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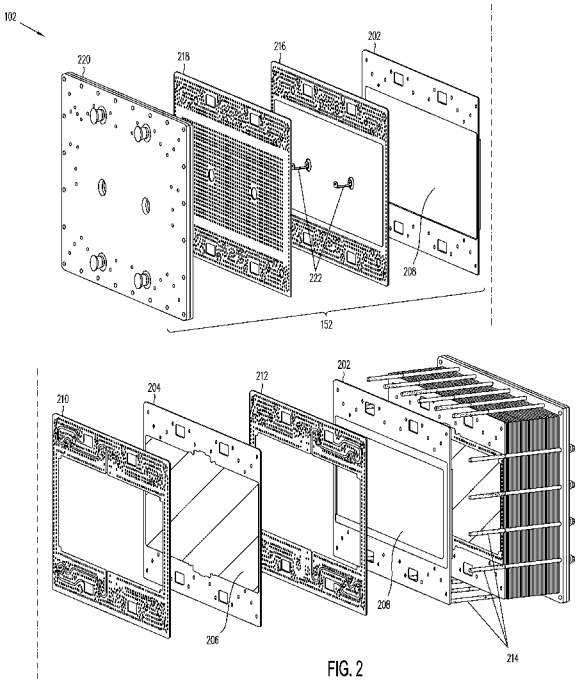

FIG. 2

(57) Abstract: A Flow Cell System that utilizes a Vanadium Chemistry is provided. The flow cell system includes a stack, electrolyte heat exchangers, and a controller executing a state machine. A stack for a flow cell system having an end plate structure comprising a conducting plate and a gasket frame including fluid manifolds. An electrolyte heat exchanger including flow field media; and heat transfer sheets separating the flow field media, and wherein electrolyte and a heat exchange fluid can be flowed through the electrolyte heat exchanger. A controller according to the present invention can include an initialization state; a charge state; a discharge state; a float state; a hibernate state; and a shutdown state.

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VANADIUM FLOW CELL

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RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 61/645,495, filed May 10, 2012, and to U.S. Nonprovisional Application No. 13/842,446, filed March 15, 2013, the entire contents of which are hereby incorporated by reference in their entirety.

BACKGROUND

1. TECHNICAL FIELD

[0002] The present disclosure relates to a flow cell system and, in particular, to a flow cell system that uses a Vanadium based chemistry.

2. DISCUSSION OF RELATED ART

[0003] There is an increasing demand for novel and innovative electric power storage systems. Redox flow cell batteries have become an attractive means for such energy storage. In certain applications, a redox flow cell battery may include one or more redox flow cells. Each of the redox flow cells may include positive and negative electrodes disposed in separate half-cell compartments. The two half-cells may be separated by a porous or ion-selective membrane, through which ions are transferred during a redox reaction. Electrolytes (anolyte and catholyte) are flowed through the half-cells as the redox reaction occurs, often with an external pumping system. In this manner, the membrane in a redox flow cell battery operates in an aqueous electrolyte environment.

[0004] In order to provide a consistent supply of energy, it is important that many

of the components of the redox flow cell battery system are performing properly. Redox flow cell battery performance, for example, may change based on parameters such as the state of charge, temperature, electrolyte level, concentration of electrolyte and fault conditions such as leaks, pump problems, and power supply failure for powering electronics.

[0005] Vanadium based flow cell system have been proposed for some time. However, there have been many challenges in developing a Vanadium based system that would be economically feasible. These challenges include, for example, the high cost of the Vanadium electrolyte, the high cost of appropriate membranes, the low energy density of dilute electrolyte, thermal management, impurity levels in the Vanadium, inconsistent performance, stack leakage, membrane performance such as fouling, electrode performance such as delamination and oxidation, rebalance cell technologies, and system monitoring and operation.

[0006] Therefore, there is a need for better redox flow cell battery systems.

SUMMARY

[0007] In accordance with some embodiments, a flow system includes a flow stack, a cooling heat exchanger, and a controller executing a state machine. A stack for a flow cell system having an end plate structure according to some embodiments includes a conducting plate; an insulating end plate, the insulating end plate having a pocket to receive an insert; a frame with an electrode; a felt; and a gasket formed over the felt, wherein a tunnel is formed in the fluid flow across the felt. An electrolyte heat exchanger according to some embodiments of the present invention includes flow field media; and heat transfer sheets separating the flow field media, wherein electrolyte and a heat exchange fluid can be flowed through the electrolyte heat exchanger. A controller according to the present invention can include an initialization state; a charge state; a

discharge state; a float state; a hibernate state; and a shutdown state, wherein transitions are made between the states.

[0008] These and other embodiments will be described in further detail below with respect to the following figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1A illustrates a flow cell system according to some embodiments of the present invention.

[0010] FIG. 1B illustrates the chemistry for a flow cell system as shown in FIG. 1A.

[0011] FIG. 2 illustrates an example of a stack according to some embodiments of the present invention.

[0012] FIG. 3 illustrates an expanded depiction of a portion of a gasket in the stack illustrated in FIG. 2.

[0013] FIG. 4 illustrates an embodiment of end plate according to some embodiments of the present invention.

[0014] FIG. 5 illustrates a cross section of an end plate according to some embodiments of the present invention.

[0015] FIG. 6 further illustrates an end plate according to some embodiments of the present invention.

[0016] FIGs. 7A and 7B further illustrate an end plate according to some embodiments of the present invention.

[0017] FIGs. 8A and 8B further illustrate an end plate according to some embodiments of the present invention.

[0018] FIGs. 9A and 9B illustrate some embodiments of an electrolyte heat exchanger as illustrated in FIG. 1A.

[0019] FIG. 10 illustrates a state machine that can be utilized to control the flow cell system shown in FIG. 1A.

[0020] The drawings may be better understood by reading the following detailed description. The drawings are not to scale.

DETAILED DESCRIPTION

[0021] A Vanadium Flow Cell system that utilizes vanadium based chemistry is disclosed. Groups have investigated vanadium/vanadium electrolytes in H_2SO_4. In that effort, V_2O_5 + V_2O_3 +H_2SO_4 yields $VOSO_4$. An electrochemical reduction of V_2O_5+H_2SO_4 can also yield $VOSO_4$. However, preparation of the electrolyte has proved difficult and impractical. Another group has tried a mixture of H2SO4 and HCl by dissolving $VOSO_4$ in HCl. However, again the electrolyte has proved to be expensive and impractical to prepare sulfate free formulation.

[0022] Figure 1A conceptually illustrates a flow cell system 100 according to some embodiments of the present invention. As shown in figure 1A, flow cell system 100 includes a stack 102. Stack 102 is a stacked arrangement of individual flow cells 146, each flow cell 146 including two half-cells separated by a membrane 148. Membrane 148 can be an ion permeable membrane as described, for example, in U.S. Patent No. 7,927,731, which is herein incorporated by reference in its entirety. Further, each half-cell of cell 146 includes an electrode 150. The end cells include end electrodes 152 and 154. A controller 142 is coupled to end electrodes 152 and 154 to control charge into and out of stack 102. Controller 142 provides charge from stack 102 to terminals 156 and 158 when system 100 is discharging and receives charge from terminals 156 and 158 to provide to stack 102 when charging. Terminals 156 and 158

are, in turn, coupled to supply current to a load when system 100 is discharging and coupled to a current source (e.g., a wind generator, solar cells, diesel generator, power grid, or other source of power) for charging of system 100.

[0023] As illustrated in Figure 1A, electrolyte solutions are flowed through each of the half cells of cells 146. A catholyte is flowed through one of the half-cells and an anolyte is flowed through the other of the half cells. Although other chemistries have been proposed for use in system 100, in some embodiments a Vanadium based chemistry is utilized to hold charge and provide charge from stack 102. The Vanadium chemistry involves the reaction of $V^{3+} + e^- \rightarrow V^{2+}$ in the negative half-cell of cell 146 and $VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$ ($V^{4+} \rightarrow V^{5+} + e^-$) in the positive half cell of cell 146. The theoretical open circuit voltage of each cell in stack 102 utilizing the Vanadium chemistry is then 1.25V, (-0.25 V from one half-cell and 1.00V from the other half-cell 108). The ions H^+ and Cl^- may traverse membrane 148 during the reaction. A Vanadium electrolyte that can be utilized in system 100 is further described in U.S. Patent Application Serial No. 13/651,230, which is herein incorporated by reference in its entirety.

[0024] As illustrated in Figure 1A, the electrolytes are stored in tanks 104 and 106. Tank 104 is fluidly coupled to stack 102 through pipes 108 and 110. The electrolyte stored in tank 104 can be pumped through stack 102 by a pump 116. Similarly, tank 106 is fluidly coupled to stack 102 through pipes 112 and 114. Electrolyte from tank 106 can be pumped through stack 102 by pump 118.

[0025] As shown in Figure 1A, system 100 is housed in a cabinet 160. During the operation of system 100, a significant amount of heat may be generated by system 100, and particularly in stack 102. In some embodiments, cooling fans 138 may be provided. A temperature control system according to some embodiments has been

described in U.S. Patent No. 7,919,204, which is herein incorporated by reference in its entirety.

[0026] As is further shown in Figure 1A, system 100 can include electrolyte cooling systems 120 and 128, which cools the electrolyte returning from stack 102 into tanks 104 and 106, respectively. As shown, electrolyte from stack 102 flowing through pipe 108 can flow through electrolyte heat exchanger 122. Similarly, electrolyte from stack 102 that flows through pipe 112 can flow through electrolyte heat exchanger 130. Each of exchangers 122 and 130 can cool electrolytes utilizing a cooling liquid that is flowed through electrolyte exchangers 122 and 130 and itself cooled by heat exchangers 126 and 136, respectively. Pumps 124 and 134, respectively, can circulate the cooling fluid through heat exchangers 126 and 136, respectively, and through heat exchangers 126 and 136, respectively.

[0027] As is further illustrated in Figure 1A, a control system 142 controls various aspects of system 100. Control system 142 controls the operation of stack 102 and electrolyte pumps 116 and 118 to charge and discharge system 100. Control system 142 can also control cooling fans 138 and cooling fluid pumps 124 and 134 to control the cooling of system 100. Control system 142 can receive signals from various sensors 140 that provide data regard the operation of system 100. Control system 142 can include, for example, a fluid level sensor such as that described in U.S. Patent Application Serial No. 12/577,147; hydrogen chlorine level detectors such as that described in U.S. Patent Application Serial No. 12/790,794; or optical leak detectors such as that described in U.S. Patent Application Serial No. 12/790,749, each of which is herein incorporated by reference in its entirety.

[0028] As discussed above, a Vanadium in HCL electrolyte can be utilized in system 100, as is further described in U.S. Patent Application Serial No. 13/651,230.

The following reactions may occur in electrochemical cells 146 of stack 102: In the positive half-cell (catholyte)

$$VOCl_2+H_2O+Cl^- \rightarrow VO_2Cl+2HCl+e^-;$$

In the negative half-cell (Anolyte)

$$VCl_3+e- \rightarrow VCl_2+Cl^-; \text{ and}$$

In the full cell 146

$$VOCl_2+H_2O+VCl_3 \rightarrow VO_2Cl+2HCl+VCl_2.$$

These reactions are illustrated diagrammatically in reaction diagram 172 in Figure 1B. The cell shown in Figure 1A may utilize different reactions and different electrolyte chemistries than those described above. The above description is for exemplary purposes only.

[0029] Figure 2 illustrates an embodiment of stack 102 such as that described, for example, in U.S. Patent Application Serial No. 12/577,134 and U.S. Patent Application Serial No. 13/350,424, each of which is herein incorporated by reference in its entirety. As shown in Figure 2, stack 102 is essentially constructed from electrode elements 202, membrane elements 204, and gaskets 210 and 212. As illustrated in Figure 2, electrode elements 202 include a frame on which an electrode material 208 is attached. Membrane elements 204 include a frame on which the membrane 206 is attached. Gaskets 210 and 212 create electrolyte fluid flows between membranes 206 and electrodes 208. As is illustrated, gaskets 210 and 212 may be identically constructed, but rotated by 180 degrees. There are passages formed such that the two electrolytes can be separately directed into the appropriate flow fields between elements.

[0030] Figure 2 further illustrates terminal 152. Terminal 152 includes an electrode 208, which in this configuration can be a charge collector. Components 216

and 218 are sandwiched between electrode 208 and end plate 220. Components 216 and 218 may be insulating seals. End plate 220 may be an aluminum end plate. Electrodes may make contact with electrode 208 and extend from end plate 220. Stack 102 is held together and tensioned by bolts 214.

[0031] Figure 3 illustrates an embodiment of gasket 210 at the interface with an electrode 208, which is a current collector, at terminal 152. As illustrated by blow-up 300, the fluid flow interface includes a channel 304 that carries electrolytic fluid between port 302and graphite current collector 208 through plastic sleeve 306 of gasket 210. Over time, there has been a tendency for electrolyte to seep into the interface between graphite current collector 208 and plastic sleeve 306, eventually causing electrolyte to leak through the current collector terminal 152.

[0032] Figure 4 illustrates an interface between gasket 210 and the current collector 208 of terminal 152 according to some embodiments of the present invention. As is illustrated in Figure 4, a tunnel 410 is provided. Tunnel 410, which includes an entrance 412 and an exit 414, creates a bypass on the flow path so that the interface between the graphite current collector 208 and the sleeve 306 is not exposed to the electrolyte and hence eliminating the possibility of an electrolyte leak. As shown in Figure 4, tunnel 410 includes an entry 412 and an exit 414, where the entry receives fluid from channel 304 in gasket 210 and the exit provides the fluid to the graphite current collector 208 through sleeve 306.

[0033] Figure 5 illustrates a cross section of an end of the stack 102. Figure 5 includes a membrane element 204, a gasket 210, an electrode element 202, and end terminal 152. As shown in Figure 5, from top to bottom, the first layer is the membrane layer, with frame 204 and membrane 206. The gasket 210 is next, gasket 210 frames a felt 502 that maintains the flow. The next layer down is another frame 202 with a

current collector electrode 208, which for example can be formed of Titanium 504 surrounded by a frame, which can be formed of Santoprene. Flow from the manifold enters the felt 502 through a tunnel 410 through the insulating endplate 218, by-passing the interface edge between the graphite 208 bipolar plate and the polypropylene sleeve of frame 202. The insulating end plate 218 may be, for example, a PVC plate. The next layer is an End gasket 216, which can be formed of Santoprene, that separates the current collector from the layer below. The next layer is the insulating end plate 218. A pressure plate 220, which can be formed of aluminum, then completes the end of the stack. As is shown in Figure 5, tunnel 410 is formed in end plate 218 with passages through frame 204 and gasket 210. The normal force on the seam between the graphite and plastic frame layers keeps that seam sealed. As shown in Figure 5, the flow by-pass (tunnel) 410 is created by having a pocket in the end plate 218 and a bridge support, which can be formed of PVC. In some embodiments, this structure seals the current collector from electrolyte without requirement for glue. Figure 6 illustrates the flow from the manifold 302 to tunnel 410 and through entry 412 and exit 414 from tunnel 410.

[0034] Addition of tunnel 410 to the end terminal 156 improves the labyrinth channel while not utilizing additional end plates. Additionally, no stack thickness increase is needed. Marginal increase in costs are realized by adding support around the entry 412 and exit 414 holes created in the graphite 208 for the tunnel, in machining a blind rectangular pocket on present PVC end plates 216, and in using an injection molded CPVC or other compatible plastic insert to provide the conduit for flow.

[0035] Figures 7A and 7B further illustrate construction of an insert pocket 702 formed in end plate 218. As is illustrated in Figure 7A, a pocket 702 is formed in the endplate and an insert 704, which provides tunnel 410, is formed that seats in pocket 702.

[0036] The resulting tunnel 410 is shown in Figure 7B. As shown in Figure 7B, end plate 218 includes insert 704. As shown in Figure 7B, a gasket layer 708 can be inserted between end plate 218 and current collector layer 216 with titanium layer 504. Various supports 706 for can be applied in exit 414 through graphite layer 208 to provide support.

[0037] Figures 8A and 8B further illustrate the insert provided in the pocket of the end plate. The compressive force goes through the top of the insert above which there is Santoprene. This force seals the gap between Graphite plate 208 and PP Sleeve .

[0038] As is further illustrated in Figure 1A, in some embodiments heat exchangers 122 and 130 are provided to cool electrolytes as they return to tanks 104 and 106, respectively. Figure 9A illustrates an embodiment of an electrolyte heat exchanger, which can be one of heat exchangers 122 or 130, according to some embodiments of the present invention. As discussed above flow batteries produce heat as well as electricity. This heat should be managed in order to optimize operation of the flow cell. Due to the aggressive nature of the electrolyte, more conventional heat exchangers made of metal cannot be used for cooling the electrolyte. Therefore, heat exchanger 900 is formed of primarily of plastics.

[0039] Some plastic heat exchangers were identified, but the cost was found to be excessive and the units were large. The heat exchangers that were investigated were all of the type called tube-in-shell heat exchangers. However, similar materials can be utilized in heat exchanger 900 as is utilized in the remainder of stack 102 because those materials withstand the chemical conditions presented by the electrolytes.

[0040] Figure 9A illustrates a plate type heat exchanger 900 according to some embodiments of the present invention. Heat exchanger 900 uses the flow battery materials and is unique in its design. Heat exchanger 900 is a liquid-to-liquid plate type

heat exchanger that transfers the process heat in the electrolyte to a conventional cooling liquid, such as glycol for example. The topology of the design can also be applied for flow batteries; modifications are required such as replacing the flow separators by membranes and bipolar plates.

[0041] As shown in Figure 9A, heat exchanger 900 is formed of alternating sheets of particular shape and size that make up the heat exchanging section. The package is flanked by a pair of pressure plates that compress the package. These have holes to accommodate tie rods and springs. In particular, as shown in Figure 9A, heat exchanger 900 is formed between pressure plates 902 and 922. Pressure plates 902 and 922 include aligned holes 920 that accommodate tie rods and springs that hold and seal heat exchanger 900. As shown in Figure 9A, a gasket 904 can be seated against pressure plate 902 and also include holes 920. Gasket 924 can be seated against pressure plate 922 and includes holes 920. Between gasket 924 and 920, flow field media 906 and heat transfer sheets 908 are positioned. Flow field media 906 is rotated by 90 degrees in each layer and each flow field media 906 is separated from the next flow field media 906 by a heat transfer sheet 908. Each of the heat transfer sheets 908 and the flow field media 906 includes manifolds 910 that all fluid to travel throughout heat exchanger 900. Pressure sheet 902 and gasket 904 do not include manifolds and seals the manifolds. Pressure sheet 922 and gasket 924 include input ports 912, 913, 916, and 918 to allow for ingress and egress of two media, one being a cooling medium and the other an electrolyte to be cooled.

[0042] When the flow medium enters inlet port 1 912 it flows through one of manifold channels 910 and then into a manifolding section within a flowfield in those flowfield media 906 that are oriented to receive and distribute the flow media from port 912. The flow medium flow through flow media 906 in contact with heat transfer sheets

908. On the opposite side of the heat transfer sheets 908, the other flow medium is flowing in contact with heat transfer sheets 908. The flow field is identical in shape and size as the first mentioned flow field but is rotated to obtain the orientation as shown. The other medium that is entering through port 2 916 follows a similar path. The fluids always stay separated and heat is transferred from one of the fluid media to the other through the heat transfer sheets. As shown in Figure 9A, flow medium 1 enters through inlet port 912 and exits through outlet port 914 and medium 2 enters through inlet port 916 and exits through outlet port 918.

[0043] The heat transferring sheets 908 can be made of plastics like polyethylene, polypropylene, pvdf, teflon, hard rubber etc. The flow fields 906 can be made of a softer material such as a soft santoprene. Alternating hard and soft materials ensures sealing between opposing liquids and the environment.

[0044] The embodiment of heat exchanger 900 as illustrated in Figure 9A employs only two different components that are two dimensional and for this reason can be fabricated at low cost. The number of alternating sheets can be varied easily to accommodate different heat transfer requirements. Assembly is easy, no special techniques are required. As common with metallic plate heat exchangers, heat exchanger 900 is compact compared to similarly rated tube-in shell-heat exchangers.

[0045] Another embodiment of heat exchanger 900 is where the flow field 906, made of a soft rubber in the previous embodiment, is replaced with a hard plastic material. The rubber performs a sealing function which, if replaced by a hard plastic, is lost. The sealing function can be replaced by gluing or welding the layers together. Elimination of the rubber may reduce cost and contamination due to the presence of rubber is eliminated.

[0046] In another embodiment of the heat exchanger 900, the electrolyte exchanges heat with air and therefore does not utilize an intermediate liquid loop. Figure 9B illustrates an exploded view of such an electrolyte heat exchanger 900. As shown in Figure 9B,

[0047] Electrolyte flows between graphite sheets 960, departing from and collecting into common manifold channels 966 and 968. The graphite sheets 960 are very good thermal conductors, particularly in the directions of the plane, which is due to its structure. The electrolyte is contained by rubber sheets 958 of particular size and shape with the purpose of directing and containing the flow through the structure that arises by stacking of graphite 960 and rubber sheets 958. The graphite sheets 960 extend out from the rubber sheets 958 thus allowing only heat and not electrolyte to be transferred to the external environment. Heat exchanger 900 is formed with end plate 958 and pressure plate 956. Side plates 962 may be utilized to direct the flow of air.

[0048] As is further shown in Figure 9B, electrolyte is flowed into and out of heat exchanger 900 through ports 952 and 954. Air flow from forced convection fans 964 provides for removal of the heat. In certain embodiments however the heat can be removed passively by orientating the graphite sheets 960 vertically and air let density differences drive the process. In this approach the fan 964 may be omitted.

[0049] The electrolyte flow is driven by an external pump that is chemically compatible with the highly aggressive electrolyte. Positive displacement pumps as well as centrifugal pumps are in existence that have this compatibility. Generally centrifugal pumps are preferred because of their longer lifetime. A disadvantage is that these pumps need to be primed. Priming in this case means that the pump needs to be filled with liquid before it can perform its function. Automated and manual priming methods are

well known and by ensuring that both electrolyte in and outlets are always below the liquid level, priming will be needed only during commissioning and for servicing.

[0050] Figure 10 illustrates a state function 1000 according to some embodiments of the present invention that can be executed on controller 142 as shown in Figure 1. Control systems for flow cells have been previously described in U.S. Patent Application Serial No. 12/790,793, which is herein incorporated by reference in its entirety.

[0051] As shown in Figure 10, controller 142 starts in system initialization 1002 on power on. In system initialization state 1002, all internal registers, memories and devices external to controller 142 are initialized for start up. Further, all hardware components are set to default states. From the system initialization state 1002, state function 1000 transitions to the ESPDongleInit state 1004.

[0052] In the ESPDongleInit state 1004, controller 142 checks for the presence of a dongle and, if not present, state function 1000 provides a warning and exits to either charge state 1014 or discharge state 1008. If the dongle is present, then the Redox Flow Battery System parameters are read from the Dongle. If a Comm bit is set, then it communicates with the external Commissioning program. It updates the system components, verifies if the Ebox was tested, checks whether any boards in the Ebox have been changed, sends out server information from the Dongle for registration if the Dongle is not registered, and waits for a time ack from the DMS board. The wait times out in one minute. From the ESPDongleINit state 1004, state function 1000 transitions to either the charge state 1014 or the discharge state 1008 depending on the En_Buck signal and DongleExBit. The DongleExbit is set when the timeout occurs or when the commissioning process is done.

[0053] In the Charge State 1014, stack 102 is charged. In general, power is taken from the BBus and is delivered to stack 102 through a constant current charging. In particular, the charging current is determined by the system type information that was obtained by reading the Dongle in the DongleInit state 1004. The following functions are then performed: The pumps, fans and blowers are all turned ON; Charging current is ramped by interaction with the Buck boost boards; The level control algorithm is initialized and is functional; The SoC of the system is calculated once the steady charging current is established (the stack voltage can be used for calculating the SoC); The ESR of the System is calculated once the SoC of the System crosses the SoCthreshold; The temperature of the Electrolyte is recorded; The Cooling system (heat exchanger) algorithm is turned on based on the electrolyte temperature. Leak sensors are continuously monitored for any leaks. The following components are monitored, recorded, and reported: All fans and blower currents; All power supplies voltages on the control board; All power supplies voltages on the Buck boost boards; The temperature of the Ebox, ESP ambient and outside ESP ambient temperatures; The Bbus voltage; and External sensors like the Diesel Generator Sensor or the Electricity Board Sensor.

[0054] In discharge state 1008, the power is delivered to the Bbus from stack 102. The En-Buck signal changes from "1" to "0" when the Bbus voltage falls below the threshold voltage. Based on the En-Buck signal status the switching to Discharge state 1008 happens. Discharge state 1008 performs all of the functions of charging state 1014 except that charging current control does not happen; ESR calculation does not happen; PFC to control the Diesel Generator is performed; and if ABB is turned ON it is turned off if the SoC is high.

[0055] Float state 1006 is transitioned to from Charge state 1014 when SOC is greater than a FloatSoC value. The FloatSoC is set up by the commissioning program or

by the FRP system in the System Dongle. The Buck Boost is in the ON state and is kept ready to discharge in case BBus power disappears or falls below a threshold value. In Float state 1006, the charging current is stopped; pumps are stopped; and the fans and blowers are stopped. The temperature of the Electrolyte is recorded, the cooling system algorithm is on and the cooling system is on based on the Electrolyte temperature, the leak sensors are monitored for any leaks, and the components are monitored, recorded , and reported as was done in charge state 1014. Since the pumps are stopped, the Electrolyte in the Stack does not drain. But the Stack voltage slowly decays due to the Self discharge process. The Stack voltage is continuously monitored and when the Stack voltage falls below a threshold voltage the pumps are turned ON for about 90minutes. During this time fresh electrolyte is provided into the Stack. The SoC of the Electrolyte is calculated when the pumps are running. Once the pumps stop the fresh electrolyte stays in the stack and hence the Stack voltage is going to be higher than the threshold voltage. The Stack voltage now slowly self discharges and the voltage falls below the threshold voltage and then the pumps turn on again. This process keeps repeating until the SoC of the System falls below a threshold SoC. Once this falls below the threshold SoC the System returns to Charge mode 1014.

[0056] Hibernate state 1010 is entered from Discharge state 1008 when the SoC falls below SoCHibernatethreshold. In the Hibernate state, the pumps are turned OFF, Buck Boost is turned OFF, and the Cooling system algorithm is turned OFF. The temperature of the Electrolyte is recorded, the leak sensors are monitored for any leaks, and the components are monitored, recorded, and reported as was done in charge state 1014. State function 1000 will change from Hibernate state 1010 when the BBus power resumes or a fault occurs due to the loss of power of the stack 102 and state function 1000 transitions to shutdown 1012.

[0057] State function 1000 transitions to Shutdown state 1012 from any other state when an Error occurs. In this state all functions are disabled except for the monitoring functionality. The recovery from Shutdown state 1012 occurs by turning ON/OFF the BTS switch when the BBus power is available, by remote SMS command, or if entry is through the hibernate state 1010 and the BBUs voltage is greater than 52V.

[0058] In the preceding specification, various embodiments have been described with reference to the accompanying drawings. It will, however, be evident that various modifications and changes may be made thereto, and additional embodiments may be implemented, without departing from the broader scope of the invention as set for in the claims that follow. The specification and drawings are accordingly to be regarded in an illustrative rather than restrictive sense.

CLAIMS

What is claimed is:

1. A stack for a flow cell system having an end plate structure, the end plate structure comprising:

a current collection plate;

a gasket frame in contact with the current collection plate, the gasket frame including fluid manifolds;

a felt in the gasket frame;

an end plate, the current collection plate being positioned between the end plate and the gasket frame, the end plate having a pocket to receive an insert; and

an insert with the end plate that forms a tunnel structure for electrolyte flow between the gasket frame and the felt.

2. A flow cell system having an electrolyte heat exchanger, comprising:

flow field media; and

heat transfer sheets separating the flow field media,

wherein electrolyte and a heat exchange fluid can be flowed through the electrolyte heat exchanger.

3. A flow system with a controller that executes code having

an initialization state;

a ESPDongleInit state;

a charge state;

a discharge state;

a float state;

a hibernate state; and

a shutdown state, wherein transitions are made between the states.

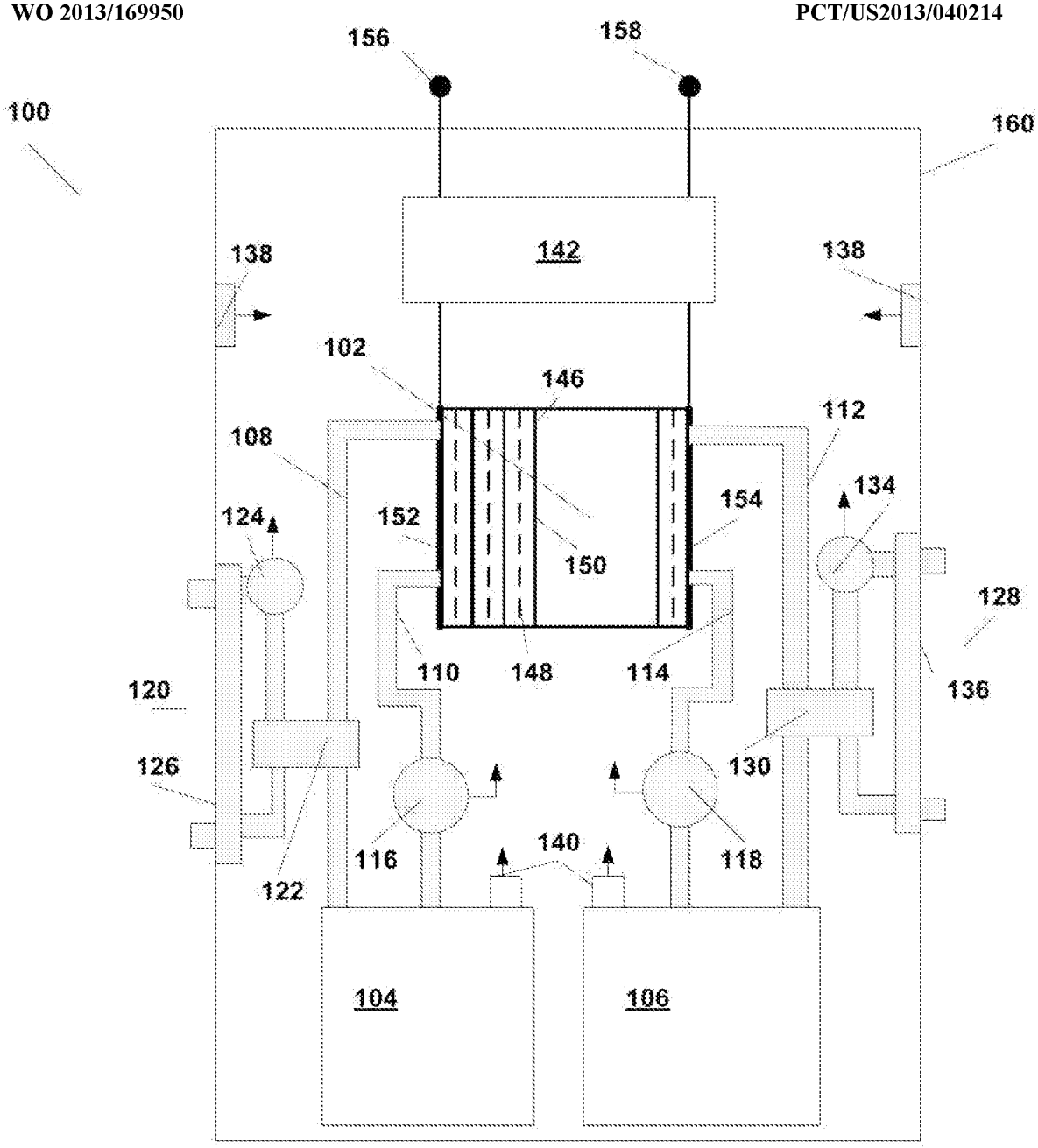

156
158
100
160
142
138
138
102
146
112
108
134
154
124
152
150
128
110
148
114
120
136
126
130
116
140
118
122
104
106

FIG. 1A

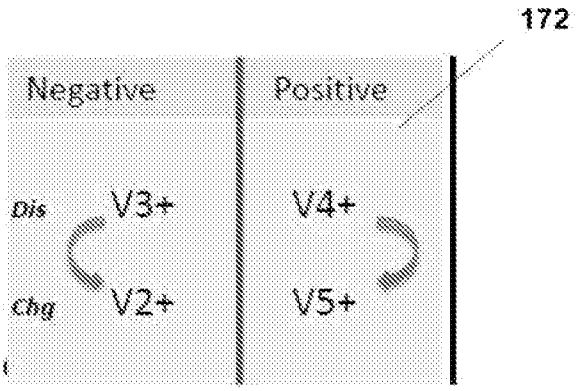

172
Negative
Positive
Dis
V3+
V4+
Chg
V2+
V5+

FIG. 1B

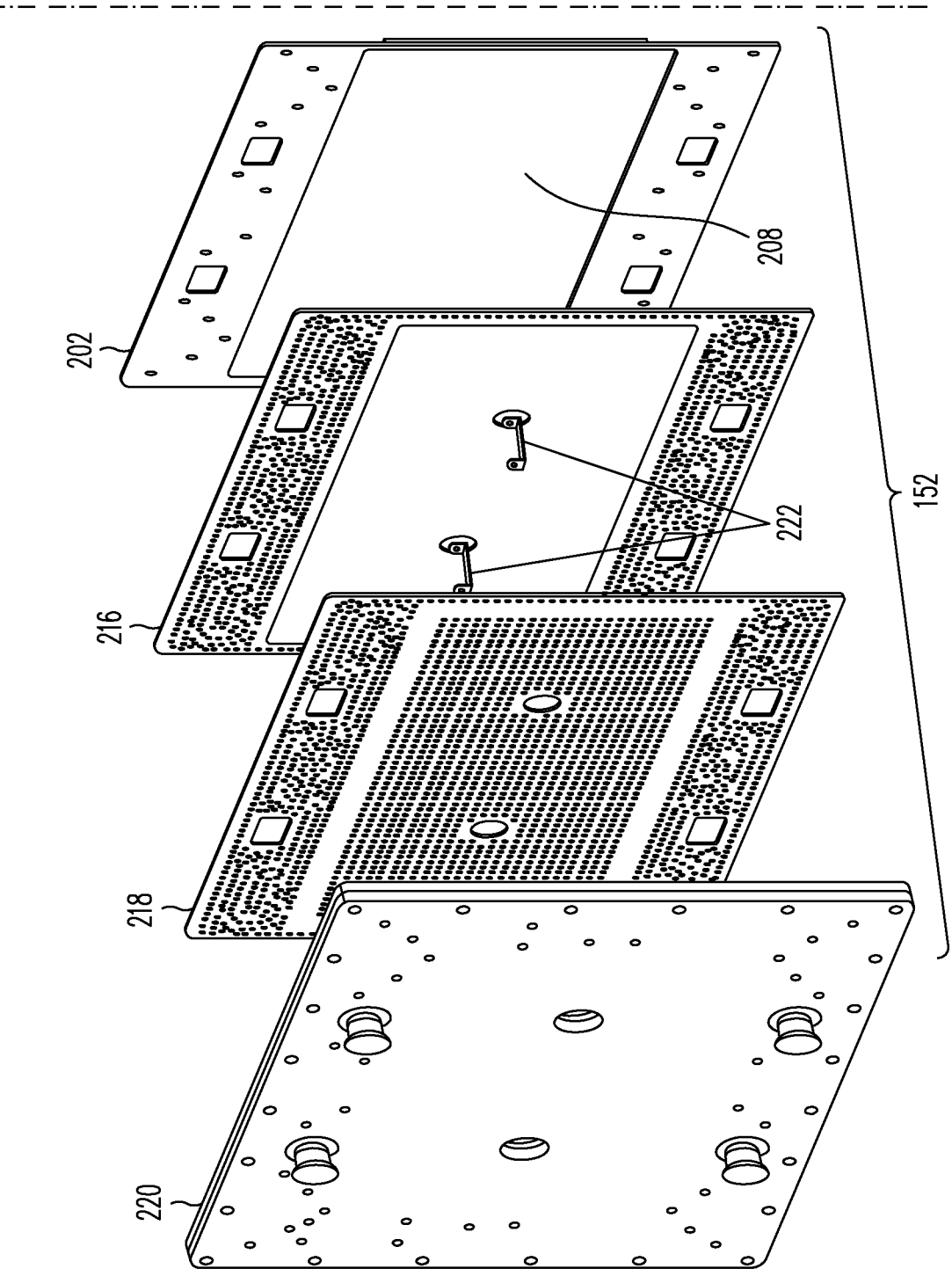


FIG. 2

Key To

FIG. 2	FIG. 2 (continued)

FIG. 2

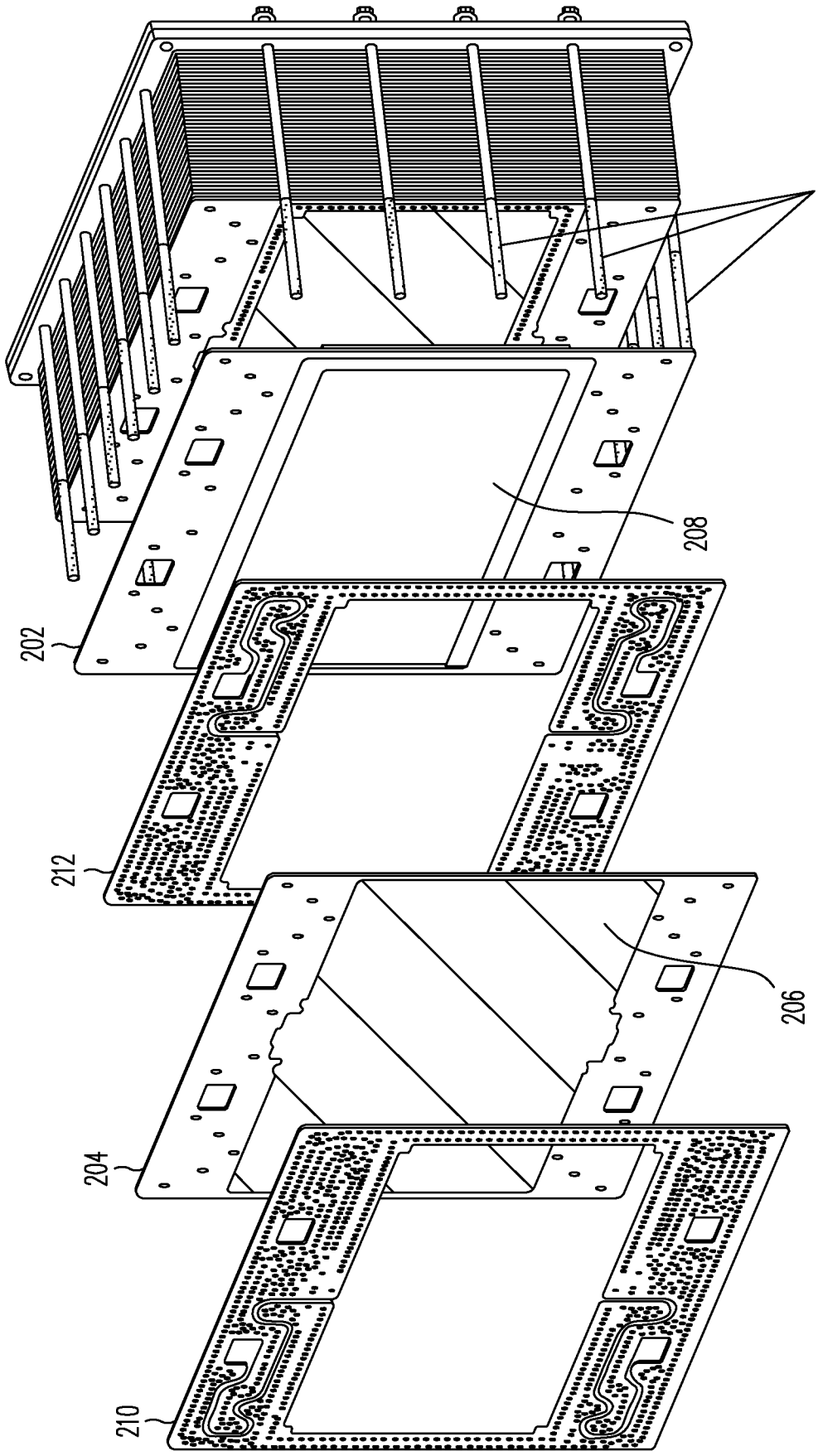


FIG. 2 (continued)

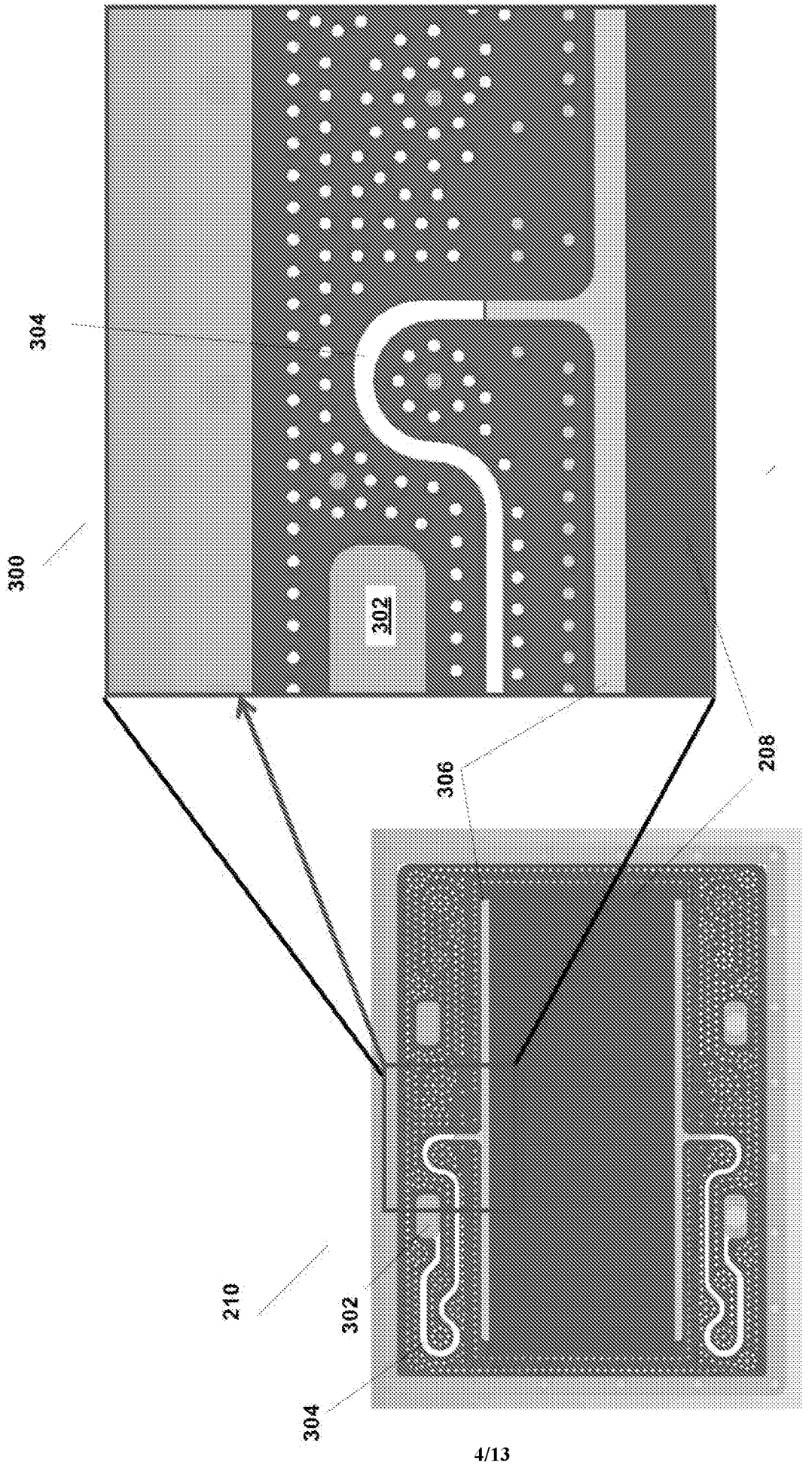


Figure 3

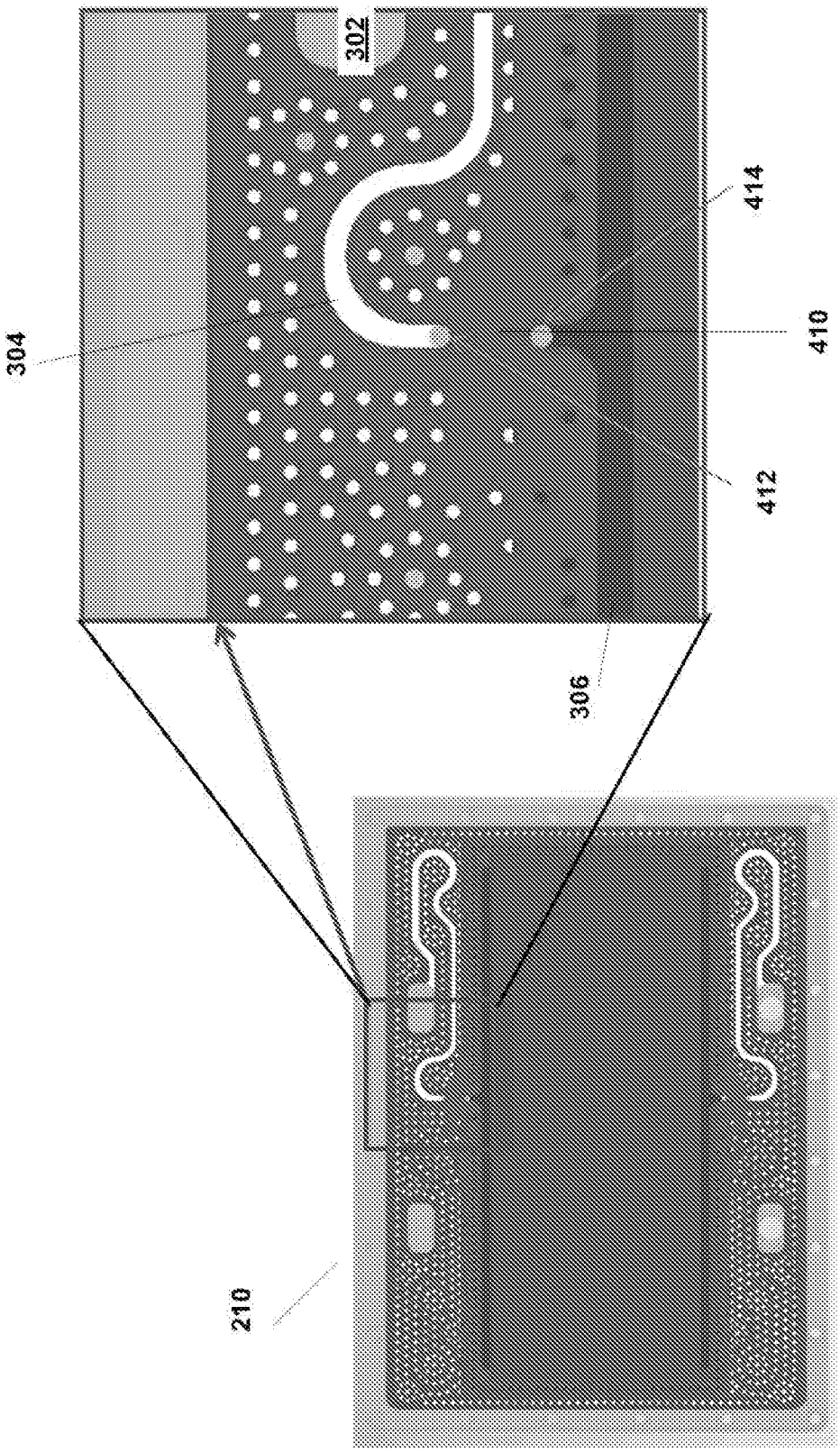


Figure 4

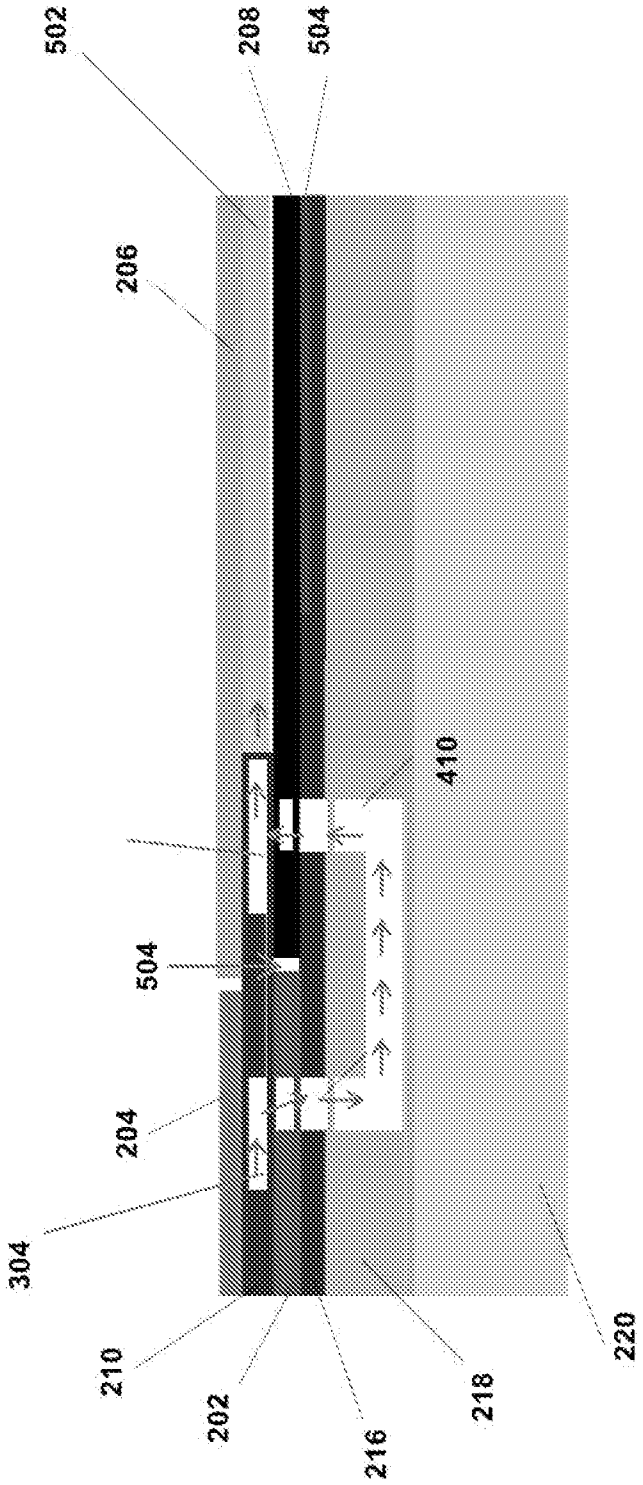
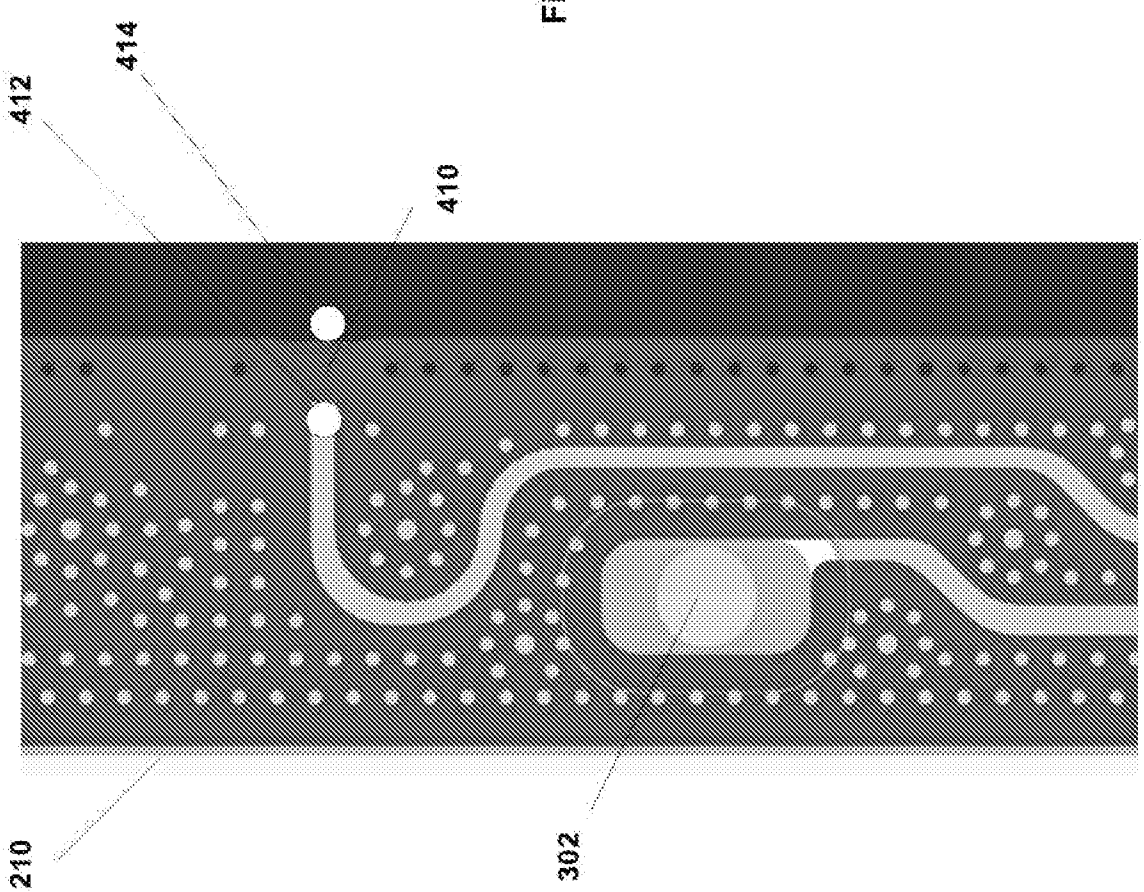


Figure 5

Figure 6



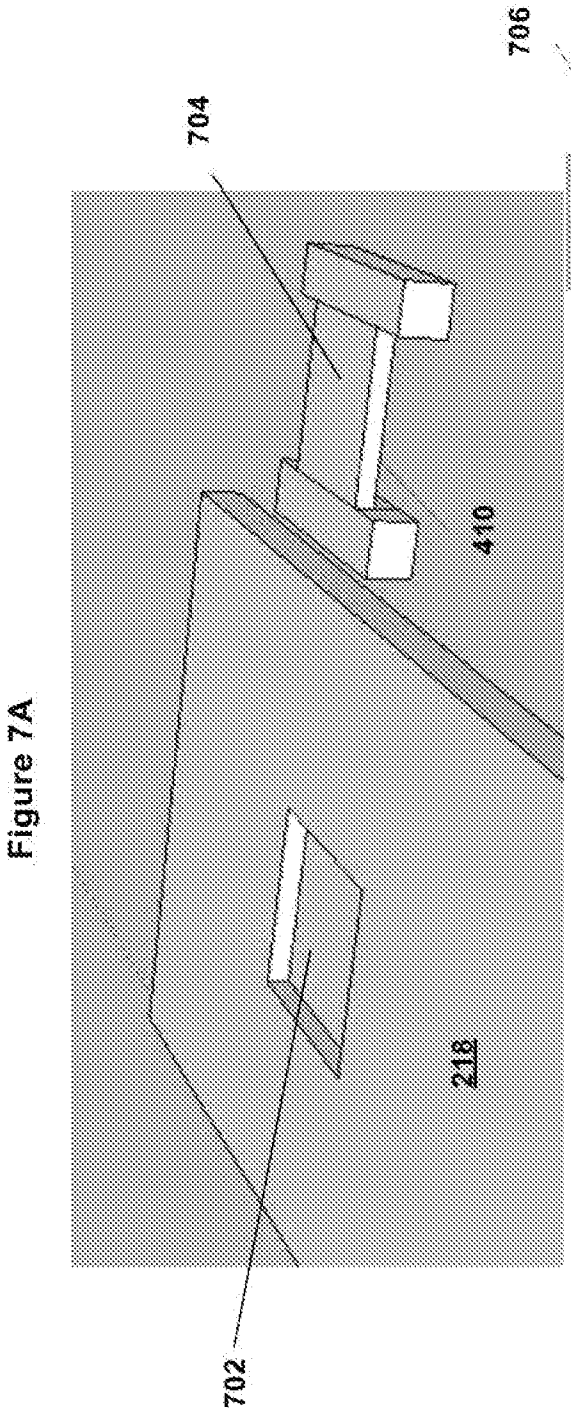


Figure 7A

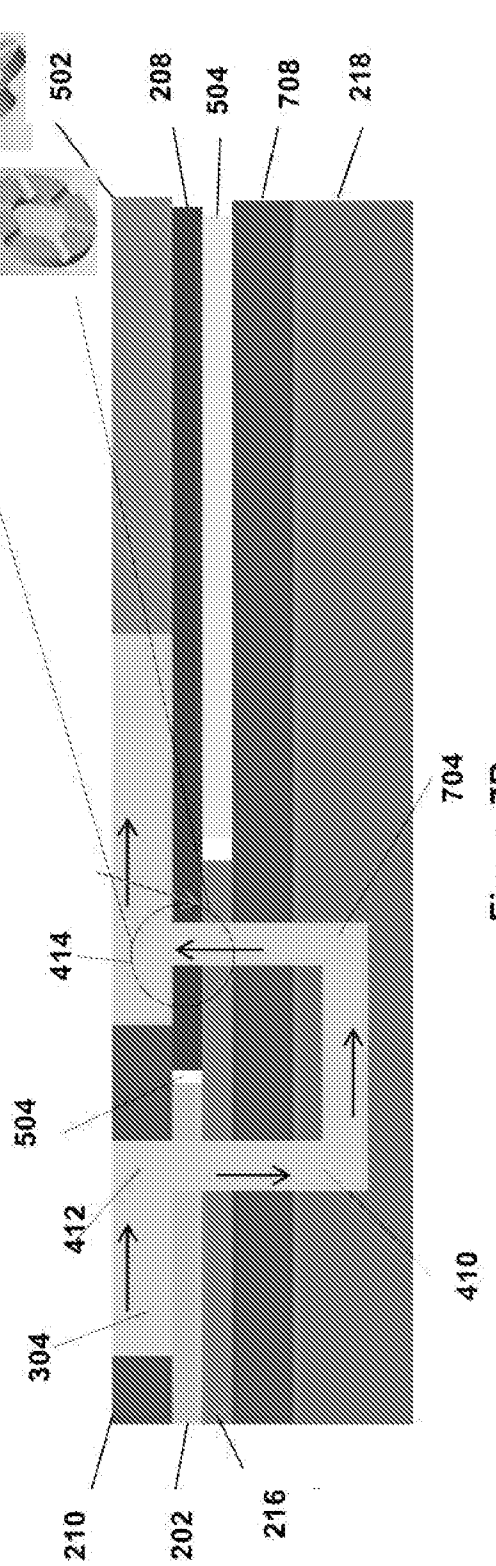


Figure 7B

Figure 8A

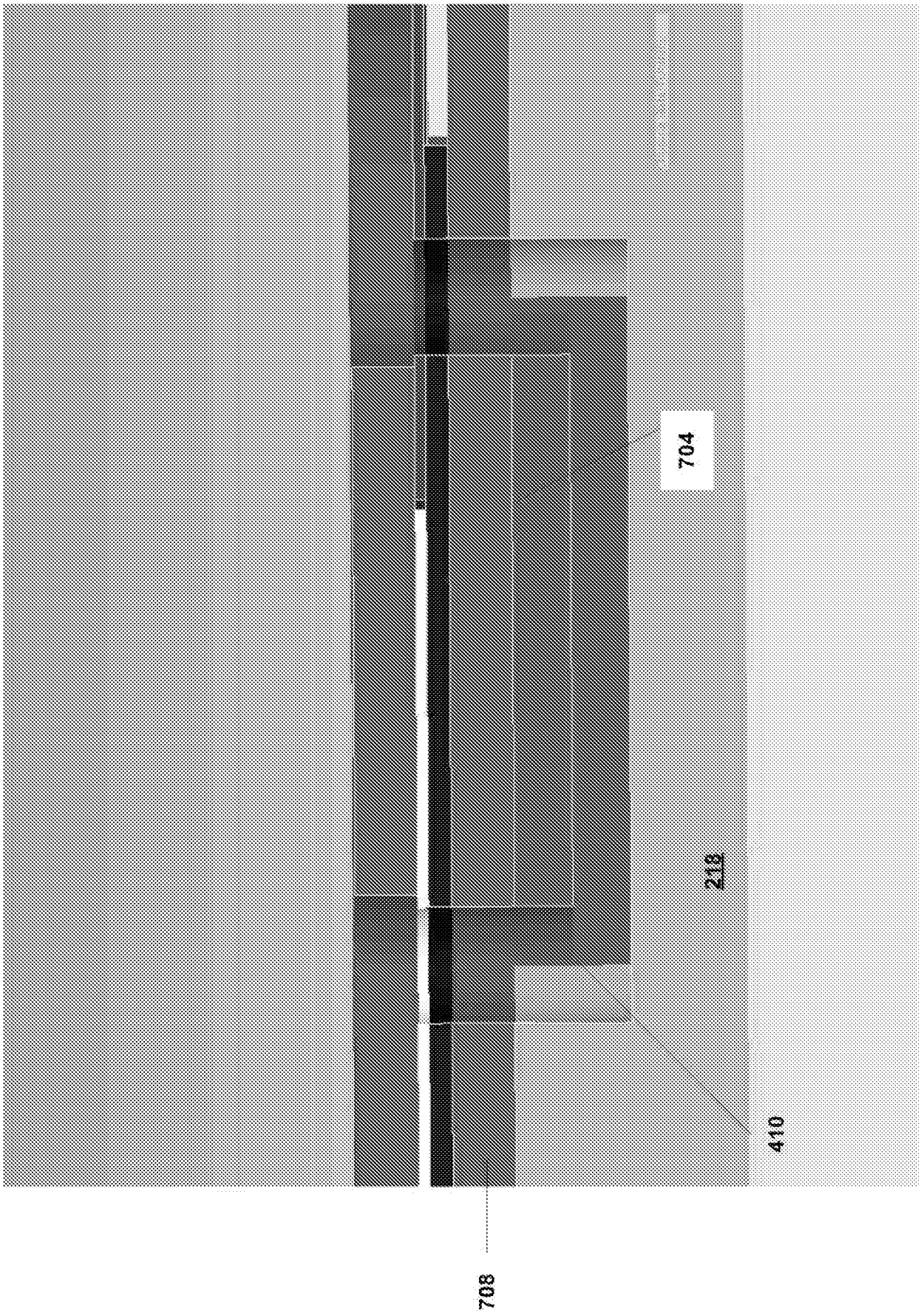


Figure 8B

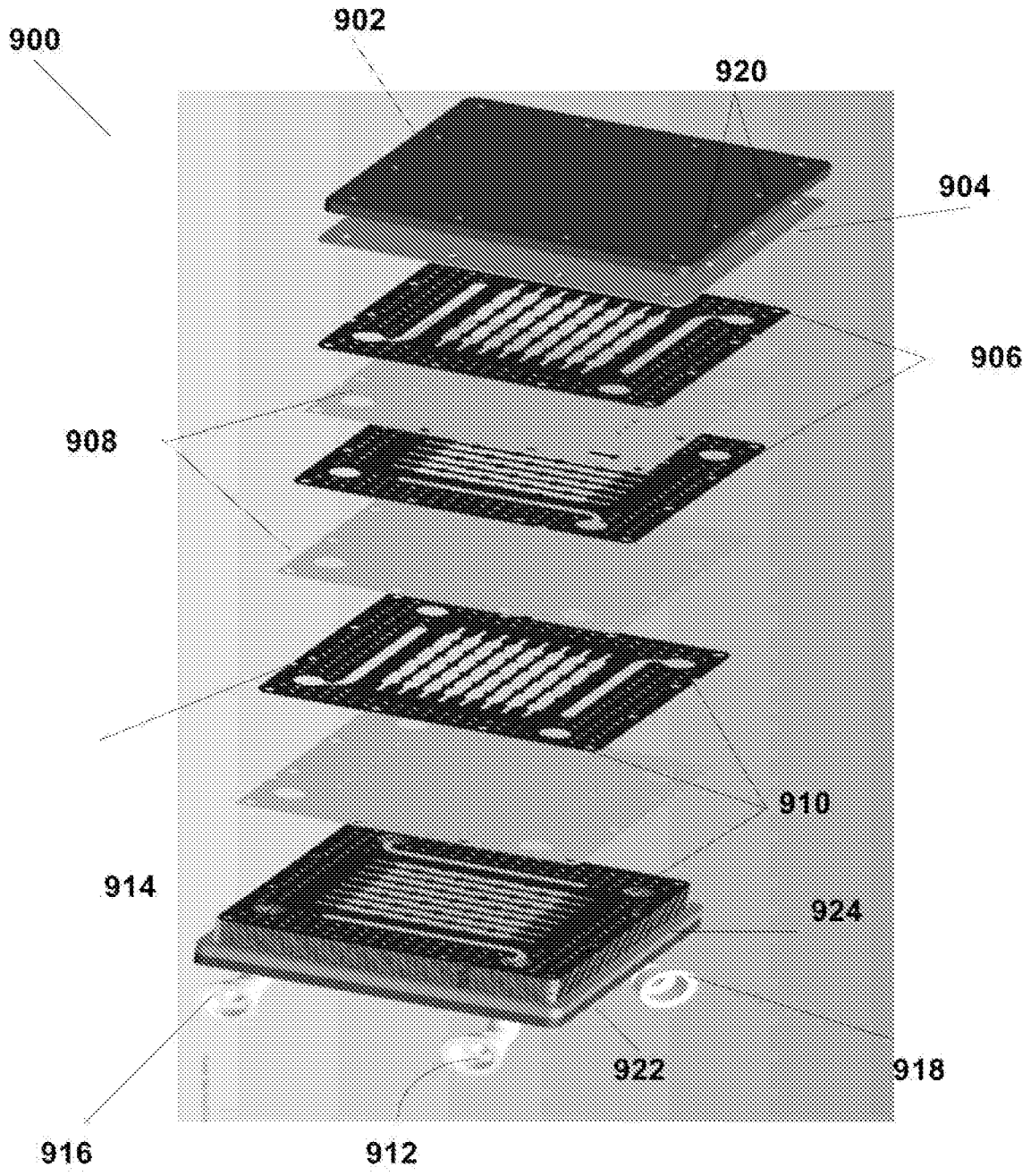


Figure 9A

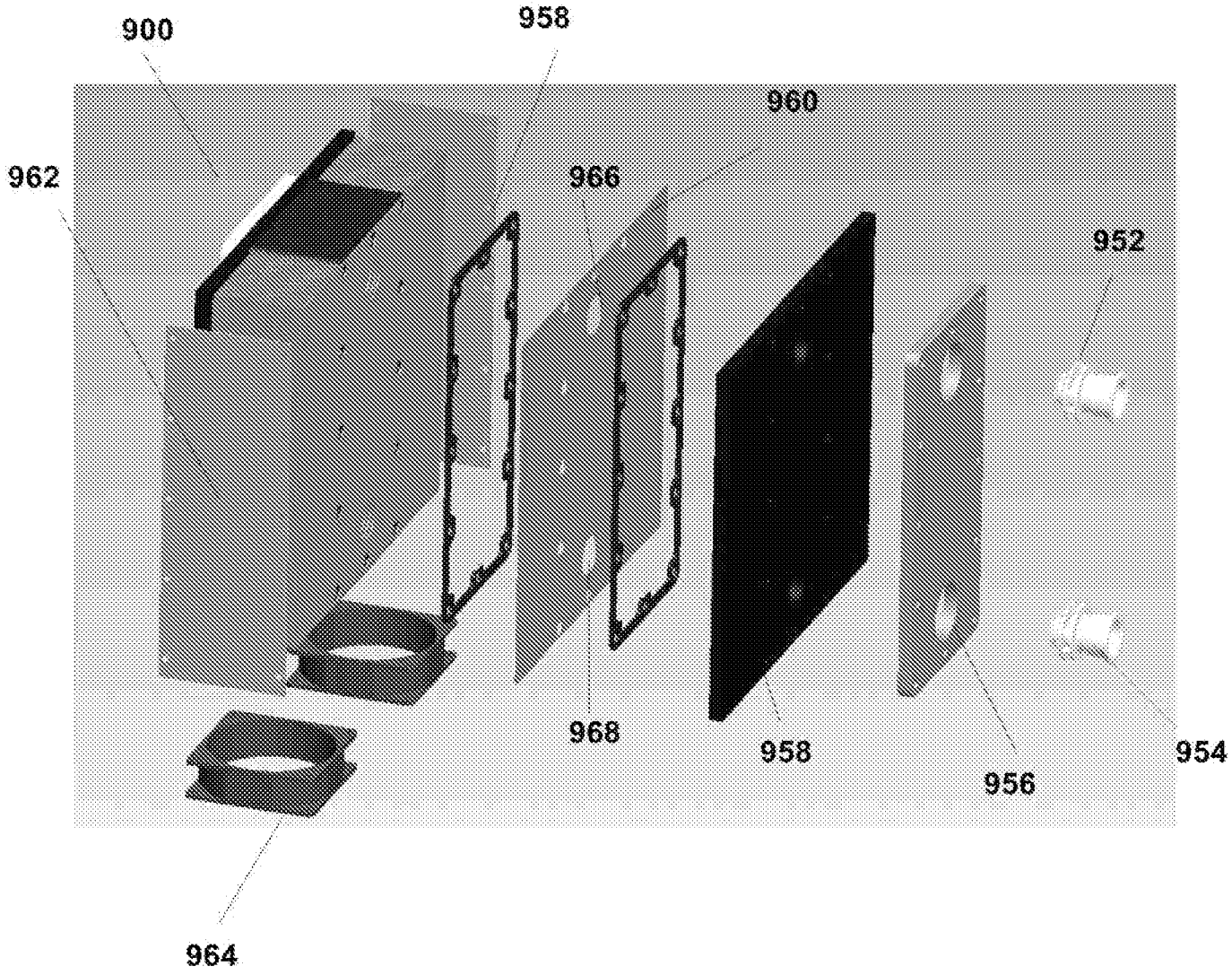


Figure 9B

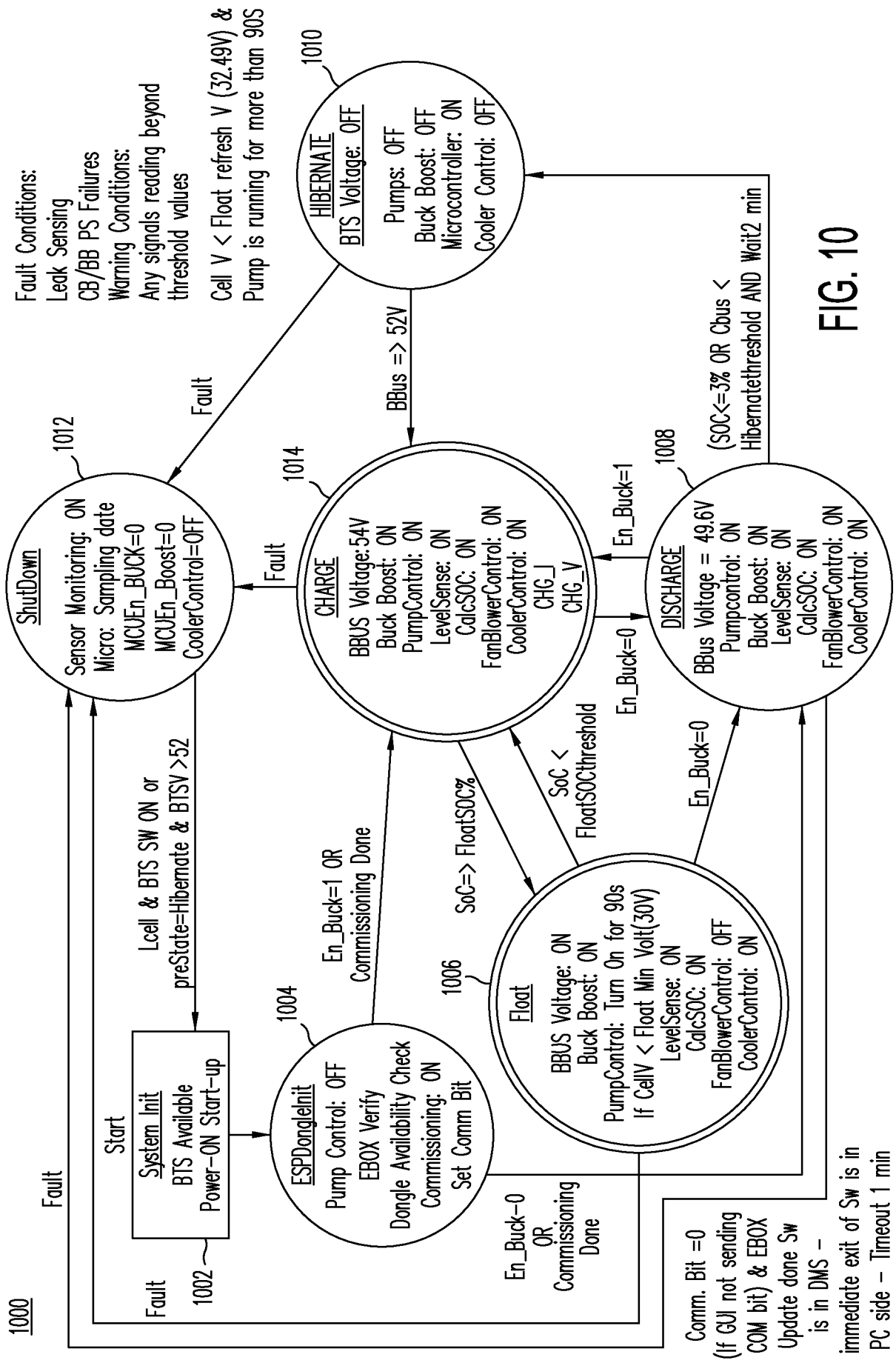

1000
Fault Conditions:
Leak Sensing
CB/BB PS Failures
Warning Conditions:
Any signals reading beyond threshold values
Cell V < Float refresh V (32.49V) & Pump is running for more than 90S
1002
System Init
BTS Available
Power-ON Start-up
Start
Fault
1004
ESPDonglelnit
Pump Control: OFF
EBOX Verify
Dongle Availability Check
Commissioning: ON
Set Comm Bit
1006
Float
BBUS Voltage: ON
Buck Boost: ON
PumpControl: Turn On for 90s
If CellV < Float Min Volt(30V)
LevelSense: ON
CalcSOC: ON
FanBlowerControl: OFF
CoolerControl: ON
1008
DISCHARGE
BBus Voltage = 49.6V
Pumpcontrol: ON
Buck Boost: ON
LevelSense: ON
CalcSOC: ON
FanBlowerControl: ON
CoolerControl: ON
1010
HIBERNATE
BTS Voltage: OFF
Pumps: OFF
Buck Boost: OFF
Microcontroller: ON
Cooler Control: OFF
1012
ShutDown
Sensor Monitoring: ON
Micro: Sampling date
MCUEn_BUCK=0
MCUEn_Boost=0
CoolerControl=OFF
1014
CHARGE
BBUS Voltage:54V
Buck Boost: ON
PumpControl: ON
LevelSense: ON
CalcSOC: ON
FanBlowerControl: ON
CoolerControl: ON
CHG_I
CHG_V
Fault
Fault
BBus => 52V
(SOC<=3% OR Cbus < Hibernatethreshold AND Wait2 min
Lcell & BTS SW ON or preState=Hibernate & BTSV >52
En_Buck=1 OR Commissioning Done
SoC=> FloatSOC%
SoC < FloatSOCthreshold
En_Buck=1
En_Buck=0
En_Buck=0
En_Buck-0 OR Commissioning Done
Comm. Bit =0 (If GUI not sending COM bit) & EBOX Update done Sw is in DMS – immediate exit of Sw is in PC side – Timeout 1 min

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/040214

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01M 8/04 (2013.01)
USPC - 429/452
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)
IPC(8) - H01M 8/02, 8/04, 8/08, 8/18, 8/24 (2013.01)
USPC - 429/408, 428, 452, 454, 457, 460

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - H01M 8/02, 8/0276, 8/04, 8/04007, 8/08 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit.com, Google Patents, Public AppFT and PatFT, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/0136455 A1 (WINTER) 03 June 2010 (03.06.2010) entire document	1
Y	WO 2012/032368 A1 (KAMPANATSANYAKORN et al) 15 March 2012 (15.03.2012) entire document	1
Y	US 2003/0118889 A1 (SMITH) 26 June 2003 (26.06.2003) entire document	1
Y	US 2009/0274940 A1 (MORITA et al) 05 November 2009 (05.11.2009) entire document	2
Y	WO 2006/045893 A1 (KIVISAARI et al) 04 May 2006 (04.05.2006) entire document	2
Y	US 2011/0074357 A1 (PARAKULAM et al) 31 March 2011 (31.03.2011) entire document	3
Y	US 2012/0040216 A1 (PARAKULAM) 16 February 2012 (16.02.2012) entire document	3

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2013	24 OCT 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

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H01M 8/20(2006.01)
H01M 8/18(2006.01)

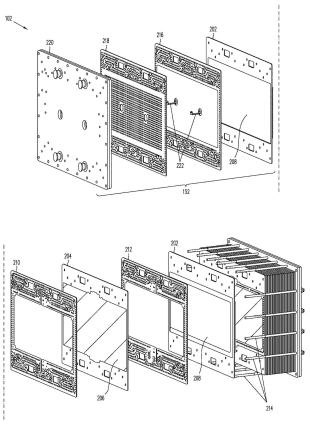
权利要求书1页 说明书7页 附图14页

(54)发明名称

钒液流电池

(57)摘要

本发明提供一种采用钒化学的液流电池系统。所述的液流电池系统包括层叠体，电解液热交换器，以及执行状态机的控制器。具有端板结构的液流电池系统用层叠体包括导电板以及包括了流体歧管的衬垫框架。电解液热交换器包括液流域介质；以及分离所述液流域介质的传热片，并且其中电解液和热交换流体可以流动穿过所述电解液热交换器。根据本发明的控制器可以包括初始化状态；充电状态；放电状态；浮动状态；休眠状态；和关闭状态。



CN 104508880 A

1.一种具有端板结构的液流电池系统用层叠体,所述端板结构包括 :

电流收集板 ;

与所述电流收集板接触的衬垫框架,所述衬垫框架包括流体歧管 ;

所述衬垫框架中的毡 ;

端板,所述电流收集板位于所述端板与所述衬垫框架之间,所述端板具有用于接收插头的袋口 ;和

插头,所述插头与所述端板形成用于电解液在所述衬垫框架与所述毡之间流动的隧道结构。

2.一种具有电解液热交换器的液流电池系统,包括 :

液流域介质 ;和

分离所述液流域介质的传热片,

其中电解液和热交换流体可以流动穿过所述电解液热交换器。

3.一种具有控制器的液流系统,所述控制器执行具有以下状态的代码 :

初始化状态 ;

ESP 软件狗初始化状态 ;

充电状态 ;

放电状态 ;

浮动状态 ;

休眠状态 ;和

关闭状态,其中在所述状态之间进行转换。

钒液流电池

[0001] 相关申请

[0002] 本申请要求2012年5月10日提交的美国临时申请号61/645,495的优先权，并且要求2013年3月15日提交的美国非临时申请号13/842,446的优先权，它们的全部内容通过引用作为整体结合在此。

[0003] 背景

[0004] 1. 技术领域

[0005] 本公开内容涉及液流电池系统并且，特别是，涉及使用基于钒的化学的液流电池系统。

[0006] 2. 相关技术公开

[0007] 对于新的和创造性的电能储存系统存在增加的需求。氧化还原液流电池的电池组对于这种能量储存成为有吸引力的方式。在特定的应用中，氧化还原液流电池的电池组可以包括一个或多个氧化还原液流电池。氧化还原液流电池的每一个可以包括放置在分开的半电池隔间中的正和负电极。两个半电池可以由多孔或离子选择性膜分隔，在氧化还原反应过程中离子从其传递穿过。当氧化还原反应发生时，电解液（阳极电解液和阴极电解液）通常借助于外部泵送系统流动穿过半电池。以这种方式，氧化还原液流电池电池组中的膜在水性电解液环境中运行。

[0008] 为了提供能量的持续供给，重要的是氧化还原液流电池电池组系统的多个组件适当地发挥功能。氧化还原液流电池电池组性能，例如，可以基于参数如充电状态、温度、电解液液面、电解液的浓度和故障情况如泄漏、泵问题和用于给电子器件供电的电源故障改变。

[0009] 已经提出了基于钒的液流电池系统一段时间。然而，在开发经济可行的基于钒的系统上存在很多挑战。这些挑战包括，例如，钒电解液的高成本、适当的膜的高成本、稀电解液的低能量密度、热管理、钒中的杂质水平、不一致的性能、层叠体泄漏、膜性能如垢化、电极性能如剥离和氧化、再平衡电池技术，以及系统监控和操作。

[0010] 因此，对于更好的氧化还原液流电池电池组系统存在需要。

[0011] 概述

[0012] 根据一些实施方案，液流系统包括液流层叠体，冷却热交换器，以及执行状态机的控制器。根据一些实施方案的具有端板结构的液流电池系统用层叠体包括导电板；绝缘端板，所述绝缘端板具有用于接收插头的袋口；具有电极的框架；毡；和在毡上形成的衬垫，其中在流动跨越毡的流体中形成隧道。根据本发明的一些实施方案的电解液热交换器包括液流域介质；和分离液流域介质的传热片，其中电解液和热交换流体可以流动穿过电解液热交换器。根据本发明的控制器可以包括初始化状态；充电状态；放电状态；浮动状态；休眠状态；和关闭状态，其中在各状态之间进行转换。

[0013] 下面将参考附图进一步详细描述这些和其他实施方案。

[0014] 附图简述

[0015] 图1A示例根据本发明的一些实施方案的液流电池系统。

[0016] 图1B示例如图1A中所示的用于液流电池系统的化学原理。

[0017] 图 2 示例根据本发明的一些实施方案的层叠体的实例。

[0018] 图 3 示例图 2 中所示的层叠体中的衬垫的一部分的放大图。

[0019] 图 4 示例根据本发明的一些实施方案的端板的实施方案。

[0020] 图 5 示例根据本发明的一些实施方案的端板的截面。

[0021] 图 6 还示例了根据本发明的一些实施方案的端板。

[0022] 图 7A 和 7B 进一步示例根据本发明的一些实施方案的端板。

[0023] 图 8A 和 8B 进一步示例根据本发明的一些实施方案的端板。

[0024] 图 9A 和 9B 示例了如图 1A 中所示的电解液热交换器的一些实施方案。

[0025] 图 10 示例可以用于控制图 1A 中所示的液流电池系统的状态机。

[0026] 通过阅读以下详述可以更好地理解附图。附图不是按比例绘制的。

[0027] 详述

[0028] 公开了采用基于钒的化学的钒液流电池系统。一个组研究了 H_2SO_4中的钒 / 钒电解液。在该努力中，$V_2O_5+V_2O_3+H_2SO_4$产生 $VOSO_4$。$V_2O_5+H_2SO_4$的电化学还原还可以产生 $VOSO_4$。然而，电解液的制备被证明是困难的并且不实际的。另一个组尝试了通过将 $VOSO_4$溶解在 HCl 中的 H2SO4 和 HCl 的混合物。然而，再一次，电解液被证明是昂贵的并且制备无硫酸盐制剂是不实际的。

[0029] 图 1A 概念性示例了根据本发明的一些实施方案的液流电池系统 100。如图 1A 中所示，液流电池系统 100 包括层叠体 102。层叠体 102 是单独的液流电池 146 的层叠排列，每个液流电池 146 包括由膜 148 分离的两个半电池。膜 148 可以是例如通过引用以其全部结合在此的美国专利号 7,927,731 中所描述的离子渗透膜。此外，电池 146 的每个半电池包括电极 150。端电池包括端电极 152 和 154。控制器 142 连接至端电极 152 和 154，以控制电荷进入和离开层叠体 102。当系统 100 放电时，控制器 142 将电荷从层叠体 102 提供至端子 156 和 158，并且当充电时从端子 156 和 158 接收电荷以提供至层叠体 102。端子 156 和 158 进一步连接以当系统 100 放电时将电流提供至负载，并且连接至电源（例如，风力发电机、太阳能发电机，柴油发电机、电网或其他电源）用于系统 100 的充电。

[0030] 如图 1A 中所示，电解液溶液流动穿过电池 146 的半电池的每一个。阴极电解液流动穿过半电池中的中一个并且阴极电解液流动穿过半电池的中另一个。虽然已经提出了其他化学原理用于在系统 100 中使用，在一些实施方案中，采用基于钒的化学原理以保持电荷并从层叠体 102 提供电荷。钒化学原理包括电池 146 的负半电池中的反应 $V^{3+}+e^- \rightarrow V^{2+}$，以及电池 146 的正半电池中的 $VO^{2+}+H_2O \rightarrow VO_2^{+}+2H^{+}+e^-$($V^{4+} \rightarrow V^{5+}+e^-$)。那么采用钒化学原理的层叠体 102 中的每个电池的理论开路电压是 1.25V，（来自一个半电池是 -0.25V，并且来自另一个半电池 108 是 1.00V)。离子 H^+和 Cl^-可以在反应过程中穿过膜 148。可以在系统 100 中采用的钒电解液进一步描述在通过引用以其全部结合在此的美国专利申请号 13/651,230 中。

[0031] 如图 1A 中所示，电解液储存在槽 104 和 106 中。槽 104 穿过管 108 和 110 而流体连接至层叠体 102。可以将储存在槽 104 中的电解液通过泵 116 泵送穿过层叠体 102。类似地，槽 106 穿过管 112 和 114 流体连接至层叠体 102。来自槽 106 的电解液可以通过泵 118 泵送穿过层叠体 102。

[0032] 如图 1A 中所示，系统 100 位于柜橱 160 中。在系统 100 的操作过程中，可以由系

统 100，并且特别是在层叠体 102 中产生显著量的热。在一些实施方案中，可以提供冷却风扇 138。根据一些实施方案的温度控制系统已经描述在通过引用以其全部结合在此的美国专利号 7,919,204 中。

[0033] 如图 1A 中进一步所示，系统 100 可以包括电解液冷却系统 120 和 128，其分别将从层叠体 102 返回至槽 104 和 106 中的电解液冷却。如所示，从层叠体 102 流动穿过管 108 的电解液可以流动穿过电解液热交换器 122。类似地，从层叠体 102 流动穿过管 112 的电解液可以流动穿过电解液热交换器 130。交换器 122 和 130 的每一个可以采用流动穿过电解液交换器 122 和 130 的冷却液体冷却电解液，并且自身分别由热交换器 126 和 136 冷却。泵 124 和 134 可以分别将冷却流体分别循环穿过热交换器 126 和 136，并且分别穿过热交换器 126 和 136。

[0034] 如图 1A 中进一步所示，控制系统 142 控制系统 100 的多个方面。控制系统 142 控制层叠体 102 和电解液泵 116 和 118 的操作，以将系统 100 充电和放电。控制系统 142 还可以控制冷却风扇 138 和冷却流体泵 124 和 134，以控制系统 100 的冷却。控制系统 142 可以由提供关于系统 100 的操作的数据的多个传感器 140 接收信号。控制系统 142 可以包括，例如，如美国专利申请号 12/577,147 中描述的流体液面传感器；如美国专利申请号 12/790,794 中描述的氢氯液面检测器；或如美国专利申请号 12/790,749 中描述的光学泄漏检测器，其每一个通过引用以其全部结合在此。

[0035] 如上所述，在系统 100 中可以采用 HCL 电解液中的钒，如美国专利申请号 13/651,230 中进一步描述的。以下反应可以出现在层叠体 102 的电化学电池 146 中：在正半电池（阴极电解液）中

[0036] $VOCl_2+H_2O+Cl^- \rightarrow VO_2Cl+2HCl+e^-$；

[0037] 在负半电池（阳极电解液）中

[0038] $VCl_3+e- \rightarrow VCl_2+Cl^-$；和

[0039] 在全电池 146 中

[0040] $VOCl_2+H_2O+VCl_3 \rightarrow VO_2Cl+2HCl+VCl_2$。

[0041] 这些反应图示在图 1B 中的反应图 172 中。图 1A 中所示的电池可以采用与上面描述的那些不同的反应和不同的电解液化学。以上说明书仅用于示例目的。

[0042] 图 2 示例如描述在例如每一个通过引用以其全部结合在此的美国专利申请号 12/577,134 和美国专利申请号 13/350,424 中的层叠体 102 的实施方案。如图 2 中所示，层叠体 102 主要由电极元件 202、膜元件 204 和衬垫 210 和 212 构成。如图 2 中所示，电极元件 202 包括在其上附加电极材料 208 的框架。膜元件 204 包括在其上附加膜 206 的框架。衬垫 210 和 212 在膜 206 与电极 208 之间建立电解液流体液流。如所示，衬垫 210 和 212 可以相同地构造，但是旋转 180 度。存在形成的通道，以使得可以将两种电解液分别引入至元件之间的合适的液流域之中。

[0043] 图 2 进一步示例端子 152。端子 152 包括电极 208，其在该构造中可以是集电器。组件 216 和 218 夹在电极 208 与端板 220 之间。组件 216 和 218 可以是绝缘密封。端板 220 可以是铝端板。电极可以与电极 208 接触并且从端板 220 延伸出。层叠体 102 保持在一起并且由闩 214 拉紧。

[0044] 图 3 示例在与电极 208 的界面处的衬垫 210 的实施方案，其为集流器，在端子 152

处。如由交点 300 所示，流体流动界面包括在端袋口 302 与石墨集流器 208 之间穿过衬垫 210 的塑料套管 306 的携带电解质流体的通道 304。随时间，存在电解液渗出至石墨集流器 208 与塑料套管 306 之间的界面的倾向，最终导致电解液泄漏穿过集流器端子 152。

[0045] 图 4 示例根据本发明的一些实施方案的衬垫 210 与端子 152 的集流器 208 之间的界面。如图 4 中所示，提供隧道 410。包括入口 412 和出口 414 的隧道 410 在液流通道上建立旁路，以使得石墨集流器 208 与套管 306 之间的界面不暴露至电解液并且因此消除了电解液泄漏的可能性。如图 4 中所示，隧道 410 包括入口 412 和出口 414，其中入口从衬垫 210 中的通道 304 接收流体，并且出口将流体穿过套管 306 提供至石墨集流器 208。

[0046] 图 5 示例层叠体 102 的端的截面。图 5 包括膜元件 204、衬垫 210、电极元件 202 和端子 152。如图 5 中所示，从上至下，第一层是具有框架 204 和膜 206 的膜层。衬垫 210 是下一个，衬垫 210 支撑保持液流的毡 502。下面的下一个层是具有集流器电极 208 的另一个框架 202，其例如可以由通过可以由 Santoprene 形成的框架环绕的钛 504 形成。来自歧管的液流穿过从绝缘端板 218 穿过的隧道 410 进入毡 502，绕开石墨 208 双极板与框架 202 的聚丙烯套管之间的界面边缘。绝缘端板 218 可以是，例如，PVC 板。下一个层是端衬垫 216，其可以由将集流器从下面的层分离的 Santoprene 形成。下一个层是绝缘端板 218。可以由铝形成的压力板 220 之后完成层叠体的末端。如图 5 中所示，隧道 410 在端板 218 中形成，具有通道穿过框架 204 和衬垫 210。石墨和塑料框架层之间的接缝上的法向力将接缝保持密封。如图 5 中所示，液流旁路（隧道）410 通过在端板 218 和桥支撑体中具有可以由 PVC 形成的袋口而建立。在一些实施方案中，该结构将集流器从电解液密封，而不需要胶。图 6 示例从歧管 302 至隧道 410 并且从隧道 410 穿过入口 412 和出口 414 的液流。

[0047] 隧道 410 至端子 156 的加入改进了迷宫通道同时不采用另外的端板。此外，不需要层叠体厚度的增加。成本上的边际增加通过下列方式实现：在石墨 208 中产生的入口 412 和出口 414 孔周围增加支撑体以用于隧道，在目前的 PVC 端板 216 上机械加工盲矩形袋口，以及使用注入模制 CPVC 或其他一致的塑料插头来提供用于流动的通道。

[0048] 图 7A 和 7B 进一步示例在端板 218 中形成的插头袋口 702 的构造。如图 7A 中所示，在端板中形成袋口 702，并且形成提供隧道 410 的插头 704，其位于袋口 702 中。

[0049] 所得到的隧道 410 在图 7B 中给出。如图 7B 中所示，端板 218 包括插头 704。如图 7B 中所示，衬垫层 708 可以插在端板 218 与具有钛层 504 的集流器层 216 之间。多个支撑体 706 可以应用在出口 414 中，穿过石墨层 208 以提供支撑体。

[0050] 图 8A 和 8B 进一步示例在端板的袋口中提供的插头。压缩力穿过插头的顶部，其上存在 Santoprene。该力密封石墨板 208 与 PP 套管之间的空隙。

[0051] 如图 1A 中进一步所示的，在一些实施方案中，提供热交换器 122 和 130 以当电解液分别返回至槽 104 和 106 时将其冷却。图 9A 示例电解液热交换器的实施方案，根据本发明的一些实施方案，其可以是热交换器 122 或 130 中的一个。如上所述，液流电池组产生热和电。应当利用这种热以便最优化液流电池的运行。归因于电解液的腐蚀性，由金属制成的更普通的热交换器不可以用于冷却电解液。因此，热交换器 900 主要由塑料形成。

[0052] 一些塑料热交换器是已知的，但是发现成本过高并且这些单位过大。所研究的热交换器全部是所谓的管壳型热交换器。然而，在热交换器 900 中可以采用如在层叠体 102 的余下部分中采用的相似的材料，因为那些材料耐受由电解液提供的化学条件。

[0053] 图 9A 示例根据本发明的一些实施方案的板型热交换器 900。热交换器 900 使用液流电池组材料并且在其设计上是独特的。热交换器 900 是液体至液体板型热交换器，其将电解液中的工艺热传送至传统的冷却液体，例如二醇。该设计的布局也可以应用于液流电池组；需要进行修改，如将液流分隔器由膜和双极板替换。

[0054] 如图 9A 中所示，热交换器 900 由构成热交换段的特定形状和尺寸的交替片形成。包装由压缩该包装的一对压板从侧面夹住。压板具有孔以容纳连杆和弹簧。特别是，如图 9A 中所示，在压力板 902 与 922 之间形成热交换器 900。压力板 902 和 922 包括容纳保持和密封热交换器 900 的拉杆和弹簧的对齐的孔 920。如图 9A 中所示，可以将衬垫 904 垫在压力板 902 上并且其也包括孔 920。可以将衬垫 924 垫在压力板 922 上并且其包括孔 920。液流域介质 906 和传热片 908 位于在衬垫 924 与 920 之间。液流域介质 906 在每个层中旋转 90 度并且每个液流域介质 906 通过热传热片 908 与下一个液流域介质 906 分离。传热片 908 和液流域介质 906 的每一个包括歧管 910，所有流体行进穿过热交换器 900 离开。压力片 902 和衬垫 904 不包括歧管并且密封歧管。压力片 922 和衬垫 924 包括输入口 912、913、916 和 918 以允许两种介质的进入和离开，一种是冷却介质并且另一种是所要冷却的电解液。

[0055] 当液流介质进入入口 1912 时，它流动穿过歧管通道 910 中的一个并且之后进入那些液流域介质 906 中的液流域内的歧管段中，其定向为接收和分配来自端口 912 的液流介质。液流介质流动穿过与传热片 908 接触的液流介质 906。在传热片 908 的相反侧，另一种液流介质与传热片 908 接触流动。该液流域在形状和尺寸上与首先提到的液流域相同，但是被旋转以获得如所示的方向。穿过端口 2916 进入的另一种介质遵循相似的路径。流体总是保持分离并且热从一种流体介质传递至穿过传热片的另一种。如图 9A 中所示，液流介质 1 穿过入口端口 912 进入并且穿过出口端口 914 离开，并且介质 2 穿过入口端口 916 进入并且穿过出口端口 918 离开。

[0056] 传热片 908 可以由塑料如聚乙烯、聚丙烯、pvdf、特弗隆、硬橡胶等制成。液流域 906 可以由较软的材料如软 santoprene 制成。交替的硬和软材料确保对于液体和环境的密封。

[0057] 如图 9A 中所示的热交换器 900 的实施方案仅采用两个二维的不同的组件，并且因为该原因可以以低成本制造。交替的片的数目可以简单地变化以容纳不同的热传递需求。组装是简单的，不需要特殊的技术。如对于金属板热交换器普遍的，热交换器 900 与类似等级的管壳式热交换器比较是紧凑的。

[0058] 热交换器 900 的另一个实施方案是将其中由之前的实施方案中由软橡胶制成的液流域 906 用硬塑料材料替换。橡胶发挥密封功能，如果由硬塑料替换，这种功能将损失。密封功能可以通过将各层粘合或焊接在一起代替。橡胶的去除可以降低成本，并且消除归因于橡胶的存在的污染。

[0059] 在热交换器 900 的另一个实施方案中，电解液与空气交换热并且因此不采用中间液体回路。图 9B 示例这种电解液热交换器 900 的分解图。如图 9B 中所示，电解液在石墨片 960 之间流动，离开并且被收集至公共歧管通道 966 和 968 中。石墨片 960 是非常好的热导体，特别是在平面方向上，这归因于其结构。电解液被包含在特定尺寸和形状的橡胶片 958 中，目的是引导和含有穿过通过石墨 960 和橡胶片 958 的层叠而出现的结构的液流。石

墨片 960 从橡胶片 958 延伸出，因此仅允许热并且不允许电解液被传递至外部环境。热交换器 900 形成有端板 958 和压力板 956。可以采用侧板 962 以引导空气的流动。

[0060] 如图 9B 中进一步所示，电解液穿过端口 952 和 954 流动进入和离开热交换器 900。来自强制对流风扇 964 的空气流动提供热的移除。然而在特定实施方案中，热可以通过将石墨片 960 垂直地定向而被动地移除，并且空气排放密度差驱动该过程。在这种方案中，可以省略风扇 964。

[0061] 电解液液流由与高度腐蚀性的电解液化学相容的外部泵驱动。存在具有这种相容性的正位移泵和离心泵。一般离心泵因为它们更长的寿命而是优选的。缺点是这些泵需要被预灌注。在这种情况下，预灌注意味着需要将泵在其可以履行其功能之前用液体填充。自动化的和手工预灌注方法是公知的，并且通过确保电解液入口和出口总是低于液体液面，将仅在投产和用于维修时需要预灌注。

[0062] 图 10 示例可以在如图 1 中所示的控制器 142 上执行的根据本发明的一些实施方案的状态函数 1000。用于液流电池的控制系统之前描述在通过引用以其全部内容结合在此的美国专利申请号 12/790,793 中。

[0063] 如图 10 中所示，在打开电源时，控制器 142 以系统初始化 1002 开始。在系统初始化状态 1002 中，将所有内部寄存器、存储器和控制器 142 外部的器件初始化用于启动。此外，将所有硬件组件设定为默认状态。从系统初始化状态 1002，状态函数 1000 转换至 ESP 软件狗初始化状态 (ESPDongleInit state)1004。

[0064] 在 ESP 软件狗初始化状态 1004 下，控制器 142 检查软件狗的存在并且，如果不存在，状态函数 1000 提供警告并且退出至或者充电状态 1014 或者放电状态 1008。如果软件狗存在，那么将氧化还原液流电池组系统参数从软件狗读出。如果设定了 Comm 位，那么它与外部启动程序通讯。它更新系统分量，检查是否测试过 Ebox，检查 Ebox 中的任何板是否改变，如果软件狗没有注册则从软件狗送出服务器信息用于注册，并且等待来自 DMS 板的时间应答。等待在一分钟后超时。从 ESP 软件狗初始化状态 1004，状态函数 1000 依赖于 En_Buck 信号和软件狗 ExBit 转换至或者充电状态 1014 或者放电状态 1008。当出现超时的时候或当完成启动过程时，设定软件狗 Exbit。

[0065] 在充电状态 1014 中，层叠体 102 被充电。通常，功率取自 BBus 并且通过恒电流充电被送至层叠体 102。特别是，充电电流由通过在软件狗初始化状态 1004 中读取软件狗获得的系统类型信息决定。之后进行以下功能 ：将泵、风扇和鼓风机全部打开 ；将充电电流通过与 Buck Boost 板相互作用上升 ；将液面控制算法初始化并函数化 ；在建立稳定的充电电流时计算系统的 SoC(层叠体电压可以用于计算 SoC) ；在系统的 SoC 与 SoC 阈值相交时计算系统的 ESR ；记录电解液的温度 ；基于电解液温度打开冷却系统 (热交换器) 算法。泄露传感器持续监控任何泄露。监控、记录并报告以下组件 ：所有风扇和鼓风机电流 ；控制板上的所有电源电压 ；Buck Boost 板上的所有电源电压 ；Ebox 的温度、ESP 环境和 ESP 外部环境温度 ；Bbus 电压 ；以及外部传感器如柴油发电机传感器或电路板传感器。

[0066] 在放电状态 1008 中，将功率由层叠体 102 递送至 Bbus。当 Bbus 电压降低低于阈值电压时，En-Buck 信号由“1”改变至“0”。基于 En-Buck 信号，发生状态至放电状态 1008 的改变。放电状态 1008 履行充电状态 1014 的所有功能，下列情况除外 ：不发生充电电流控制 ；不发生 ESR 计算 ；进行控制柴油发电机的 PFC ；并且如果 ABB 打开，如果 SoC 高则将其关

闭。

[0067] 当 SOC 大于 FloatSoC 值时，从充电状态 1014 转换至浮动状态 1006。FloatSoC 由启动程序设定，或通过系统软件狗中的 FRP 系统设定。Buck Boost 位于打开 ON 状态并且准备好在 BBus 功率消失或降低至阈值之下的情况下放电。在浮动状态 1006 下，充电电流停止；泵停止；并且风扇和鼓风机停止。记录电解液的温度，冷却系统算法打开并且基于电解液温度打开冷却系统，泄露传感器监控任何泄露，并且如在充电状态 1014 下那样监控、记录并报告各组件。因为泵停止，层叠体中的电解液不排出。但是层叠体电压归因于自放电过程缓慢地降低。连续地监控层叠体电压并且当层叠体电压降至低于阈值电压时，将泵打开约 90 分钟。在该时间过程中，将新鲜电解液提供至层叠体中。当泵运行时，计算电解液的 SoC。在泵停止之后，新鲜的电解液停留在层叠体中，并且因此层叠体电压将变得高于阈值电压。层叠体电压现在缓慢地自放电，并且电压降低至低于阈值电压，并且之后再次打开泵。该过程保持重复，直至系统的 SoC 降低至低于阈值 SoC。当其降低至低于阈值 SoC 时，系统转向充电模式 1014。

[0068] 当 SoC 降低至低于 SoC 休眠阈值时，由放电状态 1008 进入休眠状态 1010。在休眠状态下，泵关闭，Buck Boost 关闭，并且冷却系统算法关闭。记录电解液的温度，泄露传感器监控任何泄露，并且如在充电状态 1014 下所进行的那样监控、记录并报告各组件。当 BBus 功率恢复时或归因于层叠体 102 的功率损失出错时，状态函数 1000 将从休眠状态 1010 改变，并且状态函数 1000 转换至关闭 1012。

[0069] 当出错时，状态函数 1000 从任何其他状态转换至关闭状态 1012。在该状态下，除了监控功能之外，所有功能失效。从关闭状态 1012 的恢复当 BBus 功率可得时通过打开 / 关闭 BTS 开关出现，通过遥控 SMS 命令出现，或者如果通过休眠状态 1010 进入并且 BBU 电压大于 52V 则出现。

[0070] 在之前的说明书中，已经参考附图描述了不同的实施方案。然而，在不背离后面的权利要求中给出的本发明的较宽权利范围的情况下，显然的是可以对其做出多种修改和变更，并且可以实施另外的实施方案。说明书和附图因此被认为是描述性的而不是限制性的意义。

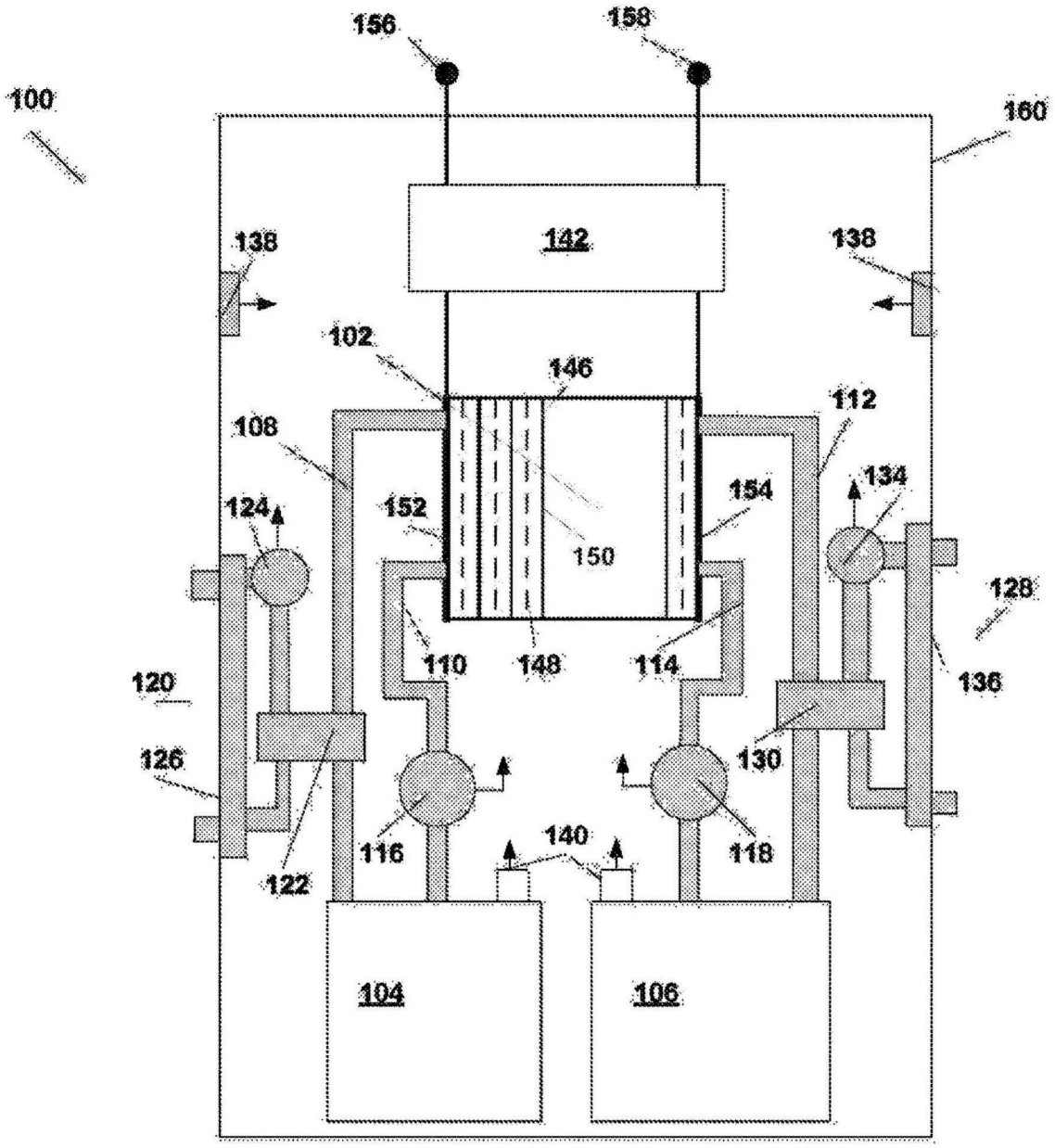

156
158
100
160
142
138
138
102
146
112
108
134
154
124
152
150
128
110
148
114
120
136
126
130
116
140
118
122
104
106

图 1A

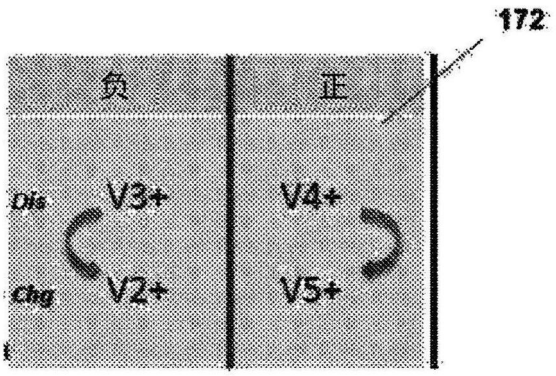


图 1B

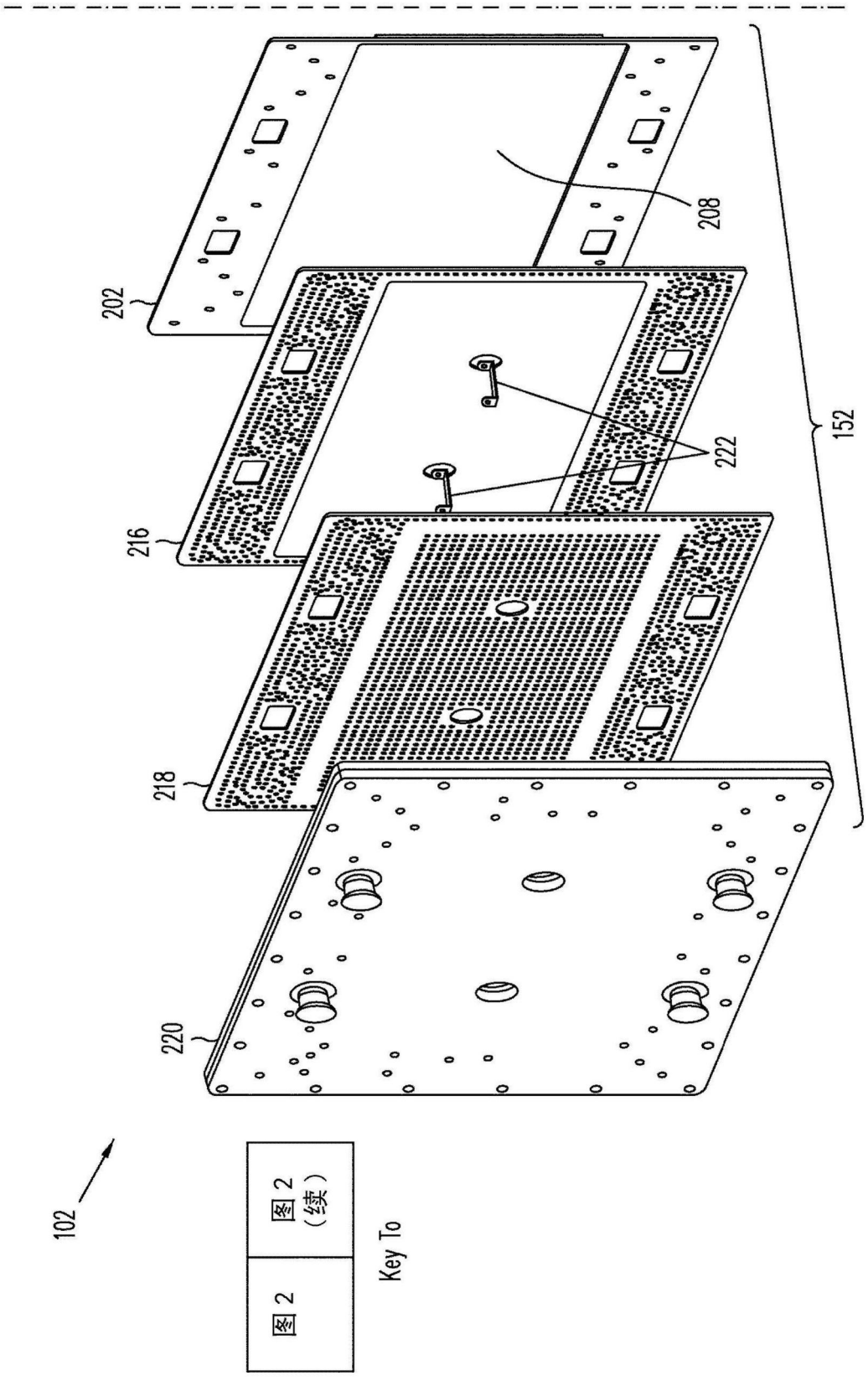


图 2

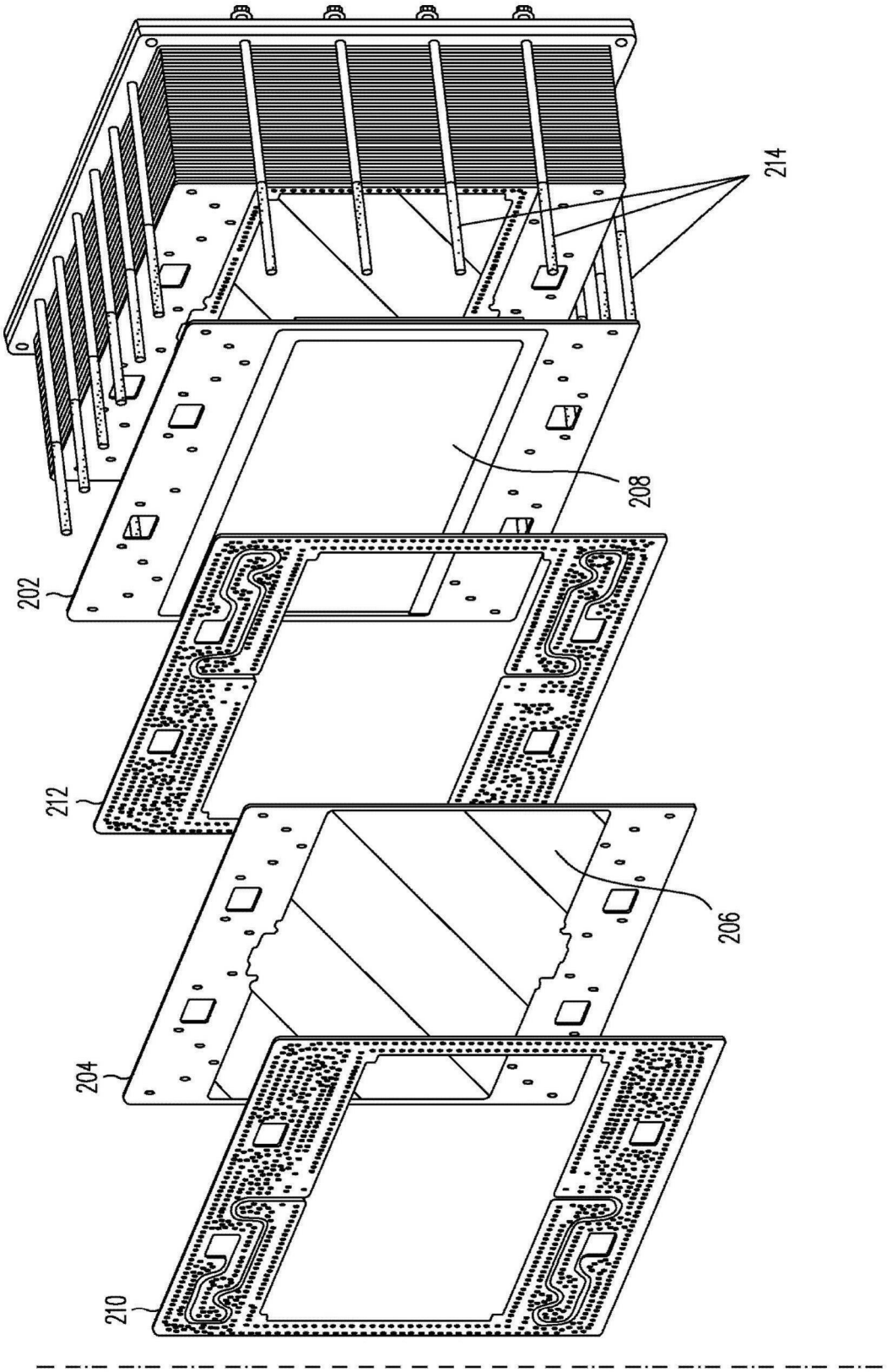


图 2(续)

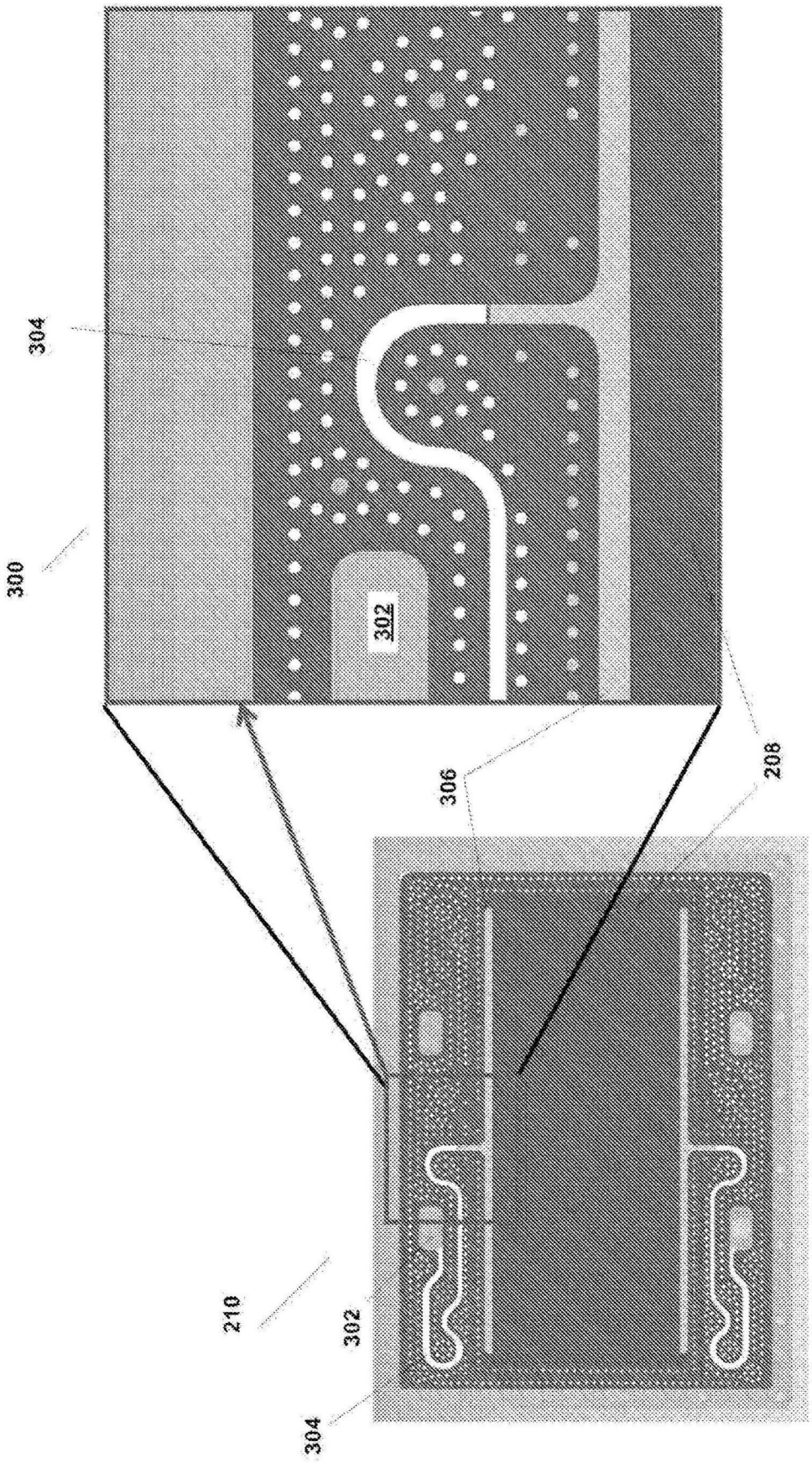


图 3

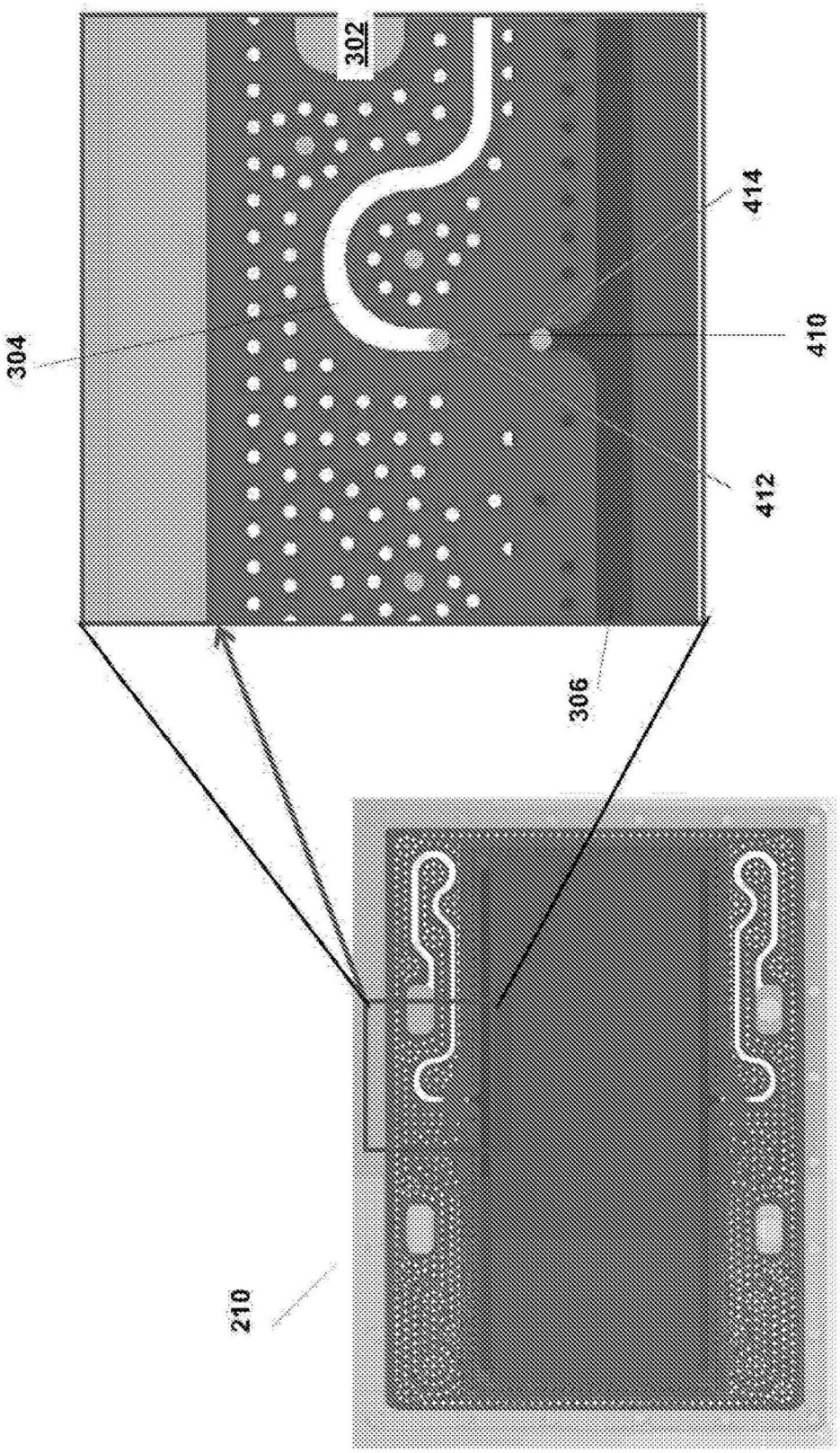


图 4

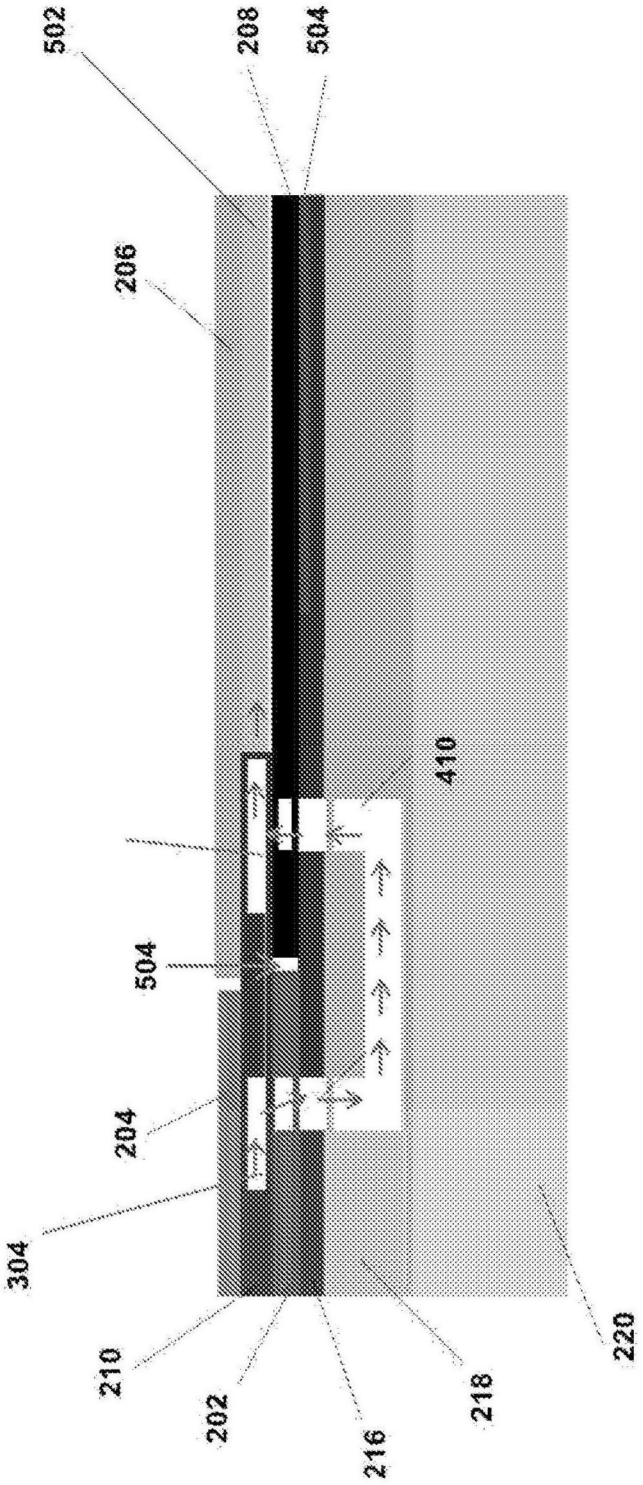


图 5

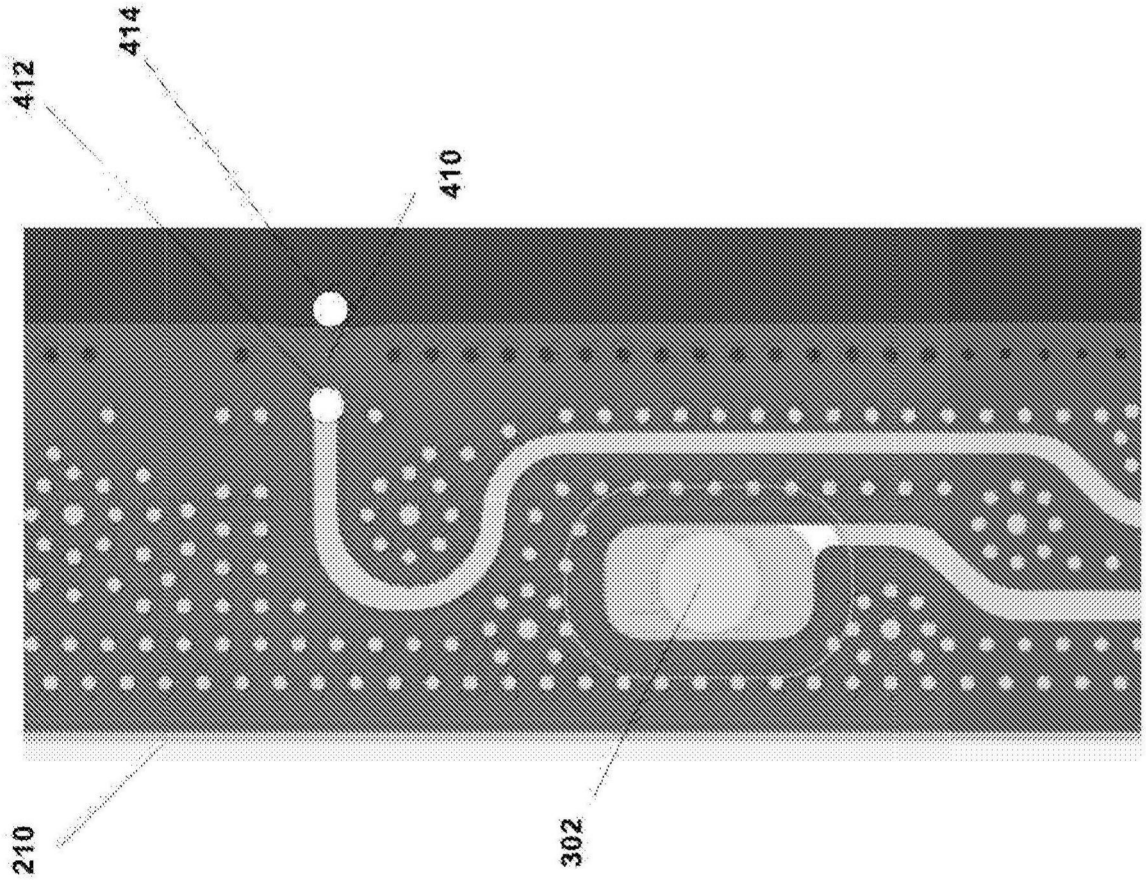


图 6

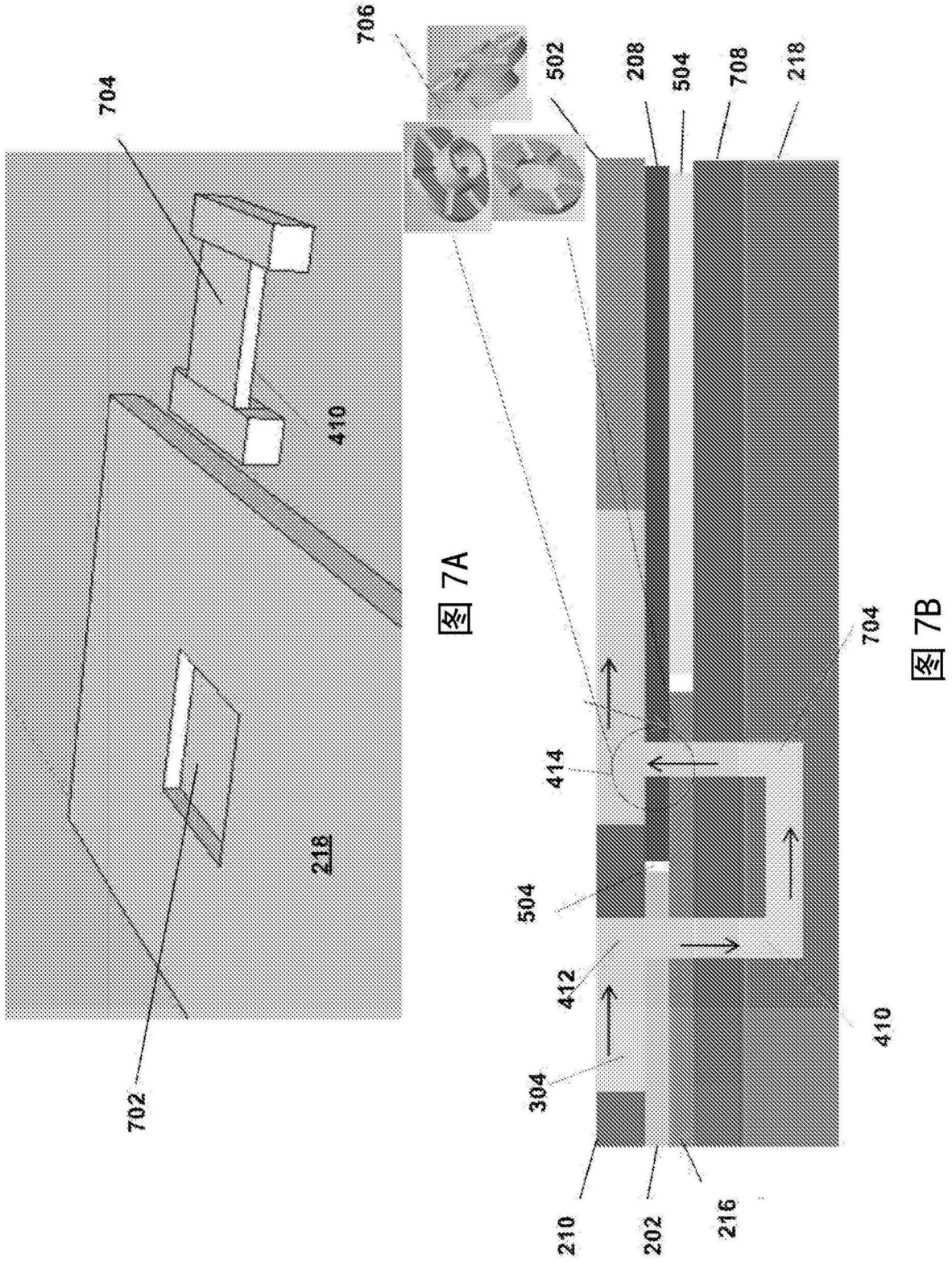

706
704
502
208
504
708
218
410
218
702
414
504
412
304
210
202
216
704
410

图 7A

图 7B

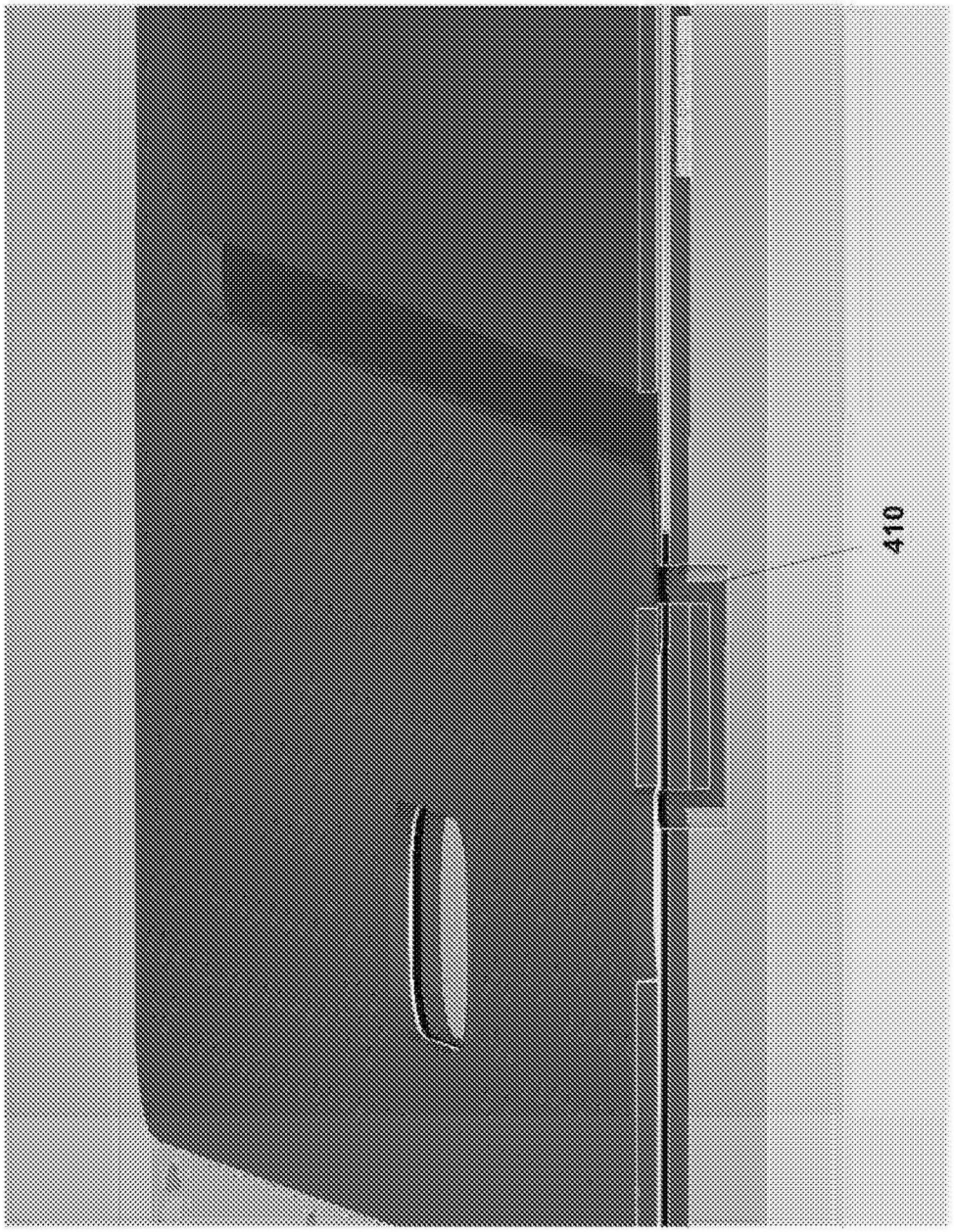


图 8A

图 8B

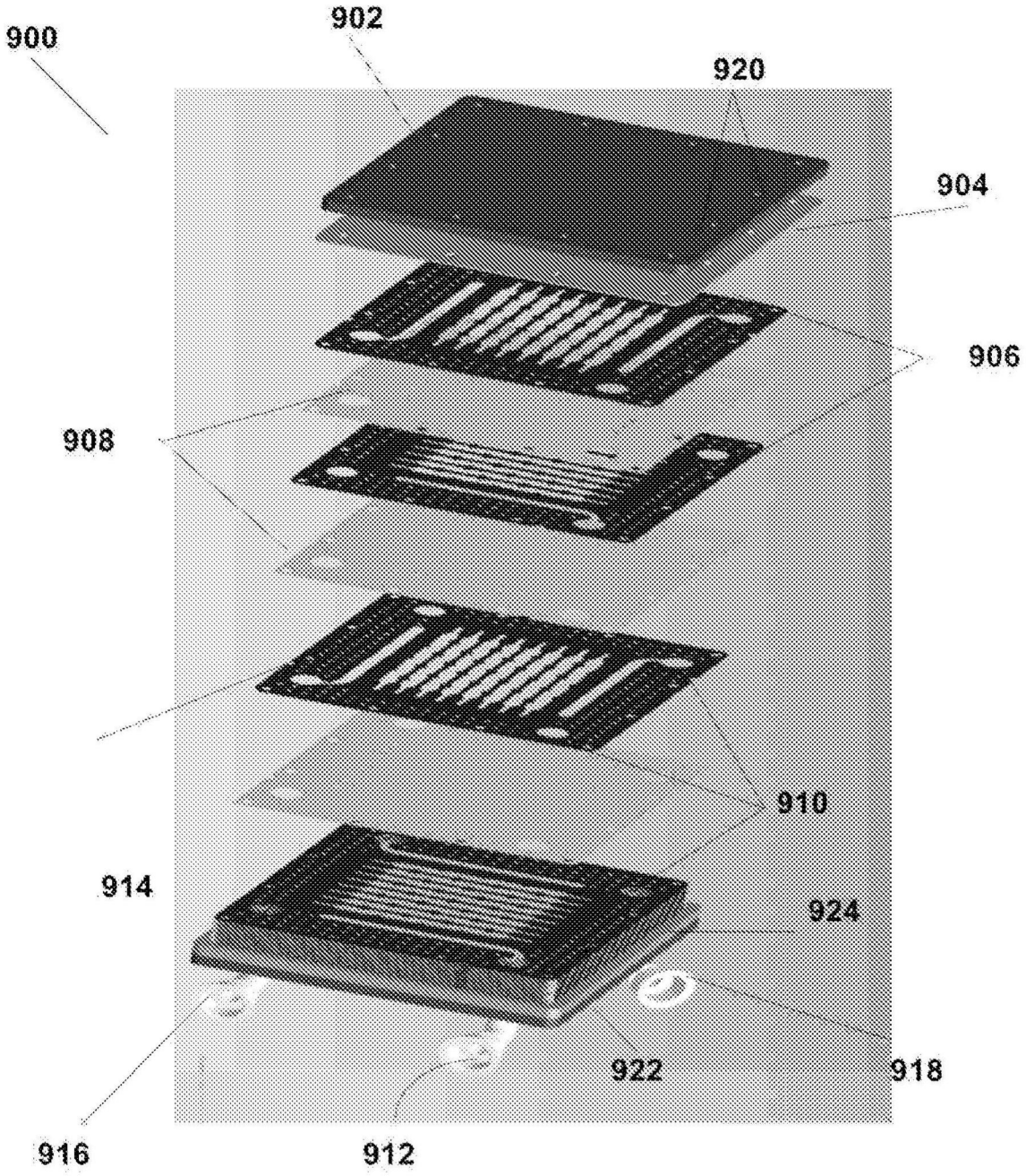


图 9A

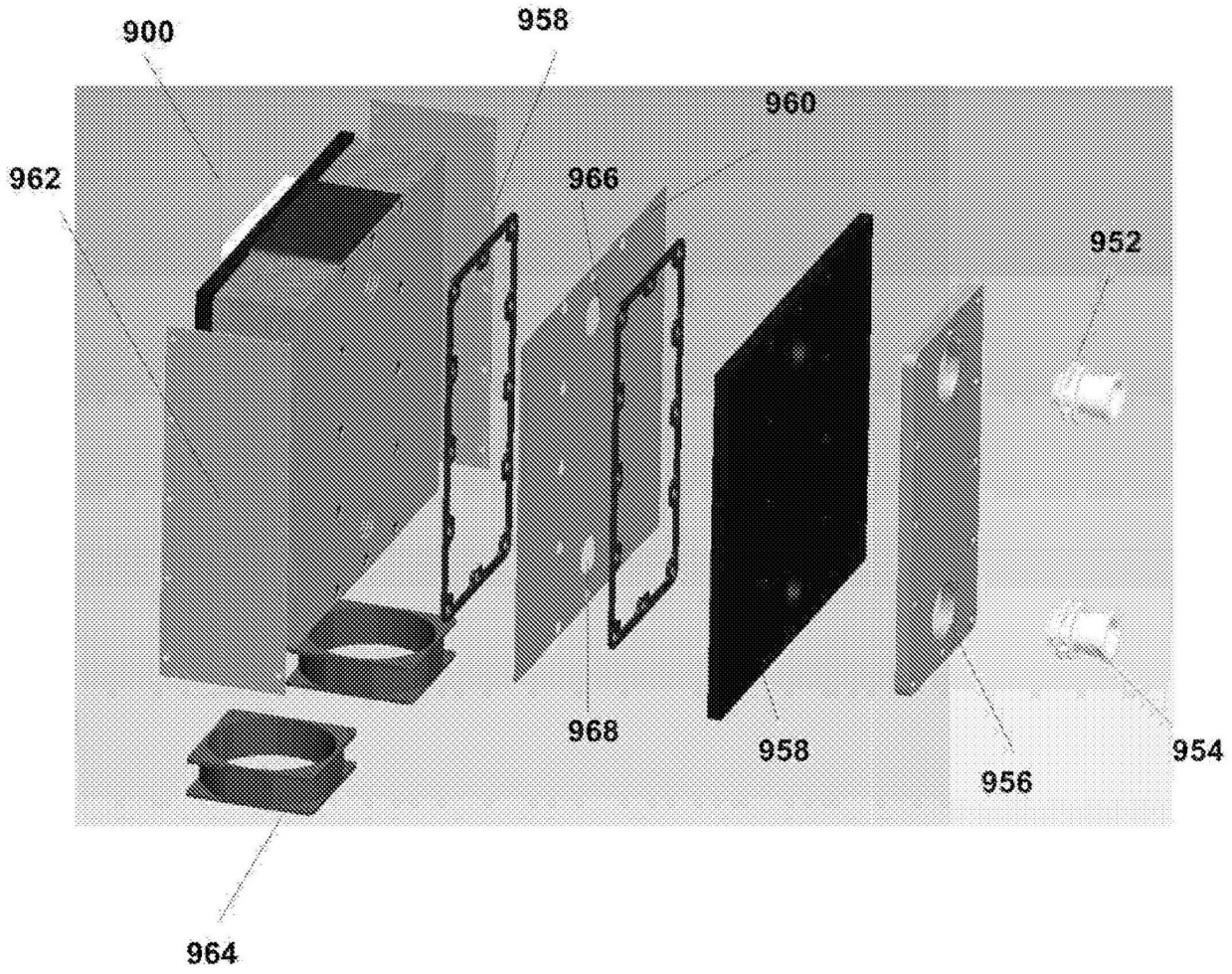


图 9B

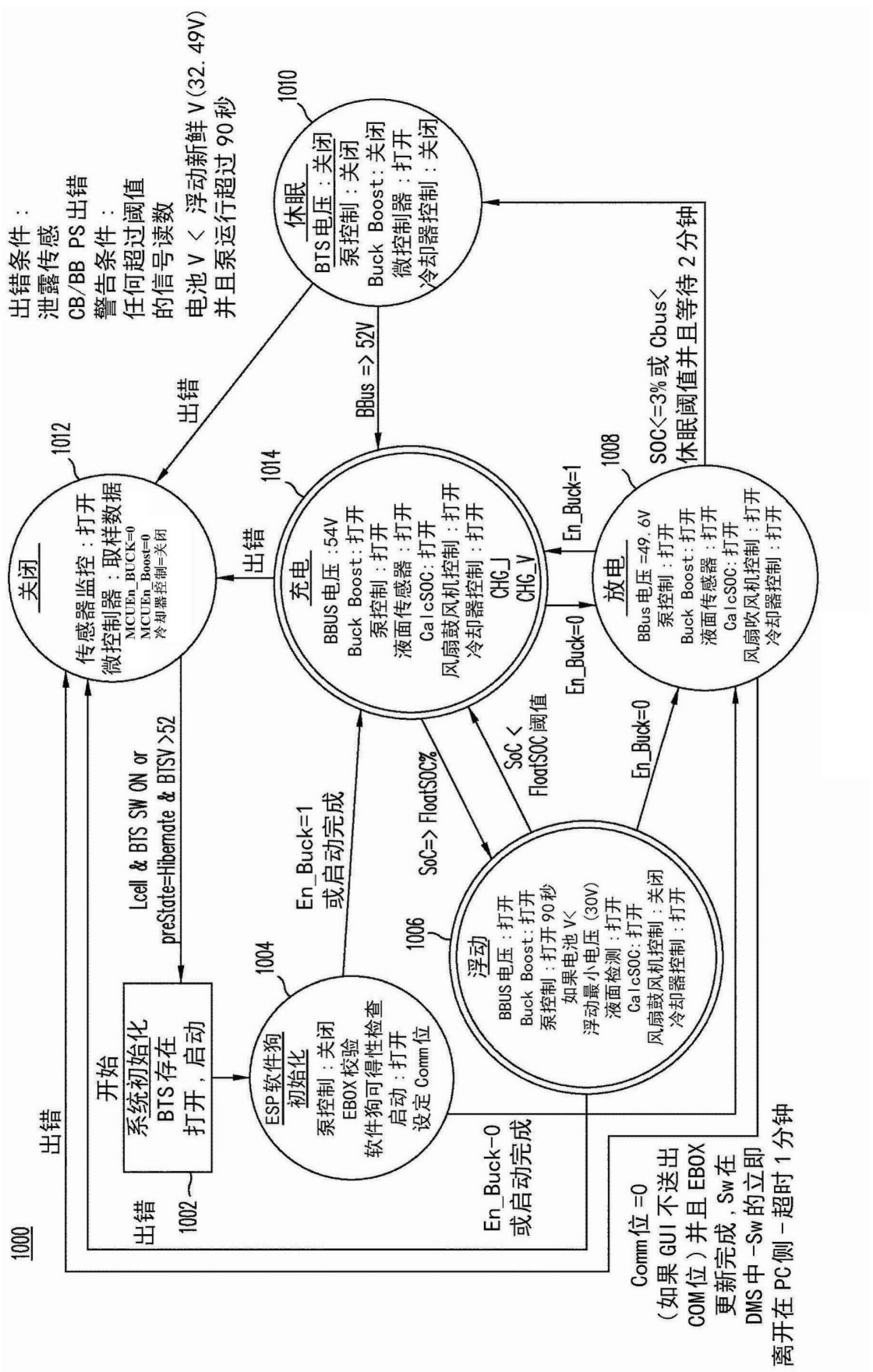

1000
出错
开始
系统初始化
BTS 存在
打开，启动
1002
出错
Lcell & BTS SW ON or
preState=Hibernate & BTSV >52
1004
ESP 软件狗
初始化
泵控制：关闭
EBOX 校验
软件狗可得性检查
启动：打开
设定 Comm 位
En_Buck=1
或启动完成
1006
浮动
BBUS 电压：打开
Buck Boost：打开
泵控制：打开 90 秒
如果电池 V<
浮动最小电压（30V）
液面检测：打开
CalcSOC：打开
风扇鼓风机控制：关闭
冷却器控制：打开
SoC=> FloatSOC%
SoC <
FloatSOC 阈值
1008
放电
BBus 电压 =49.6V
泵控制：打开
Buck Boost：打开
液面传感器：打开
CalcSOC：打开
风扇吹风机控制：打开
冷却器控制：打开
En_Buck=0
En_Buck=1
SOC<=3% 或 Cbus<
休眠阈值并且等待 2 分钟
1010
休眠
BTS 电压：关闭
泵控制：关闭
Buck Boost：关闭
微控制器：打开
冷却器控制：关闭
BBus => 52V
1012
关闭
传感器监控：打开
微控制器：取样数据
MCUEn_BUCK=0
MCUEn_Boost=0
冷却器控制=关闭
出错
1014
充电
BBUS 电压：54V
Buck Boost：打开
泵控制：打开
液面传感器：打开
CalcSOC：打开
风扇鼓风机控制：打开
冷却器控制：打开
CHG_I
CHG_V
出错
出错条件：
泄露传感
CB/BB PS 出错
警告条件：
任何超过阈值
的信号读数
电池 V < 浮动新鲜 V（32.49V）
并且泵运行超过 90 秒
En_Buck=0
或启动完成
Comm 位 =0
（如果 GUI 不送出
COM 位）并且 EBOX
更新完成，Sw 在
DMS 中 -Sw 的立即
离开在 PC 侧 - 超时 1 分钟

图 10

Abstract

A Flow Cell System that utilizes a Vanadium Chemistry is provided. The flow cell system includes a stack, electrolyte heat exchangers, and a controller executing a state machine. A stack for a flow cell system having an end plate structure comprising a conducting plate and a gasket frame including fluid manifolds. An electrolyte heat exchanger including flow field media; and heat transfer sheets separating the flow field media, and wherein electrolyte and a heat exchange fluid can be flowed through the electrolyte heat exchanger. A controller according to the present invention can include an initialization state; a charge state; a discharge state; a float state; a hibernate state; and a shutdown state.