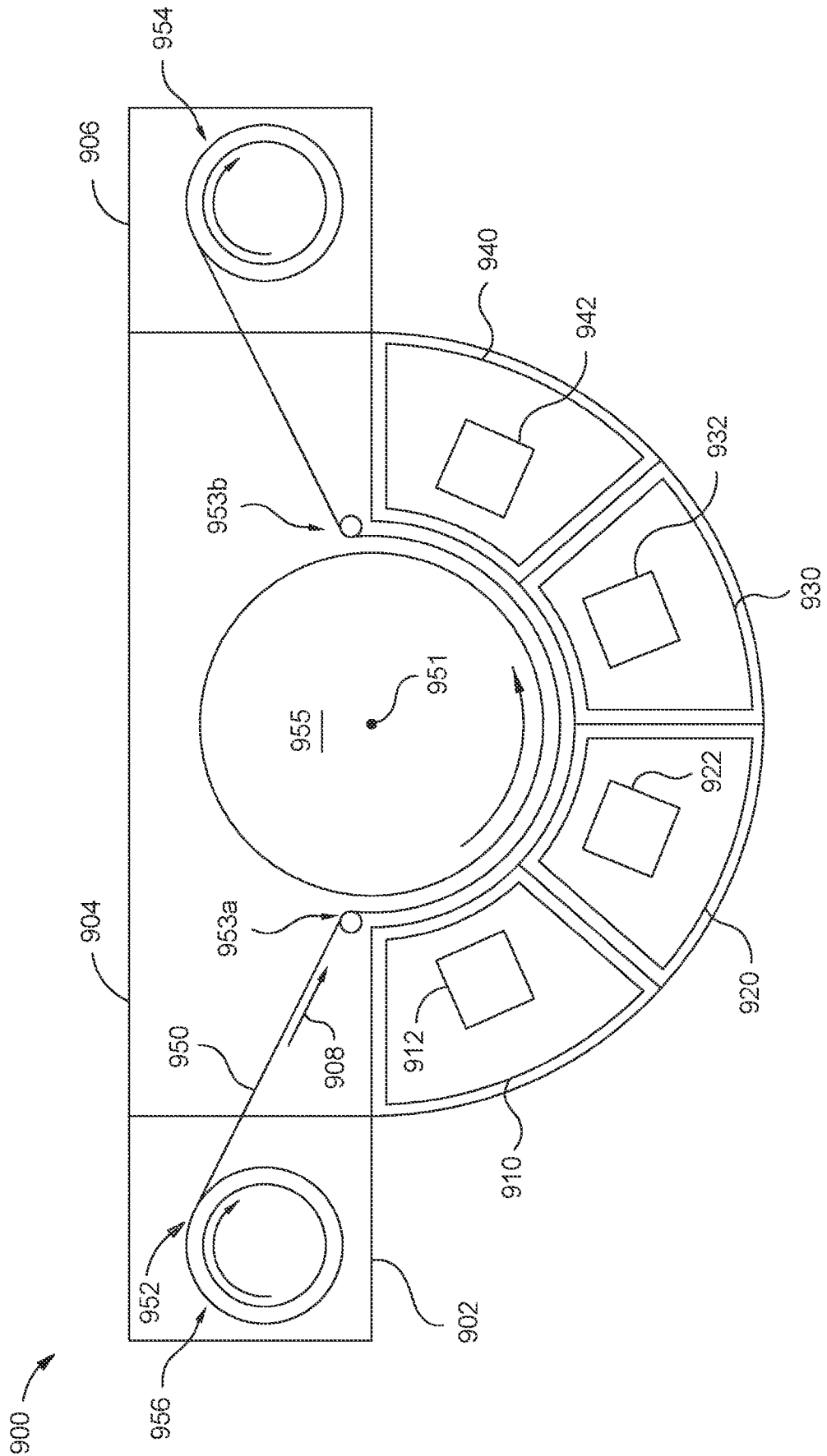


FIG. 9

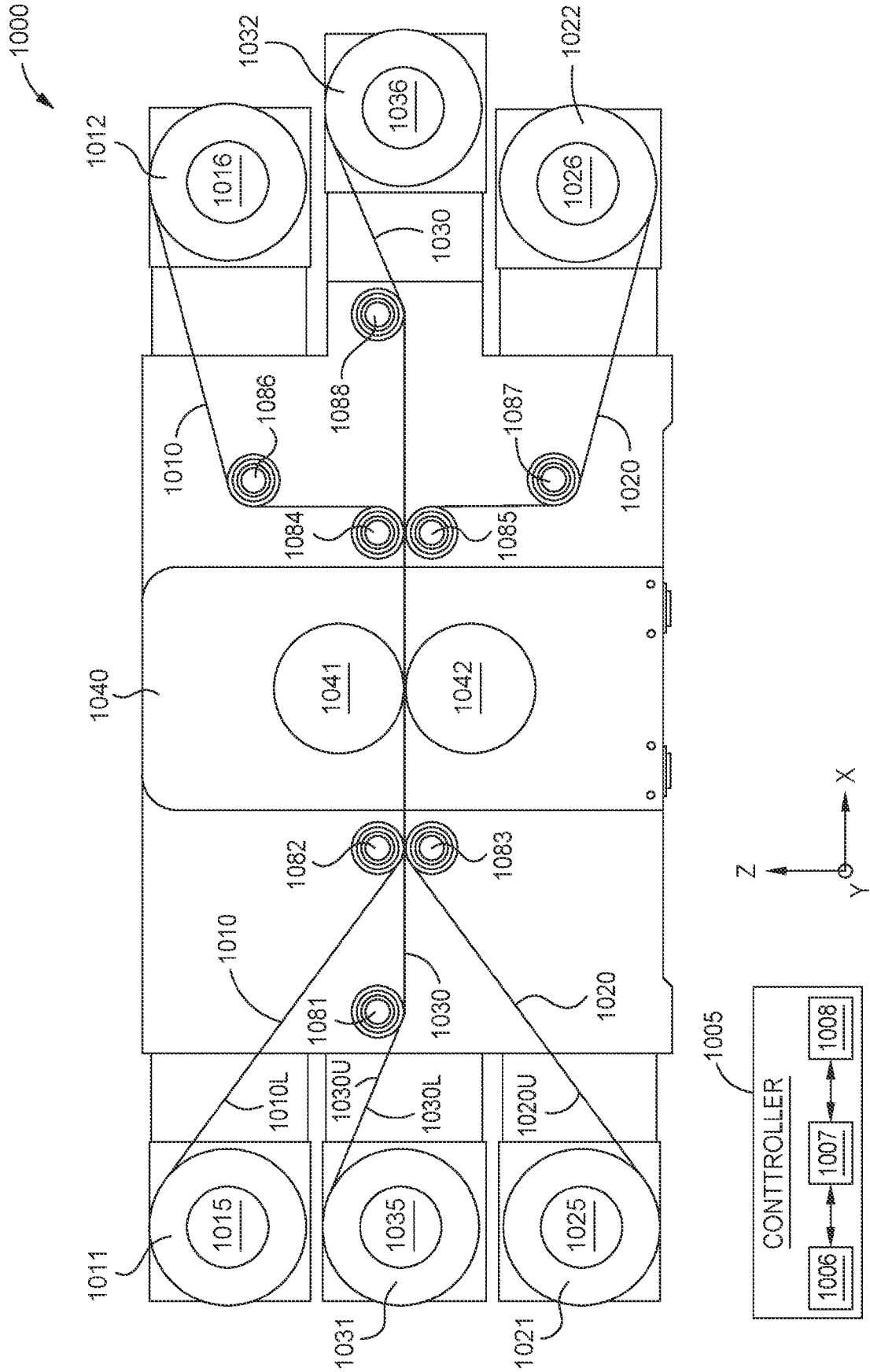


FIG. 10

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/022723

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
<b>H01M 4/139(2010.01)i; H01M 4/04(2006.01)i; H01M 10/42(2006.01)i; H01M 10/0562(2010.01)i; H01M 4/02(2006.01)i</b>		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) H01M 4/139(2010.01); C23C 14/00(2006.01); C23C 14/56(2006.01); H01M 10/052(2010.01); H01M 10/0525(2010.01); H01M 10/42(2006.01); H01M 4/13(2010.01); H01M 4/134(2010.01); H01M 4/36(2006.01); H01M 4/38(2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: battery, lithium, electrolyte layer, release layer, flexible layer, interface layer, alkali metal, film stack, dielectric material		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	WO 2017-054889 A1 (APPLIED MATERIALS, INC.) 06 April 2017 (2017-04-06) paragraphs [0015], [0017], [0030]-[0037], [0041]-[0050], [0055]-[0060], [0079]-[0083]; and figures 1, 3A-4B, 6, 8	1-4,12-15,20  5-11,16-19
Y	KR 10-2020-0089719 A (FUJIFILM CORPORATION) 27 July 2020 (2020-07-27) paragraphs [0079]-[0111], [0113], [0474]-[0476], [0498]-[0506]; and figures 1-3	1-4,12-15,20
Y	KR 10-2020-0087437 A (LG CHEM, LTD.) 21 July 2020 (2020-07-21) paragraphs [0069], [0070], [0072]-[0078], [0083]-[0085], [0087]-[0090], [0092]-[0094]	1-4,12-15,20
A	KR 10-2011-0121690 A (ZEON CORPORATION) 08 November 2011 (2011-11-08) the whole document	1-20
A	WO 2022-158375 A1 (SANYO ELECTRIC CO., LTD.) 28 July 2022 (2022-07-28) the whole document	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “D” document cited by the applicant in the international application “E” earlier application or patent but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family		
Date of the actual completion of the international search <b>17 July 2024</b>		Date of mailing of the international search report <b>18 July 2024</b>
Name and mailing address of the ISA/KR <b>Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea</b> Facsimile No. +82-42-481-8578		Authorized officer <b>HEO, Joo Hyung</b> Telephone No. +82-42-481-5373

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/US2024/022723**

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				KR	10-2018-0063250	A	11 June 2018				
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				JP	6985426	B2	22 December 2021				
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KR	10-2020-0087437	A	21 July 2020	CN	111868974	A	30 October 2020				
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				HU	E062138	T2	28 September 2023				
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WO	2022-158375	A1	28 July 2022	CN	116711098	A	05 September 2023				
				EP	4283702	A1	29 November 2023				
				US	2024-0063377	A1	22 February 2024				
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