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(54) METHODS, SYSTEMS, AND DEVICES FOR IONOCALORIC HEATING AND COOLING

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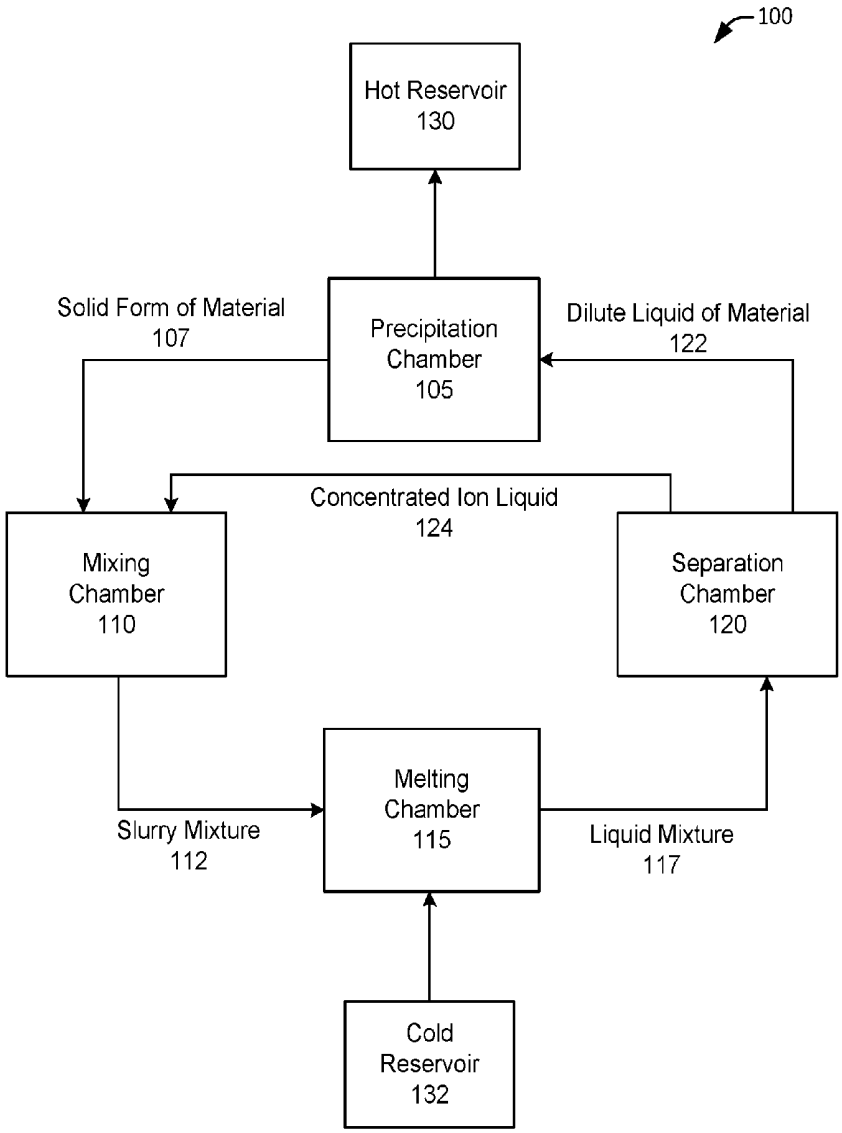
(57) **ABSTRACT**

Disclosed herein are methods, systems, and devices heating and cooling via an ionocaloric cycle. Methods include providing a first material in a solid state, combining the first material with a second material, wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material, and allowing the first material to melt, wherein the first material extracts heat from a cold reservoir upon melting. The method further includes separating the first material from the second material by a separation technique using a voltage applied to a combination of the first material and the second material and allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir during precipitation.



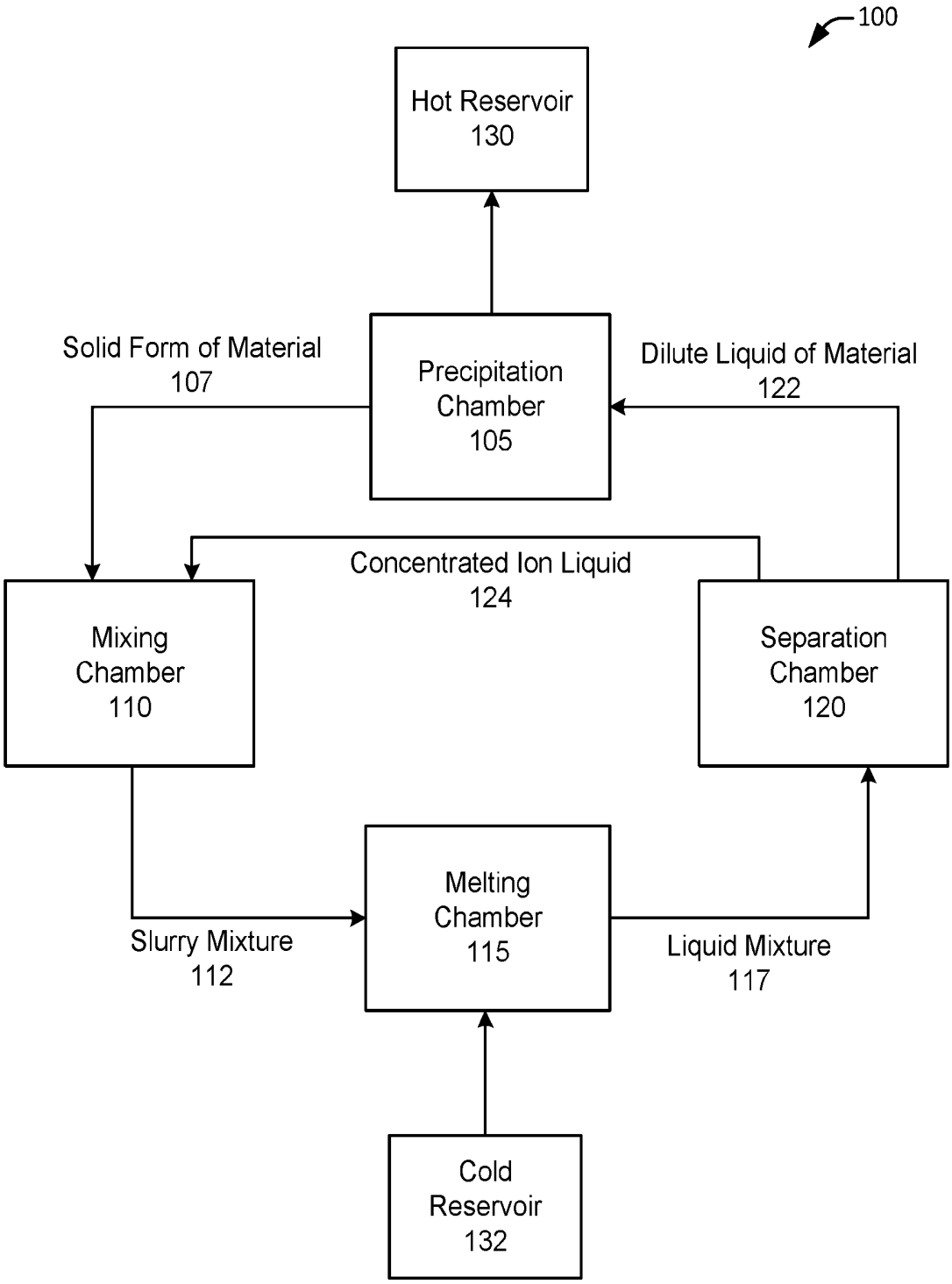

100
Hot Reservoir
130
Solid Form of Material
107
Precipitation
Chamber
105
Dilute Liquid of Material
122
Concentrated Ion Liquid
124
Mixing
Chamber
110
Separation
Chamber
120
Melting
Chamber
115
Slurry Mixture
112
Liquid Mixture
117
Cold
Reservoir
132

Figure 1

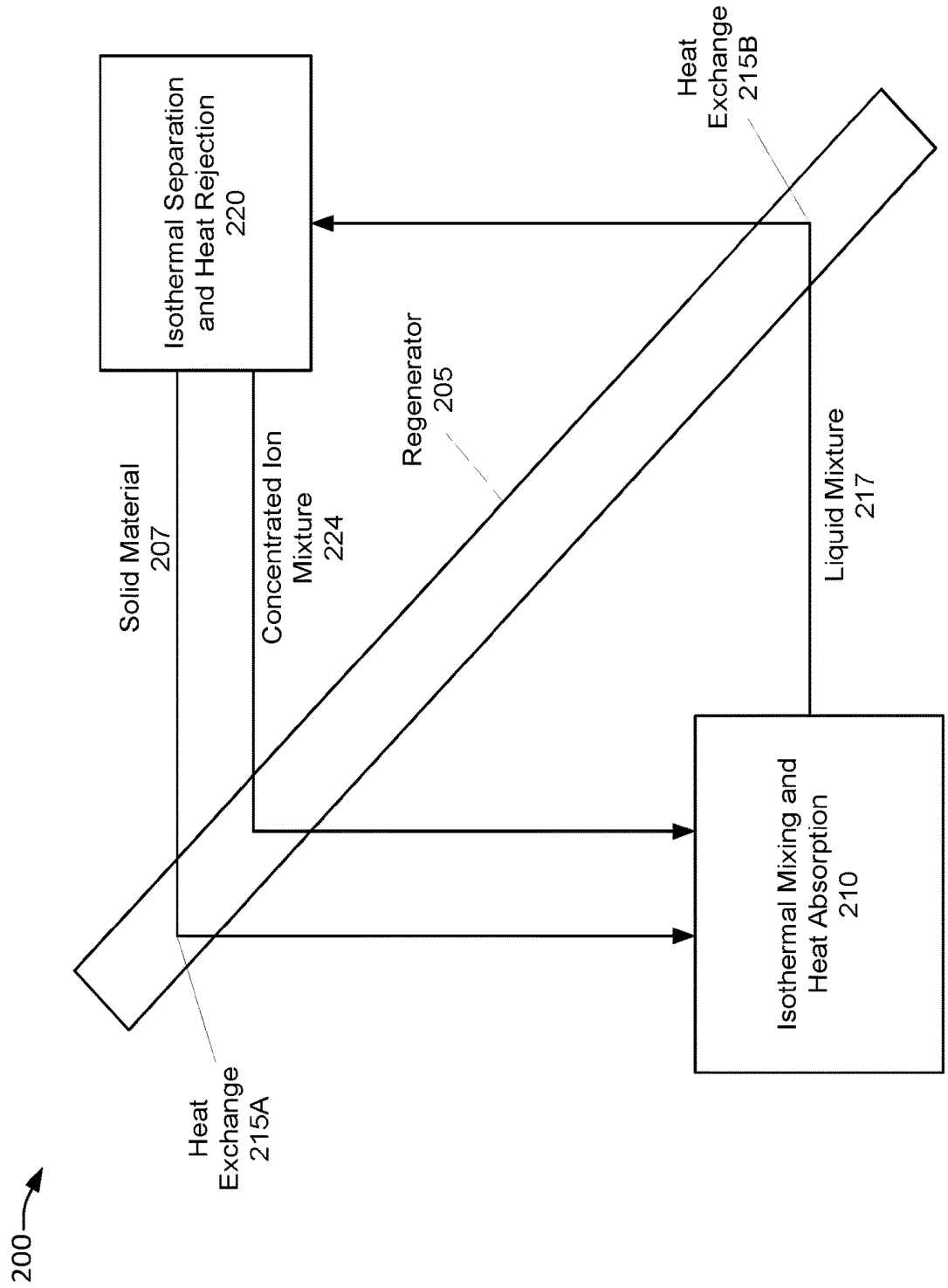

200
Isothermal Separation and Heat Rejection 220
Isothermal Mixing and Heat Absorption 210
Heat Exchange 215A
Heat Exchange 215B
Regenerator 205
Solid Material 207
Concentrated Ion Mixture 224
Liquid Mixture 217

Figure 2

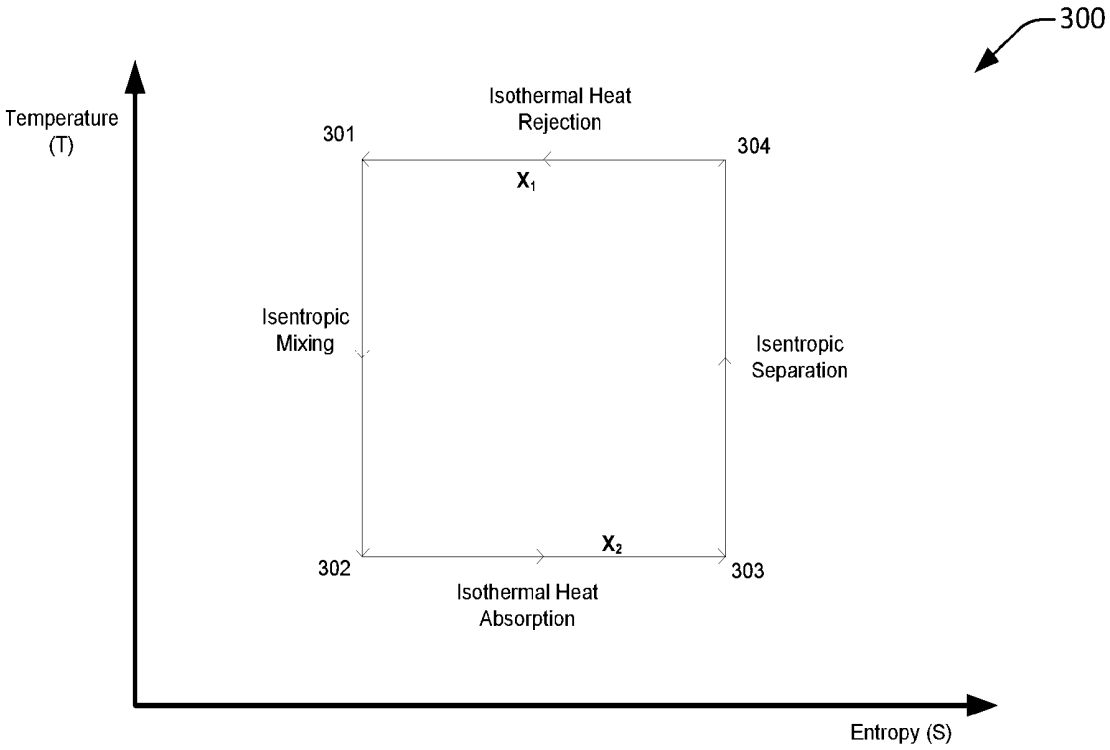


Figure 3A

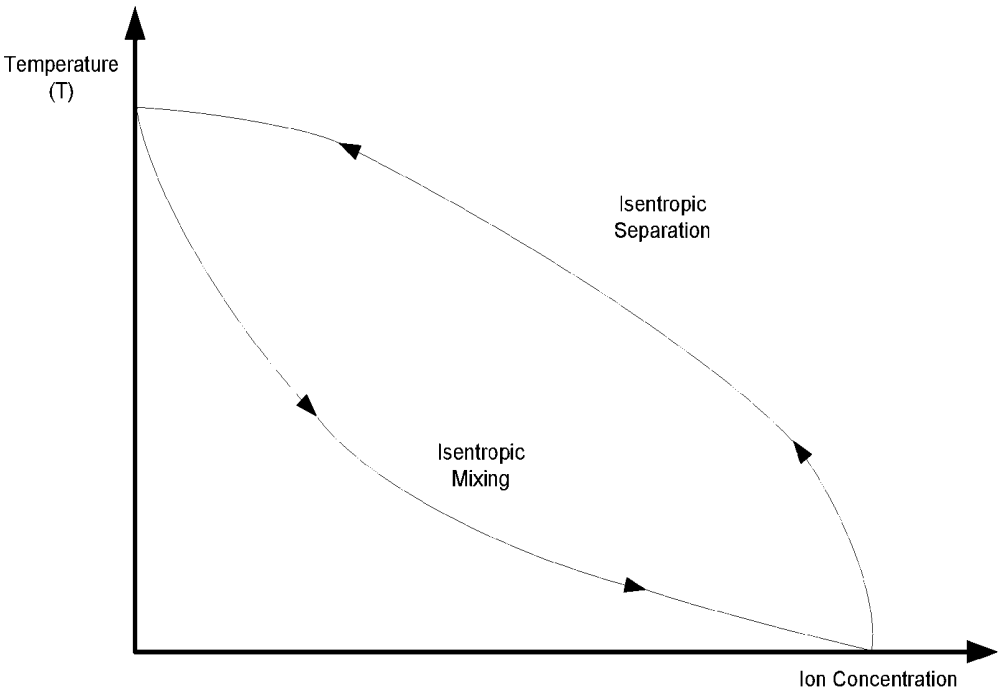


Figure 3B

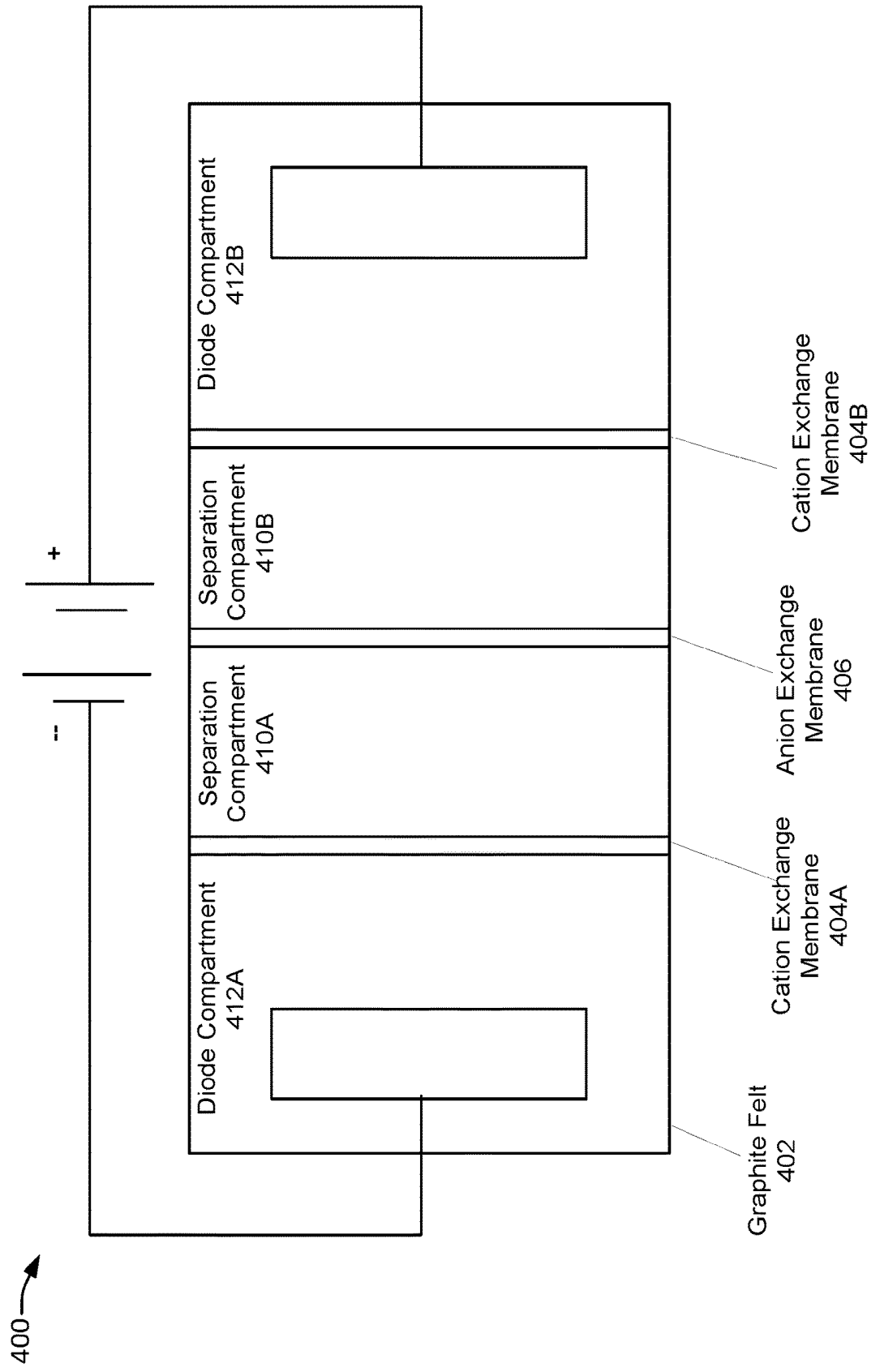

400
+
-
Diode Compartment 412A
Separation Compartment 410A
Separation Compartment 410B
Diode Compartment 412B
Graphite Felt 402
Cation Exchange Membrane 404A
Anion Exchange Membrane 406
Cation Exchange Membrane 404B

Figure 4

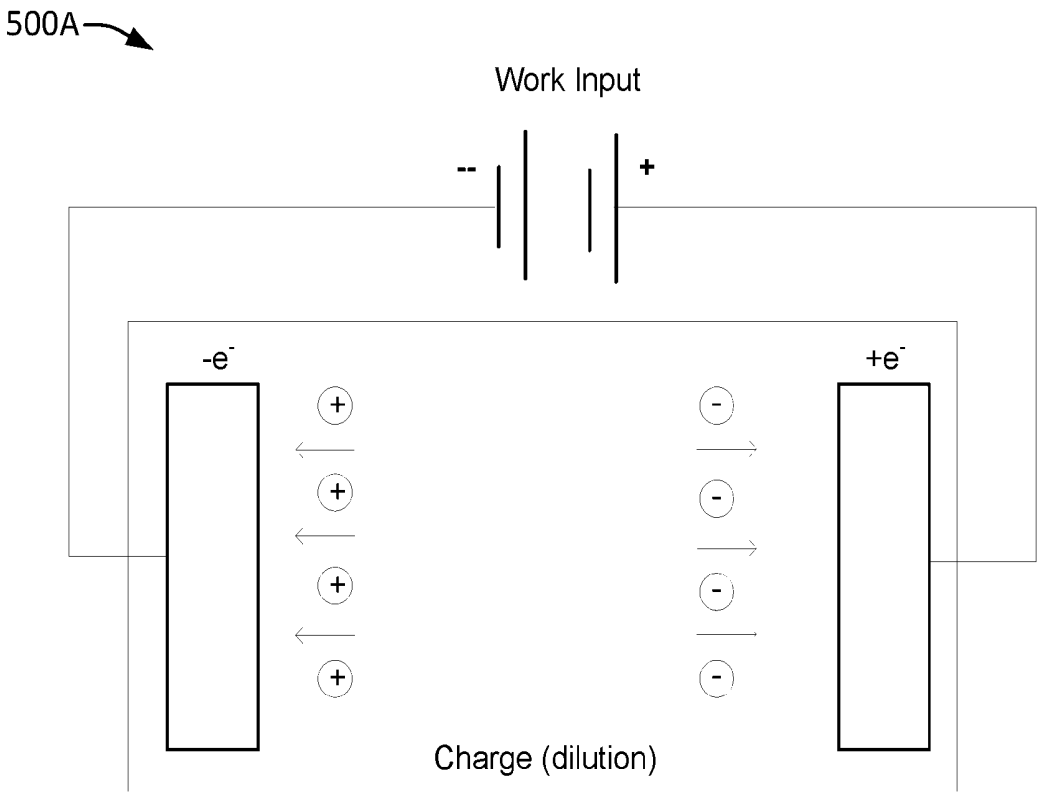


Figure 5A

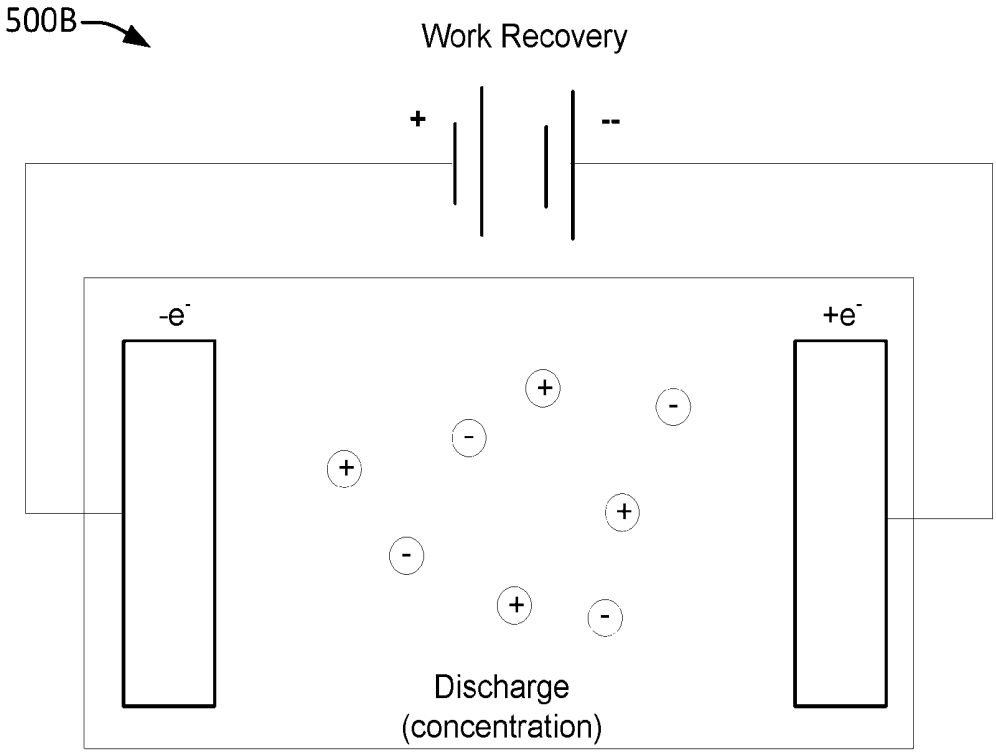


Figure 5B

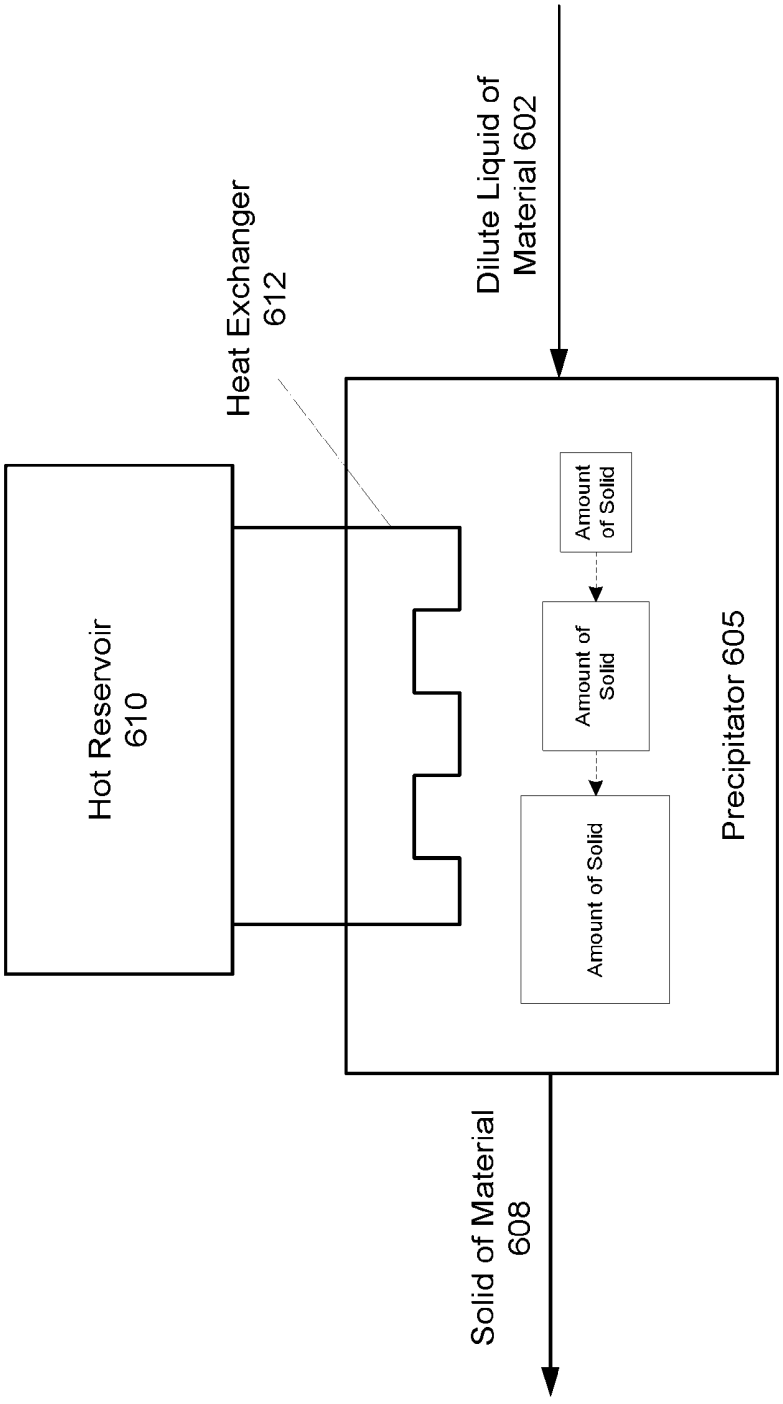

Dilute Liquid of Material 602
Heat Exchanger 612
Hot Reservoir 610
Amount of Solid
Amount of Solid
Amount of Solid
Precipitator 605
Solid of Material 608

Figure 6

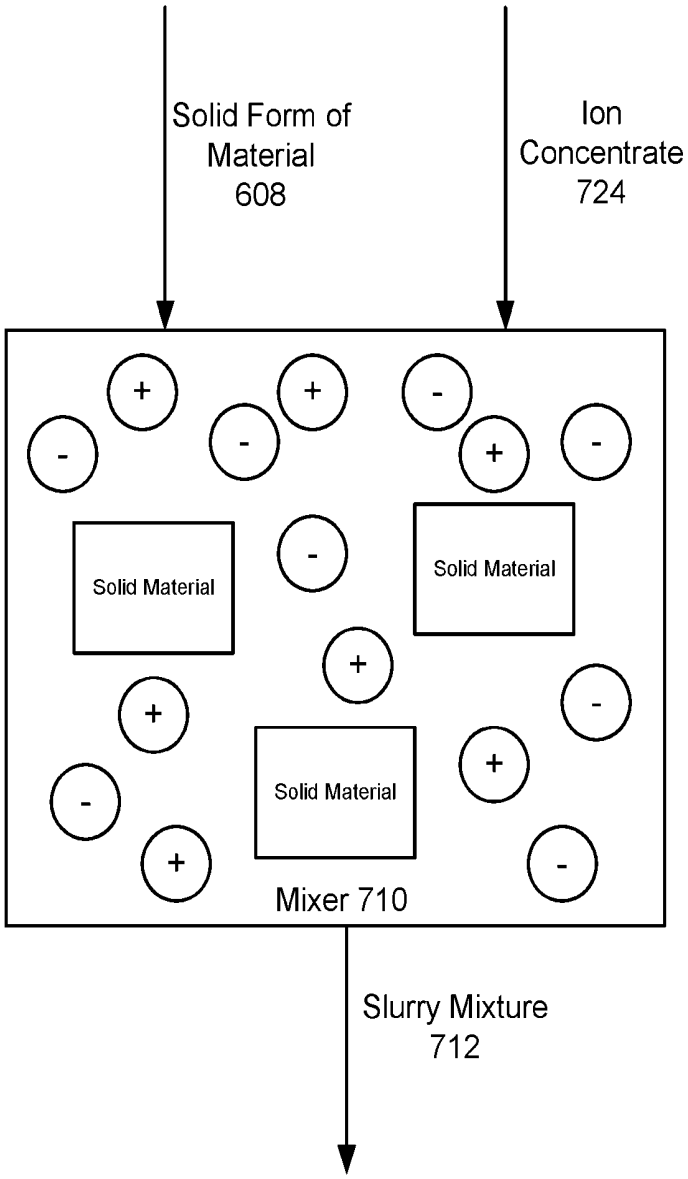

Solid Form of Material 608
Ion Concentrate 724
Solid Material
Solid Material
Solid Material
Mixer 710
Slurry Mixture 712

Figure 7

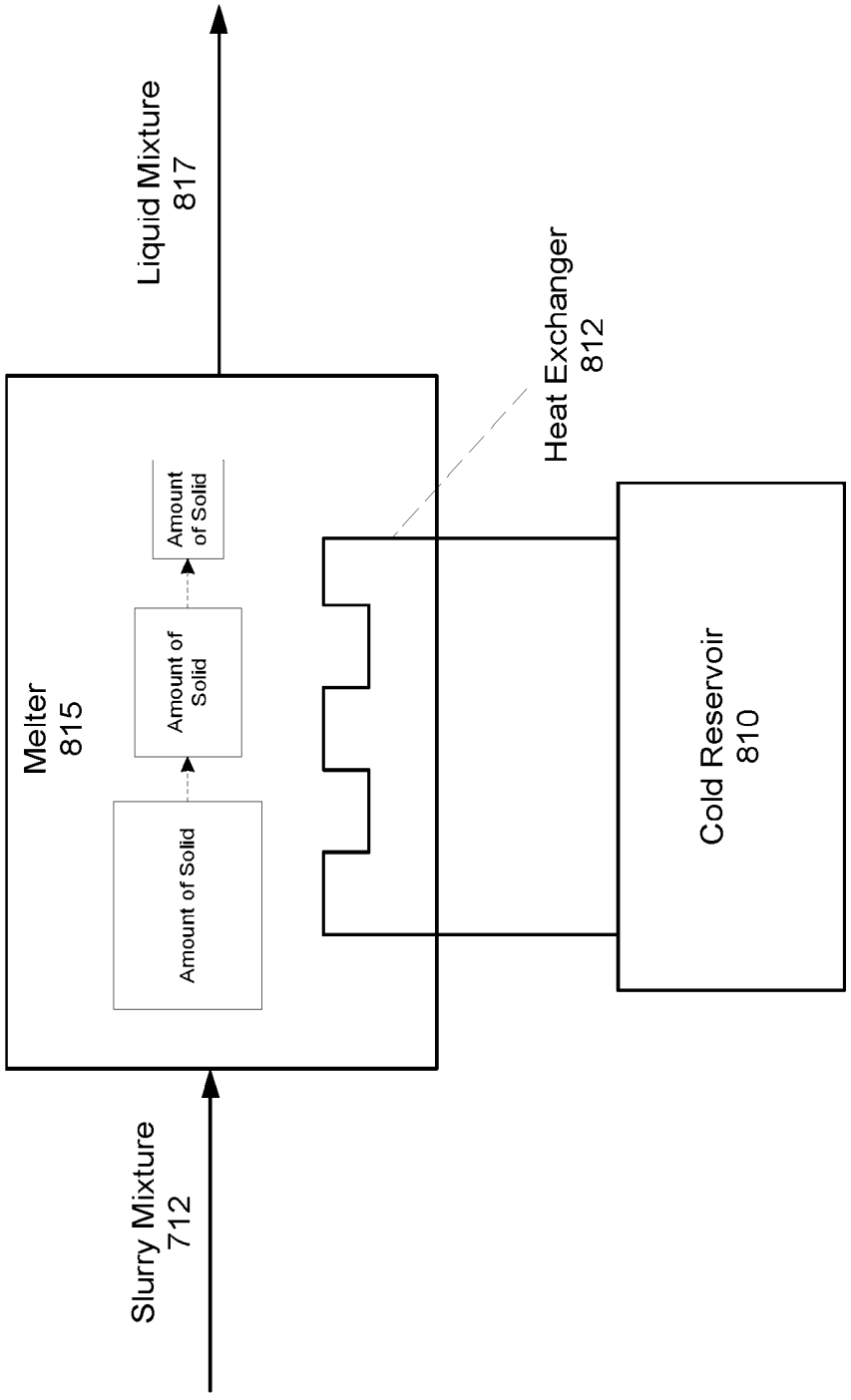

Liquid Mixture
817
Heat Exchanger
812
Melter
815
Amount of Solid
Amount of Solid
Amount of Solid
Cold Reservoir
810
Slurry Mixture
712

Figure 8

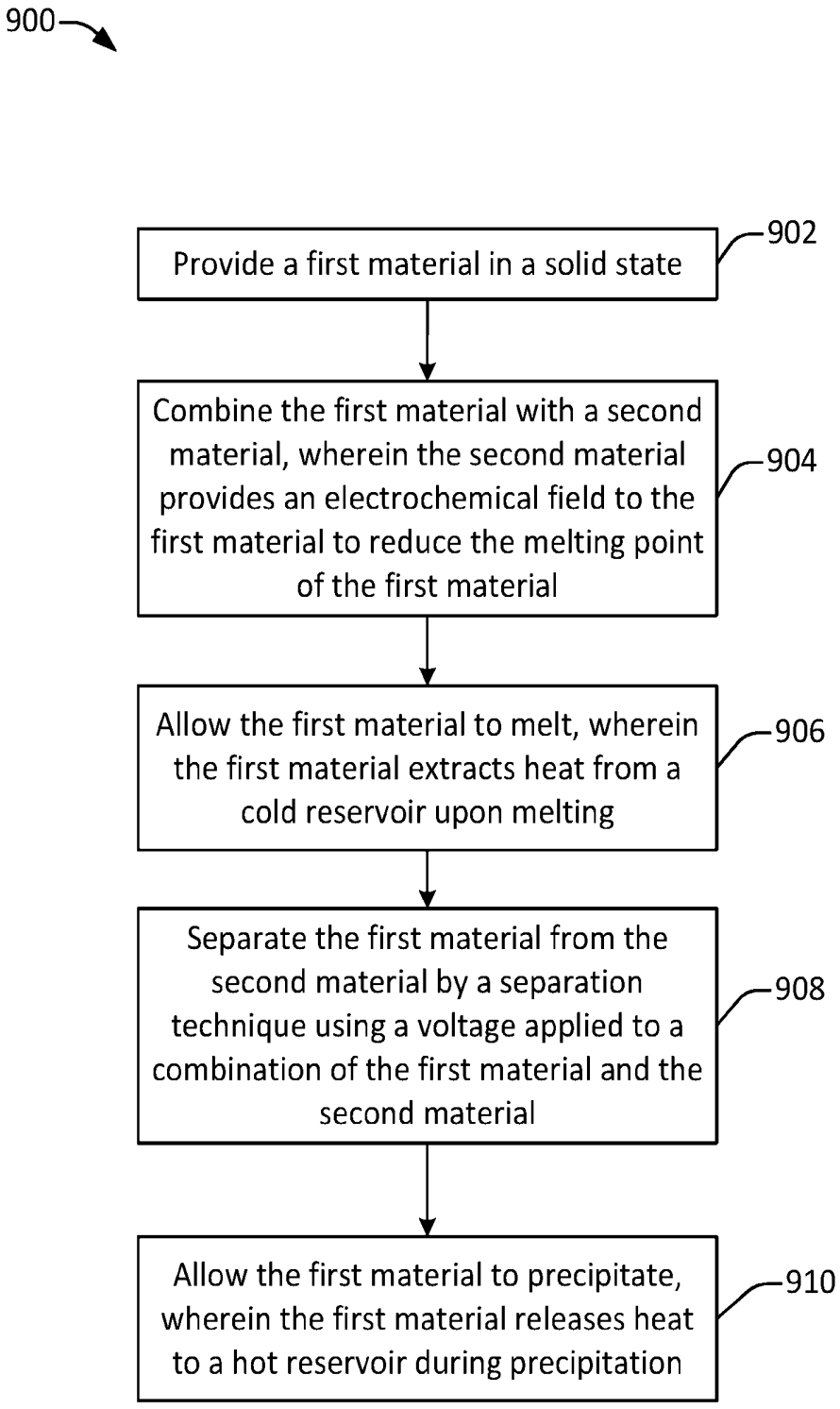

900
Provide a first material in a solid state
902
Combine the first material with a second material, wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material
904
Allow the first material to melt, wherein the first material extracts heat from a cold reservoir upon melting
906
Separate the first material from the second material by a separation technique using a voltage applied to a combination of the first material and the second material
908
Allow the first material to precipitate, wherein the first material releases heat to a hot reservoir during precipitation
910

Figure 9

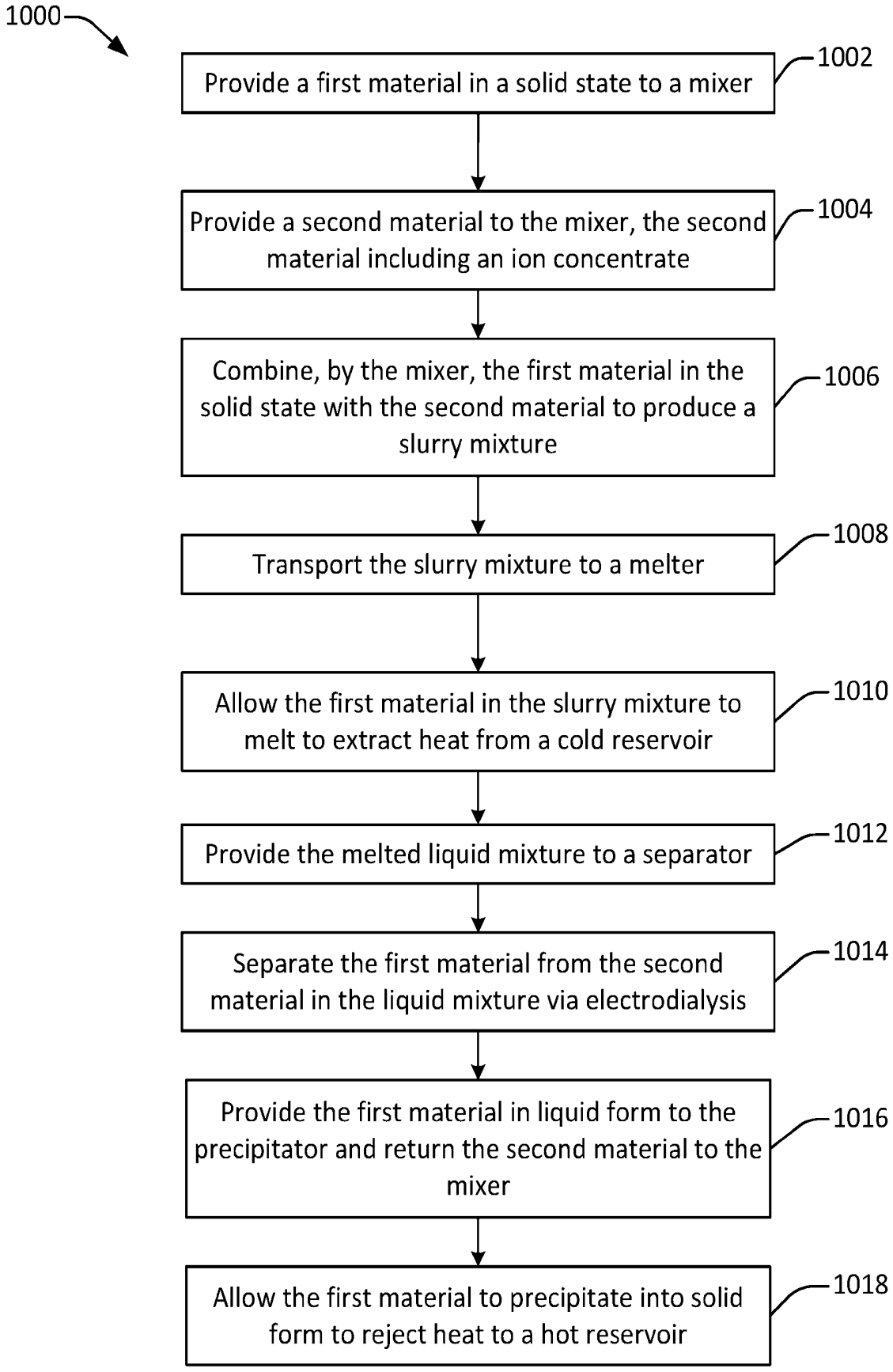

1000
Provide a first material in a solid state to a mixer
1002
Provide a second material to the mixer, the second material including an ion concentrate
1004
Combine, by the mixer, the first material in the solid state with the second material to produce a slurry mixture
1006
Transport the slurry mixture to a melter
1008
Allow the first material in the slurry mixture to melt to extract heat from a cold reservoir
1010
Provide the melted liquid mixture to a separator
1012
Separate the first material from the second material in the liquid mixture via electrodialysis
1014
Provide the first material in liquid form to the precipitator and return the second material to the mixer
1016
Allow the first material to precipitate into solid form to reject heat to a hot reservoir
1018

Figure 10

Chemical	$T_{m,o}$ *(Celsius)*	ΔH_{st} *(J/g)*	k_f
Cyclohexanol	25	17	43.47
Phenol	40.5	127	6.44
t-butanol	25.82	91	8.17
Cetyl Alcohol	49.27	238	3.63
menthol	40	80	10.19
Ethylene Carbonate	35	155	5.09
Sulfolane	27.5	10	75.15
Methyl anthranilate	24	60	12.24
p-Cresol	35	116	6.81
Guaiacol	28	120	6.28
DMSO	19	184	3.86

Figure 11

Salt	Solubility (gr/100g Ethylene Carbonate)	Ionic conductivity (μS/cm)
$ZnCl_2$	33	n/a
$HgCl_2$	49	n/a
$KCNS$	≈ 0	n/a
$KMnO_4$	≈ 0	n/a
$K_2Cr_2O_7$	≈ 0	n/a
$Cu(Br)_2$	≈ 0	n/a
NaI	37.6	11000
$NaBr$	0.31	94.6
$CaCl_2$	0.2	8.66
KI	11.16	15000

Figure 12

METHODS, SYSTEMS, AND DEVICES FOR IONOCALORIC HEATING AND COOLING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application No. 63/391,816, filed on Jul. 25, 2022, which is incorporated herein by reference in its entirety for all purposes.

STATEMENT OF GOVERNMENT SUPPORT

[0002] This invention was made with government support under Contract No. DE-AC02-05CH11231 awarded by the U.S. Department of Energy. The government has certain rights in the invention

TECHNICAL FIELD

[0003] This disclosure relates generally to heat movers, and more particularly to an ionocaloric heating and cooling cycle.

BACKGROUND

[0004] Heating and cooling systems move and transfer heat from work input into the system. Such systems may operate on one or more of several principals including phase change heat transfer via compression, air to liquid heat exchange, liquid to liquid heat exchange, etc. These heating systems can be used for climate control, refrigeration, etc.

SUMMARY

[0005] Disclosed herein are methods, systems, and devices for ionocaloric heating and cooling. Methods include providing a first material in a solid state, combining the first material with a second material, wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material and allowing the first material to melt, wherein the first material extracts heat from a cold reservoir upon melting. Methods further include separating the first material from the second material by a separation technique using a voltage applied to a combination of the first material and the second material and allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir during precipitation.

[0006] In some embodiments, the first material has a melting point at or above an ambient temperature. In some embodiments, the second material comprises an ion concentration to provide the electrochemical field. In some embodiments, the second material comprises at least one of sodium iodide, potassium iodide, magnesium nitrate, magnesium chloride, ammonium nitrate, potassium nitrate, potassium chloride, sodium thiosulfate, lithium bromide, lithium iodide, lithium chloride, lithium carbonate, water, or ethanol. In some embodiments, the separation technique comprises electrodialysis or Faradaic deionization. In some embodiments, the electrodialysis comprises separating the first material from the second material by applying the voltage across electrode compartments comprising iodide triiodide redox couples. In some embodiments, the first material comprises at least one of ethylene carbonate, magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate, Iron chloride hexahydrate, or cadmium nitrate tetrahydrate.

[0007] Systems include a mixing chamber to combine a first material in a solid state with a second material wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material and a melting chamber allowing the first material to melt, wherein the melting chamber is coupled to a cold reservoir and wherein the first material extracts heat from the cold reservoir upon melting. Systems further include a separating chamber to separate the first material from the second material via a separation technique comprising a voltage applied to a combination of the first material and the second material and a precipitation chamber allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir coupled to the precipitation chamber during precipitation.

[0008] An apparatus includes a mixer to combine a first material in a solid state with a second material wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material, a melter allowing the first material to melt, wherein the melting chamber is coupled to a cold reservoir and wherein the first material extracts heat from the cold reservoir upon melting, a separator to separate the first material from the second material via a separation technique comprising a voltage applied to a combination of the first material and the second material, and a precipitator allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir coupled to the precipitation chamber during precipitation.

[0009] Details of one or more embodiments of the subject matter described in this specification are set forth in the accompanying drawings and the description below. Other features, aspects, and advantages will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. **1** illustrates an example system for ionocaloric cooling, configured in accordance with some embodiments.

[0011] FIG. **2** illustrates an example regenerative ionocaloric cycle, in accordance with some embodiments.

[0012] FIG. **3**A illustrates a temperature-entropy diagram of an example of an ionocaloric process of heating and cooling, configured in accordance with some embodiments.

[0013] FIG. **3**B illustrates a temperature-ion concentration diagram of an example ionocaloric process of heating and cooling, configured in accordance with some embodiments.

[0014] FIG. **4** illustrates an example of a separator of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0015] FIG. **5**A illustrates another example of a separator of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0016] FIG. **5**B illustrates another example of a separator of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0017] FIG. **6** illustrates an example of a precipitator of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0018] FIG. **7** illustrates an example of a mixer of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0019] FIG. **8** illustrates an example of a melter of an ionocaloric heating and cooling system, configured in accordance with some embodiments.

[0020] FIG. **9** illustrates a flow chart of a method of ionocaloric heating and cooling, implemented in accordance with some embodiments.

[0021] FIG. **10** illustrates a flow chart of a method of ionocaloric heating and cooling, implemented in accordance with some embodiments.

[0022] FIG. **11** depicts a table of potential materials to be used for ionocaloric heating and cooling, according to some embodiments of the disclosure.

[0023] FIG. **12** depicts a table of potential ionic materials to be used for ionocaloric heating and cooling, according to some embodiments of the disclosure.

DETAILED DESCRIPTION

[0024] In the following description, numerous specific details are set forth in order to provide a thorough understanding of the presented concepts. The presented concepts may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail so as to not unnecessarily obscure the described concepts. While some concepts will be described in conjunction with the specific examples, it will be understood that these examples are not intended to be limiting.

[0025] Currently, cooling techniques are dominated by vapor compression technologies in which a gas is compressed (e.g., by heating) and then expanded (e.g. cooled). The liquids used in these vapor compression technologies include hydrofluorocarbons (HFCs) which are significant contributors to global warming and thus need to be phased out. Other liquid-based alternatives to HFCs, such as hydrofluoroolefins (HFOs), which have a lesser global warming effect but are still slightly flammable, have smaller power densities and coefficients of performance as compared to HFCs and pose other environmental concerns. Non-vapor compression based refrigeration technologies using solid-state material are being developed, however are not yet cost effective.

[0026] The ionocaloric effect is the thermal response to a changing ionic environment surrounding a solid phase, driven by an electrochemical field. Physically, the ionocaloric effect manifests within first-order phase boundaries by lowering the melting point of a solid below the ambient temperature upon the addition of ions to its surroundings (e.g., by applying an electrochemical field). Under such an applied field, the solid, which becomes most stable as a liquid, melts. Melting of the solid requires energy. Accordingly, if the system is insulated from its surroundings (e.g., adiabatic), the material in the solid form uses its own energy to melt, thus lowering its own temperature by endothermically converting some solid to the liquid phase. This process continues until the temperature of the solid is equal to the new melting temperature, which is dictated both by the strength of the applied electrochemical field and the phase boundary of the caloric material.

[0027] Various embodiments disclosed herein provide for use of the ionocaloric effect in a thermodynamic cycle for refrigeration. The thermodynamic cycle may include four steps. The first step may include mixing a caloric material in a solid form with an electrolyte solution (e.g., a liquid including an ion). The second step may include allowing the caloric material to melt and extracting heat into the caloric material from a cold reservoir. The third step may include separating the electrolyte solution from the caloric material. For example, a voltage may be applied to the mixture to separate electrolyte solution from the caloric material. The fourth step may include allowing the caloric material to precipitate or crystallize into solid form, releasing heat into a hot reservoir.

[0028] Ideal refrigerants in the ionocaloric cycle may include materials that experience large adiabatic temperature changes and isothermal entropy changes. This allows for high temperature spans and large refrigeration capacities (e.g., the amount of heat absorbed per cycle). In addition, the melting point of the materials dictates the maximum operating temperature of the cycle, so the ideal materials may have melting points above room temperature. The lowest operating temperature in the cycle is determined by either (1) the max adiabatic temperature change, or (2) the maximum melting point depression that can be achieved for a given material/salt combination.

[0029] The maximum adiabatic temperature change for the ionocaloric material, independent of the salt used in conjunction with the material, scales with the ratio of latent heat to specific heat, $\Delta T_{max} \approx \Delta H_{sl}/C_p$. However, the amount of salt needed to drive this melting point depression is related to the ionocaloric material's cryoscopic constant, $k_f = RMT^2/\Delta H_{sl}$, which can be used to relate the expected melting point depression to the molality for a given solvent/salt combination: $\Delta T_D = -ik_f[m]$, where R is the ideal gas constant, M is the molar mass of the ionocaloric material, T_m is the melting point, ΔH_{sl} is the enthalpy of fusion, i is the van't Hoff Factor (number of particles the salt dissociates into), and [m] is the molality.

[0030] These simple relations demonstrate that a material with a high enthalpy change will enable large adiabatic temperature changes but may require higher salt concentrations to move the phase boundary. To support the higher salt concentrations needed to move the phase boundaries for lower to moderate cryoscopic constant materials, the ionocaloric material may have a high salt solubility. In some examples, the material's dielectric constant can be used as a broad indicator of ability to solubilize ionic compounds. In general, materials with higher dielectric constants are more likely to exhibit high solubilities.

[0031] Therefore, ideal ionocaloric materials may have one or more of the following properties: (1) melting point greater than ambient temperature, (2) large enthalpy of fusion (3) high cryoscopic constant (4) large maximum adiabatic temperature change, and (5) large dielectric constant.

[0032] Accordingly, embodiments disclosed herein provide for heating and cooling in an ionocaloric cycle that does not use greenhouse contributing materials. Additionally, the disclosed ionocaloric cycle provides for large heating and cooling capacity at room temperature. For example, room temperature may include temperatures in the range approximately 10 degrees C. to 30 degrees C. In another example, room temperature may include temperatures in the range of 0 degrees C. to 50 degrees C. In another example, room temperature may include temperatures in the range of 18 degrees C. to 24 degrees C. Furthermore, embodiments disclosed herein allow for various applications of heating and cooling at various temperatures. In some embodiments, the process describes herein is not used for refrigeration

(e.g., embodiments are not used to provide temperatures of a cool reservoir below 0 degrees C.).

[0033] FIG. **1** illustrates an example system **100** for ionocaloric cooling, configured in accordance with some embodiments. System **100** includes a precipitation chamber **105**, a mixing chamber **110**, a melting chamber **115**, and a separation chamber **120**. In some embodiments, a solid form of a caloric material **107** may be provided to a mixing chamber **110** (e.g., from precipitation chamber **105**). In some examples, the solid form of the caloric material **107** output from the precipitation chamber **105** to the mixing chamber **110** may be a complete solid form (e.g., which may require transport via conveyor or other similar means) or may be in the form of a slurry with a portion of the slurry in solid form such that the slurry may be pumped (e.g., via piping) to the mixing chamber **110**. The caloric material may be a material with a melting point at or above ambient temperature (e.g., such that the material is in a solid state at ambient or room temperature). For example, the caloric material may be one of the materials listed in FIG. **11**. In some embodiments, the caloric material may include magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate, Iron chloride hexahydrate, cadmium nitrate tetrahydrate, room temperature liquid salts such as 1-Butyl-2,3-dimethlynlimidazolium tetrafluoroborate puruum and 1-ethyl-3-methylimidazolium nitrate, polyalcohols such as ervhritol, d-mannitol, d-dulcitol, inositol, neopentyl glycol, fatty acids such as paraffin waxes (heptadecane, octadecane) and lauric, myristic, palmitic, and stearic acids. The solid form of the caloric material **107** may be combined with an electrolyte solution (e.g., concentrated ion liquid **124**) at the mixing chamber **110**. The mixing chamber **110** may include a mechanism for mixing the electrolyte solution with the caloric material. Once mixed, a slurry mixture **112** of the combined caloric material and electrolyte solution is provided to the melting chamber **115**. The melting chamber **115** may be coupled to a cold reservoir **132**. Although depicted as separate, in some embodiments, the mixing chamber **110** and the melting chamber **115** may be a single integrated unit or chamber for mixing and melting of the caloric material. As the caloric material melts due to the electrochemical field provided by the electrolyte solution, the caloric material may drop in temperature due to the phase change. The caloric material may thus extract heat from the cold reservoir **132**. Although depicted as separate, the cold reservoir **132** may be incorporated with the melting chamber **115** as a single integrated unit. The resulting liquid mixture **117** is then transported to a separation chamber **120** where a separation process is applied to the liquid mixture **117** of the caloric material and ion liquid. The separation process applied within the separation chamber **120** may include a voltage applied across the liquid mixture. For example, the separation process may include electrodialysis, as described in more detail with respect to FIG. **3**. In some examples, the separation process may include distillation, reverse osmosis, other voltage applied separation process, or any other process for separation of mixed materials. The separation chamber **120** may thus separate the liquid mixture into a dilute liquid of the caloric material **122** and a concentrated ion liquid **124**. The dilute liquid of caloric material **122** may then be provided to the precipitation chamber **105** where the material is allowed to precipitate (e.g., crystallize). Precipitate and crystallize may be used interchangeably herein to mean converting a material from a liquid form to a solid form. Accordingly, the precipitation chamber may also be referred to as a crystallization chamber. The precipitation chamber **105** may be coupled to a hot reservoir **130**. As the caloric material precipitates and crystallized in the precipitation chamber **105**, the material rejects heat that is extracted into the hot reservoir at 20-200° C. **130**. Although depicted as separate, the hot reservoir **130** may be incorporated with the precipitation chamber **105** as a single integrated unit. The concentrated ion liquid **124** is then provided directly back to the mixing chamber **110** to continue the cycle.

[0034] In some embodiments, the caloric material may be a material with a melting point above room temperature, a eutectic well below room temperature, and a high enthalpy of fusion as well as high cryoscopic constants so that large temperature changes can be achieved using small amounts of electrolytes. In some embodiments, the caloric material may be ethylene carbonate (EC) and the ionic material may be sodium iodide (NaI). The (EC-NaI) ionocaloric system may include a pure melting point of T_{melt}=36.4° C., a eutectic transition at $T_{eutectic}$=6.4° C., and a relatively high latent heat of fusion ΔH_{fus}=204.6 J mL−1 (as compared with ΔH_{fusion}≈330 J mL-1 for water, which has one of the highest entropies of fusion of known near-room temperature molecules). The EC-NaI system is a CO_2-negative, environmentally benign, nonhazardous, zero-GWP, nontoxic, and nonflammable mixture. EC is a common additive to battery electrolytes (e.g., lithiumion), can be made stable over a long lifetime, and has shown good cyclability and stability.

[0035] Additionally, in some embodiments the ionocaloric cycle may include adding water to a salt hydrate in a solid form at the mixing chamber **110** and providing the mixture to the melting chamber **115**. The melting point of the salt hydrate may be reduced by the added water, similar to the addition of ions to a caloric material as described herein. Accordingly, the salt hydrate is cooled when the water is added via the same ionocaloric principles described herein. The salt hydrate mixture may then extract heat from the cold reservoir **132** and be passed to the separation chamber **120**. The separation chamber **120** may perform a separation technique to separate the water from the salt hydrate. For example, the separation technique may include operations such as evaporation, distillation, filtering (e.g., reverse osmosis), or any other separation technique. The separated water may be retuRN ed directly to the mixing chamber **110** for further cycles while the concentrated salt hydrate liquid may be provided to the precipitation chamber **105** where it is allowed to crystallize and release heat to the hot reservoir **130**. The cycle may then be repeated by providing the solid form of the salt hydrate from the precipitation chamber **105** to the mixing chamber **110**.

[0036] FIG. **2** illustrates an example regenerative ionocaloric cycle **200**, in accordance with some embodiments. The cycle **200** includes isothermal mixing and heat absorption **210** where a solid material **207** (e.g., solid form of material **107** of FIG. **1**) is mixed with a concentrated ion mixture **224** to reduce a melting point of the solid material and absorb heat as the solid material is converted to a liquid. The isothermal mixing and heat absorption **210** may correspond to processes occurring at mixing chamber **110** and melting chamber **115** as described with respect to FIG. **1**. In some examples, the isothermal mixing and heat absorption **210** results in a liquid mixture **217**. The liquid mixture **217** may

run through a heat exchange **215**B where the liquid mixture absorbs heat from the regenerator **205**. Isothermal separation and heat rejection **220** may be performed on the liquid mixture **217**. For example, the liquid mixture **217** may be separated back into the solid material **207** and the concentrated ion mixture **224**. During the isothermal separation and heat rejection **220** the crystallization of the solid material (e.g., due to the return of the melting point to above ambient temperature0 may cause the solid material **207** to reject heat (e.g., to a hot reservoir). In some embodiments, the isothermal separation and heat rejection **220** may correspond to processes occurring at the separation chamber **120** and the precipitation chamber **105** as described with respect to FIG. **1**. The solid material **207** may be transported through heat exchange **215**A where heat is given to the regenerator **205** from the solid material **207**. The cycle **200** may then repeat as the solid material **207** is again mixed with the concentrated ion mixture **224** at the isothermal mixing and heat absorption **210** stage.

[0037] FIG. **3**A illustrates a diagram of an ionocaloric cooling cycle according to embodiments of the present disclosure. The depicted diagram includes entropy (S) on the x-axis and temperature of a caloric material on the y-axis. The cycle may begin at point **301**, where the caloric material is in a solid state with a constant concentration of ion liquid X_1, where X_1 may be zero or at least negligible. Isentropic mixing is then performed where an increasing amount of ionic material (e.g., ion liquid or electrolyte solution) is added to and mixed with the caloric material. As the amount of ionic material increases, the melting point of the caloric material is reduced to point **302**, where the melting point is reduced to a desired temperature based on the implementation or design of the cycle. As discussed above, in an adiabatic environment the caloric material has to use its own internal heat energy to produce the phase change to liquid form, thus cooling the caloric material to the new melting point. The melting point may be based on the caloric properties of the caloric material and the concentration of ions in the mixture. For example, the concentration of ions X_2 at point **302** may drop the melting point of the caloric material to below ambient temperature to cause the phase change. Once at point **302**, the caloric material may absorb heat isothermally (e.g., while maintaining the melting point temperature) due to the internal energy required to produce the phase change. At point **303**, once isothermal heat absorption has occurred, the ion material is separated from the caloric material (e.g., isentropic separation.) In some embodiments, the ions may be removed from the caloric material via an applied voltage to the mixture. In some embodiments, the ions are removed via a form of electrodialysis, as discussed in more detail below with respect to FIG. **3**. At point **304**, once the ion material is separated from the caloric material, the melting point of the material may return to the original temperature, thus causing a phase change back into a solid. For example, the liquid caloric material may precipitate or crystallize and reject heat as it does so. The crystallization may occur isothermally as the caloric material rejects heat collected between points **302** and **303**. The cycle may then return to point **301** where the caloric material is returned to a solid state.

[0038] FIG. **3**B illustrates an ionocaloric cycle with respect to ion concentration in a caloric material, according to some embodiments of the present disclosure. The depicted diagram includes ion concentration on the x-axis and temperature of a caloric material on the y-axis. As can be seen, the temperature of the caloric material drops as isentropic mixing occurs with increasing concentrations of the ion material. Additionally, as the ion concentration is reduced during isentropic separation the caloric material increases back to its original temperature.

[0039] FIG. **4** illustrates a diagram of an example of a separator **400** of an ionocaloric heating and cooling system, according to some embodiments of the present disclosure. The separator **400** includes a diode compartments **412**A-B, separation compartment **410**A-B, cation exchange membranes **404**A-B and anion exchange membrane **406**. In some examples, the cation exchange membranes **404**A-B may alternatively be an anion exchange membrane and the anion exchange **406** may be a cation exchange membrane. The diode compartments **412**A-B may each include a graphite felt **402** across which a voltage is applied. In some examples, the voltage may be relatively small (e.g., between approximately 0.01 Volts to 2 Volts) In some examples, the voltage may be about 0.4 Volts. Additionally, the diode compartments **412**A-B may include a redox coupled (e.g., iodide triiodide redox couples). In some embodiments, the diode compartments **412**A may include graphite felt, graphite paper, carbon felt, carbon paper, stainless steel foil and/or mesh, nickel foil and/or mesh/foam, platinum coated foils, and ferricyanide/feroocyanide and bromine/bromide redox couples.

[0040] In some embodiments, the separator **400** may receive a liquid mixture of a caloric material and an ion liquid. The separator **400** may initially receive the liquid mixture in equal concentrations in the separation compartments **410**A-B. The voltage applied to the graphite felt **402** in the diode compartments **412**A-B may cause one or more chemical reactions that drive cations across the cation exchange membrane **404**A from separation compartment **410**A to diode compartment **412**A and across cation exchange membrane **404**B from diode compartment **412**B to separation compartment **410**B. The cation exchange may further drive anions across anion exchange membrane **406** from separation compartment **410**A to separation compartment **410**B. After sufficient time of applying the voltage, the result may be that only the caloric material remains in separation compartment **410**A while the separation compartment **410**B includes only an ion concentration. Thus, the caloric material separated in liquid form may be provided to a precipitator to return to solid form once the electrochemical field has been removed and the melting point is once again above ambient temperature. The ion concentration can be returned to a mixer for reuse in the ionocaloric cycle.

[0041] In some embodiments, the electrode compartments are filled with 0.5 M NaI_3 and 1.5 M NaI, forming a symmetric cell. Current is driven across the cell using an iodide triiodide redox couple. At the negative electrode, triiodide is reduced, following

$$I_3^- + 2e^- \rightarrow 3I^-,$$

and at the positive electrode, iodide is oxidized such that

$$3I^- \rightarrow I_3^- + 2e^-.$$

The reactions may be symmetric and thus the change in Gibbs free energy between the oxidized and reduced states is zero. Accordingly, the reaction proceeds at any non-zero voltage applied across the electrodes. At higher potentials [~1V higher than the iodide triiodide couple versus saturated calomel electrode (SCE)], triiodide is further oxidized to pure iodine,

$$2I_3^- \rightarrow 3I_2 + 2e^-.$$

I_2 is soluble in EC, so it dissolves back into the electrode solution and, upon circulation, either combines with an I^- to reform

$$I_3^-$$

or gets reduced at the negative electrode to the same result. Positive ions (Na^+) will then be driven toward the negative electrode upon reduction of

$$I_3^-.$$

Na^+ can cross the cation-exchange membranes but are prevented from crossing the anion-exchange membrane (e.g., by Donnan exclusion). Likewise, the negative I^- ions will be driven toward the positive electrode upon oxidation of I^- and may cross the anion-exchange membrane, but they are prevented from crossing the cation-exchange membranes. Because the membranes are selective to only one type of ion, one compartment will eventually become completely depleted of ions while the other becomes concentrated.

[0042] FIGS. **5**A and **5**B illustrate a separator using capacitive deionization or Faradaic deionization, according to some embodiments. As depicted in **5**A, a voltage may be applied across electrodes which causes ions in the solution to drift toward the electrodes depending on the charge of the ions. Accordingly, the ions may be drawn out of the solution toward the electrodes causing dilution of the caloric material. The diluted caloric material may then be transported from the separator (e.g., to a crystallizer/precipitator). As depicted in FIG. **5**B, once the diluted caloric material is removed, the voltage on the electrodes may be reversed to undo the work performed on the ions. The result may be a concentrated electrolyte solution of ions which may be provided to a mixer, as described with respect to FIG. **1**.

[0043] FIG. **6** illustrates an example of a precipitator of an ionocaloric heating and cooling system, configured in accordance with some embodiments. As depicted, a precipitator **605** may be coupled to a hot reservoir **610** (e.g., via a heat exchanger **612**). Precipitator **605** may be the same or similar to precipitation chamber **105** as described with respect to FIG. **1**. The precipitator **605** may receive the dilute liquid of caloric material **602** and allow the caloric material **602** to precipitate (e.g., crystallize). As the caloric material precipitates, it rejects excess heat to remain at the same temperature (e.g., the melting point/freezing point) as its entropy decreases. The precipitator **605** may operate at ambient temperature without additional cooling applied to the precipitator **605**. Once the precipitator **605** may then output the solid caloric material **608** to be returned to a mixer (e.g., as described in FIG. **7** below). In some embodiments, the hot reservoir **610** may be used for heating in any potential context such as in a boiler, hot water heater, central air, air source steam generating heat pumps, or any other use. For example, an air source steam generating heat pump may extract heat from air heated by the ionocaloric heating cycle. The heat extracted by the air source steam generating heat pump may be used to generate steam from the high concentration of heat provided by the ionocaloric heating cycle.

[0044] FIG. **7** illustrates an example of a mixer **710** of an ionocaloric heating and cooling system, configured in accordance with some embodiments. Mixer **710** may be the same or similar to mixing chamber **110** describe with respect to FIG. **1**. Mixer **710** may receive the solid form of the caloric material **608** (e.g., from a precipitator or other source). The mixer **710** may further receive an ion concentrate **724**, such an ion liquid (e.g., a solution including a large concentration of ions). In some embodiments, the mixer **710** may include a mechanical means to mix the ion concentrate **724** with the solid material. For example, a stirring mechanism may be included in the mixer **710**. The combination of solid material and ion concentrate **724** may be output from the mixer **710** as a slurry mixture **712** before the solid material has the opportunity to melt due to the lowered melting point of the caloric material in the presence of the electrochemical field applied by the ion concentrate. In some embodiments, although depicted separately, the mixer and the melter may be combined into a single chamber or component. For example, the mixer may be used to continuously mix or stir the slurry mixture to maintain consistent and even mixture as the caloric material melts.

[0045] FIG. **8** illustrates an example of a melter **815** of an ionocaloric heating and cooling system, configured in accordance with some embodiments. As depicted, a melter **815** may be coupled to a cold reservoir **810** (e.g., via a heat exchanger **812**). Melter **815** may be the same or similar to melting chamber **115** as described with respect to FIG. **1**. Melter **815** may receive a slurry mixture **512** (e.g., from a mixer). The melter **815** may be thermally insulated and may be coupled to a cold reservoir **810**. Accordingly, as the caloric material melts it absorbs heat from the cold reservoir via a heat exchanger **812**. Heat may be extracted from the cold reservoir **810** by the melting caloric material until the caloric material is completely melted resulting in a liquid mixture **817**. The liquid mixture **817** may then be output from the melter **815** to a separator (e.g., as described in FIG. **4** or **5**.) The cold reservoir **810** may be used in any process of cooling such as refrigeration, central air cooling, electronics cooling, or any other cooling application.

[0046] FIG. **9** illustrates a flow chart of a method of ionocaloric heating and cooling, implemented in accordance with some embodiments. In various embodiments, a method, such as method **900**, may be implemented to provide heating or cooling via an ionocaloric cycle. With reference to FIG. **9**, method **900** illustrates example functions or processes used by various embodiments. Although

specific function blocks ("blocks") are disclosed in method **900**, such blocks are examples. That is, embodiments are well suited to performing various other blocks or variations of the blocks recited in method **900**. It is appreciated that the blocks in method **900** may be performed in an order different than presented, and that not all of the blocks in method **900** may be performed.

[0047] Accordingly, method **900** may commence with operation **902** during which a first material in a solid state is provided. The first material may include one of the materials listed in FIG. **11**. For example, the first material may be ethylene carbonate. Alternatively, the first material may be magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate. Iron chloride hexahydrate, cadmium nitrate tetrahydrate, room temperature liquid salts such as 1-Butyl-2,3-dimethlynlimidazolium tetrafluoroborate puruum and 1-ethyl-3-methylimidazolium nitrate, polyalcohols such as eryhritol, d-mannitol, d-dulcitol, inositol, neopentyl glycol, fatty acids such as paraffin waxes (heptadecane, octadecane) and lauric, myristic, palmitic, and stearic acids. In some examples, the first material may be provided via mechanical means such as a conveyor, piping, pump, gravity, etc. In some embodiments, the first material may be provided in many smaller pieces of the solid material, in one large solid form, or in various shapes and sizes of the solid form of the first material. For example, the first material may be in the form of a slurry (e.g., a partial solid, partial liquid) rather than a full solid to allow the first material to be pumped from a precipitator/crystallizer to a mixer/melter. In some examples, the first material may be a salt hydrate.

[0048] Method **900** may proceed to operation **904** during which the first material is combined with a second material. The second material may provide an electrochemical field to the first material to reduce the melting point of the first material. In some examples, the second material includes an ion concentration. For example, the second material may include one or more of the ionic materials or salts provided in FIG. **12**. For example, the second material may be sodium iodide. Alternatively, the second material may be magnesium nitrate, magnesium chloride, ammonium nitrate, potassium nitrate, potassium chloride, sodium thiosulfate, lithium bromide, lithium iodide, lithium chloride, lithium carbonate, water, and ethanol. Accordingly, the ion concentration mixed with the first material may apply the electrochemical field to the first material, thus lowering a melting point of the first material. The original melting point of the first material may be at or above ambient temperature while the new melting point after mixture with the ion concentration may be below ambient temperature. In some examples in which the first material is a salt hydrate, the second material may be water (e.g., concentrated water). For example, the water may apply an electrochemical field to the salt hydrate, reducing the melting point of the salt hydrate and cooling the mixture.

[0049] Method **900** may proceed to operation **906** during which the first material is allowed to melt. The first material may extract heat from a cold reservoir upon melting. Because the melting point of the first material is lowered by the application of the electrochemical field, the first material becomes more stable as a liquid rather than a solid. Thus, the first material uses its internal heat energy to phase change to the liquid. Accordingly, the first material may absorb energy until the first material is completely converted into the liquid phase. In some embodiments, the cold reservoir may be used to perform a cooling application, such as central air conditioning, refrigeration, electronics cooling, or any other use of large cooling capacity.

[0050] Method **900** may proceed to operation **908**, during which the first material is separated from the second material by a separation technique using a voltage applied to the combination of the first material and the second material. Any voltage applied separation technique may be used to separate the second material from the first material. In some embodiments, the separation technique may include electrodialysis in which the voltage is applied to the liquid mixture via electrode compartments of iodide triiodide redox couples. In other embodiments, the separation technique may include faradaic deionization in which the voltage is applied to the liquid mixture via electro-active electrodes, which serve to modulate the salt concentration through ion conversion within the electrodes themselves. In some embodiments, the separation technique may include evaporation, distillation, filtering, reverse-osmosis, or any other methods to separate a salt hydrate from water.

[0051] Method **900** may proceed to operation **910**, during which the first material is allowed to precipitate. The first material may release heat to a hot reservoir during precipitation. Once the second material is separated from the first material, the melting point and freezing point of the first material may return to above ambient temperature (e.g., room temperature). Accordingly, the material may release excess energy as it crystallized back into the solid form. In some embodiments the hot reservoir may be used to perform a heating application, such as for steam generation, central air heating, or any other use of large heat input capability.

[0052] FIG. **10** illustrates a flow chart of a method of ionocaloric heating and cooling, implemented in accordance with some embodiments. In various embodiments, a method, such as method **900**, may be implemented to provide heating or cooling via an ionocaloric cycle. With reference to FIG. **10**, method **1000** illustrates example functions or processes used by various embodiments. Although specific function blocks ("blocks") are disclosed in method **1000**, such blocks are examples. That is, embodiments are well suited to performing various other blocks or variations of the blocks recited in method **1000**. It is appreciated that the blocks in method **1000** may be performed in an order different than presented, and that not all of the blocks in method **1000** may be performed.

[0053] Accordingly, method **1000** may commence with operation **1002** during which a first material in a solid state is provided to a mixer. Method **1000** may proceed to operation **1004**, during which a second material is provide to the mixer. The second material may include an ion concentration. Method **1000** may proceed to operation **1006**, during which the mixer combines the first material in the solid state with the second material to produce a slurry mixture. Method **1000** may proceed to operation **1008**, during which the slurry mixture is transported to a melter. Method **1000** may proceed to operation **1010**, during which the first material in the slurry mixture is allowed to melt, extracting heat from a cold reservoir. Method **1000** may proceed to operation **1012**, during which the melted liquid mixture is provided to a separator. Method **1000** may proceed to operation **1014**, during which the first material in the liquid mixture is separated from the second material via electro-

dialysis. Method **1000** may proceed to operation **1016**, during which the first material in the liquid form is provided to a precipitator and the second material in the form of an ion concentrate is returned to the mixer. Method **1000** may proceed to operation **1018**, during which the first material is allowed to precipitate and reject heat to a hot reservoir.

[0054] Although the foregoing concepts have been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. It should be noted that there are many alternative ways of implementing the processes, systems, and apparatus. Accordingly, the present examples are to be considered as illustrative and not restrictive.

What is claimed is:

1. A method of caloric cooling comprising:

providing a first material in a solid state;

combining the first material with a second material, wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material;

allowing the first material to melt, wherein the first material extracts heat from a cold reservoir upon melting;

separating the first material from the second material by a separation technique using a voltage applied to a combination of the first material and the second material; and

allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir during precipitation.

2. The method of claim **1**, wherein the first material has a melting point at or above an ambient temperature.

3. The method of claim **1**, wherein the second material comprises an ion concentration to provide the electrochemical field.

4. The method of claim **1**, wherein the second material comprises at least one of sodium iodide, potassium iodide, magnesium nitrate, magnesium chloride, ammonium nitrate, potassium nitrate, potassium chloride, sodium thiosulfate, lithium bromide, lithium iodide, lithium chloride, lithium carbonate, water, or ethanol.

5. The method of claim **1**, wherein the separation technique comprises electrodialysis or Faradaic deionization.

6. The method of claim **5**, wherein the electrodialysis comprises separating the first material from the second material by applying the voltage across electrode compartments comprising iodide triiodide redox couples.

7. The method of claim **1**, wherein the first material comprises at least one of ethylene carbonate, magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate, Iron chloride hexahydrate, or cadmium nitrate tetrahydrate.

8. A system comprising:

a mixing chamber to combine a first material in a solid state with a second material wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material;

a melting chamber allowing the first material to melt, wherein the melting chamber is coupled to a cold reservoir and wherein the first material extracts heat from the cold reservoir upon melting;

a separating chamber to separate the first material from the second material via a separation technique comprising a voltage applied to a combination of the first material and the second material; and

a precipitation chamber allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir coupled to the precipitation chamber during precipitation.

9. The system of claim **8**, wherein the first material has a melting point at or above an ambient temperature.

10. The system of claim **8**, wherein the second material comprises an ion concentration to provide the electrochemical field.

11. The system of claim **8**, wherein second material comprises at least one of sodium iodide, potassium iodide, magnesium nitrate, magnesium chloride, ammonium nitrate, potassium nitrate, potassium chloride, sodium thiosulfate, lithium bromide, lithium iodide, lithium chloride, lithium carbonate, water, or ethanol.

12. The system of claim **8**, wherein the separation technique comprises electrodialysis or Faradaic deionization.

13. The system of claim **12**, wherein the electrodialysis comprises separating the first material from the second material by applying the voltage across electrode compartments comprising iodide triiodide redox couples.

14. The system of claim **8**, wherein the first material comprises at least one of ethylene carbonate, magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate, Iron chloride hexahydrate, or cadmium nitrate tetrahydrate.

15. An apparatus comprising:

a mixer to combine a first material in a solid state with a second material wherein the second material provides an electrochemical field to the first material to reduce the melting point of the first material;

a melter allowing the first material to melt, wherein the melting chamber is coupled to a cold reservoir and wherein the first material extracts heat from the cold reservoir upon melting;

a separator to separate the first material from the second material via a separation technique comprising a voltage applied to a combination of the first material and the second material; and

a precipitator allowing the first material to precipitate, wherein the first material releases heat to a hot reservoir coupled to the precipitation chamber during precipitation.

16. The apparatus of claim **15**, wherein the first material has a melting point at or above an ambient temperature.

17. The apparatus of claim **15**, wherein the second material comprises an ion concentration to provide the electrochemical field.

18. The apparatus of claim **15**, wherein the second material comprises at least one of sodium iodide, potassium iodide, magnesium nitrate, magnesium chloride, ammonium nitrate, potassium nitrate, potassium chloride, sodium thiosulfate, lithium bromide, lithium iodide, lithium chloride, lithium carbonate, water, or ethanol and wherein the first material comprises at least one of ethylene carbonate, magnesium nitrate hexahydrate, magnesium chloride hexahydrate, sodium thiosulfate hexahydrate, sodium acetate trihydrate, nickel nitrate hexahydrate, iron nitrate hexahydrate, Iron chloride hexahydrate, or cadmium nitrate tetrahydrate.

19. The apparatus of claim **15**, wherein the separation technique comprises electrodialysis or Faradaic deionization.

20. The apparatus of claim **19**, wherein the electrodialysis comprises separating the first material from the second material by applying the voltage across electrode compartments comprising iodide triiodide redox couples.

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