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FIG. 1

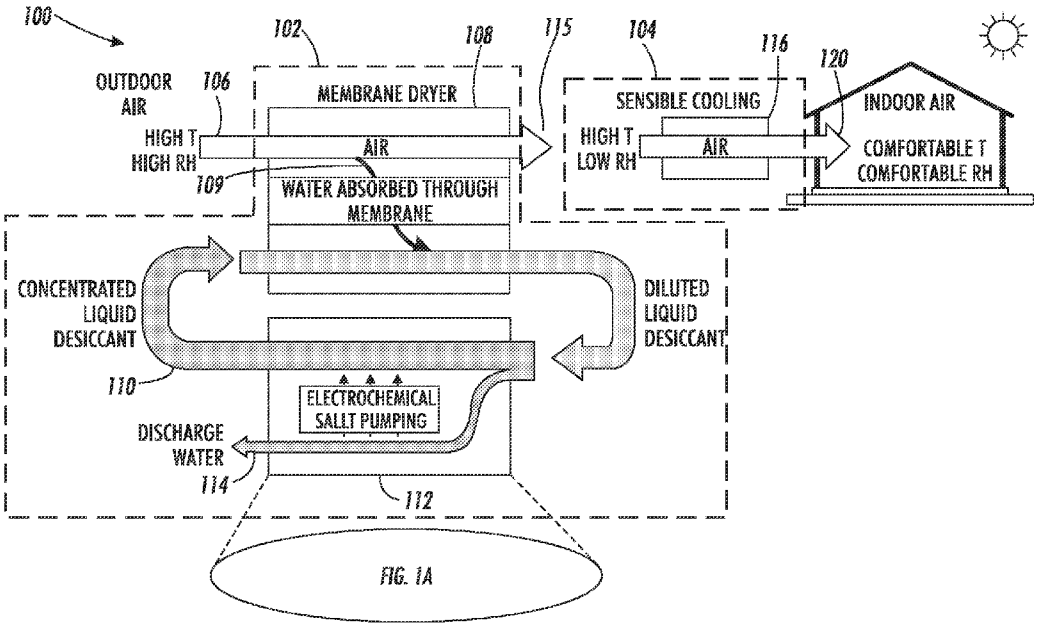


FIG. 1A

(57) Abstract: Air flows across an air-liquid interface such that liquid desiccant flowing through the interface absorbs water from the air and is thereby diluted to form an output stream. The output stream is circulated through an electrodialytic stack having a central ionic exchange membrane and first and second outer ionic exchange membranes. A redox shuttle loop circulates around the first and second outer ionic exchange membranes. A voltage is applied across the electrodialytic stack, which regenerates the liquid desiccant.

[Continued on next page]

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ELECTRODIALYTIC LIQUID DESICCANT DEHUMIDIFYING SYSTEM

[0001] The present disclosure is directed to an electrodialytic liquid desiccant dehumidifying system. In one embodiment, a liquid desiccant system includes an electrodialytic stack with a liquid desiccant loop having a diluted stream and a concentrated stream of liquid desiccant separated by a central ionic exchange membrane. A redox shuttle loop with first and second redox streams is separated from the diluted stream and the concentrated stream of the liquid desiccant loop by respective first and second outer ionic exchange membranes of a different type than the central ionic exchange membrane.

[0002] The liquid desiccant system includes first and second electrodes that are operable to apply a voltage across the electrodialytic stack. The system has an air-liquid interface in fluid communication with the concentrated stream of the liquid desiccant. The air-liquid interface exposes the concentrated stream of the liquid desiccant to air flowing across the air-liquid interface, the concentrated stream being diluted via absorption of water from the air to form an output stream.

[0003] The liquid desiccant system may include a first pump that circulates the liquid desiccant through the electrodialytic stack and the air-liquid interface. The output stream from the air-liquid interface may be split into the diluted stream and the concentrated stream upon entry into the electrodialytic stack. A second pump may be used to circulate the first and second redox streams across the first and second outer ion exchange membranes.

[0004] In another embodiment, a method involves circulating a liquid desiccant through an air-liquid interface. Air flows across the air-liquid interface such that the liquid desiccant absorbs water from the air. The liquid desiccant is diluted via the absorption of the water to form an output stream. The output stream is split to a diluted stream and a concentrated stream at an input to an electrodialytic stack. The electrodialytic stack has a central ionic exchange membrane and first and second outer ionic exchange membrane of a different type than the central ionic exchange membrane. The diluted stream flows between the central ionic exchange membrane and the first outer ionic exchange membrane and the concentrated stream flows between the central ionic exchange membrane and the second outer ionic exchange membrane. A redox shuttle loop circulates around the first and second outer ionic exchange membranes. A voltage is applied across the electrodialytic stack, e.g., to cause ionic movement across the central ionic exchange membrane and the first outer ionic

exchange membrane resulting in a desiccant concentrate moving from the diluted stream to the redox shuttle loop and to the concentrated stream.

[0005] FIGS. 1 and 1A are diagrams of a liquid desiccant system according to an example embodiment;

[0006] FIG. 2 is a perspective view of an air conditioning system according to an example embodiment;

[0007] FIG. 3 is a block diagram of an air conditioning system according to an example embodiment;

[0008] FIG. 4 is a diagram of a liquid desiccant system according to an example embodiment;

[0009] FIGS. 5A and 5B are diagrams of electrodialytic stacks according to example embodiments;

[0010] FIG. 6 is a diagram of a heat exchanger used with an air-liquid interface according to an example embodiment;

[0011] FIG. 7 is a diagram of a multi-stage electrodialytic stack according to an example embodiment; and

[0012] FIG. 8 is a flowchart of a method according to an example embodiment.

[0013] The present disclosure relates to liquid desiccant systems. A liquid desiccant system may be used in, among other things, heating, ventilation, and air-conditioning (HVAC). Air conditioning is responsible for nearly 10% of U.S. electricity consumption, with dehumidification accounting for more than half of the load in humid regions. The present disclosure describes an efficient thermodynamic approach to dehumidification for air conditioning. Generally, a system includes a membrane dehumidifier in tandem with a redox-assisted electrodialysis liquid desiccant concentrator.

[0014] The systems described herein take advantage of a redox-assisted electrodialysis process that enables a membrane-based liquid desiccant air conditioning system. In this redox-assisted electrodialysis (ED) process, an aqueous solution of a redox-active species is circulated between the anode and cathode of an electrochemical stack to concentrate ionic solutions, eliminating thermodynamic phase changes driven by heat or pressure necessary for vapor compression (VC) or desiccant based air conditioning. Liquid desiccants (e.g., aqueous solutions of lithium chloride, LiCl) will absorb moisture from air across a membrane interface. Diluted liquid desiccants will be efficiently re-concentrated, avoiding the latent heat input required to evaporate water. It is estimated that the enhanced efficiency of this new proposed cycle leads to 1.5 Quads of energy savings yearly by 2030.

[0015] In FIG. 1, a diagram illustrates an electrodialytic liquid desiccant air conditioning (ELDAC) system 100 according to an example embodiment. The system 100 includes a desiccant section 102 and a cooling section 104. In the desiccant section 102, outdoor air 106 (and/or recirculated air) is forced across a liquid-carrying membrane dryer 108, also referred to herein as an air-liquid interface. The air 106 may be outside air of high temperature and high relative humidity (RH). Water 109 from the air 106 is absorbed at the membrane interface 108 into a concentrated liquid desiccant 110, e.g., of aqueous LiCl, is then passed through a redox-assisted regenerator 112 to separate dilute stream 114 (e.g., discharge water) and re-concentrate the desiccant stream 110. Other concentrates may be used for the desiccant instead of LiCl, e.g., NaCl, LiBr, and $CaCl_2$.

[0016] The humidity is reduced in the air 115 leaving the desiccant section 102, wherein it is cooled by the cooling section 104. This cooling section 104 may include an evaporator 116 and other components not shown (e.g., condenser, compressor). Because the air 115 entering the cooling section 104 has lower relative humidity compared to the outside/recirculated air 106, the evaporator 116 is more efficient and can reduce the temperature of the cooled air 120 by a greater amount than if the evaporator 116 had to also condense moisture from the incoming air 115. Experimental results measuring the energy used by redox-assisted electrodialysis to concentrate ionic aqueous solutions show that ELDAC system 100 can have a regeneration specific heat input (RSHI) less than 0.05 kBTU/lb, which is up to 30 times lower than currently used thermal regeneration methods.

[0017] As seen in the detail view 122 of FIG. 1A, redox-assisted regenerator 112 has two outer ion exchange membranes 124 that separate the outer redox channels 126 from the inner concentrate 110 and dilute 114 streams. In this example the outer ion exchange membranes 124 are configured as anion exchange membranes (AEM). The concentrate 110 and dilute 114 streams are separated by a central ion exchange membrane 130, which in this example is a cation exchange membrane (CEM). In other configurations, the central ion exchange membrane 130 may be an AEM and the outer membranes 124 may be CEMs.

[0018] An external voltage 132 induces oxidation or reduction in redox-active shuttle molecules, driving ion movement across the membranes 124, 130 without splitting water or producing other gaseous by products (e.g. chlorine) and creating two streams: re-concentrated desiccant 110 and discharge water 114. This goal can be achieved over multiple stages. One proposed redox shuttle is a positively charged ferrocene derivative such as (bis(trimethylammoniopropyl)ferrocene/ bis(trimethylammoniopropyl) ferrocenium, $[BTMAP\text{-}Fc]^{2+}$/$[BTMAP\text{-}Fc]^{3+}$) 134, which is non-toxic, highly stable, has very rapid

electrochemical kinetics and negligible membrane permeability. Other redox shuttle solutions may include ferrocyanide/ferricyanide ($[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$) or a negatively charged ferrocene derivative. The moving parts of the system may include low pressure pumps for liquid circulation and fans for air circulation.

[0019] In FIG. 2, a perspective view shows details of an ELDAC system 200 according to an example embodiment. In FIG. 3, a block diagram shows functional relations between some of the components shown in FIG. 2, as well as showing other components according to additional embodiments. The system 200 includes an enclosure 202 that holds various functional components and provides air duct paths. Humidified air 214 (e.g., outside and/or return air) is directed through a first duct 220 via an air blower 212. This air 214 is forced across an air-liquid interface dehumidifier 206. In this example, the dehumidifier 206 is configured as a rectangular membrane element that fills the first duct 220.

[0020] Within a frame 206a of the dehumidifier 206 are one or more planar membranes 206b through which liquid desiccant is circulated. In other embodiments, hollow tube, liquid-to-air surfaces, liquid spray, may be used in the dehumidifier 206 instead of or in addition to a planar membrane 206b. Movement of the fluid desiccant through the membrane 206b may be accomplished using any combination of capillary action, gravity feed, direct pumping of the liquid, etc. A grill 206c may be provided for mechanical support of the membrane 206b to reduce flexing caused by air pressure from air flow 214. A liquid pump 207 is used to move the liquid desiccant from an optional storage tank 210 to the membrane dehumidifier 206, where it absorbs water from the air 214 and is fed back to a redox-assisted regenerator 208. The redox-assisted generator 208 separates water from the liquid desiccant, where the separated water is discharged via a drain 209. Note that while the components 207, 208, 210 and associated piping are shown outside the enclosure 202 for convenience of illustration, they may be partially or fully located within the enclosure 202.

[0021] The air 216 that has passed through the membrane dehumidifier 206 has low RH and so can be more efficiently processed by a sensible heat remover 204, e.g., an evaporator of a refrigerant-cycle air conditioner. The cooled air 218 that has passed through the sensible heat remover 204 passes through supply duct 220 where it exits the enclosure 202 and is used to cool a target space, e.g., building, vehicle, etc.

[0022] Note that in FIG. 3, a redox storage tank 300 is shown in fluid communication with the LD regenerator 208. The ELDAC system 200 may include one or both of the redox and desiccant reservoirs 300, 210. Note that the desiccant storage 210 may store fluid for both the concentrate stream and dilute stream (e.g., streams 110 and 114 in FIG. 1), by using

separate reservoirs or a single reservoir with two or more partitions. The redox storage 300 may similarly store concentrated and dilute parts of the redox stream (e.g., bottom and top parts of stream 126 shown in FIG. 1). These reservoirs 210, 300 may be used as buffers in some embodiments. For example, if the water draining from the ELDAC system 200 does not equal the water being absorbed from the air, one of concentrated or diluted desiccant (or a combination of both) may be drawn from the reservoir 210 to ensure the desiccant loop maintains the desired concentrate levels and/or flow rates.

[0023] The reservoirs 210, 300 may be of sufficient capacity to be used for other purposes besides dehumidification. For example, as is described in U.S. Patent Application 16/200,289 (Attorney docket number 20171214US03 / PARC.225U1), an electrodialytic battery 302 may use the redox solutions 300 to generate electricity, thus recovering some of the electricity used in dehumidification. Such processes may be run together with or separately from dehumidification. For example, electricity generation may occur at night when the system is lightly utilized or shut off.

[0024] In FIG. 4, a diagram shows additional details of a liquid desiccant system according to an example embodiment. An electrodialytic stack 400 provides an enclosure for a liquid desiccant loop 402 and a redox shuttle loop 404. The loops 402, 404 are separated within the housing 400 by outer exchange membranes 406 and diluted/concentrate paths 402a, 402b of the liquid desiccant loop 402 are separated by a central exchange membrane 408. The fluids in the loops 402, 404 are driven by pumps 412, 410, respectively.

[0025] The liquid desiccant loop 402 starts with concentrated liquid desiccant at point 402c. The desiccant loop 402 includes an aqueous ionic solution such as lithium chloride in water. Typical starting concentrations will be ~30% desiccant by weight. The concentrated desiccant solution is brought into contact with an air-to-membrane interface/exchanger 414, such as the membrane dehumidifier 206 shown in FIGS. 2 and 3. At the exchanger 414, higher RH air 416 enters and lower RH air 418 leaves. Water vapor 420 from the air is pulled across a water selective membrane 422 (or other liquid-air interface) at the exchanger 414 by the desiccant thereby diluting the desiccant solution which exits at a lower concentration at point 402d.

[0026] At the electrodialytic stack 400, the lower concentration liquid desiccant solution 402d is split at junction 402e split into separate streams 402a, 402b that are brought into contact with the membranes 406, 408of the stack 400. Stream 402b is concentrated as it passes through the stack 400 and reenters the pump 412 having the same concentration as

point 402c. The other stream 402a is diluted as it passes through the stack 400 and leaves as a highly diluted stream of water which can be drained, stored, or used for some other purpose.

[0027] The pump 410 circulates the redox shuttle between points 404a and 404b, whereupon it comes into contact with electrodes 424. A voltage 426 applied across the electrodialytic stack drives ions from stream 402a to stream 402b, from stream 402a into stream 404b, and from stream 404a into stream 402b. In each case, driving the ions through the membranes 406, 408 affects the concentration. An alternate embodiment of an electrodialytic stack 500 is shown in FIG. 5A using LiCl as the desiccant concentrate and $[BTMAP\text{-}Fc]^{2+}/[BTMAP\text{-}Fc]^{3+}$ as the redox shuttle. The LiCl desiccant concentrate is split into a desalinate/diluted stream and a concentrated stream 504 by a central ionic exchange membrane 506, in this case a CEM. A redox shuttle loop 508 has first and second redox streams 508a-b separated from the diluted stream and the concentrated stream of the liquid desiccant loop by respective first and second outer ionic exchange membranes 507, 509 of a different type (in this case an AEM) than the central ionic exchange membrane 506.

[0028] Another alternate embodiment of an electrodialytic stack 510 is shown in FIG. 5B using LiCl as the desiccant concentrate and $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ as the redox shuttle. The LiCl desiccant concentrate is split into a desalinate/diluted stream and a concentrated stream 514 by a central ionic exchange membrane 516, in this case an AEM. A redox shuttle loop 518 has first and second redox streams 518a-b separated from the diluted stream and the concentrated stream of the liquid desiccant loop by respective first and second outer ionic exchange membranes 517, 519 of a different type (in this case a CEM) than the central ionic exchange membrane 516. Note that the electrodialytic stacks 500, 510 shown in FIGS. 5A and 5B can be used in any of the dehumidification loops shown herein.

[0029] The dehumidification part of the above-described system requires only input electricity for driving pumps and the electrodialytic stack as well as an input air stream to be dehumidified. There will be outlet streams of water and low RH air. The system is intended for use for dehumidification, although it may be adapted for additional uses, e.g., generating electricity from stored redox solution. A benefit is provided because ELDAC requires significantly less energy than existing dehumidification systems due to the use of electrodialytic concentration at zero or near-zero overpotential. Because the system does not rely on water splitting to drive ion motion, ELDAC does not generate any toxic or flammable gases (e.g. chlorine or hydrogen) when used on concentrated salt solutions unlike other electrochemical processes like conventional electrodialysis. An example application could be

using ELDAC upstream from a normal air conditioner to eliminate the latent heat load to the air conditioner and lower air conditioning bills.

[0030] The absorption of the moisture in the liquid desiccant is exothermic, such that it will increase the temperature of the air-liquid interface that carries the liquid desiccant. This increase in temperature could result in increased loads on a sensible cooling section that receives air that passes through the air-liquid interface. In FIG. 6, a diagram shows a system for removing heat from an air-liquid interface 600 according to an example embodiment. A heat exchanger 602 is thermally coupled to heat transfer elements 604 that are distributed through parts (e.g., the membrane) of the interface 600.

[0031] The heat transfer elements 604 may be conductive strips (e.g., metals, carbon nanotubes, etc.), gas-filled or liquid-filled passive heat pipes (e.g., thermosiphon), tubes through which a gas or liquid is pumped, radiative heat absorbers, or other heat-carrying structures known in the art. The heat carried through elements 604 is delivered to the heat exchanger 602, which is subjected to a cooling flow 606. The cooling flow 606 is a gas or liquid flow that carries heat away from the heat exchanger 602 and ultimately may dump the heat to an ambient heat sink (e.g., air, soil, water). In other embodiments, the heat 608 may be transferred (e.g., along heat transfer path 610) to other heat sinks, such as an electrodialytic stack 612 (which may be the same stack that provides desiccant to the interface 600 or a different stack) and/or the discharge water 614 from the system (e.g., discharge water 114 in FIG. 1).

[0032] In the previous example, an electrodialytic stack included a single redox loop. In other embodiments, a stack may include multiple redox loops and associated ionic membranes to further increase the level of dilution/concentration and/or to increase the amount of desiccant flow that can be treated. In FIG. 7, a block diagram shows a dual-stage electrodialytic stack 700 according to an example embodiment.

[0033] The electrodialytic stack 700 processes a liquid desiccant loop 702 that is split into a diluted stream 702a and a concentrated stream 702b that passes through a first stage 704. Stream 702a exiting stage 704 is further split into a second diluted stream 702d and a second concentrated stream 702e that passes through a second stage 706. Stream 702e exiting stage 706 is at a lower concentration than stream 702b exiting stage 704 and can be remixed with output stream 702c and reintroduced to the previous stage 704 instead of being remixed with 702b and reintroduced to the air-liquid interface 708. To maximize efficiency, the desiccant concentrations in streams 702c and 702e are about equivalent (e.g., within 0-20%).

[0034] Each of the stages 704, 706 has a central ionic exchange membrane 704a, 706a that separates the diluted streams 702a, 702d and the concentrated streams 702b, 702e. Each of the stages 704, 706 has a redox shuttle loop 704b, 706b with first and second redox streams 704ba, 704bb, 706ba, 706bb separated from the diluted streams 702a, 702d and the concentrated streams 702b, 702e of the liquid desiccant loop 702 by respective first and second outer ionic exchange membranes 704c, 704d, 706c, 706d. The stages 704, 706 each include first and second electrodes 704e, 704f, 706e, 706f that are operable to apply a voltage across the stages 704, 706 of the electrodialytic stack 700.

[0035] An air-liquid interface 708 is in fluid communication with the concentrated stream 702b of the liquid desiccant exiting the first stage 704. The air-liquid interface 708 exposes the concentrated stream 702b of the liquid desiccant to air flowing across the air-liquid interface 708, the concentrated stream being diluted via absorption of water from the air to form an output stream 702c. The output stream 702c is combined with the output stream 702e exiting the second stage 706. A first pump 712 circulates the liquid desiccant through the electrodialytic stack 700 and the air-liquid interface 708. After being combined with output stream 702e, the output stream 702c from the air-liquid interface 708 is split into the diluted stream 702a and the concentrated stream 702b upon entry into the electrodialytic stack 700.

[0036] The voltages across the electrodes 704e, 704f, 706e, 706f cause ionic movement across the central ionic exchange membranes 704a, 706a and the first outer ionic exchange membrane 704c, 706c resulting in a desiccant concentrate moving from the first diluted stream 702a to the first redox stream 704ba of stage 704 and to the first concentrated stream 702b, and similarly from the second diluted stream 702d to the first redox stream 706ba of stage 706 and to the second concentrated stream 702e. Second pumps 714, 716 circulate the redox shuttle loops 704b, 706b such that first redox streams 704ba, 706ba and second redox streams 704bb, 706bb flow across the respective first outer ion exchange membranes 704c, 706c and second outer ion exchange membranes 704d, 706d. The voltages will also cause a second (and similar) ionic movement across the second outer exchange membranes 704d, 706d that results in movement of the desiccant concentrate from the second redox streams 704bb, 706bb to the concentrated streams 702b, 702e.

[0037] Note that the stages 704, 706 may be the same or different. For example, each stage 704 may use a different combination of redox shuttle solution, center and outer exchange membrane type, voltage, membrane geometry, desiccant flow geometry, redox flow rate, etc. In this way, the stages 704, 706 can be optimized for different expected

concentrations within the parts of the diluted streams 702a, 702d and concentrated streams 702b, 702e. The stages 704, 706 may operate at the same time, and one or the other may be shut off under some conditions. For example, if the concentrate level within the diluted stream 702a is below some threshold, one of the stages 704, 706 may be shut off to save energy and reduce wear. If the concentrate level within the diluted stream 702a goes above this threshold, the deactivated stage 704, 706 can be restarted.

[0038] The embodiment shown in FIG. 7 can be extended to more than two stages 704, 706. Further, while the stages 704, 706 are shown as part of a single electrodialytic stack unit 700, they may be implemented as separate enclosures that are coupled, e.g., by piping to carry the streams 702a, 702b, 702d, 702e of the desiccant loop 702. In one embodiment, one redox pump may be used instead of the two pumps 714, 716, e.g., by running loops 704b, 706b in parallel or in series. Note that a multistage electrodialytic stack such as shown in FIG. 7 may be used in any of the embodiments shown previously (e.g., FIGS. 1-5) and may incorporate any features shown in those and other figures, e.g., fluid storage reservoirs, heat exchangers, etc.

[0039] In FIG. 8, a flowchart shows a method according to an example embodiment. The method involves circulating 800 a liquid desiccant through an air-liquid interface. Air is caused to flow 801 across the air-liquid interface such that the liquid desiccant absorbs water from the air. The liquid desiccant is diluted via the absorption of the water to form an output stream. The output stream is split 802 into a diluted stream and a concentrated stream at an input to an electrodialytic stack. The electrodialytic stack has a central ionic exchange membrane and first and second outer ionic exchange membranes of a different type (e.g., cation or anion) than the central ionic exchange membrane.

[0040] The diluted stream is caused to flow 803 between the central ionic exchange membrane and the first outer ionic exchange membrane. The concentrated stream is caused to flow 804 between the central ionic exchange membrane and the second outer ionic exchange membrane. A redox shuttle loop is circulated 805 around the first and second outer ionic exchange membranes. A voltage is applied 806 across the electrodialytic stack to cause ionic movement across the central ionic exchange membrane and the first outer ionic exchange membrane. This movement results in a desiccant concentrate moving from the diluted stream to the redox shuttle loop and to the concentrated stream.

[0041] Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary,

the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

CLAIMS:

1. A liquid desiccant system, comprising:

an electrodialytic stack comprising:

a liquid desiccant loop with a diluted stream and a concentrated stream of liquid desiccant separated by a central ionic exchange membrane;

a redox shuttle loop with first and second redox streams separated from the diluted stream and the concentrated stream of the liquid desiccant loop by respective first and second outer ionic exchange membranes of a different type than the central ionic exchange membrane; and

first and second electrodes that are operable to apply a voltage across the electrodialytic stack; and

an air-liquid interface in fluid communication with the concentrated stream of the liquid desiccant, the air-liquid interface exposing the concentrated stream of the liquid desiccant to air flowing across the air-liquid interface, the concentrated stream being diluted via absorption of water from the air to form an output stream, the output stream being circulated back into the liquid desiccant loop of the electrodialytic stack.

2. The liquid desiccant system of claim 1, further comprising:

a first pump that circulates the liquid desiccant through the electrodialytic stack and the air-liquid interface, the output stream from the air-liquid interface being split into the diluted stream and the concentrated stream upon entry into the electrodialytic stack; and

a second pump that circulates the first and second redox streams across the first and second outer ion exchange membranes.

3. The liquid desiccant system of claim 1, wherein the voltage causes:

a first ionic movement across the central ionic exchange membrane and the first outer ionic exchange membrane resulting in a desiccant concentrate moving from the diluted stream to the first redox stream and to the concentrated stream; and

a second ionic movement across the second outer exchange membrane that causes movement of the desiccant concentrate from the second redox stream to the concentrated stream.

4. The liquid desiccant system of claim 1, wherein the central ionic exchange membrane comprises a cation exchange membrane and wherein the first and second outer ionic exchange membranes comprise anion exchange membranes.

5. The liquid desiccant system of claim 3, wherein the desiccant concentrate comprises LiCl and wherein the redox shuttle loop comprises a positively charged ferrocene derivative.

6. The liquid desiccant system of claim 1, wherein the central ionic exchange membrane comprises an anion exchange membrane and wherein the first and second outer ionic exchange membranes comprise cation exchange membranes.

7. The liquid desiccant system of claim 5, wherein the desiccant concentrate comprises LiCl and wherein the redox shuttle loop comprises ferrocyanide/ferricyanide $[Fe(CN)_6]^{4-/3-}$ or a negatively charged ferrocene derivative.

8. The liquid desiccant system of claim 1, further comprising heat transfer elements in thermal communications with the air-liquid interface, the heat transfer elements carrying heat generated from the absorption of the water from the air into the output stream at the air-liquid interface to a heat sink.

9. The liquid desiccant system of claim 1, further comprising a reservoir that stores a portion of at least one of the diluted stream and the concentrated stream of the liquid desiccant, the stored portion being added to the liquid desiccant loop if the water absorbed from the air does not equal an amount of water added to the diluted stream.

10. The liquid desiccant system of claim 1, further comprising an electrodialytic battery in fluid communication with a reservoir storing a portion of fluid from the redox shuttle loop, the stored portion being used to generate electricity via the electrodialytic battery.

11. The liquid desiccant system of claim 1, further comprising:

a second redox shuttle loop with third and fourth redox streams separated from a second dilute stream and a second concentrate stream of the liquid desiccant loop by respective third and fourth outer ionic exchange membranes; and

a second central ionic exchange membrane between the third and fourth outer ionic exchange membranes, the voltage causing second ionic movement across the second central ionic exchange membrane and the third outer ionic exchange membrane that causes desiccant concentrates from the second diluted stream to be moved to the third redox stream and to the second concentrated stream.

12. The liquid desiccant system of claim 11, wherein the dilute stream of the liquid desiccant loop is split into the second dilute stream and the second concentrated stream as it exits from membrane contact with the redox shuttle loop such that the second diluted stream flows between the second central ionic exchange membrane and the third outer ionic exchange membrane and the second concentrated stream flows between the second central ionic exchange membrane and the fourth outer ionic exchange membrane.

13. The liquid desiccant system of claim 12, wherein the second concentrated stream has approximately an equivalent desiccant concentrate level as the output stream and is remixed with the output stream.

14. A method comprising:

circulating a liquid desiccant through an air-liquid interface;

flowing air across the air-liquid interface such that the liquid desiccant absorbs water from the air, the liquid desiccant being diluted via the absorption of the water to form an output stream;

splitting the output stream to a diluted stream and a concentrated stream at an input to an electrodialytic stack, the electrodialytic stack having a central ionic exchange membrane and first and second outer ionic exchange membrane of a different type than the central ionic exchange membrane;

flowing the diluted stream between the central ionic exchange membrane and the first outer ionic exchange membrane;

flowing the concentrated stream between the central ionic exchange membrane and the second outer ionic exchange membrane; and

circulating a redox shuttle loop around the first and second outer ionic exchange membranes; and

applying a voltage across the electrodialytic stack.

15. The method of claim 14, wherein applying the voltage causes:

a first ionic movement across the central ionic exchange membrane and the first outer ionic exchange membrane resulting in a desiccant concentrate moving from the diluted stream to the redox shuttle loop and to the concentrated stream; and

a second ionic movement across the second outer exchange membrane that causes the desiccant concentrate to move from the redox shuttle loop to the concentrated stream.

16. The method of claim 14, wherein the central ionic exchange membrane comprises a cation exchange membrane and wherein the first and second outer ionic exchange membranes comprise anion exchange membranes.

17. The method of claim 14, further comprising draining the diluted stream from the electrodialytic stack.

18. The method of claim 14, further comprising:

storing a portion of at least one of the diluted stream and the concentrated stream of the liquid desiccant; and

determining that the water absorbed from the air does not equal the water in the diluted stream, and in response thereto, adding the stored portion to at least one of the concentrated stream and the output stream.

19. The method of claim 14, further comprising:

storing a portion of fluid from the redox shuttle loop; and

using the portion of the fluid to generate electricity via an electrodialytic battery.

20. An air conditioning system, comprising:

an electrodialytic stack comprising:

a pump-driven, liquid desiccant loop with a diluted stream and a concentrated stream of liquid desiccant separated by a central ionic exchange membrane;

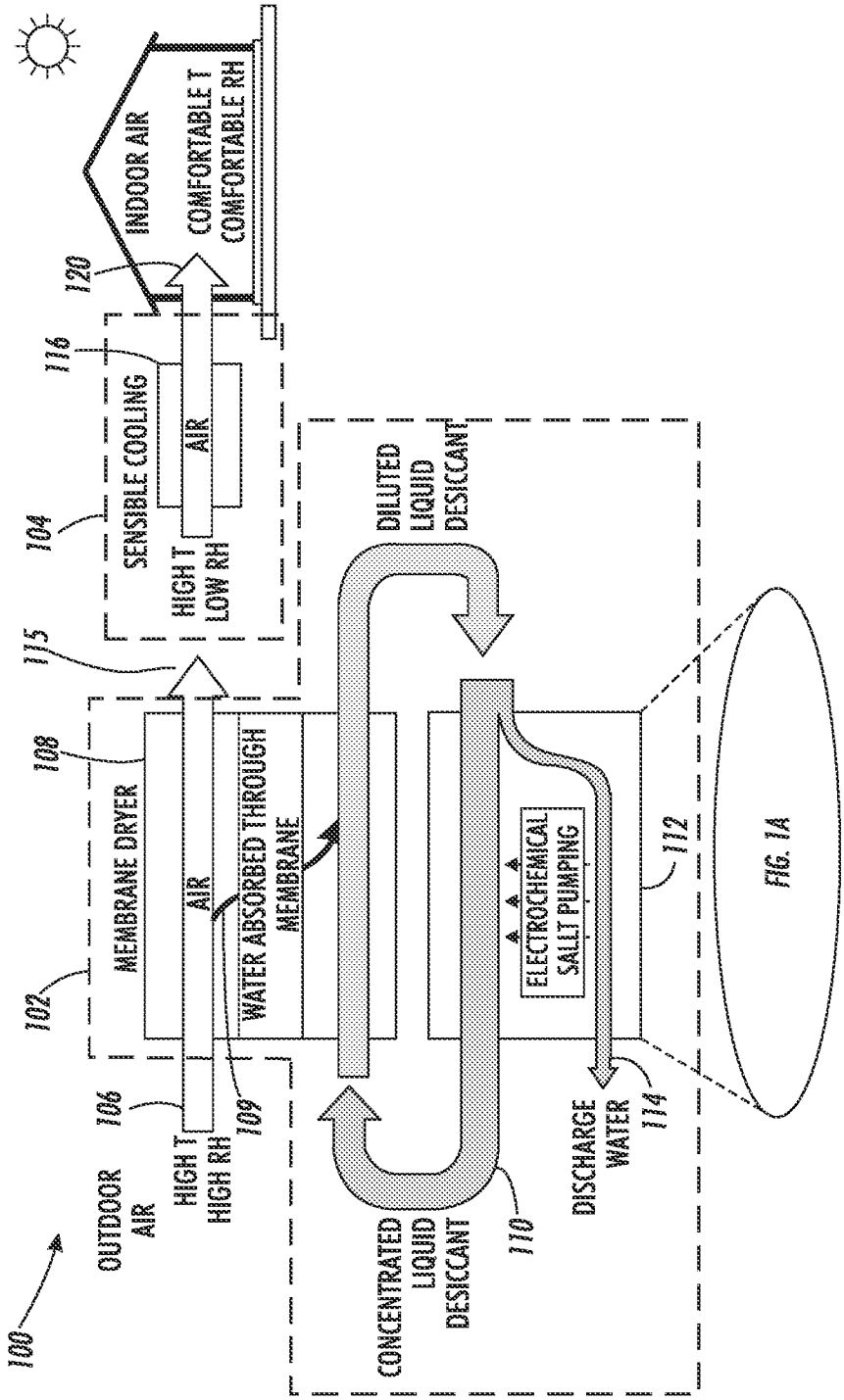
a redox shuttle loop flowing across first and second outer ionic exchange membranes of a different type than the central ionic exchange membrane, the redox shuttle loop separated from the diluted stream and the concentrated stream of the liquid desiccant loop by the first and second outer ionic exchange membranes; and

electrodes that are operable to apply a voltage across the electrodialytic stack;

an air-liquid interface in fluid communication with the concentrated stream, the concentrated stream being diluted via absorption of water from the air via the air-liquid interface to form an output stream of the liquid desiccant and a stream of dehumidified air, the output stream from the air-liquid interface being split into the diluted stream and the concentrated stream upon entry into the electrodialytic stack; and

a sensible cooling element that receives and cools the dehumidified air.

FIG. 1


100
OUTDOOR AIR
HIGH T HIGH RH
106
MEMBRANE DRYER
102
AIR
WATER ABSORBED THROUGH MEMBRANE
108
109
115
SENSIBLE COOLING
AIR
HIGH T LOW RH
104
116
INDOOR AIR
COMFORTABLE T COMFORTABLE RH
120
DILUTED LIQUID DESICCANT
CONCENTRATED LIQUID DESICCANT
110
ELECTROCHEMICAL SALT PUMPING
112
DISCHARGE WATER
114
FIG. 1A

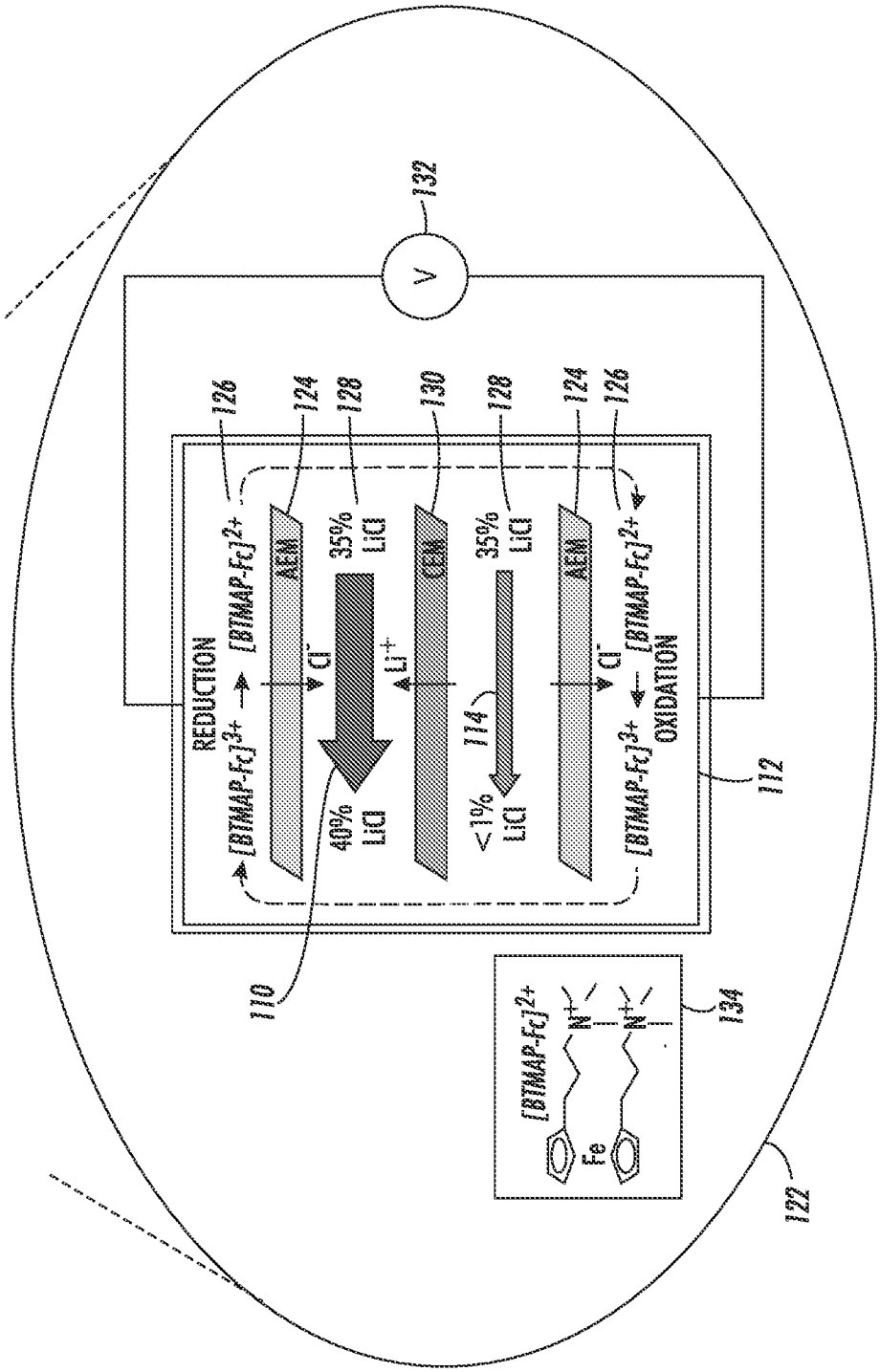

132
V
126
124
128
130
128
124
126
REDUCTION
[BTMAP-Fc]2+
[BTMAP-Fc]3+
AEM
CEM
AEM
Cl-
Li+
35% LiCl
40% LiCl
114
<1% LiCl
35% LiCl
OXIDATION
[BTMAP-Fc]2+
[BTMAP-Fc]3+
110
112
134
122
Fe

FIG. 1A

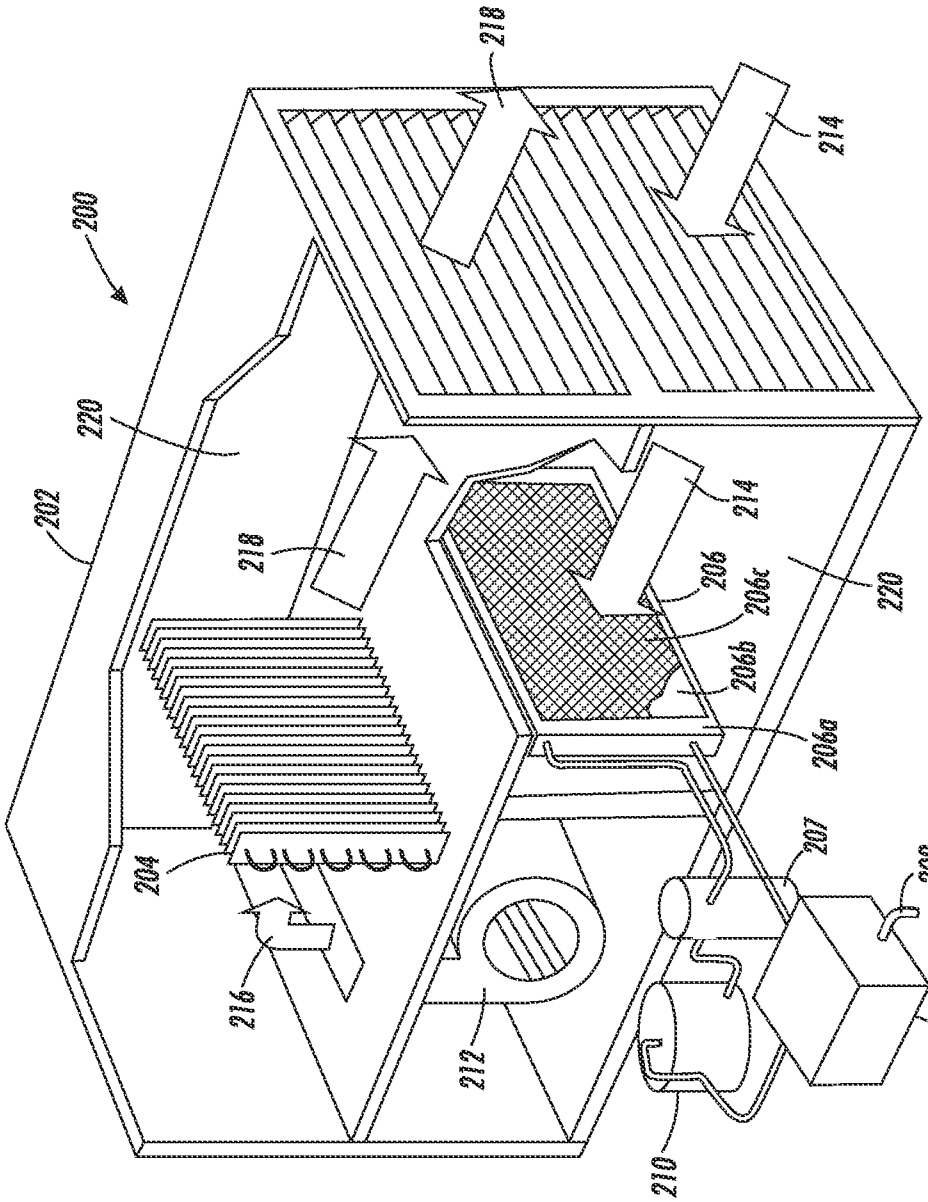

218
214
200
220
202
218
214
206
206c
220
206b
206a
207
209
204
216
212
208
210

FIG. 2

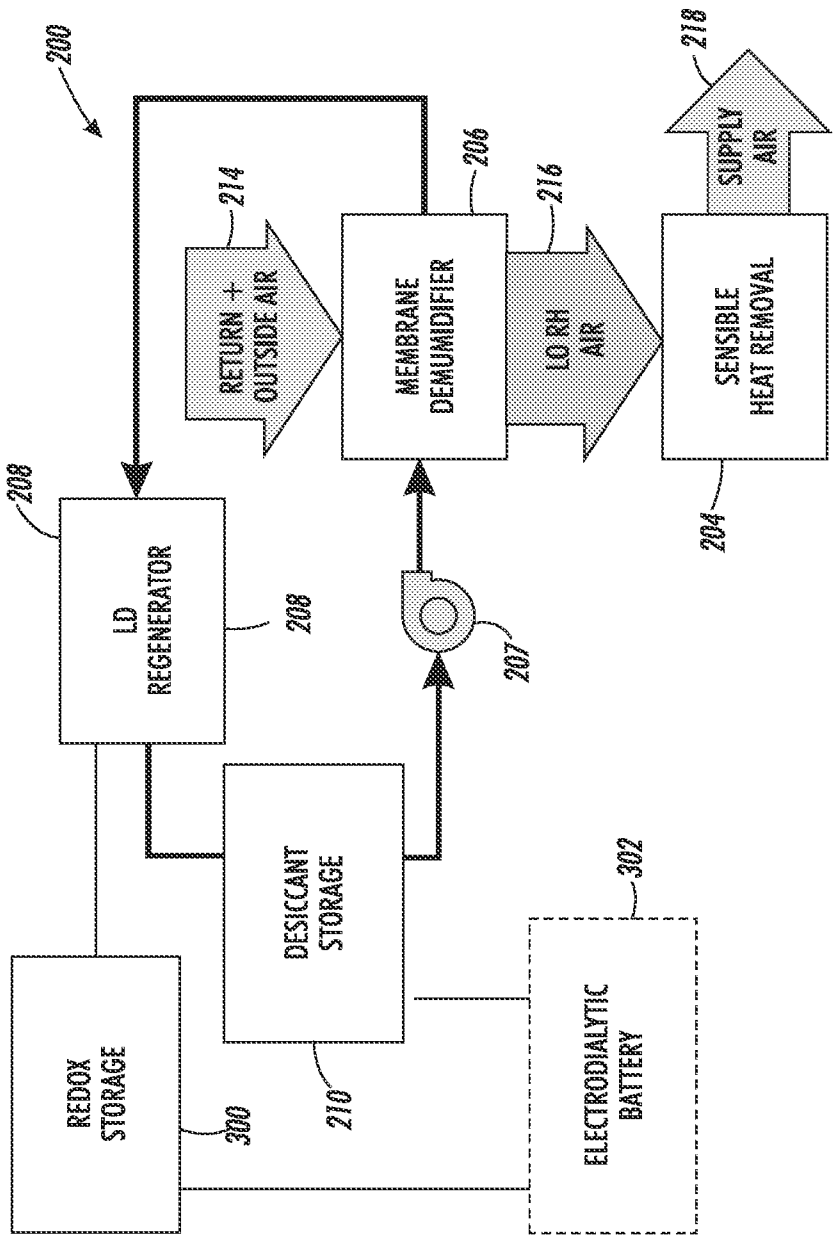

200
214
RETURN + OUTSIDE AIR
206
MEMBRANE DEHUMIDIFIER
216
LD RH AIR
218
SUPPLY AIR
SENSIBLE HEAT REMOVAL
204
208
LD REGENERATOR
208
207
DESICCANT STORAGE
210
302
ELECTRODIALYTIC BATTERY
REDOX STORAGE
300

FIG. 3

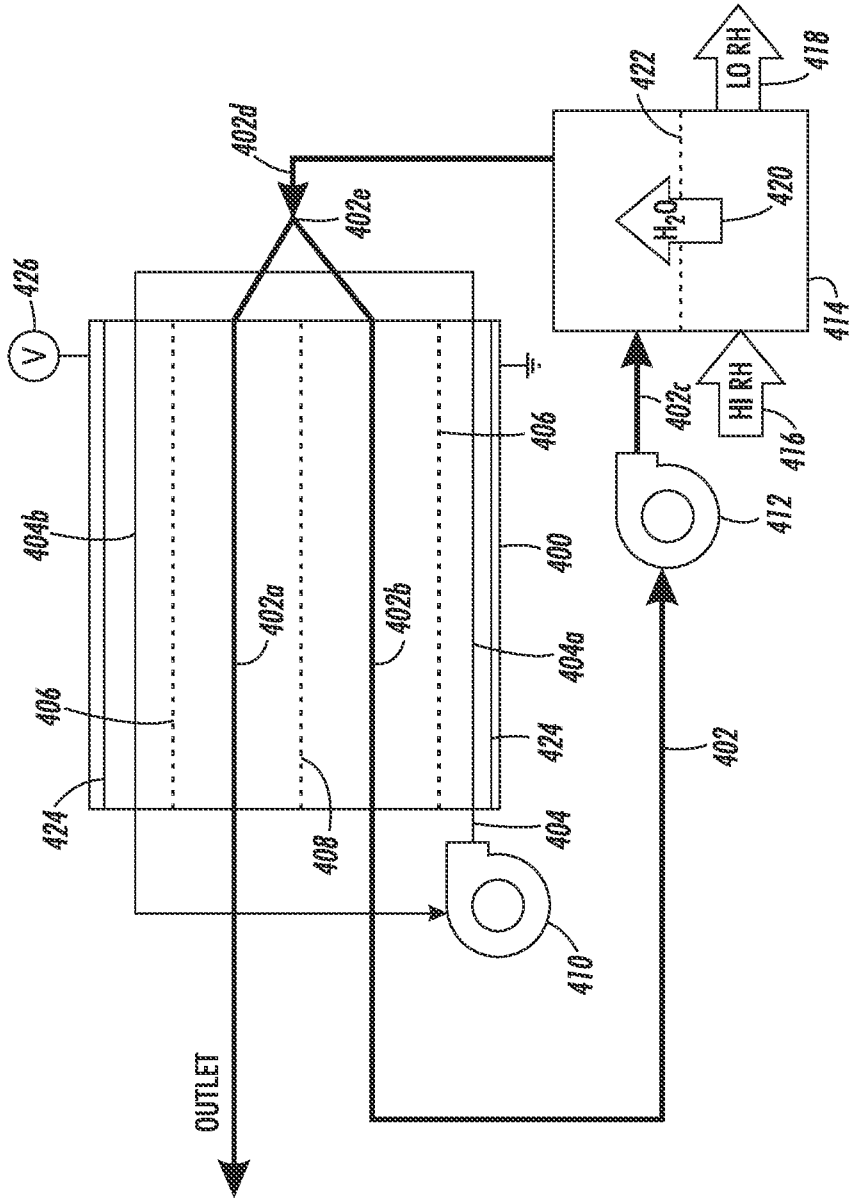

426
V
402d
402e
422
LO RH
418
H_2O
420
414
HI RH
416
402c
406
404b
400
402a
402b
404a
406
424
402
424
408
404
410
412
OUTLET

FIG. 4

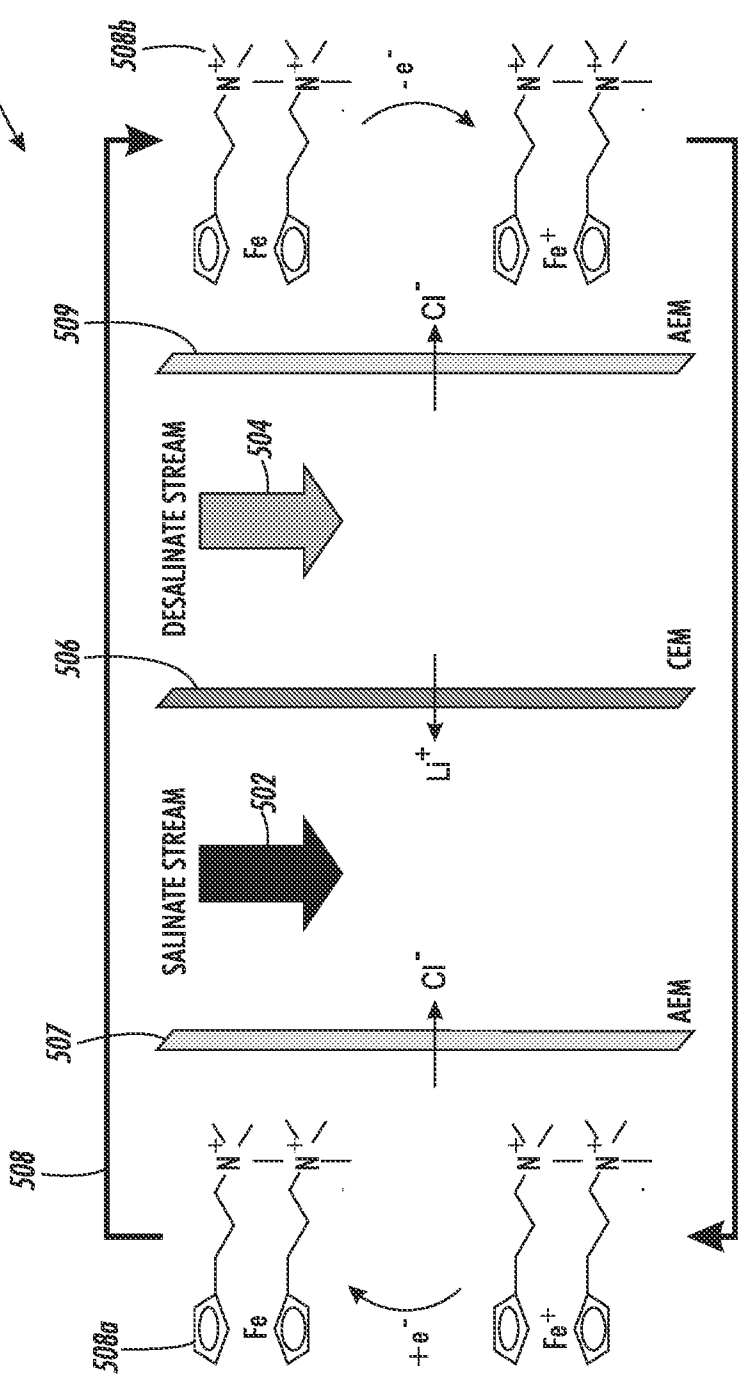

500
508b
509
507
506
508
508a
DESALINATE STREAM
504
SALINATE STREAM
502
AEM
CEM
AEM
Cl⁻
Li⁺
Cl⁻
-e⁻
+e⁻
Fe
Fe⁺
N⁺

FIG. 5A

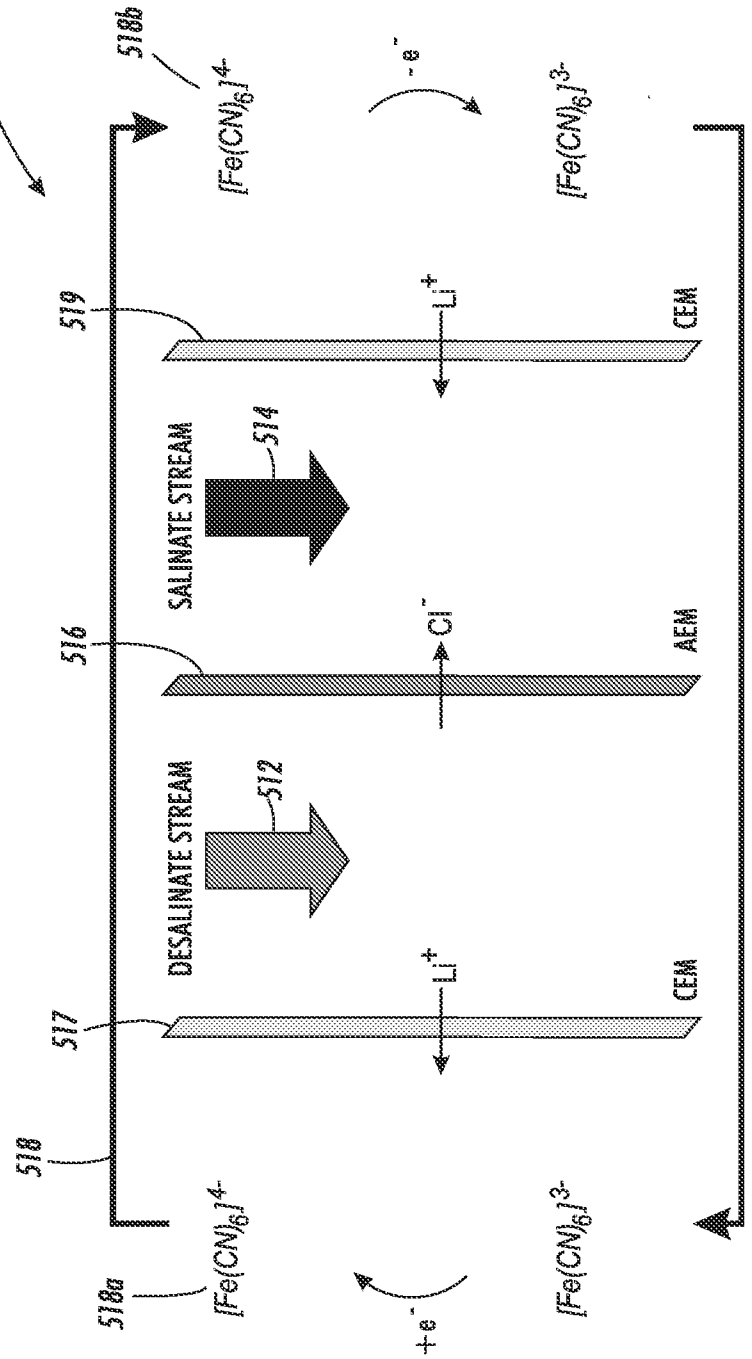

510
518b
$[Fe(CN)_6]^{4-}$
$-e^-$
$[Fe(CN)_6]^{3-}$
519
Li^+
CEM
SALINATE STREAM
514
516
Cl^-
AEM
DESALINATE STREAM
512
517
Li^+
CEM
518
$[Fe(CN)_6]^{4-}$
$+e^-$
$[Fe(CN)_6]^{3-}$
518a

FIG. 5B

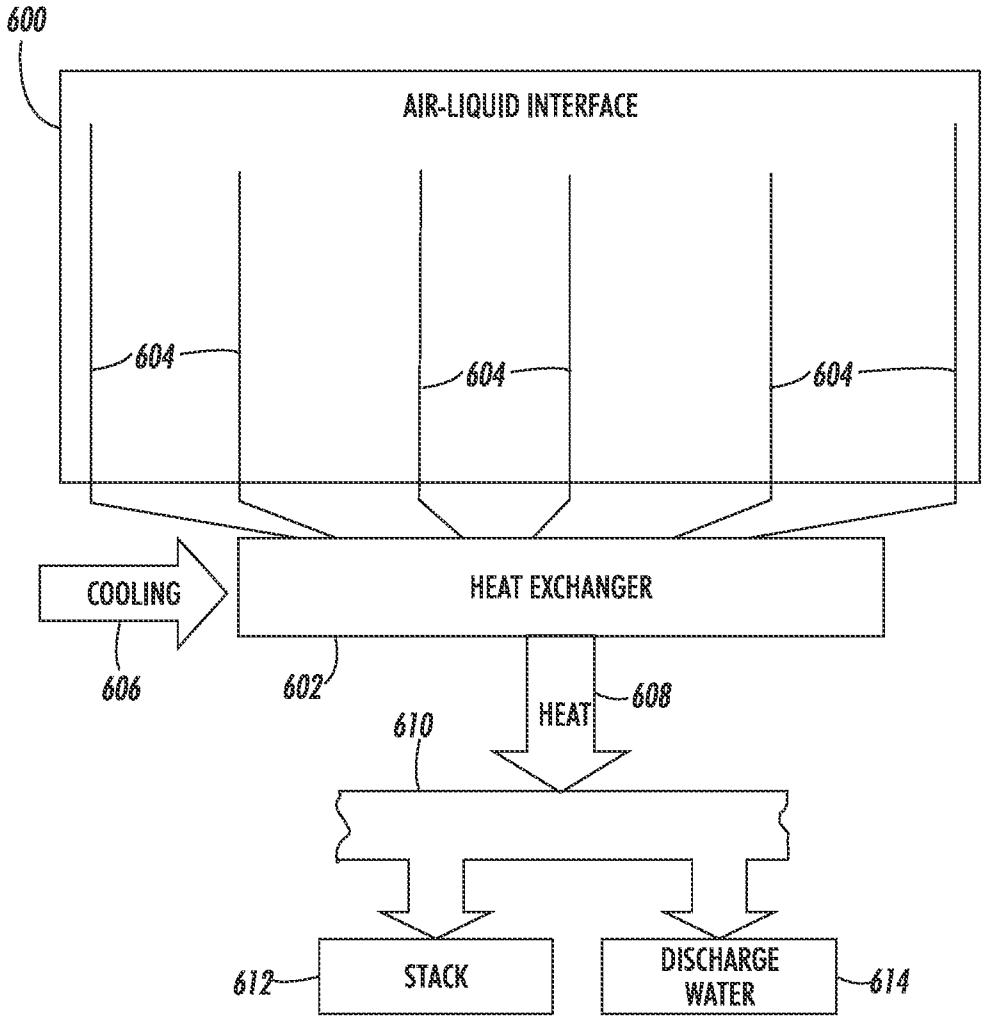

600
AIR-LIQUID INTERFACE
604
604
604
COOLING
HEAT EXCHANGER
606
602
HEAT
608
610
612
STACK
DISCHARGE WATER
614

FIG. 6

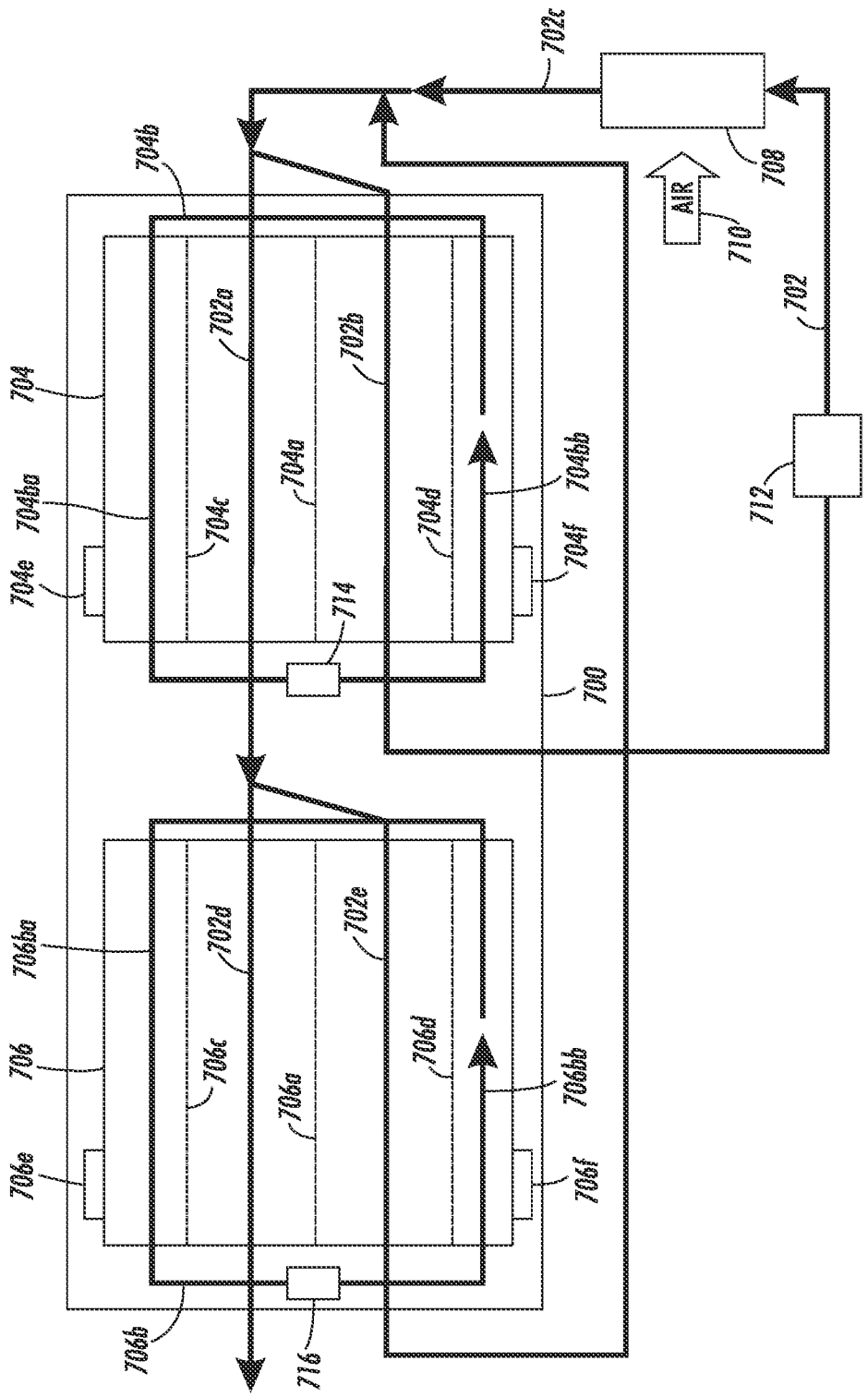

702c
708
AIR
710
702
712
704b
704
702a
702b
704a
704ba
704c
704d
704bb
704e
704f
714
700
706ba
706
706e
702d
702e
706c
706a
706d
706bb
706f
706b
716

FIG. 7

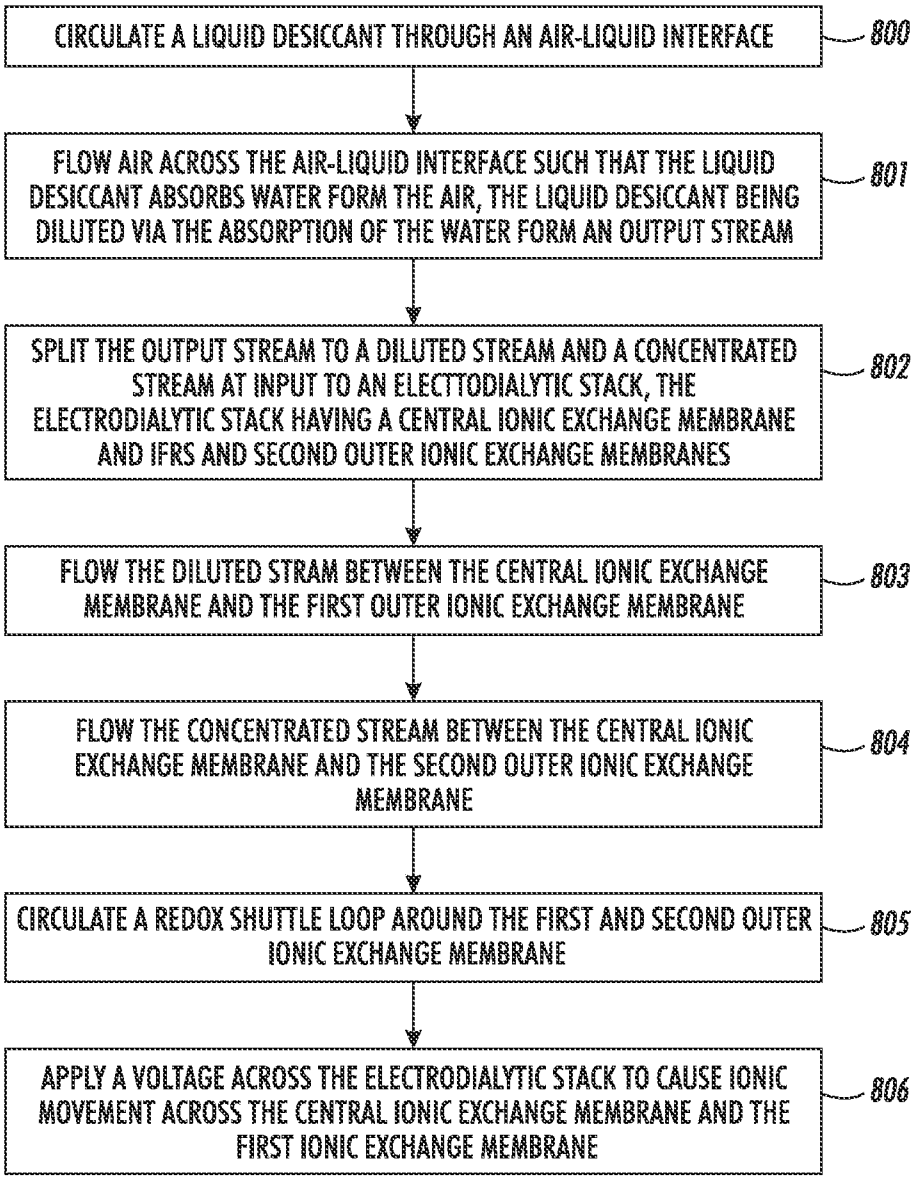

CIRCULATE A LIQUID DESICCANT THROUGH AN AIR-LIQUID INTERFACE
800
FLOW AIR ACROSS THE AIR-LIQUID INTERFACE SUCH THAT THE LIQUID DESICCANT ABSORBS WATER FORM THE AIR, THE LIQUID DESICCANT BEING DILUTED VIA THE ABSORPTION OF THE WATER FORM AN OUTPUT STREAM
801
SPLIT THE OUTPUT STREAM TO A DILUTED STREAM AND A CONCENTRATED STREAM AT INPUT TO AN ELECTTODIALYTIC STACK, THE ELECTRODIALYTIC STACK HAVING A CENTRAL IONIC EXCHANGE MEMBRANE AND IFRS AND SECOND OUTER IONIC EXCHANGE MEMBRANES
802
FLOW THE DILUTED STRAM BETWEEN THE CENTRAL IONIC EXCHANGE MEMBRANE AND THE FIRST OUTER IONIC EXCHANGE MEMBRANE
803
FLOW THE CONCENTRATED STREAM BETWEEN THE CENTRAL IONIC EXCHANGE MEMBRANE AND THE SECOND OUTER IONIC EXCHANGE MEMBRANE
804
CIRCULATE A REDOX SHUTTLE LOOP AROUND THE FIRST AND SECOND OUTER IONIC EXCHANGE MEMBRANE
805
APPLY A VOLTAGE ACROSS THE ELECTRODIALYTIC STACK TO CAUSE IONIC MOVEMENT ACROSS THE CENTRAL IONIC EXCHANGE MEMBRANE AND THE FIRST IONIC EXCHANGE MEMBRANE
806

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/062924

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D61/42 B01D61/58
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D F24F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 108 187 459 A (UNIV DONGGUAN TECHNOLOGY) 22 June 2018 (2018-06-22)	1-20
Y	embodiments 1,2; claims 1-8; figures 3,5	5,7
A	KR 2015 0034545 A (NA) 3 April 2015 (2015-04-03) figure 2	1-20
A	WO 2018/119280 A1 (UNIV IOWA RES FOUND [US]; PANI CLEAN INC [US] ET AL.) 28 June 2018 (2018-06-28) figures 4a,b	1-20

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 February 2020	09/03/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hennebrüder, K

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/062924

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCIALDONE O ET AL: "Investigation of electrode material - redox couple systems for reverse electrodialysis processes. Part II: Experiments in a stack with 10-50 ce", JOURNAL OF ELECTROANALYTICAL CHEMISTRY, ELSEVIER, AMSTERDAM, NL, vol. 704, 14 June 2013 (2013-06-14), pages 1-9, XP028698081, ISSN: 1572-6657, DOI: 10.1016/J.JELECHEM.2013.06.001 abstract; figure 1a	1-20
A	AL-JUBAINAWI ALI ET AL: "Factors governing mass transfer during membrane electrodialysis regeneration of LiCl solution for liquid desiccant dehumidification systems", SUSTAINABLE CITIES AND SOCIETY, vol. 28, 29 August 2016 (2016-08-29), pages 30-41, XP029830807, ISSN: 2210-6707, DOI: 10.1016/J.SCS.2016.08.021 abstract; figure A2	1-20
Y	Btmap-Vi Dihydrate ET AL: "Ordering and Customer Service Neutral pH Aqueous Redox Flow Battery Materials BTMAP-Vi BTMAP-Fc BTMAP-Fc 5gB5660 [B5659] [B5660] N e w", , 1 January 2017 (2017-01-01), page 639, XP055666447, Retrieved from the Internet: URL:https://www.tcichemicals.com/pdf/FF078E.pdf the whole document	5,7
Y	WO 2014/181898 A1 (KOREA ENERGY RESEARCH INST [KR]) 13 November 2014 (2014-11-13) figure 2 the whole document	5,7
X	CN 206 055 832 U (UNIV LANZHOU JIAOTONG) 29 March 2017 (2017-03-29)	1-20
Y	paragraph [0019]; figure 1	5,7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/062924

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 108187459 A	22-06-2018	NONE	
KR 20150034545 A	03-04-2015	NONE	
WO 2018119280 A1	28-06-2018	CN 110573238 A	13-12-2019
		EP 3558498 A1	30-10-2019
		WO 2018119280 A1	28-06-2018
WO 2014181898 A1	13-11-2014	CN 105308317 A	03-02-2016
		WO 2014181898 A1	13-11-2014
CN 206055832 U	29-03-2017	NONE	