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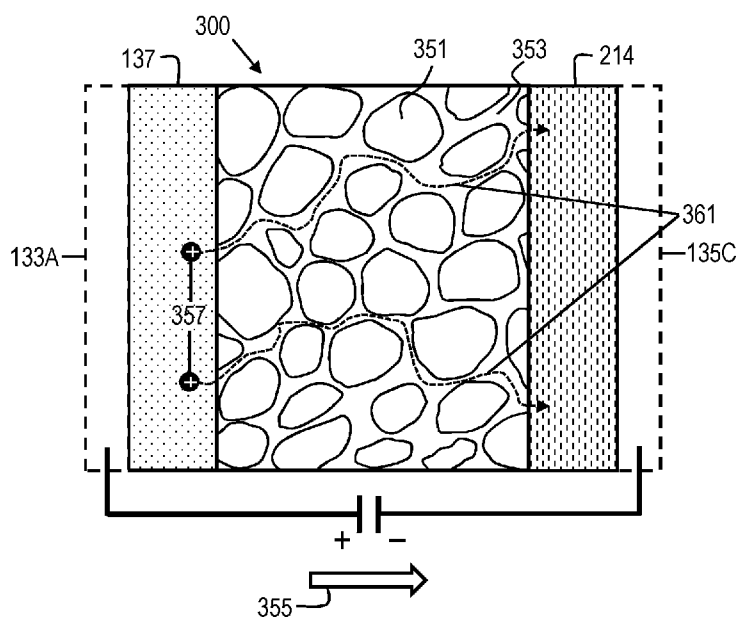


FIG. 3A

(57) Abstract: Disclosed herein are methods for modifying a glass composition, the methods including delivering a molten glass to a ceramic forming body including at least one cavity containing a first electrode and a mobile ion source or a mobile ion sink, contacting the molten glass with a second electrode, and applying an electrical field between the first and second electrodes to create an electrical potential difference sufficient to drive at least one mobile ion into or out of the molten glass through an intergranular glass phase of the ceramic forming body. Ceramic forming bodies including a crystalline phase, an intergranular glass phase, and a cavity containing a first electrode and a mobile ion source or a mobile ion sink are also disclosed. Glass sheets manufactured using the disclosed methods and forming bodies are further disclosed.



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METHODS AND APPARATUSES FOR MODIFYING A GLASS COMPOSITION DURING GLASS MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application Serial No. 62/491,357 filed on April 28, 2017 the contents of which are relied upon and incorporated herein by reference in their entirety as if fully set for the below.

FIELD OF THE DISCLOSURE

[0002] The present disclosure relates generally to methods for modifying a glass composition during a glass forming process and apparatuses for carrying out such methods, and more particularly to methods for doping or depleting a glass composition during a fusion down draw process.

BACKGROUND

[0003] High-performance display devices, such as liquid crystal displays (LCDs) and plasma displays, are commonly used in various electronics, such as cell phones, laptops, electronic tablets, televisions, and computer monitors. Currently marketed display devices can employ one or more high-precision glass sheets, for example, as substrates for electronic circuit components, light guide plates, color filters, or cover glasses, to name a few applications. The leading technology for making such high-quality glass substrates is the fusion draw process, developed by Corning Incorporated, and described, e.g., in U.S. Patent Nos. 3,338,696 and 3,682,609, which are incorporated herein by reference in their entireties.

[0004] The fusion draw process typically utilizes a forming body comprising a trough disposed in an upper portion and a lower portion having a wedge-shaped cross-section with two major forming surfaces sloping downwardly to join at a bottom edge (root). During operation, the trough is filled with molten glass, which is allowed to flow over the trough sides and down along the two forming surfaces as two molten glass streams, which ultimately converge at the root where they fuse together to form a

unitary glass ribbon. The glass ribbon can thus have two pristine external surfaces that have not been exposed to the surface of the forming body. The ribbon can then be drawn down and cooled to form a glass sheet having a desired thickness and a pristine surface quality.

[0005] Consumer demand for high-performance displays with ever growing size and image quality requirements drives the need for improved manufacturing processes for producing large, high-quality, high-precision glass sheets having various compositions. However, the glass manufacturing process is often compositionally limited by the physical properties of the glass composition, for example, the melting point and/or viscosity of the composition. For instance, it may be difficult or impossible to melt and/or fine certain glass compositions with relatively high melting points using currently available methods and equipment. Alternatively, it may be difficult or impossible to down draw some glass compositions with viscosities that are too high or too low. Glasses manufactured using the fusion down draw process may thus be compositionally limited in terms of the ability to remove or add certain components from the batch materials.

[0006] Accordingly, it would be advantageous to provide methods for modifying a glass composition during the glass manufacturing process, e.g., during the fusion down draw process. It would be also advantageous to provide forming bodies for carrying out such methods. Moreover, it would be advantageous to provide glass sheets with modified, e.g., doped or depleted, compositions that may otherwise be difficult or impossible to form using conventional down draw techniques.

SUMMARY

[0007] The disclosure relates to methods for modifying a glass composition, the methods comprising delivering a molten glass to a ceramic forming body comprising at least one cavity containing (i) a first electrode and (ii) a mobile ion source or a mobile ion sink, contacting the molten glass with a second electrode, and applying an electrical field between the first and second electrodes to create an electrical potential difference

across the ceramic forming body, wherein the electrical potential difference is sufficient to drive at least one mobile ion into or out of the molten glass through an intergranular glass phase of the ceramic forming body. The electrical potential difference may, in various embodiments, range from about 0.1 V/cm to about 20 V/cm. The methods can further comprise heating the ceramic forming body to a treatment temperature ranging from about 1000°C to about 1500°C.

[0008] According to various embodiments, the first electrode is an anode and the second electrode is a cathode. In such an exemplary configuration, the recess can contain a mobile ion source comprising at least one dopant mobile ion and the electrical potential can be sufficient to drive the dopant mobile ion out of the mobile ion source and into the molten glass through the intergranular glass phase of the ceramic forming body. The mobile ion source can be chosen from metals, metal alloys, metal oxides, metal salts, glasses, combinations thereof, mixtures thereof, and ceramic composites thereof. In various embodiments, the dopant mobile ion can include at least one of alkali metal ions, alkaline earth metal ions, transition metal ions, rare earth metal ions, and heavy metal ions. According to non-limiting embodiments, the intergranular glass phase and crystalline phase of the ceramic forming body are both substantially free of the at least one dopant mobile ion prior to application of the electric field.

[0009] In additional embodiments, the first electrode is a cathode and the second electrode is an anode. In such a non-limiting configuration, the recess can contain a mobile ion sink for receiving at least one depleted mobile ion and the electrical potential can be sufficient to drive the depleted mobile ion out of the molten glass through the intergranular glass phase of the ceramic forming body and into the mobile ion sink. The mobile ion sink be chosen from porous metal oxides, porous metals, porous glasses, porous ceramics, and combinations thereof. In various embodiments, the depleted mobile ion can include at least one of alkali metal ions, alkaline earth metal ions, and transition metal ions. According to non-limiting embodiments, the intergranular glass phase and crystalline phase of the ceramic forming body are both substantially free of the at least one dopant mobile ion prior to application of the electric field.

[0010] Also disclosed herein are ceramic forming bodies comprising a crystalline phase, an intergranular glass phase, and a cavity containing (i) a first electrode and (ii) a mobile ion source or a mobile ion sink. The cavity may be positioned in an upper trough and/or a lower wedge of the ceramic forming body. According to some embodiments, the cavity can contain at least one anode and at least one mobile ion source. In other embodiments, the cavity can contain at least one cathode and at least one mobile ion sink.

[0011] Further described herein are glass articles, such as glass sheets or ribbons, manufactured using the methods and forming bodies disclosed herein. The glass sheet can comprise a first major surface layer, a second major surface layer, and a central region disposed therebetween, the central region comprising a first concentration of at least one mobile ion that is different from a second concentration of the at least one mobile ion in the first and second major surface layers. In various non-limiting embodiments, a thickness of the central region can range from about 1 μm to about 200 μm , or from about 1% to about 20% of the total thickness of the glass sheet. According to certain embodiments, the at least one mobile ion is chosen from alkali metal ions, alkaline earth metal ions, transition metal ions, rare earth metal ions, and heavy metal ions and the first concentration is greater than the second concentration. In further embodiments, the at least one mobile ion is chosen from alkali metal ions, alkali earth metal ions, and transition metal ions, and the first concentration is less than the second concentration.

[0012] Additional features and advantages of the disclosure will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the methods as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0013] It is to be understood that both the foregoing general description and the following detailed description present various embodiments of the disclosure, and are intended to provide an overview or framework for understanding the nature and

character of the claims. The accompanying drawings are included to provide a further understanding of the disclosure, and are incorporated into and constitute a part of this specification. The drawings illustrate various embodiments of the disclosure and together with the description serve to explain the principles and operations of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The following detailed description can be best understood when read in conjunction with the following drawings, where like structures are indicated with like reference numerals where possible and in which:

[0015] **FIG. 1A** illustrates an exemplary forming body;

[0016] **FIG. 1B** is a cross-sectional view of the forming body of **FIG. 1A**;

[0017] **FIG. 2** illustrates an exemplary glass manufacturing system;

[0018] **FIGS. 3A-B** illustrate the exemplary migration of mobile ions in a ceramic body under an electric potential difference; and

[0019] **FIG. 4** illustrates an exemplary glass sheet comprising a central region with a modified (e.g., depleted or doped) composition.

DETAILED DESCRIPTION

[0020] Disclosed herein are methods for modifying a glass composition, the methods comprising delivering a molten glass to a ceramic forming body comprising at least one cavity containing (i) a first electrode and (ii) a mobile ion source or a mobile ion sink, contacting the molten glass with a second electrode, and applying an electrical field between the first and second electrodes to create an electrical potential difference across the ceramic forming body, wherein the electrical potential difference is sufficient to drive at least one mobile ion into or out of the molten glass through an intergranular glass phase of the ceramic forming body. Ceramic forming bodies comprising a crystalline phase, an intergranular glass phase, and a cavity containing (i) a first electrode and (ii) a mobile ion source or a mobile ion sink are also disclosed. Glass articles, such as glass sheets or ribbons, manufactured using the disclosed methods and forming bodies are further disclosed.

[0021] Embodiments of the disclosure are discussed below with reference to **FIGS. 1A-B** and **FIG. 2**, which depict an exemplary forming body and glass manufacturing system, respectively, and **FIGS. 3A-B** and **FIG. 4**, which depict exemplary mobile ion migration patterns and an exemplary glass ribbon having a modified composition, respectively. The following general description is intended to provide only an overview of the claimed methods and apparatuses. Various aspects will be more specifically discussed throughout the disclosure with reference to the non-limiting embodiments, these embodiments being interchangeable with one another within the context of the disclosure.

[0022] Referring to **FIG. 1A**, during a glass manufacturing process, such as a fusion draw process, molten glass can be introduced into a forming body **100** comprising a trough **103** via an inlet **101**. Once the trough **103** is filled, the molten glass can flow over the sides of the trough and down the two opposing forming surfaces **107** before fusing together at the root **109** to form a glass ribbon **111**. The glass ribbon can then be drawn down in the direction **113** using, e.g., a roller assembly (not shown) and further processed to form a glass sheet. The forming body can further comprise ancillary components such as end caps **105** and/or edge directors **115**.

[0023] **FIG. 1B** provides a cross-sectional view of the forming body of **FIG. 1A**, in which the forming body **100** can comprise an upper trough-shaped portion **117** and a lower wedge-shaped portion **119**. The upper trough-shaped portion **117** can comprise a channel or trough **103** configured to receive the molten glass. The trough **103** can be defined by two trough walls (or weirs) **125a**, **125b** comprising interior surfaces **121a**, **121b**, and a trough bottom **123**. Although the trough is depicted as having a rectangular cross-section, with the interior surfaces forming approximately 90-degree angles with the trough bottom, other trough cross-sections are envisioned, as well as other angles between the interior surfaces and the bottom of the trough. The weirs **125a**, **125b** can further comprise exterior surfaces **127a**, **127b** which, together with the wedge outer surfaces **129a**, **129b**, can make up the two opposing forming surfaces **107**. Molten glass can flow over the weirs **125a**, **125b** and down the forming

surfaces **107** as two glass streams which can then fuse together at the root **109** to form a unitary glass ribbon **111**. The ribbon can then be drawn down in direction **113** and, in some embodiments, further processed to form a glass sheet.

[0024] The forming body **100** may, in non-limiting embodiments, comprise at least one recess or cavity **131**. The cavity can contain at least one first electrode **133**, which can be a cathode or anode, depending on the desired application. For instance, as illustrated in **FIG. 1B**, the first electrode **133** can comprise an anode and the cavity **131** can contain a mobile ion source **137** comprising at least one mobile ion that can be doped into glass in contact with the forming surface, referred to herein as a “dopant” mobile ion (see **FIG. 3A**). Alternatively, the first electrode **133** can comprise a cathode and the recess **131** can contain a mobile ion sink (not illustrated) for receiving at least one mobile ion that can be depleted from glass in contact with the forming surface, referred to herein as a “depleted” mobile ion (see **FIG. 3B**). Of course, while the cavity **131** is depicted in **FIG. 1B** as being located in the lower wedge-shaped portion **119** of the forming body **100**, it is to be understood that the cavity may be positioned in any other location within the forming body, such as in the upper trough-shaped portion **117**, e.g., in one or both of the weirs **125a**, **125b**, or any combination thereof. In certain embodiments, the cavity can comprise one or more cylindrical holes disposed internally along a length of the forming body. Exemplary diameters for such tube(s) can range from about 1 mm to about 10 cm, such as from about 5 mm to about 5 cm, from about 10 mm to about 1 cm, or from about 50 mm to about 0.5 cm, including all ranges and subranges therebetween.

[0025] Additionally, while **FIG. 1B** illustrates the first electrode **133** surrounded or encompassed by the mobile ion source **137**, it is to be understood that any other arrangement is possible and intended to fall within the scope of this disclosure, e.g., the first electrode **133** and mobile ion source **137** (or mobile ion sink) may be located adjacent to one another, such as side by side, or one on top of the other, and so forth. The forming body **100** may also comprise more than one cavity comprising an electrode and a mobile ion source or sink, and each cavity can, in some embodiments, comprise more than one electrode and/or more than one mobile ion source or sink, and so forth

without limitation. In various embodiments, the first electrode **133**, the mobile ion source **137** (or mobile ion sink), and/or the forming body **100** may be in physical contact with one another.

[0026] The forming body **100** can comprise any material suitable for use in a glass manufacturing process, for example, refractory materials such as zircon, zirconia, alumina, magnesium oxide, silicon carbide, silicon nitride, silicon oxynitride, xenotime, monazite, mullite, zeolite, solid solutions thereof, and multi-phase composites thereof. According to various embodiments, the forming body may comprise a unitary piece, e.g., one piece machined from a single source. In other embodiments, the forming body may comprise two or more pieces bonded, fused, attached, or otherwise coupled together, for instance, the trough-shaped portion and wedge-shaped portion may be two separate pieces comprising the same or different materials. The dimensions of the forming body, including the length, trough depth and width, and wedge height and width, to name a few, can vary depending on the desired application. In some embodiments, at least one dimension of the forming body, such as the length, may be greater than 1 meter (m), greater than 1.5 m, greater than 2 m, or even greater than 2.5 m. It is within the ability of one skilled in the art to select these dimensions as appropriate for a particular manufacturing process or system.

[0027] **FIG. 2** depicts an exemplary glass manufacturing system **200** for producing a glass ribbon **111**. The glass manufacturing system **200** can include a melting vessel **210**, a fining vessel (e.g., finer tube) **220**, a first connecting tube **216** connecting the melting and fining vessel, a mixing vessel **224**, and a second connecting tube **222** (with a level probe stand pipe **218** extending therefrom) connecting the fining and mixing vessels, a delivery vessel **228**, a third connecting tube **226** connecting the mixing and delivery vessels, a downcomer **232**, and a fusion draw machine (FDM) **230**, which can include an inlet pipe **234**, a forming body **100**, and a pull roll assembly **236**.

[0028] Glass batch materials can be introduced into the melting vessel **210**, as shown by arrow **212**, to form molten glass **214**. The melting vessel **210** can comprise, in some embodiments, one or more walls constructed from refractory ceramic

bricks, e.g., fused zirconia bricks. The fining vessel **220** is connected to the melting vessel **210** by the first connecting tube **216**. The fining vessel **220** comprises a high temperature processing area that receives the molten glass from the melting vessel **210** and which can remove bubbles from the molten glass. The fining vessel **220** is connected to the mixing vessel **224** by the second connecting tube **222**. The mixing vessel **224** is connected to the delivery vessel **228** by the third connecting tube **226**. The delivery vessel **228** can deliver the molten glass through the downcomer **232** into the FDM **230**.

[0029] As described *supra*, the FDM **230** can include an inlet pipe **234**, a forming body **100**, and a pull roll assembly **236**. The inlet pipe **234** receives the molten glass from the downcomer **232**, from which the molten glass can flow to the forming body **100**. The forming body **100** can include an inlet **101** that receives the molten glass, which can then flow into the trough **103**, overflowing over the sides of the trough **103**, and running down the two opposing forming surfaces **107** before fusing together at the root **109** to form a glass ribbon **111**. In certain embodiments, the forming body **100** can comprise a refractory ceramic, e.g., zircon or alumina ceramic. The pull roll assembly **236** can transport the drawn glass ribbon **111** for further processing by additional optional apparatuses.

[0030] For example, a traveling anvil machine (TAM), which can include a scoring device for scoring the glass ribbon, such as a mechanical or laser scoring device, may be used to separate the ribbon **111** into individual sheets, which can be machined, polished, chemically strengthened, and/or otherwise surface treated, e.g., etched, using various methods and devices known in the art. Of course, while the apparatuses and methods disclosed herein are discussed with reference to fusion draw processes and systems, it is to be understood that such apparatuses and methods can also be used in conjunction with other glass forming processes, such as slot-draw and float processes, to name a few.

[0031] **FIGS. 3A-B** are schematics illustrating the exemplary migration of mobile ions through a ceramic forming body **300** under a potential gradient. The ceramic forming body **300** can include a crystalline phase **351** and a glass phase **353**.

The crystalline phase **351** may include one or more ceramic grains. The crystalline phase **351** may, in some embodiments, include a crystalline matrix or lattice having a periodic arrangement. The glass phase **353** may be amorphous, e.g., a non-periodic structure. The glass phase **353** can exhibit higher mobility or diffusivity of its constituents at elevated temperatures as compared to the crystalline phase **351**.

[0032] The glass phase **353** may be an intergranular glass phase surrounding one or more grains in the crystalline phase **351**. The glass phase **353** may thus be present in one or more grain boundary regions between adjacent grains of the crystalline phase **351**. In certain non-limiting embodiments, the glass phase **353** can comprise a silicate glass which may include silica and one or more oxides of alkali metals (e.g., Li, Na, K), alkaline earth metals (e.g., Ba, Ca, Mg, Sr), transition metals (e.g., Ag, Au, Cu, Cr, Fe, Mn, Sn, Ti), rare earth metals (e.g., Ce, La, Nd, Y), and heavy metals (e.g., Ta, W, Mo, V, Nb).

[0033] As used herein, the term “mobile ions” is used to refer to cations and anions that are mobile under a potential gradient, such as concentration gradient, a chemical potential gradient, or an electrical potential gradient. Exemplary cations that are mobile in glass under an electrical potential gradient include, but are not limited to, ions of alkali metals (e.g., Li, Na, K), ions of alkaline earth metals (e.g., Ba, Ca, Mg, Sr), ions of transition metals (e.g., Ag, Au, Cu, Cr, Fe, Mn, Sn, Ti), ions of rare earth metals (e.g., Ce, La, Nd, Y), and ions of heavy metals (e.g., Ta, W, Mo, V, Nb). Exemplary mobile anions include, but are not limited to, halides (e.g., Br, Cl, F), selenides, and sulfides. Of course, other mobile ions can migrate into or out of the molten glass and the mobile ions may exist in various oxidation states.

[0034] The glass phase **353** may have a melting temperature and/or a viscosity lower than that of the overall ceramic composition. For instance, the melting temperature of a glass phase **353** may be less than the melting temperature of the overall ceramic by several tens or even hundreds of degrees. As such, mass transport of mobile ions to or from the molten glass in contact with the forming body may be carried out via the glass phase **353** at temperatures that may not produce a noticeable

physical change in the crystalline phase **351**. For instance, dopant mobile ions from a mobile ion source located within the ceramic forming body **300** may be transported through the intergranular glass phase **353** to the molten glass **214** (see **FIG. 3A**), thus producing zones in the glass sheet that are enriched in the mobile ion(s) during the draw process. In other embodiments, mobile ions from the molten glass **214** may be transported through the glass phase **353** to a mobile ion sink located within the ceramic forming body **300** (see **FIG. 3B**), thus producing zones in the glass sheet that are depleted of the mobile ion(s) during the draw process.

[0035] Application of a potential gradient may provide, in some instances, sufficient energy for the phase decomposition of the ceramic body into its constituents. For instance, “electrolysis” is used herein to refer to an electrical potential gradient-related, electric energy-assisted phase decomposition of the ceramic material. When the energy locally provided by the electric field remains below the electrolysis threshold, e.g., less than the energy of formation of the ceramic material, the migration of ions in the ceramic material does not induce phase decomposition and leads only to a spatial redistribution of the mobile ions. A stronger local electric field may exceed the electrolysis threshold, and the local energy coupled to the potential gradient may be equal to or greater than the formation energy of a crystalline phase and may thus lead to the decomposition of that phase in the ceramic material. While the above criterion may describe a thermodynamic bulk balance, the decomposition onset of the material may be delayed due to a need of additional energy for nucleation, interface formation, and overcoming strain energies, such that higher electric field strength can be tolerated. The electric field strength and resulting current densities may thus have any suitable value below the electrolysis threshold of the ceramic material.

[0036] In the ceramic body, mobile ions may migrate under the applied electrical potential gradient towards a negative or positive potential. Different migration mechanisms can be activated, such as exchanges with point defects such as vacancies or interstitials in ordered crystalline solids or density and/or fluctuation perturbations that allow migration of more loosely bonded atoms in glassy structures. In the case of a potential gradient produced by an electric field, based on charge considerations, cations

may migrate toward an area of negative potential while anions may migrate toward an area of positive potential. Ion migration may be coupled by charge interactions and may be driven by a generalized electrochemical potential gradient. For instance, ion migration may increase with electric field strength and/or the concentration difference of the mobile ion between the mobile ion source and the molten glass during the draw process.

[0037] For example, mobile cations may be driven by a potential gradient to migrate from a positive potential to a negative potential (e.g., from anode **133A** to cathode **135C**) through the ceramic forming body **300** in the direction illustrated by the arrow **355** in **FIG. 3A**. Alternatively, mobile cations may migrate from anode **135A** to cathode **133C** through the ceramic forming body **300** in the direction illustrated by the arrow **355'** in **FIG. 3B**. Migration of mobile ions under an applied potential gradient may occur at different migration rates due to different mobilities and/or different concentrations of the individual ion species. In addition, each ion species may undergo a variety of individual coupling conditions during migration under the potential gradient that can modify the resulting effective mobility. In some embodiments, these migration rates may be used to customize or tailor the doping and/or depletion of the molten glass of mobile ion(s). Exemplary mobile ion migration rates can range from about 0.1 mm/hr to about 2 mm/hr, such as from about 0.2 mm/hr to about 1.5 mm/hr, from about 0.3 mm/hr to about 1 mm/hr, or from about 0.5 mm/hr to about 0.8 mm/hr, including all ranges and subranges therebetween.

[0038] As illustrated in **FIG. 3A**, the ceramic forming body **300** may comprise at least one cavity (not illustrated) containing a first electrode, e.g., anode **133A**, and a mobile ion source **137** comprising at least one dopant mobile ion **357**. A second electrode, e.g., cathode **135C**, may be in contact with the molten glass **214**. The dopant mobile ion(s) **357** may travel from the mobile ion source **137** through the intergranular glass phase **351** via exemplary paths **361** and into the molten glass **214** in contact with the ceramic forming body **300**. The anode **133A** and cathode **135C** may be in an operational arrangement configured to apply an electric field having a predetermined

magnitude across the ceramic forming body **300**. For example, the two electrodes **133A**, **135C** may be operably coupled to a voltage supply via lead wires. The electric field may be applied for variable time periods depending, e.g., on the other treatment parameters, such as treatment temperature, until the dopant mobile ions **357** migrate into the molten glass **214** to the desired concentration level. In some embodiments, as shown in **FIG. 3B**, the electrodes can be switched (e.g., anode **135A** and cathode **133C**) to drive mobile ions out of the molten glass **214**, through the intergranular glass phase **351** via exemplary paths **361'**, and into the mobile ion sink **139** located within a cavity of the ceramic forming body **300** as shown in **FIG. 3B**.

[0039] The cathode **133C**, **135C** and the anode **133A**, **135A** may include one or more metals including, but not limited to, platinum (Pt), nickel (Ni), or tungsten (W). In other embodiments, the cathode and anode may include carbon (C). In further embodiments, the cathode and anode may comprise electrically conducting ceramics, such as La-chromite, Sn-oxide, Ni-lanthanate, TaO_x, NbO_x, or WO_x, alone or in combination with the metallic conductors. In yet further embodiments, the cathode **133C**, **135C** and the anode **133A**, **135A** can comprise electrically conductive carbon, e.g., graphite, carbon nanotubes, or graphene, alone or in combination with the electrically conducting ceramics or the metallic conductors.

[0040] A mobile ion source **137** can be located in the cavity of the forming body and in contact with the first electrode **133** also contained in the cavity. The mobile ion source **137** can exchange material with the electrode, supply mobile ions, and support the flow of mobile ions through the intergranular glass of the forming body into the molten glass during the draw, thus changing the local composition of the glass in contact with the forming body, e.g., enriching the glass with at least one dopant mobile ion. The mobile ion source **137** can comprise any material having a sufficient concentration of at least one dopant mobile ion **357**. For instance, the mobile ion source may comprise a metal, metal alloy, metal oxide, metal salt, glass, combinations thereof, mixtures thereof, and ceramic composites thereof, such as mixtures of zirconia and metal oxide. Quantum dots comprising mobile cations or anions may also be

incorporated as the mobile ion source **137** or can be combined with other sources listed herein.

[0041] In non-limiting embodiments, the mobile ion source **137** can comprise from about 100 ppm to about 100% by weight of at least one dopant mobile ion, such as from about 1% to about 80%, from about 5% to about 60%, from about 10% to about 50%, or from about 20% to about 40% by weight of the dopant mobile ion. According to various embodiments, the at least one dopant mobile ion **357** may not be present in the ceramic forming body **300** and/or the anode **133A** prior to application of the electrical field. In other embodiments, the forming body and/or anode may comprise trace amounts of the dopant mobile ion, but such ions may not be present in amounts sufficient to effect a significant compositional change in the molten glass **214**. For instance, a ceramic composition comprising one or more tramp or trace impurities of a mobile ion (e.g., less than 100 ppm) may not provide a sufficient amount of mobile ions for use as a mobile ion source **137** in accordance with the disclosure. In additional embodiments, the first electrode (e.g., anode **133A**) may not be the source for dopant mobile ions **357**.

[0042] According to certain embodiments, the ceramic forming body **300** may comprise a hollow body having a recess or cavity filled by the anode **133A** and the mobile ion source **137**. For instance, the forming body can comprise a core, e.g., a copper core (providing Cu dopant mobile ions) or a molybdenum oxide core (providing Mo dopant mobile ions), metal salt core, glass core, and so forth without limitation. In non-limiting embodiments, the mobile ion source **137** can be replenished during operation to maintain a sufficient concentration of mobile ions. For instance, the mobile ion source **137** can be replenished manually or automatically on a scheduled, regular, or semi-regular basis. Replenishment of the mobile ion source **137** may be carried out by injecting material into the cavity during operation of the forming body, e.g., at elevated operation temperatures.

[0043] The mobile ion sink **139** can comprise any material having a sufficient capacity for accepting at least one depleted mobile ion **359** from the molten glass during

operation of the forming body. For instance, the mobile ion sink may comprise porous materials, such as a porous metal oxide, porous metal, porous glass, porous ceramic, or combinations thereof. Exemplary porous materials may have a porosity of at least about 30%, such as ranging from about 40% to about 90%, from about 50% to about 80%, or from about 60% to about 70%, including all ranges and subranges therebetween. The pores (e.g., ultramicropores, micropores, mesopores, etc.) of such materials may be filled with air or other mixtures of gases, such as gas mixtures comprising oxygen. According to various embodiments, the at least one depleted mobile ion may not be present in the ceramic forming body **300** and/or the cathode **133C** prior to application of the electrical field. In additional embodiments, the first electrode (e.g., cathode **133C**) may not serve as the sink for depleted mobile ions **359**. According to certain embodiments, the ceramic forming body **300** may comprise a hollow body having a recess or cavity filled by the cathode **133C** and the mobile ion sink **139**. In non-limiting embodiments, the mobile ion sink **139** can be regenerated during operation to maintain a sufficient capacity for accepting depleted mobile ions from the molten glass. For instance, the mobile ion sink **139** can be regenerated manually or automatically on a scheduled, regular, or semi-regular basis.

[0044] An electric potential can be applied across the ceramic body using any method known in the art. For instance, a direct current can be applied to electrodes on opposing sides of the ceramic body to produce a potential difference across the ceramic body of at least about 0.1 V (per cm of sample thickness). In certain embodiments, the electric potential can range from about 0.1 V to about 20 V, such as from about 0.5 V to about 15 V, from about 1 V to about 12 V, from about 2 V to about 11 V, from about 3 V to about 10 V, from about 4 V to about 9 V, from about 5 V to about 8 V, or from about 6 V to about 7 V (per cm of sample thickness), including all ranges and subranges therebetween.

[0045] According to non-limiting embodiments, the ceramic forming body may be heated during application of the electric potential, for instance, the ceramic forming body may be heated to temperatures greater than or equal to about 1000°C. The treatment temperature can range, in some embodiments, from about 1000°C to about

1500°C, such as from about 1100°C to about 1400°C, or from about 1200°C to about 1300°C, including all ranges and subranges therebetween. The duration of treatment can vary depending, e.g., on the applied voltage and temperature, but can range, in various non-limiting embodiments, from about 1 hour to about 1000 hours or greater, such as from about 10 hours to about 500 hours, from about 20 hours to about 360 hours, from about 30 hours to about 240 hours, from about 40 hours to about 120 hours, from about 50 hours to about 80 hours, or from about 60 hours to about 70 hours, including all ranges and subranges therebetween.

[0046] The methods and forming bodies disclosed herein may be used to manufacture glass ribbons having various compositional modifications that can be further processed to produce glass sheets having a number of mechanical, physical, and/or optical properties. As shown in **FIG. 4**, a glass sheet **400** produced according to the instant disclosure can comprise first and second major surface layers **470**, **472**, and a central region or layer **474** disposed therebetween. The central region **474** of glass sheet **400** can comprise the molten glass that was in contact with the ceramic forming body (e.g., forming surfaces **107** in **FIG. 1A**) during the down draw process, whereas the surface layers **470**, **472** can comprise the pristine surfaces that did not come into contact with the ceramic forming body. The two separate glass streams flowing down the forming surfaces of the forming body can fuse together (e.g., at the root **109** in **FIG. 1A**) to form a unitary ribbon, which can then be processed to form glass sheet **400**. The fusion point is represented by the dashed centerline in **FIG. 4**.

[0047] The central region **474**, which comprises the glass that came into contact with the forming body, can thus have a composition that is different from the surface layers **470**, **472**, which did not contact the forming body. For instance, a concentration of at least one mobile ion in the central region **474** may be higher or lower than the concentration of the mobile ion in the surface layers **470**, **472**. If the glass composition is doped with one or more mobile ions, the central region **474** can have a mobile ion concentration that is higher than that of the surface layers **470**, **472**. In some embodiments, a doped concentration gradient may exist within the central region **474**,

e.g., the dopant mobile ion may be more concentrated in the middle of the central region **474** as compared to portions adjacent to the surface layers **470**, **472**. If the glass composition is depleted of one or more mobile ions, the surface layers **470**, **472** can have a mobile ion concentration that is higher than that of the central region **474**. A depleted concentration gradient may similarly exist within the central region **474**, e.g., the depleted mobile ion may be less concentrated in the middle of the central region **474** as compared to portions adjacent to the surface layers **470**, **472**.

[0048] A thickness t_c of the central region can vary depending on the degree of mobile ion migration into or out of the molten glass during the down draw process. The central region can be defined as the portion of the glass sheet having a compositional makeup that is different from the surface layers and, as such, the thickness t_c of the central region can depend on the depth or degree to which mobile ions penetrate into the molten glass (doping) or are removed from the molten glass (depletion). In certain embodiments, the thickness t_c can range from about 1 μm to about 200 μm , such as from about 5 μm to about 100 μm , from about 10 μm to about 50 μm , from about 15 μm to about 40 μm , or from about 20 μm to about 30 μm , including all ranges and subranges therebetween. According to non-limiting embodiments, the thickness t_c of the central region can comprise from about 1% to about 20% of the total thickness T of the glass sheet, such as from about 2% to about 15%, from about 3% to about 10%, from about 4% to about 9%, from about 5% to about 8%, or from about 6% to about 7%, including all ranges and subranges therebetween.

[0049] Glass compositions that can be processed according to the methods disclosed herein can include both alkali-containing and alkali-free glasses. Non-limiting examples of such glass compositions can include, for instance, soda lime silicate, aluminosilicate, alkali-aluminosilicate, alkaline earth-aluminosilicate, borosilicate, alkali-borosilicate, alkaline earth-borosilicate, aluminoborosilicate, alkali-aluminoborosilicate, and alkaline earth-aluminoborosilicate glasses. According to various embodiments, the methods disclosed herein can be used to produce glass sheets, such as high performance display substrates or other glass substrates for use in various applications (e.g., architectural, automotive, and energy applications). Exemplary commercial

glasses include, but are not limited to, EAGLE XG[®], Lotus[™], Willow[®], Iris[™], and Gorilla[®] glasses from Corning Incorporated.

[0050] Doping may be useful for introducing one or more glass-compatible or glass-incompatible ions into the glass composition to alter the physical properties of the resulting glass sheet, e.g., to change the mechanical and/or optical properties of the glass. For instance, the central region may be modified by doping to provide a multi-layer glass sheet having alternating layers with varying mechanical and/or optical properties. Doping may also be used to introduce mobile ions that would otherwise increase the melting temperature and/or draw temperature of the glass composition (e.g., Ba, Sr, Ca, etc.). For example, while it may not be possible to melt and/or draw an initial glass composition comprising the desired dopant concentration, it may be possible to increase the concentration of such dopant ions during drawing to produce a modified glass composition.

[0051] As used herein, “glass-compatible” ions refer to mobile ions that do not result in demixing when added to the molten glass. Exemplary glass-compatible ions include ions capable of forming amorphous oxides (e.g., alkali, alkaline earth, transition, and rare earth metal ions). Glass-compatible ions can also include ions that easily crystallize, e.g., forming crystalline precipitates during draw, cool down, or optional annealing of the glass ribbon. A glass composition doped with such crystallizing ions may result in a glass sheet comprising a crystalline or semi-crystalline central region, e.g., a glass-ceramic core, with amorphous glass surface layers. The at least one dopant mobile ion may also be introduced into the central region to form magnetic nanoprecipitates. For instance, introduction of sufficient levels of iron can result in the formation of magnetite-type magnetic nanoprecipitates in the central region.

[0052] “Glass-incompatible” ions can also be doped into the glass composition, these ions resulting in demixing of the central region of the glass sheet. Exemplary glass-incompatible ions may include, but are not limited to, nucleation agents, such as cerium, rare earth, silver, copper, titanium, and zirconium ions. Doping may also be used to add anions, such as halides, selenides, or sulfides to the molten

glass, which can also serve as nucleation agents under some conditions. The resulting multi-layer glass sheet can comprise two glass surface layers with a central region or core comprising a demixed layer of glass and dopant. In some instances, a glass composition doped with metal ions, such as silver or copper, can be annealed after the down draw process such that metal in the central region migrates to the surface layers.

[0053] Depleting the molten glass of one or more mobile ions may also be useful for altering the physical properties of a glass composition, e.g., modifying the viscosity and/or mechanical properties of the glass. For instance, an alkali-rich glass composition may be depleted of alkali mobile ions during the draw process to produce a multi-layer glass sheet having alkali-rich surface layers and a central region depleted of alkali ions. Such a glass sheet can have improved mechanical strength similar to that obtained via ion exchange processes, but without the extra ion exchange step. Extraction of mobile ions from a molten glass composition may also be used to alter the viscosity of the composition. For example, it may not possible to draw silica-rich glass compositions using traditional methods due to excessive viscosity. However, a glass composition that can be drawn into a glass ribbon can be depleted of mobile ions during the draw process to produce a high viscosity silica-rich glass sheet.

[0054] According to various embodiments, the central region **474** can comprise a first concentration of at least one mobile ion that is higher than a second concentration of the at least one mobile ion in the first and second surface layers **470**, **472**. Exemplary mobile ions that may be doped into the central region **474** of the glass sheet **400** can include, but are not limited to, ions of alkali metals (e.g., Li, Na, K), ions of alkaline earth metals (e.g., Ba, Ca, Mg, Sr), ions of transition metals (e.g., Ag, Au, Cu, Cr, Fe, Mn, Sn, Ti), ions of rare earth metals (e.g., Ce, La, Nd, Y), ions of heavy metals (e.g., Ta, W, Mo, V, Nb), halides, selenides, and sulfides. By way of non-limiting example, the first mobile ion concentration may be at least about 0.0001% higher than the second mobile ion concentration, such as ranging from about 0.001% to about 10%, from about 0.01% to about 5%, from about 0.1% to about 2%, or from about 0.5% to about 1% higher, including all ranges and subranges therebetween.

[0055] In other non-limiting embodiments, the central region **474** can comprise a first concentration of at least one mobile ion that is lower than a second concentration of the at least one mobile ion in the first and second surface layers **470**, **472**. Exemplary mobile ions that may be depleted from the central region can include, but are not limited to, ions of alkali metals (e.g., Li, Na, K) ions of alkaline earth metals (e.g., Ba, Ca, Mg, Sr), ions of transition metals (e.g., Ag, Au, Cu, Cr, Fe, Mn, Sn, Ti), or any other mobile cation present in the molten glass. For instance, the first mobile ion concentration may be at least about 0.0001% lower than the second mobile ion concentration, such as ranging from about 0.001% to about 10%, from about 0.01% to about 5%, from about 0.1% to about 2%, or from about 0.5% to about 1% lower, including all ranges and subranges therebetween. In some embodiments, one or more mobile cations may be depleted from the central region **474** such that the central region is enriched in silica as compared to the surface layers **470**, **472**. For example, a first silica concentration in the central region may be at least about 0.0001% higher than a second silica concentration in the surface layers, such as ranging from about 0.001% to about 10%, from about 0.01% to about 5%, from about 0.1% to about 2%, or from about 0.5% to about 1% higher, including all ranges and subranges therebetween.

[0056] The methods and apparatuses disclosed herein may provide one or more advantages over prior art draw methods. For example, it may be possible to produce glass ribbons and sheets from glass compositions that are not otherwise capable of processing via conventional draw techniques (e.g., high or low viscosity compositions and/or high melting point compositions). It may furthermore be possible to effect changes in a glass sheet without carrying out multi-step processing. For instance, a glass sheet may be mechanically strengthened during the draw process instead of carrying out a subsequent chemical or thermal strengthening step. Additionally, glass sheets having novel multi-layer structures can be produced, such as glass sheets having a ferromagnetic nanostructured core layer. Such multi-layer glass sheets, including sheets comprising a glass ceramic core with amorphous glass

cladding layers can also be produced via a single-step, single-draw process, as compared to other complex multi-step or multi-draw processes.

[0057] Multi-layer structures having layers with one or more different physical, chemical, and/or optical properties can also be produced without a lamination step, which may improve the mechanical stability of the resulting glass article. For instance, a glass sheet as disclosed herein can comprise a central layer and surface layers that are integrally fused together, e.g., during the draw process, as opposed to separately formed layers that are subsequently laminated or otherwise bonded together by conventional techniques. The multi-layer glass sheets disclosed may thus comprise a unitary sheet having different regions of mobile ion concentration, rather than a composite sheet comprising separately bonded layers. The integral fusion of layers together may provide a multi-layer glass structure with enhanced mechanical strength as compared to a laminated structure that can be separated under mechanical stress.

[0058] It will be appreciated that the various disclosed embodiments may involve particular features, elements or steps that are described in connection with that particular embodiment. It will also be appreciated that a particular feature, element or step, although described in relation to one particular embodiment, may be interchanged or combined with alternate embodiments in various non-illustrated combinations or permutations.

[0059] It is also to be understood that, as used herein the terms “the,” “a,” or “an,” mean “at least one,” and should not be limited to “only one” unless explicitly indicated to the contrary. Thus, for example, reference to “a component” includes examples having two or more such components unless the context clearly indicates otherwise.

[0060] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, examples include from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further

understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0061] The terms “substantial,” “substantially,” and variations thereof as used herein are intended to note that a described feature is equal or approximately equal to a value or description. Moreover, “substantially similar” is intended to denote that two values are equal or approximately equal. In some embodiments, “substantially similar” may denote values within about 10% of each other, such as within about 5% of each other, or within about 2% of each other.

[0062] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that any particular order be inferred.

[0063] While various features, elements or steps of particular embodiments may be disclosed using the transitional phrase “comprising,” it is to be understood that alternative embodiments, including those that may be described using the transitional phrases “consisting” or “consisting essentially of,” are implied. Thus, for example, implied alternative embodiments to a method that comprises A+B+C include embodiments where a method consists of A+B+C and embodiments where a method consists essentially of A+B+C.

[0064] It will be apparent to those skilled in the art that various modifications and variations can be made to the present disclosure without departing from the spirit and scope of the disclosure. Since modifications combinations, sub-combinations and variations of the disclosed embodiments incorporating the spirit and substance of the disclosure may occur to persons skilled in the art, the disclosure should be construed to include everything within the scope of the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. A method for modifying a glass composition, the method comprising:
delivering a molten glass to a ceramic forming body, the ceramic forming body comprising a recess containing (i) a first electrode and (ii) a mobile ion source or a mobile ion sink;
contacting the molten glass with a second electrode; and
applying an electrical field between the first and second electrodes to create an electrical potential difference across the ceramic forming body sufficient to drive at least one mobile ion into or out of the molten glass through an intergranular glass phase of the ceramic forming body.
2. The method of claim 1, wherein the first electrode is an anode and the second electrode is a cathode.
3. The method of claim 2, wherein the recess contains a mobile ion source comprising at least one dopant mobile ion, and the electrical potential difference is sufficient to drive the at least one dopant mobile ion from the mobile ion source through the intergranular glass phase and into the molten glass.
4. The method of claim 3, wherein the at least one mobile ion source is chosen from the group consisting of metals, metal alloys, metal oxides, metal salts, glasses, combinations thereof, mixtures thereof, and ceramic composites thereof.
5. The method of claim 3, wherein the at least one dopant mobile ion is chosen from the group consisting of alkali metal ions, alkaline earth metal ions, transition metal ions, rare earth metal ions, and heavy metal ions.

6. The method of claim 3, wherein the intergranular glass phase and a crystalline phase of the ceramic forming body are both substantially free of the at least one dopant mobile ion prior to application of the electric field.
7. The method of claim 1, wherein the first electrode is a cathode and the second electrode is an anode.
8. The method of claim 7, wherein the recess contains a mobile ion sink for accepting at least one depleted mobile ion, and the electrical potential difference is sufficient to drive the at least one depleted mobile ion out of the molten glass phase and into the at least one mobile ion sink through the intergranular glass phase.
9. The method of claim 8, wherein the at least one mobile ion sink is chosen from the group consisting of porous metal oxides, porous metals, porous glasses, porous ceramics, and combinations thereof.
10. The method of claim 8, wherein the at least one depleted mobile ion is chosen from the group consisting of alkali metal ions, alkaline earth metal ions, and transition metal ions.
11. The method of claim 1, further comprising heating the ceramic forming body to a treatment temperature ranging from about 1000°C to about 1500°C.
12. The method of claim 1, wherein the electric potential difference ranges from about 0.1 V/cm to about 20 V/cm.
13. A ceramic forming body comprising a crystalline phase, an intergranular glass phase, and a cavity containing (i) at least one electrode and (ii) at least one mobile ion source or at least one mobile ion sink.

14. The ceramic forming body of claim 13, wherein the cavity is positioned in an upper trough of the ceramic forming body, in a lower wedge of the ceramic forming body, or both.
15. The ceramic forming body of claim 13, wherein the cavity contains at least one anode and at least one mobile ion source.
16. The ceramic forming body of claim 13, wherein the cavity contains at least one cathode and at least one mobile ion sink.
17. The ceramic forming body of claim 13, wherein the mobile ion is chosen from the group consisting of alkali metal ions, alkaline earth metal ions, transition metal ions, rare earth metal ions, and heavy metal ions.
18. The ceramic forming body of claim 13, wherein the mobile ion source comprises at least one mobile ion, and the crystalline phase and the intergranular glass phase are both substantially free of the at least one mobile ion.
19. A glass sheet comprising:
a first major surface layer,
a second major surface layer, and
a central region disposed therebetween, the central region comprising a first concentration of at least one mobile ion that is different from a second concentration of the at least one mobile ion in either one or both of the first and second major surface layers.
20. The glass sheet of claim 19, wherein a thickness of the central region ranges from about 1 μm to about 200 μm .

21. The glass sheet of claim 19, wherein a thickness of the central region comprises from about 1% to about 20% of the total thickness of the glass sheet.

22. The glass sheet of claim 19, wherein the at least one mobile ion is chosen from the group consisting of alkali metal ions, alkaline earth metal ions, transition metal ions, rare earth metal ions, and heavy metal ions, and the first concentration is greater than the second concentration.

23. The glass sheet of claim 19, wherein the at least one mobile ion is chosen from alkali metal ions, alkaline earth metal ions, and transition metal ions, and the first concentration is less than the second concentration.

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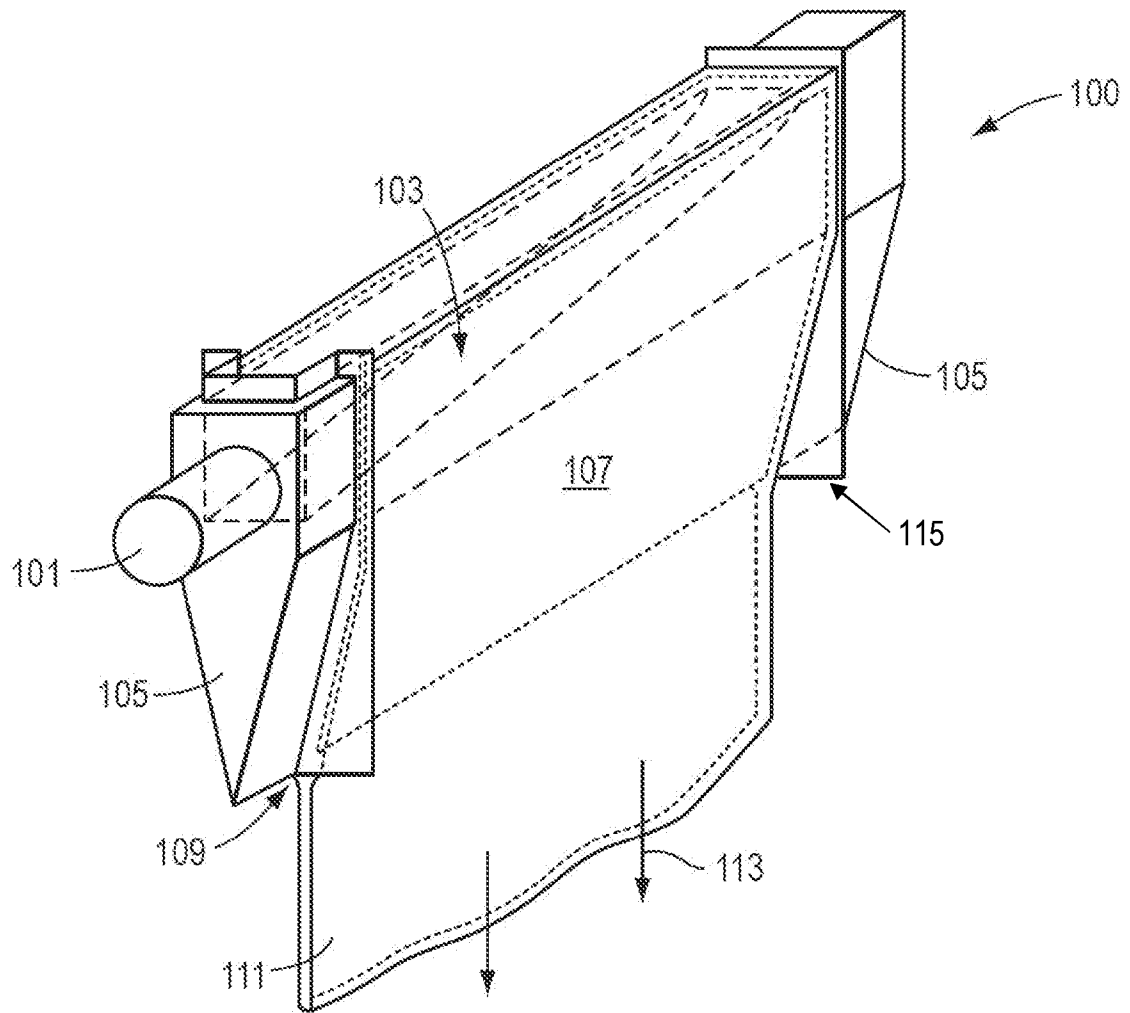


FIG. 1A

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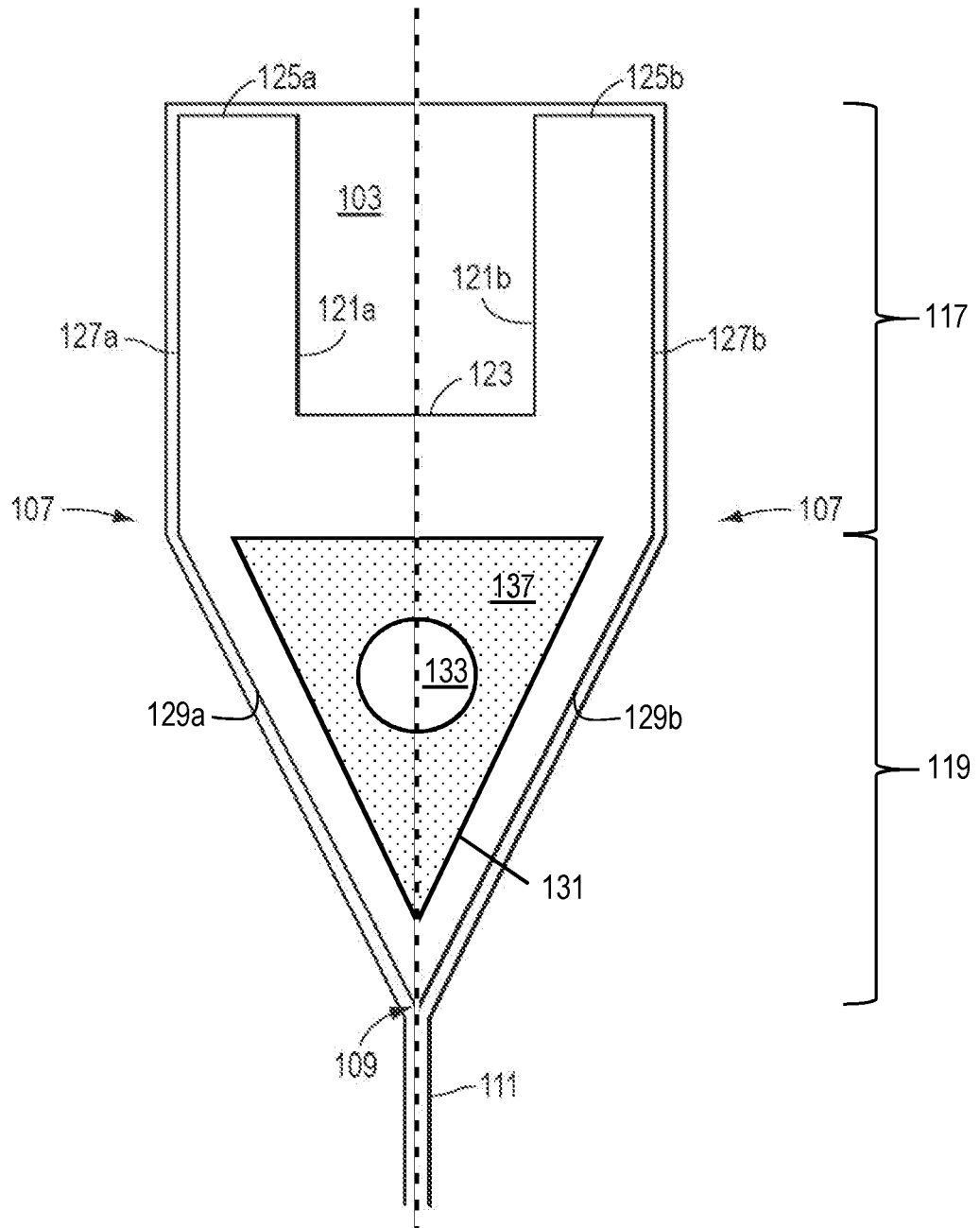


FIG. 1B

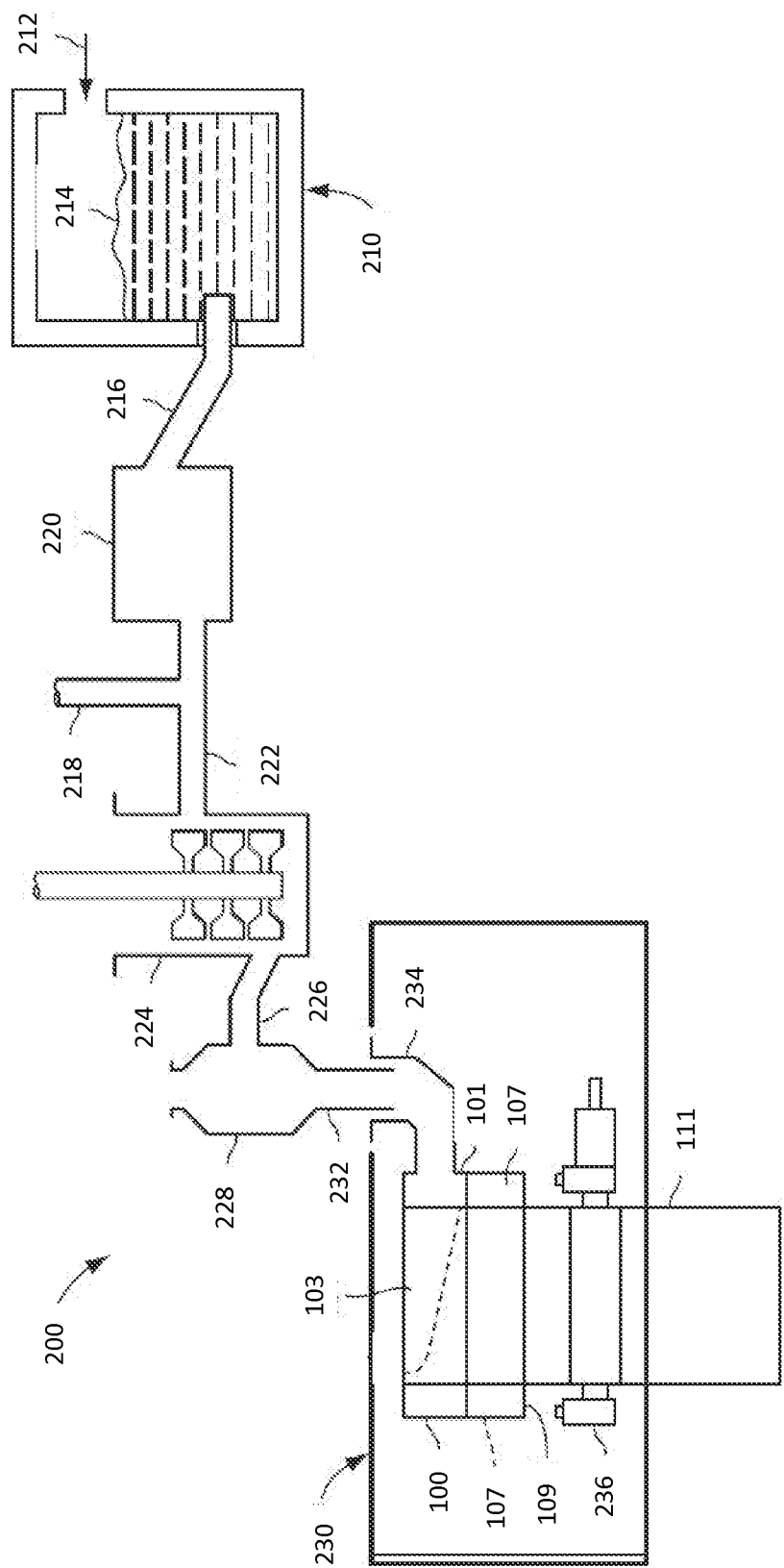


FIG. 2

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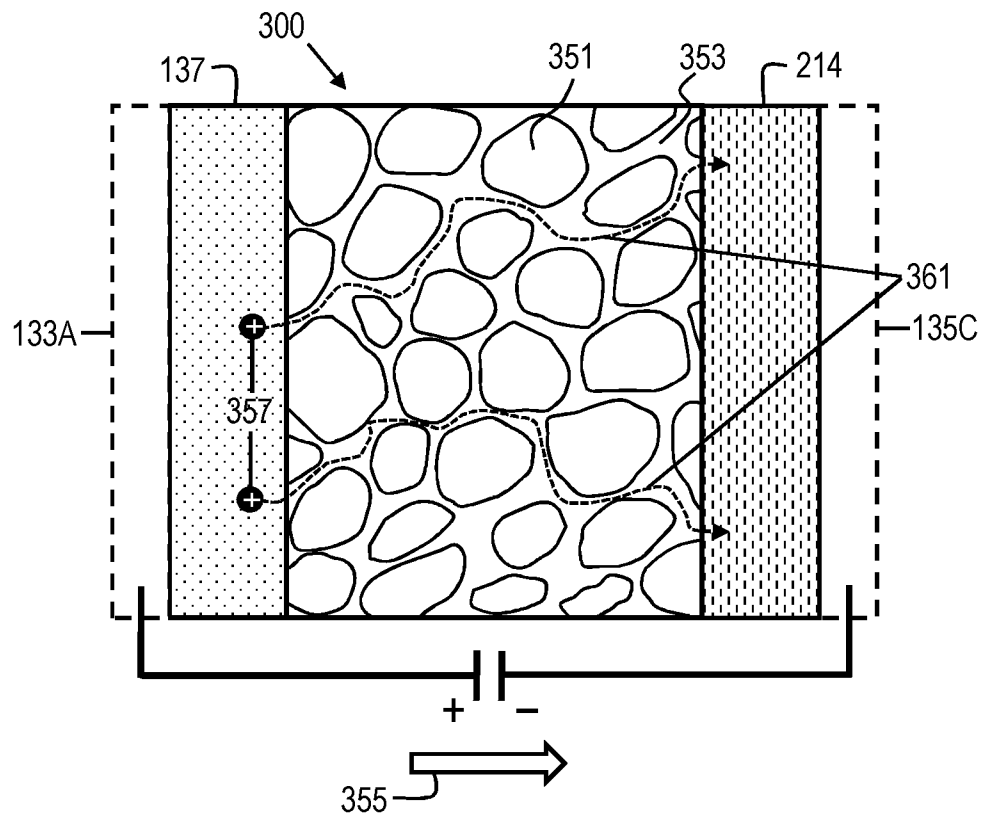


FIG. 3A

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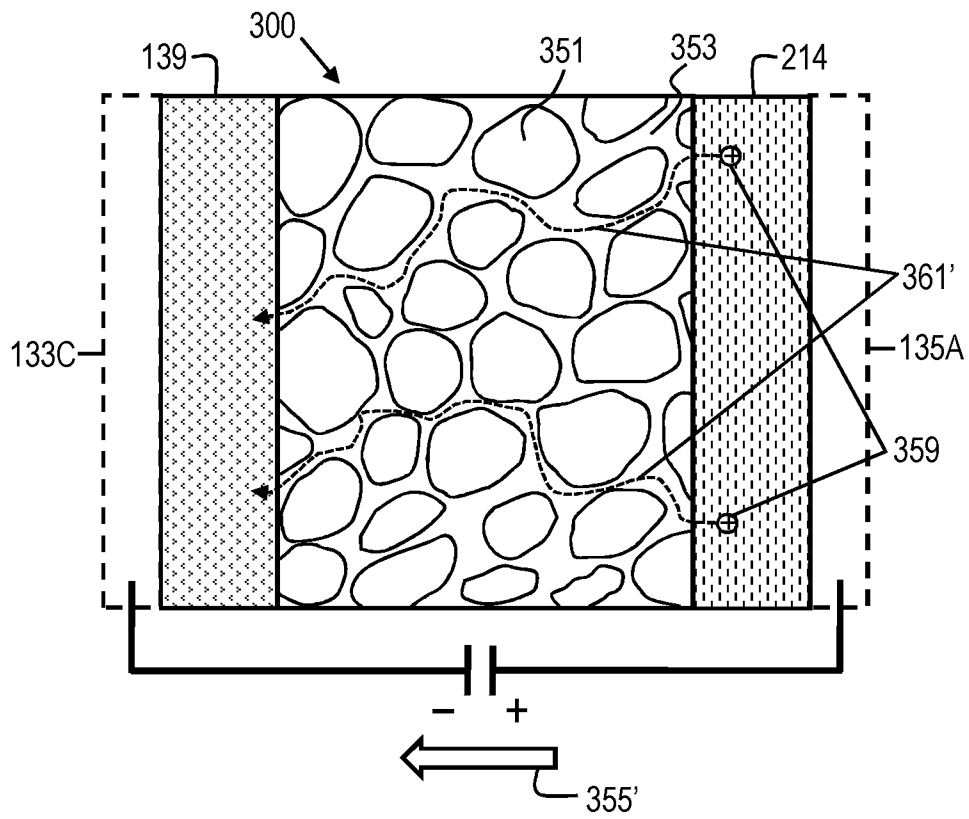


FIG. 3B

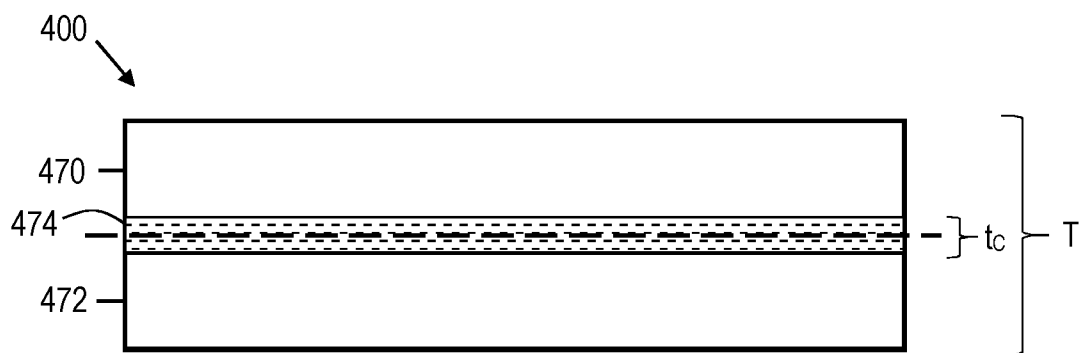


FIG. 4