

ELECTROCHEMICAL SYSTEM FOR LOW ENERGY AND HIGH EFFICIENCY
WATER DESALINATION

Cross-Reference to Related Application

- 5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10201904355T, filed 15 May 2019, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

- 10 [0002] The present disclosure relates to an electrode module operable for electrodialysis. The present disclosure also relates to an electrodialysis system comprising the electrode module, and a method of controlling desalination efficiency in electrodialysis involving the electrode module.

15 **Background**

- [0003] About 70% of the world is covered by water but only 2.5% of the water may be qualified as fresh water, from which only 0.007% may be useful for consumption. Based on this, fresh water may be deemed a scarcity, and fresh water scarcity affects likely more than 40% of the global population and may be aggravated by a growing
20 population, climate change and inadequate infrastructure. It has been unfortunate for millions of people to die each year from diseases associated with inadequate water supply, sanitation and hygiene. This is in spite of almost half of the world's population living in close proximity to the coastline, having access to seawater that constitutes about over 95% of Earth's water.
- 25 [0004] As almost half of the world's population stay near the coastline, seawater desalination may be considered a promising solution to the worldwide water crisis. However, implementation of existing desalination technologies for freshwater production remains limited by, for example, its significant energy consumption. Despite this, electrodialysis (ED) may be one of the most popular desalination techniques, next
30 to reversed osmosis (RO), nanofiltration (NF), ion-exchange resins, and flash distillation. In ED, ions migrate from a diluate to a concentrate solution through cation- and anion-exchange membranes upon a potential difference applied between the

cathode and anode situated at the sides of the membranes. In contrast to filtration techniques (e.g. RO, NF) where clean water may be transported through a filtration membrane, ED may be much more tolerant of processing various feed water quality, as the electric field generated between the cathode and anode may affect small hydrophilic ions to a greater extent over other compounds and therefore membrane fouling may be profoundly reduced. Furthermore, the deposits formed at the membrane can be easily removed in ED by occasionally and conveniently reversing polarity of the applied potential. However, significant drawbacks of existing ED may include a relatively high electricity consumption and low salt removal efficiency, hence becoming limited to the processing of low salinity feeds.

[0005] There is thus a need to provide a solution that addresses one or more of the limitations mentioned above. The solution should at least provide for an ED system that allows for precise control of the desired level of desalination efficiency as a direct function of the applied voltage.

Summary

[0006] In a first aspect, there is provided for an electrode module operable for electrodialysis, the electrode module comprising:

a substrate; and

an array of electrodes arranged on the substrate, wherein each of the electrodes is shaped as a planar sheet and each planar sheet is a segment of the array of electrodes, wherein each segment is arranged apart from another segment, and wherein each segment has a different planar surface area from another segment.

[0007] In another aspect, there is provided for an electrodialysis system comprising:

one or more electrodialysis cells, wherein each of the one or more electrodialysis cells comprise:

an anode electrically coupled to a cathode, wherein each of the anode and the cathode comprises the electrode module described in various embodiments of the first aspect; and

a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and

the cathode are arranged for segments of the anode and segments of the cathode having identical planar surface area face each other.

[0008] In another aspect, there is provided for a method of controlling desalination efficiency in electrodialysis comprising:

applying a voltage to one or more electrodialysis cells, wherein each of the one or more electrodialysis cells comprise:

an anode electrically coupled to a cathode, wherein each of the anode and the cathode comprises the electrode module described in various embodiments of the first aspect; and

a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and the cathode are arranged for segments of the anode and segments of the cathode having identical planar surface area face each other; and

operating a pair of segments of the array of electrodes at a different potential difference from another pair of segments, wherein one pair of segments comprises a segment from the anode and another segment of identical planar surface area from the cathode.

Brief Description of the Drawings

[0009] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0010] FIG. 1A shows the open circuit potential (OCP) generated for a cation concentration gradient across a cation-exchange membrane (CEM). Specifically, FIG. 1A shows the processes occurring in a system with a cation-exchange membrane. I^+ denotes cation, A^- denotes a counter-anion, R^- denotes a negatively charged functional group of the cation-exchange membrane, which may be sulfonic groups chemically bound to a polymeric chain of the membrane, and C_{I^+} denotes the concentration of the cation I^+ in the solution.

[0011] FIG. 1B depicts migration of cations across the CEM upon an applied voltage (E).

[0012] FIG. 2A shows the geometry of an electrode array of one non-limiting embodiment of the present disclosure. The numbers 1-4 each represent a segment of the electrode array working at theoretical applied potentials of 60, 120, 180 and 240 mV, removing 66%, 22%, 8% and 3% of NaCl, respectively, which in turn represents
 5 reduction to 0.2 M, 0.06 M, 0.02 M and 0.006 M NaCl, respectively. A pair of conductometric electrodes (i.e. conductometric cells), formed of platinum as an example, may be incorporated between segments of the electrode array to monitor the progress of desalination.

[0013] FIG. 2B is a plot of energy efficiency of the present electrodialysis system. For
 10 the Ag/AgCl single-electrode system, the energy consumption rate was 3.9 kWh/m³. However, in the Ag/AgCl system comprising the electrode array, the energy consumption becomes closer to a theoretical ideal system, and with the number of segments (stages) involved in the process, e.g. for a 4 stage system, the energy consumption rate gets reduced to 1.4 kWh/m³.

[0014] FIG. 2C is a plot of electromotive force (EMF) measured in mV against a single
 15 junction Ag/AgCl reference electrode as a function of the logarithm of concentration of chloride ion in a bulk solution, which follows the Nernst equation: $OCP = E^0 + \frac{59}{-z} \log a_A$, wherein OCP represents open circuit potential, E^0 represents a standard electrode potential, while z and a_A represent the charge and activity of the potential-generating anion, respectively. The inset shows a fast and stable dynamic response of
 20 the present silver/silver chloride electrode to the changes in chloride concentration in the solution.

[0015] FIG. 2D is a plot of voltage applied against the logarithm of concentration
 gradient across a cation-exchange membrane that follows the equation (derived from
 25 Nernst equation): $E = OCP + 59 \log \frac{\Delta a_{C2} \cdot \Delta a_{A2}}{\Delta a_{A1} \cdot \Delta a_{C1}}$, wherein E represents the effective electrode potential, wherein OCP represents open circuit potential and the equation for OCP is already defined above for FIG. 2C, Δa_{A1} , Δa_{C1} , Δa_{C2} and Δa_{A2} represent the intended change in activities of chloride and counter cation on both sides of the membrane, respectively. Specifically, FIG. 2D can be theoretically derived based on a
 30 known relationship between the voltage applied and the logarithm of chloride concentration, for example, from the plot and values shown in FIG. 2C.

[0016] FIG. 3A shows the process occurring in an embodiment of the present symmetrical electrodialysis system with application of an effective voltage, e.g. +0.24 V.

[0017] FIG. 3B shows the process occurring in an embodiment of the present symmetrical electrodialysis system with reversal of the voltage polarity, e.g. -0.24 V.

[0018] FIG. 4 shows a non-limiting example of a designed stacking of multiple cells. The left image (A) shows a side cross-sectional view of the stacked cells and the right image (B) shows a top-down view of the stacked cells. Each cell has an anode and a cathode, wherein each of the anode and cathode has an array of four electrodes (four segments). SW denotes seawater, D denotes diluate, and B denotes brine.

[0019] FIG. 5 shows a dissection of the assembly of FIG. 4.

[0020] FIG. 6A shows photo images of a prototype developed for desalination based on the present electrodialysis system using the present electrode module. The left image shows chloridation of the electrodes (deposition of AgCl layer) which is, for example, to be performed before the cell assembly. The middle image shows a pair of conductometric electrodes disposed between two segments of the electrode array. The right image shows a complete assembly of the prototype.

[0021] FIG. 6B shows the configuration of the electrode module used in the prototype of FIG. 6A. C1 to C16 denote pairs of conductometric electrodes disposed between two segments of the electrode array. The segments are the electrodes having different planar surface areas denoted by E1 to E8. The arrows denote flow of the electrolyte (e.g. solution to be treated).

[0022] FIG. 7A is a plot of current (A) against time (seconds). Specifically, FIG. 7A shows the behavior of electrodialytic systems operated based on the three different processes indicated in the plot as the desalination driving force, which includes (i) faradaic process using electrodes of the second kind, (ii) faradaic process using conventional redox electrodes, and (iii) a capacitive process. The behavior reflected assumes operating on an unlimited source of electrolyte (regardless under bulk or flow conditions, i.e. batch or continuous operations, respectively). The faradaic process using redox electrodes (e.g. platinum, graphite) provides for stable process condition, which can be observed from the consistent current readings in FIG. 7A. For capacitive process, it is observed that the current drop after initial operations and the process shuts

down. In the faradaic process using electrodes of the second kind, a comparable surface area of the electrode can accept much larger quantities of ions compared to capacitive processes, as the ions are built into the structure of the electrode and charge neutralized by silver oxidation results in stable current through the whole process. The electrode of the “second kind” herein refers to an electrode composed of a metal covered with a layer of an insoluble salt of the metal.

[0023] FIG. 7B is a plot of voltage (V) against time (seconds). Specifically, FIG. 7B shows the behavior of electrodialytic systems operated based on the three different processes indicated in the plot as the desalination driving force, which includes (i) faradaic process using electrodes of the second kind, (ii) faradaic process using conventional redox electrodes, and (iii) a capacitive process. The behavior reflected assumes operating on an unlimited source of electrolyte (regardless under bulk or flow conditions, i.e. batch or continuous operations, respectively). FIG. 7B shows that the faradaic process using redox electrodes (e.g. platinum, graphite) operates at a higher voltage cost for the stable process condition and consistent current readings of FIG. 7A. For the capacitive process, there is initially low voltage demand, which exponentially increases with surface saturation that causes the current drop and process shut down as observed in FIG. 7A. In the faradaic process using electrodes of the second kind, a comparable surface area of the electrode can accept much larger quantities of ions compared to capacitive processes, as the ions are built into the structure of the electrode and charge neutralized by silver oxidation results in low voltage demand (in FIG. 7B) and the stable current through the whole process as already shown in FIG. 7A.

[0024] FIG. 8 shows the configuration of a planar electrodialysis flow-cell of the present disclosure. The top and bottom images show the top-down and bottom-up views of part B of the flow-cell, respectively. The middle image shows the cross-sectional view from a side of the flow-cell.

[0025] FIG. 9 shows an alternative configuration of planar electrodialysis flow-cell of FIG. 8, wherein the Ag/AgCl electrode and spacer is replaced with an Ag/AgCl porous electrode.

[0026] FIG. 10 shows recycling of silver to form the porous Ag/AgCl porous electrode of FIG. 9. Specifically, silver metal scraps are dissolved in aqueous nitric acid to form silver nitrate. Aqueous sodium chloride is then added and AgCl is precipitated. The

precipitated AgCl is dried and mixed with, for example, crystalline sodium chloride, and the mixture is subjected to elevated pressure and temperature (abbreviated as P/T) to sinter the amorphous AgCl precipitate and to form a porous Ag/AgCl electrode after the sodium chloride template is dissolved. The porous electrode can be configured into
5 the electrode array of FIG. 2A.

[0027] FIG. 11 is a table comparing the economic viability of an electrodialysis system of the present disclosure, operably involving the present electrode array, for treating seawater and brackish water, compared to traditional seawater and brackish reverse osmosis and reverse electrodialysis. The comparison includes an electrodialysis system
10 of the present disclosure, operably involving a porous version of the present electrode array (see last row). * denotes use of recycled silver based on the method of FIG. 10. The price of silver used in the calculation was 1000 SGD/kg and the price of recycled silver (assuming 75% of pure silver recovered from scrap) is SGD 519.14 SGD/kg.

[0028] FIG. 12 demonstrates for the faradaic capacity of Ag/AgCl via alternating
15 current cycling, wherein an Ag/AgCl wire electrode is used.

[0029] FIG. 13 is a plot of the galvanostatic voltammetry of the Ag/AgCl wire electrode of FIG. 12.

[0030] FIG. 14 illustrates the oxidation and reduction mechanism of silver using an Ag/AgCl electrode surface.

20 [0031] FIG. 15A shows the electrolytic desalination (battery charging) of a desalination battery operating based on the present electrode.

[0032] FIG. 15B shows the galvanic regeneration (battery discharging) of a desalination battery operating based on the present electrode.

25 Detailed Description

[0033] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced.

[0034] Features that are described in the context of an embodiment may
30 correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other

embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0035] The present disclosure relates to an electrode module operable for
5 electro dialysis. The electrode module is operable as an anode or a cathode in electro dialysis. The electrode module may comprise an array of electrodes that may be interchangeably termed herein an “electrode array”. The array of electrodes may comprise one or more electrodes, and each of the one or more electrodes may be referred to as a segment of the electrode array. The electrodes forming the electrode
10 array may be of planar configuration. In other words, each of the electrodes may be configured as a planar element, such as a planar layer or a planar sheet. As the electrodes are planar, the electrode module may be configured to have a planar configuration. Accordingly, each segment may have a planar surface area. In the array of electrodes, each of the segment has different planar surface area from another segment.
15 Holistically, the present electrode module has a plurality of planar segments, wherein each planar segment acts as an electrode in an array of electrodes.

[0036] Typically, the minimum energy consumption rate for desalinating a cubic meter of water may be 1.06 kWh/m^3 according to theoretical thermodynamics calculations. Comparatively, the energy consumption rate for existing seawater reverse osmosis
20 treatment plant tends to range from 3 to 4 kWh/m^3 . In a Ag/AgCl one-electrode system, the energy consumption rate may be about 4 kWh/m^3 . However, a Ag/AgCl system operably using electrode array of the present disclosure is able to attain an energy consumption rate of 1.6 kWh/m^3 .

[0037] Advantageously, to obtain a desalination efficiency of at least 99.5%, an
25 electro dialysis system using the present electrode module may require about 10% of the energy consumed for an electro dialysis system using a single stage system based on e.g. existing one-piece graphite electrode.

[0038] Other advantages of the present electrode module, an electro dialysis system and a method of controlling desalination efficiency in electro dialysis, both of which
30 operated using the present electrode module, include reduced post-treatment requirements such as no need for pH adjustment or re-mineralization, low pressure operations and hence reduced capital cost, operable using cheap and durable ion-

selective exchange membrane, very low fouling with clean-in-place cleaning (i.e. without disassembly of system and/or electrode module for cleaning), operable with a significantly smaller footprint due to, for example, integration of the electrode array into a single stackable module, and flexibility of switching operations between
5 electrodialysis and reverse electrodialysis (RED).

[0039] Details of various embodiments of the electrode module of the first aspect, the present electrodialysis system and method, and advantages associated with the various embodiments are now described below.

[0040] In various embodiments of the first aspect, there is provided an electrode module operable for electrodialysis. The electrode module may include a substrate, and an array of electrodes arranged on the substrate, wherein each of the electrodes may be shaped as a planar sheet and each planar sheet may be a segment of the array of electrodes, wherein each segment may be arranged apart from another segment, and wherein each segment may have a different planar surface area from another segment. Said differently, the electrode module may be operable as an anode or a cathode. Each electrode module comprises an array of electrodes, wherein the electrodes in the array may be of a planar configuration and are of different sizes. A planar electrode of the present disclosure is configured as a planar layer or planar sheet, and hence termed to be of a planar configuration. As the electrodes are planar, the electrode module may also be configured to have a planar configuration. A planar configuration is advantageous as it allows for stacking of various electrodes modules without resulting in a significant thickness.

[0041] Each segment of the electrode module may be operable to have a voltage applied
10 to facilitate deposition of anions, e.g. chloride anions, at each electrode operating as the anode. Each segment of the electrode module may be operable to have a voltage applied which may be based on each segment's planar surface area. The voltage applied specifically to each segment may differ. For example, the amount of anions (e.g. chloride anions) deposited at each electrode may be a function of (i) the voltage applied
15 and (ii) concentration of anions (e.g. chloride anions) in the solution to be electrodialysed and which the electrodes are in contact with, wherein the ratio of the different planar surface areas of the segments is proportional, or preferably proportional, to a ratio of the amounts of anions (e.g. chloride anions) deposited. That

is to say, the anions (e.g. chloride anions) deposited at the electrodes may be defined as an anion quantity ratio (e.g. chloride anions quantity ratio), which may be proportional, or preferably proportional, to a ratio of the different planar surface area of the segments. The amount of anions (e.g. chloride anions) deposited as a function of (i) and (ii) may be quantified or determined using the Nernst equation, which is described in the examples section herein. Said differently, each segment may be operable to have an amount of electrical charge passing through which may be proportional to the anion (e.g. chloride ion) concentration of the solution in contact with each respective segment and the voltage applied, which may be the case for optimized flow rate. As a non-limiting example to illustrate this, a theoretical potential difference of 240 mV (considering only the electrodes and membrane potentials) may have to be applied. This theoretical potential differences applies for a conventional electrode, that is, an electrode used as a single piece of component instead of being formed of an array of electrodes. However, with the present electrode array that has segments of different planar surface area, to remove 66% of the salt, only about one quarter of the theoretically calculated voltage may need to be applied (60 mV). Accordingly, removal of 22% and 8% of the salt may require half and three quarters of the theoretical voltage, respectively, and only 3% to 4% of a sample to be treated may require the full potential of 240 mV to be applied. In other words, if a single conventional electrode is used, energy consumption is not saved as 240 mV has to be applied to the entire electrode. Meanwhile, in the present electrode module, each electrode segment allows for a lesser amount of voltage to be applied to achieve an even higher operation efficiency, reducing energy used. To ensure similar current densities and therefore similar silver oxidation rate for the segments in the array, the ratios of the surface area of the segments in the array may reflect the ratios of the desalination efficiency from respective segments, e.g. for removal of about 66%, about 22%, about 8% and about 4% of chloride ions from the solution, a ratio of 66:22:8:4 of the surface areas of the segments may be defined. During operation of the present electrode module, the removal of, for example, chloride ions from the solution or the water to be treated, may comprise deposition of chloride ions at the surface of the electrodes in the present electrode module. In other words, each segment may be operable to have a different voltage applied to facilitate deposition of an amount of chloride ions at each electrode, wherein the amount of chloride ions

deposited at the electrodes defines a chloride ion quantity ratio which may be proportional to a ratio of the different planar surface area of the segments. The reduction in chloride ion concentration in the solution or water to be treated may be a function of the voltage applied. An example of the chloride ion quantity ratio and the ratio of the different planar surface of the segments has already been described above, e.g. 66:22:8:4. This ratio may depend on the number of segments present in the array of electrodes.

[0042] In various embodiments, each of the electrodes may comprise any suitable material that is conductive, sparingly soluble in the solution to be electrodialed, and is a redox reversible metal compound. Such a material may be or may comprise, for example, a metal, a metal chloride, a metal cyanide, a metal thiocyanide, a metal sulfide, a metal hydroxide, and/or a metal oxide. Electrodes formed of such materials may be suitable for use with other electrolyte systems. For example, an electrode of silver and silver chloride may be used for desalination, wherein chloride ions are to be removed.

In other instances where desalination is not the application, and a different electrolyte system is to be worked with, other electrodes, for example, those of a metal cyanide, a metal thiocyanide, a metal sulfide, a metal hydroxide, and/or a metal oxide may be more suitable. In various embodiments, each of the electrodes may comprise silver, mercury, and/or a chloride thereof. For example, each of the electrodes may comprise silver chloride or mercury chloride. The mercury chloride may be a mercury (I) chloride. In other words, each segment may comprise silver, mercury, or a chloride thereof. Each of the electrode, and hence the segment, may be an electrode of the second “kind”, which refers to an electrode composed of a metal covered with a layer of an insoluble salt of the metal. In this regard, each of the electrodes may comprise a layer of an insoluble salt, wherein the insoluble salt may comprise silver chloride or mercury (I) chloride. Additionally, an electrode of the second “kind” configured as a segment disclosed herein is of a thin-layer planar configuration, which advantageously mitigates or eliminates problems associated with dead volumes of electrolytes in an electrodialysis cell that may occur for electrodes in the form of thick bars. With the thin-layer planar configuration of the electrode of the second “kind”, the configuration or arrangement of a channel in an electrodialysis can be designed in a straightforward manner without the need to consider additional designs as an attempt for resolving the

issue of dead volumes. Advantageously, the insoluble salts do not dissolve easily upon contact with an electrolyte, such as brine or seawater, allowing for electrodialysis to be operated over a long period. In various embodiments, the insoluble salt may produce an anion upon receiving negative electrical charges when the electrode module operates as a cathode – this represents the cathodic process, or each of the electrodes may accept an anion to form the layer of insoluble salt upon releasing negative electrical charges when the electrode module operates as an anode – this represents the anodic process. For example, for an insoluble salt that may comprise silver chloride or mercury (I) chloride, the anion may be chloride ion. While mercury (I) chloride may be deemed toxic, an electrode comprising such an insoluble salt may still be used for applications that is not limited by its toxicity and tolerate its use.

[0043] The present electrode module may have a substrate as mentioned above. The substrate may comprise an electrically non-conductive and water insoluble material. The electrical non-conductive and water insoluble material may comprise or may be a polymer, a glass, a ceramic, or a combination thereof. The substrate may be in the form of sheets, tubes, bundle, or rolls, etc. Preferably, the substrate may be a planar substrate.

[0044] The electrode module in various embodiments of the first aspect may further comprise a pair of conductometric electrodes, wherein the pair of conductometric electrodes may be disposed in a space between two segments. The pair of conductometric electrodes may be used to monitor for concentrations of ions in the electrolyte or solutions in contact with the electrodes. The term “conductometric” herein includes within its meaning a reference to a component for measuring electrical conductivity from concentration of a substance. The pair of conductometric electrodes may each comprise a conductive material that remains inert during operation to measure conductivity of the solution, which may be, for example, proportional to concentration of chloride ions measured. The conductive material may comprise or may be platinum, gold, stainless steel, conductive carbon material such as graphite, or Ag/AgCl. The conductive material used may depend on the solution or water to be treated.

[0045] In various embodiments, the electrode module may be operable as an anode or a cathode at a voltage ranging from about 0 mV to about 300 mV, about 0 mV to about 240 mV, and/or may be operable as an anode or a cathode that withstands even higher voltages. The electrode module may be operable for higher voltages, e.g. about 500

mV, which may depend on the specific needs of the applications that the electrode module operates in. The voltage applied may depend on (i) the concentration of the electrolyte or solution and (ii) the desired desalination degree. The actual effective voltage required may be slightly higher than the theoretical one due to the resistance of the solution. For example, a voltage of 120 mV may be applied for every order of magnitude concentration change and that additional over-potentials may be accounted for. A range of voltages of up to 240 mV may be applied to reduce, e.g. chloride concentration in desalination operation, by two orders of magnitude, which may represent 99% desalination efficiency, but higher voltages may be applied in consideration of non-faradaic processes or if a higher rate of desalination happens to be required. Advantageously, the planar configuration of the present electrode module, which is operable with a thin (tens to hundreds micrometers) electrolyte layer, is able to reduce this factor, i.e. the resistance and hence the energy consumption, to a minimum. Nevertheless, the present electrode module is versatile in that voltage adjustments may be independently applied for each segment to be optimally operable in terms of energy consumption at each desalination stage. The voltage range of about 0 mV to about 300 mV, and even about 0 mV to about 240 mV, may be advantageous in that a high operating voltage is not required and energy consumption is therefore reduced.

[0046] The present disclosure also provides for an electrodialysis system. The electrodialysis system may comprise one or more electrodialysis cells, wherein each of the one or more electrodialysis cells may comprise an anode electrically coupled to a cathode, wherein each of the anode and the cathode may comprise or may be the electrode module described in various embodiments of the first aspect, and a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and the cathode may be arranged for segments of the anode and segments of the cathode having identical planar surface area face each other.

[0047] Embodiments and advantages described for various embodiments of the electrode module of the first aspect can be analogously valid for the present electrodialysis system subsequently described herein, and vice versa. As the various

embodiments and advantages have already been described above and examples demonstrated herein, they shall not be iterated for brevity.

[0048] As mentioned above, the electrode module may be operated as an anode or as a cathode. In other words, two electrode modules may be configured for use in an
5 electrodialysis cell, one operable as the anode and the other as the cathode. The segments of an electrode module operates either as an anode if the electrode module is operated as the anode or as a cathode if the electrode module is operated as the cathode, and two segments may cooperate as a pair accordingly when the two electrode modules are arranged accordingly. Different voltage may be applied to each pair of segments
10 when two electrode modules are paired. For example, a pair of segments from the two electrode modules may be configured in an electrodialysis cell to form a closed ionic/electronic circuit (the circuit may be partially ionic and partially electronic), wherein one segment acts as a positive terminal and the other a negative terminal such that the positive and negative terminal are connected to a power source with controlled
15 voltage and/or controlled current density, e.g. a potentiostat or a battery, and there may be multiple pairs of segments. Each of the pairs of segments may be controlled separately as each pair of segments may operate as an individual circuit that receives current of a tunable voltage, wherein the tunable voltage may be different voltages applied to different pairs of segments even when the tunable voltage is operated from a
20 single device that supplies the current. This is advantageous as both the present electrode module and electrodialysis cells of the present electrodialysis system are versatile in that voltage adjustments may be independently applied for each pair of segments to be optimally operable in terms of energy consumption at each desalination stage.

25 [0049] In various embodiments, each of the one or more electrodialysis cells may be operable to have a first voltage applied thereto in a first direction which produces the anion in the concentrate channel from the layer of insoluble salt at the cathode. This may represent the cathodic process under normal operations of the electrodialysis system. In the first direction, the first voltage applied may have a positive value. In
30 addition, for voltage applied in a direction, the voltage applied may be different for each segment. For example, the first voltage applied in the first direction may comprise different voltages applied to different segments. This saves on the energy consumed as

the voltage applied can be individually tuned for each segment such that a segment operable with a lower voltage need not be applied with a higher voltage required for operating another segment.

[0050] In various embodiments, each of the one or more electrodialysis cells may be operable to have a second voltage applied thereto in a second direction which regenerates the layer of insoluble salt at the anode. This may represent the anodic process. In the second direction, the voltage polarity is reversed from that used in a normal operation. This helps to regenerate the electrodes, including the insoluble salt layer coating each of the electrodes. Hence, the present electrodialysis system is versatile and advantageous in that it can be operated for regeneration of electrodes, and desalination of seawater can still be carried out at the same time, without compromising performance of the system. The advantage of being able to regenerate electrodes also reduces maintenance downtime and cost for replacement electrodes. Similarly, for the second voltage applied in the second direction, the voltage applied may be different for each segment. For example, the second voltage applied in the second direction may comprise different voltages applied to different segments. As already mentioned above, this saves on the energy consumed as the voltage applied can be individually tuned for each segment such that a segment operable with a lower voltage need not be applied with a higher voltage required for operating another segment.

[0051] In various embodiments, the concentrate channel and/or the diluate channel may comprise a thickness ranging from 10 μm to 1000 μm , 10 μm to 300 μm , 10 μm to 200 μm , etc. Such thicknesses render the channels structurally thin, which is advantageous, as it renders an electrodialysis cell to have not just a smaller footprint but also better desalination efficiency. The advantage of better desalination efficiency arising from the thinner channels is described in the examples section herein. In various embodiments, the one or more electrodialysis cells may include two to ten electrodialysis cells which are stacked together and have a total thickness of at most 1 mm. Advantageously, as the channels are already structurally thinned, the multiple stacked electrodialysis cells can be structurally thin as well without any compromise in desalination efficiency. Nevertheless, the number of electrodialysis cells stacked may be varied depending on application needs and the total thickness may thus vary. For example, the number of cells stacked may be more than 10. In various embodiments, a spacer may be disposed

in the concentrate channel and/or the diluate channel. The spacer helps to promote turbulence of the liquid flowing in the respective channels so that the respective ions in the liquid may be contacted with the electrodes of the array. Alternatively, the spacer and the electrode may be combined as a single entity to form a porous electrode. Said
5 differently, each of the segment in the array may be a porous planar electrode. This further reduces overall thickness of the electrodialysis system.

[0052] In various embodiments, each of the anode and the cathode may have a conductive paste or a conductive film disposed in contact therewith. This allows for the anode and the cathode to be electrically connected, including connection to a voltage
10 source and/or a voltmeter, for electrodialysis operation. Nevertheless, the conductive contact may not be limited to the conductive paste or the conductive film, as long as each of the anodes and each of the cathodes are electrically connected for the present electrodialysis system to be operable.

[0053] In various embodiments, the present electrodialysis system may be operable for
15 desalination of seawater, or as a pre-treatment prior to desalination of seawater, or as a battery.

[0054] The present disclosure further provides for a method of controlling desalination efficiency in electrodialysis. The method may comprise applying a voltage to one or more electrodialysis cells, wherein each of the one or more electrodialysis cells may
20 comprise an anode electrically coupled to a cathode, wherein each of the anode and the cathode may comprise the electrode module described in various embodiments of the first aspect, and a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and the cathode may be arranged for segments of the anode and segments of the cathode
25 having identical planar surface area face each other, and operating a pair of segments of the array of electrodes at a different potential difference from another pair of segments, wherein one pair of segments may comprise a segment from the anode and another segment of identical planar surface area from the cathode.

[0055] Embodiments and advantages described for various embodiments of the
30 electrode module of the first aspect and the present electrodialysis system can be analogously valid for the method of controlling desalination efficiency in electrodialysis subsequently described herein, and vice versa. As the various

embodiments and advantages have already been described above and examples demonstrated herein, they shall not be iterated for brevity.

[0056] In various embodiments, applying the voltage may comprise applying a first voltage in a first direction which produces the anion in the concentrate channel from the layer of insoluble salt at the cathode. This may represent the cathodic process under normal operations of the electrodialysis system. In the first direction, the first voltage applied may have a positive value.

[0057] In various embodiments, applying the voltage may comprise applying a second voltage in a second direction which regenerates the layer of insoluble salt at the anode. This may represent the anodic process. In the second direction, the voltage polarity is reversed from that used in a normal operation. This helps to regenerate the electrodes, including the insoluble salt layer coating each of the electrodes. Hence, the present electrodialysis system is versatile and advantageous in that it can be operated for various modes, e.g. for desalination of seawater and for regeneration of electrodes, without compromising performance of the system. The advantage of being able to regenerate electrodes also reduces maintenance downtime and cost for replacement electrodes.

[0058] In various embodiments, operating a pair of segments of the array of electrodes at a different potential difference from another pair of segments may comprise, as a non-limiting example, operating a first pair of segments at a first potential difference ranging from 60 mV to 90 mV, 60 mV to 80 mV, 60 mV to 70 mV, e.g. 60 mV, operating a second pair of segments at a second potential difference ranging from 120 mV to 160 mV, 120 mV to 150 mV, 120 mV to 140 mV, 120 mV to 130 mV, e.g. 120 mV, operating a third pair of segments at a third potential difference ranging from 180 mV to 230 mV, 180 mV to 220 mV, 180 mV to 210 mV, 180 mV to 200 mV, 180 mV to 190 mV, e.g. 180 mV, and operating a fourth pair of segments at a fourth potential difference ranging from 240 mV to 300 mV, 240 mV to 290 mV, 240 mV to 280 mV, 240 mV to 270 mV, 240 mV to 260 mV, 240 mV to 250 mV, e.g. 240 mV. The first pair of segments operated at the first potential difference may, for example, reduce chloride concentration by 66% for desalination. The second pair of segments operated at the second potential difference may, for example, reduce chloride concentration by 22% for desalination. The third pair of segments operated at the third potential

difference may, for example, reduce chloride concentration by 8% for desalination. The fourth pair of segments operated at the fourth potential difference may, for example, reduce chloride concentration by 3% for desalination. The voltages used for respective segments may be altered based on the number of segments configured in the present electrode module. As already described above, such an operation is advantageous, i.e. if a single conventional electrode is used, energy consumption is not saved as 240 mV has to be applied to the entire electrode, but for the present electrode module, each electrode segment allows for a lesser amount of voltage to be applied to achieve an even higher operation efficiency, reducing energy used.

10 [0059] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0060] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0061] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance. The variance may be $\pm 20\%$, $\pm 10\%$, $\pm 5\%$, $\pm 1\%$, $\pm 0.5\%$, etc.

20 [0062] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0063] Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

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Examples

[0064] The present disclosure relates to an electrodialysis system and method that allow a precise control of the desired level of desalination efficiency as a direct function of the applied voltage. The present system may comprise one or more cells, wherein each cell has an anode and a cathode. Both the anode and cathode may be an array of electrodes. The array of electrodes may be called herein an electrode module, that is, each of the anode and cathode may be an electrode module. Said differently, using the

anode as an example, the anode may be formed of one or more electrodes, wherein each electrode may represent a segment of the array.

[0065] The present electrodialysis system may comprise channels that are each of a thin layer which allows for continuous flow of the solution or water to be treated (i.e. electrolyte). As opposed to a bulk solution electrolysis system wherein a reactor is sized for a significant volume of electrolyte to be treated. The present electrodialysis system conserves footprint as only thin-layered channels are required for treating the electrolyte. The electrolyte may be seawater as a non-limiting example.

[0066] The present electrodialysis system may include one or more arrays of, for example, silver/silver chloride (Ag/AgCl) electrodes which provide for desalination efficiency of at least 99.5 % at an energy consumption level that may be at 10% of what is used in conventional electrodialysis technologies, or even lesser. Compared to electrodes made of noble material (e.g. platinum, glassy carbon), the present electrodes of the second kind, e.g. Ag/AgCl electrode, are operable without the need for harsh electrolytes (e.g. NaOH, H₂SO₄) and yet provide the advantage mentioned above. As such harsh electrolytes may be extremely concentrated, reactive, abrasive and/or corrosive, circumventing them is another advantage afforded by the present system, method and electrodes. Without such electrolytes, less chemicals are needed to operate the present system and diluate solution contamination is also avoided.

[0067] The present electrodialysis system and method, including the present electrodes, are described in further details, by way of non-limiting examples, as set forth below.

[0068] Example 1A: General Discussion of the Present System and Method

[0069] Electrodes of the present system and method are distinct from redox electrodes typically used in electrodialysis. Redox electrodes do not undergo oxidation or reduction, but instead facilitate the oxidation and/or reduction reactions in the electrolyte in the vicinity of the electrode and therefore need to be in contact with the electrolyte containing oxidizable/reducible substances to be operable. However, electrodes of the present disclosure undergo reversible oxidation while producing a layer of an insoluble salt of its own metal at the electrode surface. The one or more materials may be an electrically conductive material, e.g. a metal like silver or mercury.

[0070] As a non-limiting example, the present electrode may be a silver/silver chloride (Ag/AgCl) electrode, or a calomel (Hg/Hg₂Cl₂) electrode. That is, the electrode is

formed of silver and mercury, and covered with a layer of its insoluble salt (i.e. AgCl and Hg₂Cl₂, respectively).

[0071] The potential of the present electrode, including Ag/AgCl and Hg/Hg₂Cl₂ electrodes, changes linearly with the logarithm of the concentration of the anion “A” that forms the layer of insoluble salt, and may be defined by the Nernst equation (units in mV):

$$E = E^0 + \frac{59}{-z} \log a_A$$

[0072] where E represents the effective electrode potential (referred herein as voltage in the case of processes involving current, or open circuit potential (OCP) in the case of passive potentiometric techniques), E^0 represents a standard electrode potential, while z and a_A represent the charge and activity of the potential-generating anion, respectively. Passive potentiometric techniques measure the potential of a solution between two electrodes without exerting an effect on the solution.

[0073] If a pair of such electrodes is separated by a cation-selective (also termed herein “cation exchange”) membrane, the potential difference between the electrodes may be defined by the following equation (e.g. for two cation-selective membranes):

$$E = E^0 + \frac{59}{-z_A} \log a_{A1} - \frac{59}{z_C} \log a_{C1} + \frac{59}{z_C} \log a_{C2} - \frac{59}{-z_A} \log a_{A2}$$

[0074] which for single charged (i.e. monovalent) ions may be simplified to (modified Nernst equation):

$$E = E^0 + 59(-\log a_{A1} - \log a_{C1} + \log a_{C2} + \log a_{A2}) = E^0 + 59 \log \frac{a_{C2} \cdot a_{A2}}{a_{A1} \cdot a_{C1}}$$

[0075] where z_A and z_C represent, respectively, numerical charge of the anion and cation for potential generation, while a_{A1} , a_{C1} , a_{C2} and a_{A2} represent activities of those ions on both sides of the membrane, respectively. For example, for silver cations, z_A then equals to 1, wherein the polarity of the charge has been taken into account in the above equation.

[0076] The relationship between the potential generated and ionic activity may be used to induce migration of ions through the membrane with an imposed voltage. The bigger the deviation from the measured OCP, the bigger the ionic flux. A schematic example of the process is depicted in FIG. 1A and 1B. If the thickness of the sample layer (or sample solution) is reduced to less than the thickness of the diffusion layer, the process

can be completed in a matter of seconds at close to theoretical efficiencies (e.g. 99.5%) due to significant suppression of concentration overpotentials. The sample layer (or sample solution) refers to the electrolyte. The diffusion layer refers to a layer of electrolyte that happens to be proximal to or in vicinity of the electrode. Hence, it would be advantageous to limit the thickness of channels of the electrodialysis system (both concentrate and diluate) to the thickness of diffusion layer (e.g. tens to hundreds of micrometers) to achieve a high efficiency. That is to say, the present electrode array, present system and method not only benefit from having a smaller footprint through use of thinner channels, but also better desalination efficiency with the thinner channels. Advantageously, this allows for multiple stacked electrodialysis cells to be thinner, and yet have even better efficiency, as the channels are already structurally thinned.

[0077] Example 1B: Electrode Array of Present System and Method

[0078] The present system and method are operable for large scale desalination – the present system and method can produce potable water at high production rate and low energy demand. The present system may have a planar design, wherein the electrodes, e.g. Ag/AgCl electrodes, are arranged as an array of electrodes (FIG. 2A). The present array of electrodes may be termed herein as an “electrode array”. Such an array may be referred herein as an “electrode module”. Each of the electrodes in the array may be referred to as a “segment” of the electrode array.

[0079] The discussion in this paragraph specifically illustrates for a non-limiting arrangement of the electrodes in the array without taking into consideration the membranes. A further discussion of the array of electrodes, incorporating the membrane, follows thereafter. As mentioned earlier, the concentration gradient created across the cation exchange membrane (CEM) is a logarithmic function of applied potential. Assuming the desired desalination efficiency to be of 99% (2 orders of magnitude concentration difference), the theoretical applied potential difference may be 240 mV (considering only the electrodes and membrane potentials). To remove 66% of the salt (half order of magnitude concentration difference), however, only one quarter of the theoretically calculated voltage needs to be applied (60 mV). Removal of 22% and 8% of the salt required half and three quarters of the theoretical voltage, respectively. Only 3% to 4% of the sample treated this way required the full potential of 240 mV to be applied. Such advantages are achieved by using the present array of

electrodes, which comprises segments instead of a single electrode (FIG. 2A). The present array of electrodes only uses 36.5% of the energy required for a single uniform electrode system (FIG. 2B). For concentrated electrolytes like seawater, the process may be limited by mass transport through the membrane, and in this connection, the geometrical arrangement of the electrode array is configurable to address this limitation as well. The surface area of each segment of the electrode array should be “proportional” to the amount of charge passing through them (FIG. 2A), wherein the the lowest potential can be applied to the electrode having the largest planar surface area for removal of majority of the ions from the solution, while the highest potential can be applied to remove residual ions and therefore sized much smaller to accommodate the significantly smaller quantities of ions. In addition, the present array allows for a pair of thin “line” of electrodes, e.g. platinum (Pt) electrodes, to be employed between segments of the present electrode array. That is to say, such a pair of Pt “thin line electrodes” may be arranged therein to operate as conductometric system to monitor the progress and efficiency of chloride ion removal from the system during operation. Such electrodes are herein referred as “thin line”, as they are configured to be sufficiently thin to arranged in the gaps between segments. Preferably, a pair of conductimetric electrodes may be used as the “thin line electrode” to monitor concentration of passing solutions, e.g. concentrate and diluate.

[0080] The transfer of cations, e.g. sodium ions (Na^+), across the CEM may be facilitated by (i) oxidation of a metal, e.g. metallic silver to silver cation (Ag^+) which leads to formation of a silver chloride layer (at anode), and (ii) reduction of Ag^+ in silver chloride to metallic silver and release of chloride anion to the solution (at cathode). Therefore, the capacity of the present system to transfer the sodium ion may be limited to the amount of metallic silver in the anode and silver chloride in the cathode. Near the capacity limits, the electrodes need to be regenerated, that is, reversing polarity of the applied potential.

[0081] The present system may be compared to a tubular system. The tubular system is not symmetrical in that a thin layer of electrolyte is disposed at one side of the membrane and bulk electrolyte is disposed at the other side. Regeneration of the Ag/AgCl electrode was still possible but did not allow for simultaneous desalination of the electrolyte at the other side of the membrane. The present system, however, has a

planar and symmetrical arrangement, wherein regeneration of the electrodes (both cathode and anode) can be achieved by switching the diluate (treated water) and the concentrate (brine) channels (also termed herein “compartments”) together with the voltage polarity, as depicted in FIG. 3A and 3B. This switching and reversal of voltage polarity allows the original cathode to act as a “temporary” anode and generate the AgCl that was lost, and when normal operation reverts, the “temporary” anode operates as the original cathode. Due to versatility of the present system, the arrangement requires no extra energy and/or time as the electrodes’ regeneration in the present system is conveniently operable. The reversal of voltage polarity may also mitigate membrane fouling at the same time during electrode regeneration.

[0082] The planar configuration of the present system allows for stacking, which makes it directly scalable. FIG. 4 shows a non-limiting example of the arrangement of the electrodes in the present array of the system disclosed herein. FIG. 5 shows a dissection of the arrangement in FIG. 4, in which segmentation of the electrodes (Ag/AgCl) is also shown. Since each of the electrodes (i.e. segments) are of a thin planar layer, a stacking of multiple cells, e.g. 2 to 10 cells (depending on the cell design), may have an advantageous thickness of up to, for example, only 1 mm. That is to say, the entire electrodialysis system, even when comprised of multiple cells stacked together, only has a thickness of 1 mm (see FIG. 4). Each cell may comprise a Ag/AgCl anode, a Ag/AgCl cathode, a CEM arranged between the anode and cathode to define two channels (or two compartments), one channel (or one compartment) for flow (or housing) of a stripping solution (or electrolyte if measuring open circuit potential) and the other for the sample to be treated.

[0083] Example 2: Faradaic Capacity of AgCl

[0084] The faradaic capacity of AgCl is discussed in this example. An Ag/AgCl wire electrode was used to demonstrate for its faradaic capacity, and the alternating current cycling results are shown in FIG. 12. After 10 hrs of galvanostatic chloride deposition at 0.2 mA/cm^2 , the electrode was subjected to 10 mins of alternating negative (-0.2 mA) and positive ($+0.2 \text{ mA}$) currents cycling. In each step, the same amount of charge is passed ($\pm 0.12 \text{ C}$). The observed reduction in the generated voltage is attributed to the improved ionic conductivity within the AgCl layer which is attributed to the increase in surface porosity and granular order.

[0085] Results of galvanostatic voltammetry performed in the +/- 1 mA current density range (per 1 cm² of electrode surface) is shown in FIG. 13. From the change of the slope of the V/I relation, it is observed that the ionic resistance of the electrode has decreased 2.5 times after 10 hrs of slow galvanostatic chloride deposition/silver oxidation. In this regard, the oxidation and reduction mechanisms of silver at low voltages/current densities are discussed in the following example (also see FIG. 14). The results demonstrated applicability of silver, and silver-based, electrodes for use in continuous electrolysis. At lower current densities, not only does the silver remain conductive but its conductivity gets improved due to increasing surface porosity. This addresses the concern that passivation of silver surface renders silver unsuitable for electrolysis.

[0086] Example 3: Oxidation/Reduction of Silver at Low Voltages

[0087] The trend in electrodialysis desalination/desalination batteries appears to be drawn toward capacitive processes using new engineered materials. Silver has been historically used for high power batteries in military application due to high initial oxidation rate of silver. However, due to passivation, those batteries were efficient specifically for very short periods only (i.e. pulses). Hence, silver was abandoned for its application in commercial batteries.

[0088] However, slow oxidation at low voltages/current densities do not lead to silver passivation, and this has been investigated and demonstrated herewith. Further, it was observed that subsequent reduction and re-oxidation improves electrochemical properties of silver. Unlike other electrodialysis systems suitable for treating only brackish water, the present electrodialysis system, which may utilize Ag/AgCl electrodes, is not only great for seawater desalination, but also has great potential use in batteries and reverse electrodialysis. Moreover, as AgCl is photosensitive, light can be used to reduce it to silver, pushing the equilibrium of the present desalination system against the concentration gradient, which provides for potential application in solar energy harvesting and storage using the present desalination system (charging of the battery).

[0089] As mentioned above, the oxidation and reduction of silver at low voltages/current densities have been investigated. FIG. 14 illustrates the oxidation and reduction mechanism. During oxidation, dissolution of silver occurs. However, in the presence of chloride ions, AgCl gets precipitated. As diffusion of silver through AgCl

layer is lower than diffusion through created pores, porosity of the electrode surface may increase. Reduction of AgCl may lead to granulation of the electrode surface, and rapid oxidation may lead to depletion of chloride ions in the proximity of the electrode that may render overpotentials and loss of silver. The results therefore demonstrate for the applicability of silver in electrolytical applications.

[0090] Example 4A: Prototype Testing Protocol

[0091] A prototype of the present electrodialysis system using the present electrode module was developed. Photo images of the prototype and the electrode module are shown in FIG. 6A. The configuration of the electrode module in the prototype is shown in FIG. 6B.

[0092] Based on FIG. 6B, the conductivity was measured between adjacent conductometric electrodes, C1 and C3, C2 and C4, C5 and C7, etc., and between opposite electrode segments, e.g. E1 and E2, E3 and E4, etc. The electrodes forming the segments may be termed herein as amperometric electrodes. To make washing of the electrodes easier, electrolytes with lower concentration of salts may be started with. For example, in the calibration for conductivity measurement, NaCl solutions containing 6 mM, 20 mM, 60 mM, 200 mM and 600 mM of NaCl may be first prepared. Each of these solutions may then be passed through the cell and conductivity readings may be taken from each pair of electrodes (conductometric and/or even amperometric readings). The steps for calibration may be repeated 3 times as an example. The very last pair of conductometric electrodes can be used for monitoring whether the concentration has stabilized before taking any conductivity readings to ensure no error in measurements.

[0093] For operation of the prototype, electrolysis can be carried out between the amperometric electrode pairs: E1 and E2, E3 and E4, etc. At the same time, the conductivity measured from each pair of conductometric electrodes located right after the respective amperometric electrodes (e.g. a working anode in the dilute compartment) can be obtained. For example, if voltage is applied between E1 and E2 to oxidize E1 (anode), conductivity may be measured between C1 and C3. An example of the steps taken for testing out desalination on the prototype are described as follow.

[0094] An electrolyte containing 0.6 M NaCl may be passed into the prototype. Subsequently, voltages of 40 mV, 60 mV, 80 mV and 100 mV may be applied to the

amperometric electrodes. The readings may be recorded to generate a current versus time plot using a computer, and the conductivity of the treated solution from the conductometric electrodes may also be plotted using a computer. These steps may be repeated for a 0.2 M NaCl solution, applying 100 mV, 120 mV, 140 mV and 160 mV at the respective amperometric electrodes. These steps may also be applied for a 0.06 M NaCl solution with application of 160 mV, 180 mV, 200 mV and 220 mV to the respective amperometric electrodes. Similarly, these steps may be applied for a 0.02 M NaCl solution with application of 220 mV, 240 mV, 260 mV and 280 mV to the respective amperometric electrodes. Each of these steps may be repeated for at least 3 times to ensure the data is reproducible. Once these steps are completed, it can be determined that the prototype is operable. For compiling the readings and plotting the results, the computers may be installed with an Arduino software that renders such a function.

[0095] Example 4B: Application as Battery

[0096] In capacitive desalination batteries, the charging process relies on the formation of a monolayer of the same-charged ions at the electrode/solution interface, and therefore it may be limited by the specific surface area of the electrode, which in turn is reflected in the significant size and price of such batteries. However, in the case of electrodes of the second kind, which refers to an electrode composed of a metal covered with a layer of an insoluble salt of the metal, the energy can be stored in the concentration gradient between the diluate and concentrate solutions instead of the electrode itself, thereby substantially reducing the amount of silver used and hence, the cost of the desalination battery. FIG. 15A and FIG. 15B show the electrolytic desalination (battery charging) and galvanic regeneration (battery discharging) of a desalination battery operating based on the present electrode.

[0097] Example 4C: Commercial and Potential Applications

[0098] In summary, the present electrode module operable for electrodialysis includes a planar silver/silver chloride electrode that may function as an anode or a cathode, wherein the planar electrode may exist as electrode array comprising segments with varying surface areas, wherein the surface area of each segment of the electrode array may be proportional to the amount of charge passing through them, and wherein the

electrode array may comprise a pair of conductometric electrodes located between the desalination Ag/AgCl segments.

[0099] The electrode module may be operable in an electrodialysis cell comprising a feed (diluate) compartment, the feed (diluate) compartment positioned between an anode and a cation exchange membrane, a concentrate (brine) compartment, the concentrate (brine) compartment positioned between the cation exchange membrane and a cathode, wherein the anode and cathode comprise a pair of symmetrical and planar silver/silver chloride working electrodes, wherein the anode and cathode are connected by an external electrical circuit, wherein a potential may be applied in a first direction across the electrodialysis cell to generate an electric field in a first direction and a reversed potential may be applied across the electrodialysis cell to generate an electric field in a reversed direction. Multiple electrodialysis cells with alternating configuration may be arranged into an electrodialysis stack (i.e. system). Each pair of electrodialysis cells may further comprise a non-conductive substrate. The electrodialysis cells may be operably used in desalination of seawater.

[00100] The method disclosed herein provides for controlling desalination efficiency in electrodialysis, wherein the method involves a pair of silver/silver chloride planar electrodes as cathode and anode, applying a voltage across the pair of silver/silver chloride electrodes, and having the electrodes operated with the voltage based on the modified Nernst equation already discussed above.

[00101] The electrode module, electrodialysis system and method of the present disclosure are suitable for off-the-grid water desalination for agricultural application, where certain levels of dissolved organics can be disregarded. In potable water production, the present system is ideal as a pre-treatment for reverse osmosis, as it substantially reduces overall treatment energy consumption. Moreover, the present system is ideal for electrodialytic energy generation (reversed electrodialysis (RED)). Due to the low voltage current requirements, the present system can be powered directly by integrated photovoltaic panels when applied off-grid. Efficiency of the present system, and its freshwater production rate, can conveniently accommodate or cater to the availability of sunlight – which is practical for agricultural applications.

[00102] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various

changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. An electrode module operable for electrodialysis, the electrode module comprising:
 - a substrate; and
 - an array of electrodes arranged on the substrate, wherein each of the electrodes is shaped as a planar sheet and each planar sheet is a segment of the array of electrodes, wherein each segment is arranged apart from another segment, and wherein each segment has a different planar surface area from another segment.
2. The electrode module of claim 1, wherein each of the electrodes comprises a metal, a metal chloride, a metal cyanide, a metal thiocyanide, a metal sulfide, a metal hydroxide, and/or a metal oxide.
3. The electrode module of claim 1 or 2, wherein each of the electrode comprises silver, mercury, and/or a chloride thereof.
4. The electrode module of any one of claims 1 to 3, wherein each of the electrodes comprises a layer of an insoluble salt, wherein:
 - the insoluble salt produces an anion upon receiving negative electrical charges when the electrode module operates as a cathode; or
 - each of the electrodes accepts anions to form the layer of insoluble salt upon releasing negative electrical charges when the electrode module operates as an anode;
 - wherein the insoluble salt comprises silver chloride or mercury (I) chloride.
5. The electrode module of claim 4, wherein each segment is operable to have a different voltage applied to facilitate deposition of the anions at each electrode operating as the anode.
6. The electrode module of claim 4 or 5, wherein the anions deposited at the electrodes define an anion quantity ratio which is proportional to a ratio of the different planar surface area of the segments.

7. The electrode module of any one of claims 1 to 6, wherein the substrate comprises an electrically non-conductive and water insoluble material, wherein the electrical non-conductive and water insoluble material comprise a polymer, a glass, a ceramic, or a combination thereof.
8. The electrode module of any one of claims 1 to 7, further comprising a pair of conductometric electrodes, wherein the pair of conductometric electrodes is disposed in a space between two segments.
9. The electrode module of claim 8, wherein the pair of conductometric electrodes each comprises a conductive material, wherein the conductive material comprises platinum, gold, stainless steel, conductive carbon material, or Ag/AgCl.
10. The electrode module of any one of claims 1 to 9, wherein the electrode module is operable as an anode or a cathode at a voltage ranging from 0 mV to 300 mV.
11. An electrodialysis system comprising:
one or more electrodialysis cells, wherein each of the one or more electrodialysis cells comprise:
an anode electrically coupled to a cathode, wherein each of the anode and the cathode comprises the electrode module of any one of claims 1 to 8; and
a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and the cathode are arranged for segments of the anode and segments of the cathode having identical planar surface area face each other.
12. The electrodialysis system of claim 11, wherein each of the one or more electrodialysis cells is operable to have a first voltage applied thereto in a first direction which produces the anion in the concentrate channel from the layer of insoluble salt at the cathode.

13. The electrodialysis system of claim 11 or 12, wherein each of the one or more electrodialysis cells is operable to have a second voltage applied thereto in a second direction which regenerates the layer of insoluble salt at the anode.
14. The electrodialysis system of any one of claims 11 to 13, wherein the concentrate channel and/or the diluate channel comprise a thickness ranging from 10 μm to 1000 μm .
15. The electrodialysis system of any one of claims 11 to 14, wherein a spacer is disposed in the concentrate channel and/or the diluate channel.
16. The electrodialysis system of any one of claims 11 to 15, wherein each of the anode and the cathode has a conductive paste or a conductive film disposed in contact therewith.
17. The electrodialysis system of any one of claims 11 to 16, wherein the electrodialysis system is operable for desalination of seawater, or as a pre-treatment prior to desalination of seawater, or as a battery.
18. A method of controlling desalination efficiency in electrodialysis comprising:
applying a voltage to one or more electrodialysis cells, wherein each of the one or more electrodialysis cells comprise:
an anode electrically coupled to a cathode, wherein each of the anode and the cathode comprises the electrode module of any one of claims 1 to 8; and
a cation-selective membrane arranged between the anode and the cathode to define a concentrate channel and a diluate channel, wherein the anode and the cathode are arranged for segments of the anode and segments of the cathode having identical planar surface area face each other; and
operating a pair of segments of the array of electrodes at a different potential difference from another pair of segments, wherein one pair of segments comprises a segment from the anode and another segment of identical planar surface area from the cathode.

19. The method of claim 18, wherein applying the voltage comprises applying a first voltage in a first direction which produces the anion in the concentrate channel from the layer of insoluble salt at the cathode.

20. The method of claim 18 or 19, wherein applying the voltage comprises applying a second voltage in a second direction which regenerates the layer of insoluble salt at the anode.

21. The method of any one of claims 18 to 20, wherein operating a pair of segments of the array of electrodes at a different potential difference from another pair of segments comprises:

operating a first pair of segments at a first potential difference ranging from 60 mV to 90 mV;

operating a second pair of segments at a second potential difference ranging from 120 mV to 160 mV;

operating a third pair of segments at a third potential difference ranging from 180 mV to 230 mV; and

operating a fourth pair of segments at a fourth potential difference ranging from 240 mV to 300 mV.