

ENHANCEMENT OF SPECIFIC ION RECOVERY AND MITIGATION OF SCALING/FOULING IN ELECTRODIALYSIS STACKS

RELATED APPLICATION

[0001] This application claims the benefit of priority to the Singapore application no. 10202302277U filed August 11, 2023, the contents of which are hereby incorporated herein by reference in their entirety for all purposes.

TECHNICAL FIELD

[0002] The present disclosure relates generically to the technical field of electrodialysis, and more particularly to methods and stacks for enhancing specific ion enrichment and the mitigation of scaling/fouling in electrodialysis apparatus.

BACKGROUND

[0003] Electrodialysis (ED) is an electrically driven membrane separation process that selectively separate charged species from uncharged species and solvent. ED has many advantages over other membrane separation processes, including low energy and maintenance cost, low requirements for pretreatment, and high membrane life. Therefore, it can be used for various applications such as desalination, wastewater treatment, nutrient recovery, food processing. Although ED has received wide applications, its performance is influenced by some issues, including scaling/fouling and ion leakage into electrode chamber.

SUMMARY

[0004] In one aspect, an electrodialysis stack includes a cathode, an anode, and a membrane stack. The membrane stack includes a first mediation chamber and a second mediation chamber. The cathode is disposed in an electrode solution in a cathode chamber. The anode is disposed in the electrode solution in an anode chamber. The membrane stack includes a plurality of chambers defined by a corresponding plurality of membranes. The plurality of membranes are alternately disposed ones of one or more cation exchange membranes and one or more anion exchange membranes. The first mediation chamber is interposed between the

cathode chamber and a first chamber of the plurality of chambers. A first membrane of the membrane stack is disposed between a first stream in the first chamber and a mediation solution in the first mediation chamber. A cathode chamber membrane is disposed between the first mediation chamber and the cathode chamber. The second mediation chamber is interposed between the anode chamber and a last chamber of the plurality of chambers. A last membrane of the membrane stack is disposed between a last stream in the last chamber and a mediation solution in the second mediation chamber. An anode chamber membrane is disposed between the second mediation chamber and the anode chamber.

[0005] The electrodialysis stack in which a transport path of the selected ions from any one of the first stream and the last stream to the electrode solution in a respective one of the cathode chamber and the anode chamber is blocked by a respective one of the first mediation chamber and the second mediation chamber, and wherein the mediation solution is a recirculating stream distinct from any one of a concentrate stream and a dilute stream, the concentrate stream and the dilute stream being respective streams flowing through respective ones of the plurality of chambers.

[0006] The electrodialysis stack in which a selected ion transport from the membrane stack into the electrode solution is blocked from occurring across at least one of the following: (i) the cathode chamber membrane and/or the anode chamber membrane, and (ii) the first membrane and/or the last membrane.

[0007] Each of the first membrane and the last membrane may be selected to block selected ions from transporting into the first mediation chamber and the second mediation chamber, respectively.

[0008] According to some embodiments, the first membrane may be a cation exchange membrane selected to block the selected anions from transporting from the first mediation chamber into the first chamber, in which the last membrane is a cation exchange membrane selected to block the selected anions from transporting from the last chamber into the last mediation chamber.

[0009] According to some other embodiments, the first membrane may be an anion exchange membrane selected to block the selected cations from transporting from the first chamber into the first mediation chamber, in which the last membrane is an

anion exchange membrane selected to block the selected cations from transporting from the last mediation chamber into the last chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Various embodiments of the present disclosure will be described with reference to the following figures:

[0011] **FIG. 1A** to **FIG. 1C** are schematic diagrams of electrodialysis stacks including normal cation exchange membranes (M1) and normal anion exchange membranes (M2). **FIG. 1A** shows an example in which M1 is placed near each electrode. **FIG. 1B** shows an example in which M2 is placed near each electrode. **FIG. 1C** shows the example of **FIG. 1A** in which the mediation chamber and/or electrode chambers are characterized by a presence of similar monovalent cations.

[0012] **FIG. 2A** to **FIG. 2C** are schematic diagrams of electrodialysis stacks including normal cation exchange membranes (M1), normal anion exchange membranes (M2), and monovalent selective anion exchange membranes (M3). **FIG. 2A** shows an example in which M1 is placed near each electrode. **FIG. 2B** shows an example in which (b) M2 is placed near each electrode. **FIG. 2C** shows the example of **FIG. 2A** in which the mediation chamber and/or electrode chambers are characterized by a presence of similar monovalent cations.

[0013] **FIG. 3A** to **FIG. 3C** are schematic diagrams of electrodialysis stacks including normal cation exchange membranes, normal anion exchange membranes, and monovalent selective cation exchange membranes. **FIG. 3A** shows an example in which M1 is placed near each electrode. **FIG. 3B** shows an example in which M2 is placed near each electrode. **FIG. 3C** shows the example of **FIG. 3A** in which the mediation chamber and/or electrode chambers are characterized by a presence of similar monovalent cations.

[0014] **FIG. 4A** is a schematic diagram of an electrodialysis stack comprising normal cation exchange membranes, normal anion exchange membranes, monovalent selective cation exchange membranes, and monovalent selective anion exchange membrane. **FIG. 4B** is a schematic diagram of an electrodialysis stack of **FIG. 4A** in which the mediation chamber and/or electrode chambers are characterized by a presence of similar monovalent cations.

[0015] **FIG. 5** is a plot of experimental results showing the concentration of $\text{NH}_4^+\text{-N}$ in each stream during electrodialysis for nutrient recovery from a wastewater.

[0016] **FIG. 6** is a plot of experimental results showing the concentration of phosphate in each stream during electrodialysis for nutrient recovery from a wastewater.

[0017] **FIG. 7** is a plot of experimental results showing the concentration of Mg^{2+} in each stream during electrodialysis for nutrient recovery from a wastewater.

[0018] **FIG. 8** is a plot of experimental results showing the concentration of Ca^{2+} in each stream during electrodialysis for nutrient recovery from a wastewater.

[0019] **FIG. 9** is a plot of experimental results showing the total organic carbon (TOC) in each stream during electrodialysis for nutrient recovery from a wastewater.

[0020] **FIG. 10** is a schematic diagram of an electrodialysis configuration. ES: electrode solution in cathode chamber 1 and anode chamber 6; DS: dilute solution in chambers 2 and 4; CS: concentrate solution in chambers 3 and 5. CEM1, the CEM near the cathode; CEM2, the CEM near the anode; CEM3, the center CEM; AEM1, the AEM near the cathode; AEM2, the AEM near anode.

[0021] **FIG. 11** is a plot showing stack voltage during ED desalination of different treated solution in which SW refers to synthetic seawater and NaCl refers to a sodium chloride solution with the same conductivity as the synthetic seawater (51.5 mS/cm).

[0022] **FIG. 12** is a plot showing water transport during ED for NaCl and SW desalination in which SW refers to synthetic seawater and NaCl refers to a sodium chloride solution with the same conductivity as the synthetic seawater (51.5 mS/cm).

[0023] **FIGs. 13A and 13B** show (**FIG. 13A**) Desalination efficiency (DE) and (**FIG. 13B**) system electrical resistance (SER) during the ED desalination of different solutions in which SW refers to synthetic seawater and NaCl refers to a sodium chloride solution with the same conductivity as the synthetic seawater (51.5 mS/cm).

[0024] **FIGs. 14A to 14F** show the characterization of scaling on the cathode, spacer, and CEM in cathode chamber after ED desalination tests. Photographs of the (**FIG. 14A**) cathode, (**FIG. 14B**) spacer in cathode chamber, and (**FIG. 14C**)

surface of CEM1 (**FIG. 10**) facing cathode chamber. (**FIG. 14D**) SEM image of pristine CEM. (**FIG. 14E1**) SEM image, (**FIG. 14E2**) EDX mapping of Mg distribution, and (**FIG. 14E3**) EDX analysis of elemental composition on the surface of CEM1 facing cathode chamber. (**FIG. 14F**) X-ray diffraction spectra for the precipitates collected in the electrode chamber, the CEM1 facing cathode chamber, and the pristine CEM. SW, synthetic seawater. The arrows in **FIG. 14A** to **FIG. 14C** show the flow direction of cathode solution.

[0025] **FIGs. 15A** to **15B2** are photos of (**FIG. 15A**) cathode and (**FIG. 15B1**) anode before experiment. **FIG. 15B2** is a photo of anode after ED desalination of SW.

[0026] **FIG. 15C** shows EDX analysis of elemental composition on the surface of pristine CEM (CJMC-4).

[0027] **FIGs. 16A** and **16B** are photos of the surface of (**FIG. 16A**) CEM1 and (**FIG. 16B**) AEM1 facing chamber 2 (i.e., the dilute chamber near cathode) after ED desalination of SW.

[0028] **FIGs. 17A1** to **17B3** are FESEM-EDS images and elemental analyses of the surfaces of CEM1 and AEM1 facing the dilute chamber 2 after ED desalination tests. **FIG. 17A1** is an SEM image, **FIG. 17A2** is an EDX mapping of Mg distribution, and **FIG. 17A3** is an EDX analysis of elemental composition on the surface of CEM1 facing the dilute chamber after ED for SW desalination. **FIG. 17B1** is an SEM image, **FIG. 17B2** is an EDX mapping of Mg distribution, and **FIG. 17B3** is an EDX analysis of elemental composition on the surface of AEM1 facing the dilute chamber after ED for SW desalination.

[0029] **FIGs. 18A** and **18B** are (**FIG. 18A**) SEM images and (**FIG. 18B**) EDX analysis of elemental composition on the surface of the pristine AEM (CJMA-4).

[0030] **FIGs. 19A** and **19B** are (**FIG. 19A**) SEM images and (**FIG. 19B**) EDX analysis of elemental composition on the surface of CEM2 facing chamber 5 (i.e., the concentrate solution) after ED desalination of SW.

[0031] **FIGs. 20A** and **20B** are (**FIG. 20A**) SEM images and (**FIG. 20B**) EDX analysis of elemental composition on the surface of CEM2 facing anode chamber after ED desalination of SW.

[0032] **FIGs. 21A and 21B** are (**FIG. 21A**) SEM images and (**FIG. 21B**) EDX analysis of elemental composition on the surface of CEM3 (the CEM in the center) facing chamber 3 (i.e., the concentrate solution) after ED desalination of SW.

[0033] **FIGs. 22A and 22B** are (**FIG. 22A**) SEM images and (**FIG. 22B**) EDX analysis of elemental composition on the surface of CEM3 (the CEM in the center) facing chamber 4 (i.e., the dilute solution) after ED desalination of SW.

[0034] **FIGs. 23A and 23B** are (**FIG. 23A**) SEM images and (**FIG. 23B**) EDX analysis of elemental composition on the surface of AEM1 facing chamber 3 (i.e., the concentrate solution) after ED desalination of SW.

[0035] **FIGs. 24A and 24B** are (**FIG. 24A**) SEM images and (**FIG. 24B**) EDX analysis of elemental composition on the surface of AEM2 facing chamber 4 (i.e., the dilute solution) after ED desalination of SW.

[0036] **FIGs. 25A and 25B** are (**FIG. 25A**) SEM images and (**FIG. 25B**) EDX analysis of elemental composition on the surface of AEM2 facing chamber 5 (i.e., the concentrate solution) after ED desalination of SW.

[0037] **FIGs. 26A to 26D** shows concentration of (**FIG. 26A**) magnesium ion (Mg^{2+}) and (**FIG. 26B**) calcium ion (Ca^{2+}) in concentrate solution (CS), dilute solution (DS) and electrode solution (ES) as a function of desalination efficiency (DE) during ED desalination of SW, respectively. (**FIGs. 26C, 26D**) pH changes as a function of DE during ED desalination of different solutions. NaCl, the sodium chloride solution which had the same conductivity of SW (51.5 mS/cm); CE, effluent of cathode chamber; AE: effluent of anode chamber.

[0038] **FIGs. 27A to 27D** shows the change in the number of moles of (**FIG. 27A**) calcium ion (Ca^{2+}) and (**FIG. 27B**) magnesium ion (Mg^{2+}) in concentrate solution (CS), dilute solution (DS), and electrode solution (ES) as a function of desalination efficiency (DE) during ED desalination of synthetic seawater (SW), respectively. (**FIG. 27C**) The total amount of Ca^{2+} and Mg^{2+} in all solutions as a function of DE during ED. (**FIG. 27D**) Element loss as a function of DE.

[0039] **FIG. 28** shows schematic illustrations of mechanisms of scaling formation and scaling-enhanced scaling during ED desalination.

[0040] **FIG. 29A to FIG. 29C** provide a graphical summary of the scaling BED mechanism occurring in conventional ED, BED, and SED stacks, in which BED

stack (or bipolar ED stack) refers to an ED stack using a bipolar membrane for the cathode chamber, and in which SED stack (or selective ED stack) refers to the ED stack using monovalent selective cation ion exchange membrane for the cathode chamber.

[0041] **FIG. 30** schematically illustrates an embodiment of the proposed ED stack.

[0042] **FIG. 31A** to **FIG. 31C** are schematic diagrams showing the ion transport during ED desalination of high salinity solution in conventional ED, BED, and SED stacks, respectively.

[0043] **FIG. 31D** is a schematic diagram showing the ion transport during ED desalination of high salinity solution in the proposed ED stack.

[0044] **FIG. 31E** is a schematic diagram of the BED setup for ED.

[0045] **FIG. 31F** is a schematic diagram of the SED setup for ED.

[0046] **FIG. 31G** is a schematic diagram of the EDM setup for ED, according to an embodiment of the present disclosure.

[0047] **FIG. 32A** to **FIG. 32H** are images relating to the BED stack.

[0048] **FIG. 32A1** to **FIG. 32C2** are images relating to the pristine bipolar membrane.

[0049] **FIG. 33A** to **FIG. 33F** are images relating to the SED stack.

[0050] **FIG. 33A1** to **FIG. 33B2** are images relating to the pristine monovalent-selective cation exchange membrane.

[0051] **FIG. 34A** to **FIG. 34F** are images relating to the EDM stack.

[0052] **FIG. 35A** shows the desalination efficiency (DE) during ED desalination of different feed solutions.

[0053] **FIG. 35B** shows the water transport during ED desalination of different feed solutions.

[0054] **FIG. 36A** to **FIG. 36C** illustrate the relationship between the system electrical resistance and desalination efficiency for ED desalination.

[0055] **FIG. 37A** and **FIG. 37B** show the concentration of magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}) in different solutions during ED desalination of SW.

[0056] **FIG. 38A** and **FIG. 38B** are schematic diagrams illustrating the cation transport through the BPM of the BED stack and the SCEM of the SED stack, respectively.

[0057] **FIG. 38C** is a schematic diagram illustrating the ion movements in the EDM stack with the mediating solution chambers.

[0058] **FIG. 39A** and **FIG. 39B** show changes in the pH of electrode solutions as a function of desalination efficiency during ED desalination of NaCl and SW, respectively. **FIG. 40A** and **FIG. 40B** show changes in the pH as a function of as a function of desalination efficiency during desalination for different solutions.

[0059] **FIG. 41** is a schematic diagram to better illustrate various embodiments of the proposed electrodialysis stack configured to block or prevent selected ions from entering the electrode solution.

DETAILED DESCRIPTION

[0060] The following detailed description is made with reference to the accompanying drawings, showing details and embodiments of the present disclosure for the purposes of illustration and to aid understanding, and not to be limiting. Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments, even if not explicitly described in these other embodiments. 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.

[0061] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0062] The word “exemplary” is used herein to mean “serving as an example, instance, or illustration.” Any embodiment described herein as “exemplary” is not necessarily to be construed as preferred or advantageous over other embodiments.

[0063] As used herein, the singular ‘a’ and ‘an’ may be construed as including the plural “one or more” unless apparent from the context to be otherwise.

[0064] The terms “about” and “approximately” as applied to a stated numeric value encompasses the exact value and a reasonable variance as will be

understood by one of ordinary skill in the art, and the terms “generally” and “substantially” are to be understood in a comparable manner, unless otherwise specified.

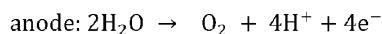
[0065] Some processes may be described in terms of steps merely to aid understanding and/or for convenient reference. The delineation between one step and another step may be described as such merely for convenient reference in the present disclosure. It will be understood that in actual implementation there may not be a clear division or transition from one step to another subsequent step. There may be a certain amount of overlap among the steps and/or more than one step may occur or be performed concurrently in time, etc.

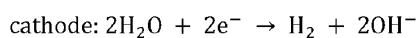
[0066] As used herein, the term “concurrent”, or “concurrently”, is used loosely to refer to two or more occurrences (or events) that at least partially overlap in time. The occurrences may or may not start at the same time instant and/or end at the same time instant.

[0067] Terms such as “first” and “second” are used in the description and claims only for the sake of brevity and clarity, and do not necessarily imply a priority or order, unless required by the context.

[0068] ED Stack

[0069] An ED stack includes five elements: (1) direct current supply, which was used to reinforce ion migration; (2) electrodes, which can provide the driving force for ion migration by fulfilling the transformation between electronic current and ionic current; (3) solvents, which serve as a continuum for ion transport; (4) electrolytes, which are served as current carrier; (5) ion exchange membranes (IEMs), the key element for separation, which allow the transport of counter ions and block the passage of co-ions. In a conventional ED stack, cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are alternately placed between the cathode and the anode, which forms different solution flow chambers alternately arranged in the stack, i.e., one cathode chamber and one anode chamber at each end of the stack, one or multiple dilute chambers, and one or multiple concentrate chambers. During the ED operation, the applied voltage may lead to the electrode reactions as follows:





[0070] The hydrogen evolution is accompanied by the generation of hydroxide ions in cathode. In addition, there will be an electric potential difference between the cathode and the anode after applying voltage. In the electric field, cations transport across CEMs toward cathode but are blocked by AEMs; anions transport across AEMs toward anode but are blocked by CEM. Finally, salt ions from dilute chambers are concentrated in concentrate chambers and the feed solutions are diluted in dilute chambers. In addition to the cation transport from dilute chamber to concentrate chamber, cations transport between treated solution and electrode solution to form a loop for current in the typical ED stack. Specifically, cations from the treated solution transport across the CEM near the cathode to the cathode solution, and cations from the anode solution transport across the CEM near the anode to treated solution. That will lead to (1) scaling on the cathode, in the cathode chamber and on the CEM near the cathode, because multivalent cations, such as Mg^{2+} and Ca^{2+} , can enter the cathode chamber and react with hydroxide ions generated during water electrolysis; (2) leakage of specific cations (e.g., nutrient ion NH_4^+) into electrode solution during the concentration of specific ions, because the transport of target cations such as NH_4^+ from electrode solution to concentrate chamber is more difficult than that of the monovalent cation in electrode solution.

[0071] Embodiments of Proposed ED Stack

[0072] Unless otherwise specified, in FIG. 1A to FIG. 4B, X represents cations; Y represents anions; Z represents non-charged species. m and n represent the valence of corresponding ions, where $m \geq 1$ and $n > 1$. A, B and C are three solutions flowing through different chambers. A1, B1 and C1 are influent of A, B and C solutions, respectively, while A2, B2 and C2 are effluent of A, B and C solutions, respectively.

[0073] FIG. 1A to FIG. 1C are schematic diagrams of an electrodialysis stack 100 including normal cation exchange membranes (M1) and normal anion exchange membranes (M2). In FIG. 1A and FIG. 1C, two M1 are placed near electrodes, and in FIG. 1B, two M2 are placed near cathode and anode. X represents cations; Y represents anions. m represents the valence of corresponding ions, where $m \geq 1$. A, B and C are three solutions flowing through

different chambers. A1, B1 and C1 are influent of A, B and C solutions, respectively, while A2, B2 and C2 are effluent of A, B and C solutions, respectively. As illustrated in **FIG. 1A**, the electrodialysis stack 100 includes a cathode **EC**, and an anode **EA**, three or more normal cation exchange membranes **M1** which allow all the cations to transport through but reject the transport of anions, two or more normal anion exchange membranes **M2** which allow all the anions to transport through but reject the transport of cations. **M1** and **M2** are placed alternately between two electrodes. Normal cation exchange membrane **M1** is placed near the anode **EA** to block the transport of anions such as chloride into electrode solution, which can prevent the formation of chlorine and help to protect the electrodes. Spacers with thickness in the range from 0.2 mm to 1 cm can be placed in the stack to form different flow channels and solution chambers. The spacers used in different flow channels and solution chambers are to enhance the hydrodynamic conditions, to reduce or eliminate the influence of concentration polarization and to reduce or eliminate fouling and scaling in the chambers and on membrane surfaces. The spacers should not cause high pressure loss along the flow channel in the solution chamber. The spacers can have different geometries including net-type, ladder-type, diamond-type, and any other types that can achieve the aforementioned functions. One or multiple spacers are placed between **M1** and **EC** to form the cathode chamber **110**, and one or multiple spacers are placed between **M1** and **EA** to form the anode chamber **120**. The chamber near cathode chamber **110** and the chamber near anode chamber **120** are defined as mediation chambers **130**. Between these two mediation chambers **130**, **M1** and **M2** are placed alternately to form one or more concentrate chambers **140** and one or more dilute chambers **150**. In a special case, no spacer is used in each chambers **130/140/150**, where the chambers **130/140/150** are formed by the shims, gaskets, O-rings and frames with a certain gap that hold ion exchange membranes.

[0074] A salt solution, such as Na_2SO_4 , with a proper initial volume and a concentration from 0.01 to 4 M is used as electrode solution (**ES**) and is recirculated in anode and cathode chambers **110/120**. A salt solution (**A**) from an external tank (not shown) is fed into the mediation chamber **130** as stream **A1** to eliminate the direct transport of cations from the concentrate stream to the electrode solution **ES**.

In particular, as illustrated more clearly in **FIG. 1C**, multivalent ions from an adjacent concentrate chamber **140** or an adjacent dilute chamber **150** are blocked from entering / not transported into the mediation chamber **130**. This in turn prevents direct transport of multivalent ions into the electrode solution **ES**. It is preferred that the cation in stream **A** solution is the same as that in electrode solution **ES**. For example, if the Na_2SO_4 is used as electrode solution, sodium salt solution such as NaCl , NaNO_3 , Na_2SO_4 , KCl , KNO_3 and K_2SO_4 solution is preferred for stream **A**. The effluent of both mediation chambers **130** (stream **A2**) can be fed back to the tank to be mixed with the remaining solution **A** to maintain the salt concentration nearly unchanged so that the salt solution **A** can be reused. Stream **B** is fed in the concentrate chamber **140** as the concentrate solution. Sometimes stream **B** can be used for the concentration and purification of certain target ions, i.e., stream **B** acts as the stripping solution by using a different solution other than stream **C**. The original influent of stream **B** can be any salt solution. For example, it can be the same as the influent of dilute stream **C** or a tap water or a clean salt solution with a relatively low concentration. The anion exchange membranes **M2** and cation exchange membranes **M1** can prevent the transport of uncharged species and/or charged species with large sizes (e.g., organic compounds, pharmaceuticals, microorganisms, virus, pathogens) from feed (dilute) stream **C** into the concentrate or stripping solution stream **B**. Therefore, when a clean stripping solution **B** (different from stream **C**) is used, the effluent of concentrated stripping solution **B1** will be highly purified without uncharged pollutants and large species such as organic compounds, pharmaceuticals, and microorganisms. The flow of concentrate/stripping stream **B** and feed effluent/dilute stream **C** can be designed as either a batch mode (i.e., the effluent stream **B2** or **C2** is fed back to an external tank to mix with stream **B1** or **C1** until a desired concentration has been achieved) or a continuous mode (i.e., the effluent stream **B2** or **C2** is not recirculated). The final effluent (stream **B2**) from the concentrate chamber is a high concentration salt solution, which can be further treated for salt production or collected for reuse or discharged. Stream **C** is the dilute stream, which can be also designed as a batch mode by recirculating it in multiple cycles till the desired dilution factor is achieved or a continuous mode by running it once through the stack. The majority of anions

and cations in stream **C** will be removed via transport through IEMs into stream **B**. Then the final effluent stream **C2** from dilute chamber can be collected or further treated for reuse or discharged after electrodialysis operation.

[0075] **FIG. 1B** is a schematic diagram of an electrodialysis stack 100 according to various embodiments. The electrodialysis stack 100 comprises normal cation exchange membranes (**M1**) and normal anion exchange membranes (**M2**). Compared with the stack in **FIG. 1A**, two anion exchange membranes **M2** are placed near the two electrodes, and one or more cation exchange membrane **M1** and anion exchange membrane **M2** are alternately placed between these two anion exchange membranes **M2** to form two mediation chambers 130, one or more concentrate chambers 140, and one or more dilute chambers 150. Similarly, stream **A** is the mediating solution, and it is preferred that (1) the anion in stream **A** solution is the same as that in electrode solution, (2) monovalent anion is used in stream **A** and electrode solution, and (3) the monovalent anion has a high diffusivity but will not be oxidized under the electrical field in ED. For example, electrode solution and Stream **A** can use Na_2SO_4 , NaNO_3 , K_2SO_4 , KNO_3 , etc., and KNO_3 or NaNO_3 solution is preferred. Stream **B** is the concentrate solution, and stream **C** is the dilute solution. The flow pattern of the stream **A**, **B** and **C** can be either batch mode or continuous mode.

[0076] During the ED operation, (1) cations can transport across normal cation exchange membrane **M1** towards cathode **EC**, but their transports are rejected by anion exchange membranes **M2**; (2) anions can transport across anion exchange membranes **M2** towards EA, but their transports are rejected by normal cation exchange membrane **M1**. Finally, (1) most of cations and anions are removed from the dilute solution (stream **C2**); (2) cations transport from stream **C** across normal cation exchange membranes **M1** and are concentrated in the concentrate solution (stream **B2**); (3) the transport of cations from solution **B** to the mediating solution (stream **A**) is rejected by the normal anion exchange membranes **M2**, i.e., divalent cations cannot enter the mediation chamber **130**, which further eliminated the transport of divalent cations into the electrode stream, and thus the potential electrode scaling is prevented; (4) a small amount of anions transport from stream **C** to mediation chamber **130** (stream **A**) in **FIG. 1A**; (5) in **FIG. 1B**, cations can enter

mediation chamber **130**, but the transport of cations from mediating solution to electrode chamber is blocked by anion exchange membrane **M2**, which can prevent the electrode scaling.

[0077] **FIG. 2A** to **FIG. 2C** are schematic diagrams of an electrodialysis stack **100** including normal cation exchange membranes (**M1**), normal anion exchange membranes (**M2**), and monovalent selective anion exchange membranes (**M3**). In **FIG. 2A** and **FIG. 2C**, two **M1** are placed near electrodes **EC** and **EA**. In **FIG. 2B**, two **M2** are placed near cathode **EC** and anode **EA**. X represents cations; Y represents anions. m and n represent the valence of corresponding ions, where $m \geq 1$ and $n > 1$. **A**, **B** and **C** are three solutions flowing through different chambers. **A1**, **B1** and **C1** are influent of **A**, **B** and **C** solutions, respectively, while **A2**, **B2** and **C2** are effluent of **A**, **B** and **C** solutions, respectively. **FIG. 2C** is similar to **FIG. 2A** but more clearly illustrates the multivalent ions being prevented from entering into the mediation chambers **130** from an adjacent concentrate chamber **140** or from an adjacent dilute chamber **150**. Compared with the stack in **FIG. 1A**, all or some of the normal anion exchange membranes are replaced by monovalent selective anion exchange membranes **M3**. One cation exchange membrane **M1** is placed near cathode (**EC**) to form cathode chamber **110**, and one cation exchange membrane **M1** is placed near anode (**EA**) to form anode chamber **120**. One mediation chamber **130** is adjacent to the cathode chamber **110**, and one mediation chamber **130** is adjacent to the anode chamber **120**. One or more concentrate chambers **140** and dilute chambers **150** are formed alternately between these two mediation chamber **130**. Stream **A** is the mediating solution, stream **B** is the concentrate solution, and stream **C** is the dilute solution. The flow pattern of the stream **A**, **B** and **C** can be either batch mode or continuous mode. The monovalent selective anion exchange membrane **M3** allows the transport of monovalent anions or small anions but reject the transport of multi-valent anions (e.g., SO_4^{2-} , PO_4^{3-} , HPO_4^{2-}) or large anions (e.g., charged organic anion, large inorganic ions H_2PO_4^-) and all the cations, which can (1) enhance the concentration of monovalent anions or small anions in the stream **B2**, (2) reduce fouling/scaling in concentration chamber and on ion exchange membranes due to reduced transport of multi-valent anions and their accumulation in concentrate chamber, and/or (3) remove small inorganic salts from stream **C2** to

improve its purity and quality. The use of mediation chambers can prevent the transport of cations from the feed to electrode solution, which can prevent electrode scaling as discussed above.

[0078] **FIG. 2B** is a schematic diagram of an electrodialysis stack 100 comprising normal cation exchange membranes (**M1**), normal anion exchange membranes (**M2**), and monovalent selective anion exchange membranes (**M3**). Compared with the stack in **FIG. 1B**, all or some of **M2** are replaced by monovalent selective anion exchange membranes **M3**. Since **M3** allows the transport of monovalent anions or small anions but reject the transport of multi-valent anions (e.g., SO_4^{2-} , PO_4^{3-} , HPO_4^{2-}) or large anions (e.g., charged organic anion, large inorganic ions such as H_2PO_4^-) and all the cations as discussed above, the advantages of the stack in **FIG. 2B** are the same as that for the stack in **FIG. 2A**, which can (1) enhance the concentration of the transport of monovalent anions or small anions, (2) reduce fouling/scaling in the electrode chamber and on the surfaces of membranes facing concentrate chambers due to reduced transport of multi-valent cations, and/or (3) remove monovalent anions from stream C2. The use of mediation chambers can prevent the transport of cations from the feed to electrode solution, which can prevent electrode scaling as discussed above.

[0079] **FIG. 3A** to **FIG. 3C** are schematic diagrams of an electrodialysis stack including normal cation exchange membranes (**M1**), normal anion exchange membranes (**M2**), and monovalent-selective cation exchange membranes (**M4**). In **FIG. 3A** and **FIG. 3C**, two cation exchange membranes **M1** are placed near electrodes. In **FIG. 3B**, two anion exchange membranes **M2** are placed near cathode **EC** and anode **EA**, respectively. X represents cations; Y represents anions; Z represents non-charged species. m and n represent the valence of corresponding ions, where $m \geq 1$ and $n > 1$. **A**, **B** and **C** are three solutions flowing through different chambers. **A1**, **B1** and **C1** are influent of **A**, **B** and **C** solutions, respectively, while **A2**, **B2** and **C2** are effluent of **A**, **B** and **C** solutions, respectively. As illustrated in **FIG. 3A**, the electrodialysis stack is similar to that depicted in **FIG. 1A** with only the exception that two or more monovalent selective cation exchange membranes **M4** are used in the stack. Normal anion exchange membranes **M2** and monovalent selective cation exchange membranes **M4** are placed alternately between two

normal cation exchange membranes **M1**. The monovalent selective cation exchange membranes **M4** allow the transport of monovalent cations but retard the transport of multi-valent cations and all the anions. This can lead to the increase in the concentration factor of target monovalent cations (e.g., NH_4^+) in the concentration chamber and also prevent the transport and accumulation of multi-valent cations (e.g., Ca^{2+} , Mg^{2+} , and heavy metal ions) and uncharged species and/or charged species with large sizes (e.g., organic compounds, pharmaceuticals, microorganisms, virus, pathogens) from feed stream into the concentrate/stripping solution stream **B**. When a clean influent stripping solution **B1** is used, the effluent stripping stream **B2** is enriched with highly purified target ionic species. The flow of solutions through each chamber of the ED stack follows the same method as that described for **FIG. 1A** to **FIG. 2C**, i.e., either batch mode or continuous mode. The stack is similar to the stack in **FIG. 1A** only except that monovalent selective cation exchange membranes **M4** are used. During the ED operation, (1) monovalent cations can transport across normal cation exchange membrane **M1** and monovalent selective cation exchange membranes **M4** towards cathode, but their transports are rejected by anion exchange membranes **M2**; (2) the transports of divalent cations are rejected by normal anion exchange membranes **M2**, and also blocked by monovalent selective cation exchange membranes **M4**; (3) anions can transport across anion exchange membranes **M2**, but their transports are rejected by both normal cation exchange membrane **M1** and monovalent selective cation exchange membranes **M4**; (4) uncharged species cannot transport across any ion exchange membranes. Finally, (1) most of divalent cations and nearly all the uncharged species are retained in the dilute solution (stream **C**); (2) monovalent cations transport from stream **C** across monovalent selective cation exchange membranes **M4** and are concentrated in the concentrate solution (stream **B**); (3) a large amount of anions transport from stream **C** across anion exchange membranes **M2** and are concentrated in the concentrate solution (stream **B**), and a small amount of anions transport from stream **C** to mediation solution chamber (stream **A**). In the example illustrated in **FIG. 3C**, multivalent ions are not present in mediation chambers **130**, the multivalent ions from the respective adjacent concentrate chamber **140** and the dilute chamber **150** having been

blocked from entering the mediation chambers. In turn, the multivalent ions are not transported into the electrode solution **ES**.

[0080] As shown in **FIG. 3B**, two anion exchange membranes **M2** are placed near cathode **EC** and anode **EA** to form respectively, cathode chamber **110** and anode chamber **120**. Two cation exchange membranes **M1** are placed near the two anion exchange membranes **M2** to form two mediation chambers **130**, respectively. Concentrate chambers **140** and dilute chambers **150** were formed by alternately placing anion exchange membranes **M2** and monovalent selective cation exchange membranes **M4**. According to the transport performance in each membrane as discussed above, the advantages of this stack include: (1) retain the divalent cations and uncharged species in the stream **C**; (2) increase the concentration of anions and mitigate the nutrient loss; (3) avoid the electrode scaling.

[0081] The normal anion exchange membranes **M2** that are near anode **EA** can be replaced by monovalent selective anion exchange membrane **M3** as shown in **FIG. 4A** and **FIG. 4B**. **FIG. 4A** is a schematic diagram of an electrodialysis stack including normal cation exchange membranes **M1**, normal anion exchange membranes **M2**, monovalent selective cation exchange membranes **M4**, and monovalent selective anion exchange membrane **M3**. **X** represents cations; **Y** represents anions; **Z** represents non-charged species. m and n represent the valence of corresponding ions, where $m \geq 1$ and $n > 1$. **A**, **B** and **C** are three solutions flowing through different chambers. **A1**, **B1** and **C1** are influent of **A**, **B** and **C** solutions, respectively, while **A2**, **B2** and **C2** are effluent of **A**, **B** and **C** solutions, respectively. **FIG. 4B** is an alternative illustration of the electrodialysis stack of **FIG. 4A** more clearly showing the larger species and multivalent ions being blocked from entering the mediation chambers **130** and hence from entering the electrode solution **ES**. As discussed before, the monovalent selective anion exchange membrane **M3** allows the transport of monovalent anions or small anions but reject the transport of multi-valent anions (e.g., SO_4^{2-} , PO_4^{3-} , HPO_4^{2-}) or large anions (e.g., charged organic anion, large inorganic ions H_2PO_4^-) and all the cations. In this case, the monovalent selective anion exchange membrane **M3** is placed between the dilute chamber **150** (stream **C**) and the mediation chamber **130** (stream **A**) near anode, which block the transport of multivalent anions and large anions. Thus, the

loss of some nutrient anions (e.g., SO_4^{2-} , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-) due to the transport from stream **C** to mediation chamber **130** (stream **A**) can be decreased. That means the stack in **FIG. 4A** and **FIG. 4B** has better performance in decreasing the loss of nutrient anions as well as all the advantages of the stack in **FIG. 3A** to **FIG. 3C**. In **FIG. 1A** to **FIG. 4B**, the pH of solutions **A**, **B** and **C** can be adjusted to enhance separation performance and reduce scaling.

[0082] Mitigating Scaling/Fouling During Desalination

[0083] For the electrodialysis stack **100** in **FIG. 1A** to **FIG. 1C**, both the influents of stream **B** and stream **C** can be saline wastewater, brackish water, seawater, brine, etc. Salt ions can transport from stream **C** to stream **B**. Additionally, divalent cations can transport from stream **C** to stream **B** but are blocked by normal anion exchange membrane **M2**. Finally, salts are removed in stream **C** and concentrated in stream **B**. The design of two mediation chambers **130** can block the transport of cations from stream **B** to cathode chamber **110**, which can prevent the electrode scaling.

[0084] Mitigating Scaling/Fouling During Monovalent Anions Recovery

[0085] The electrodialysis stack **100** in **FIG. 2A** to **FIG. 2C** can be used for the demineralization of whey. Calcium ions are the major divalent ions in whey, and lactate ions are monovalent nutrient anions. During the recovery of lactic acid from whey by ED, blocking the transport of divalent cations is necessary to prevent the electrode scaling. Since the lactate ions are monovalent, the use of monovalent selective anion exchange membrane can enhance the concentration factor of it. Stream **B** can be stripping solution such as tap water for nutrients concentration, and the stream **C** is whey to provide nutrients like nitrate. Lactate ions can transport across monovalent selective anion exchange membrane **M3** from stream **C** to stream **B**, and the monovalent selective anion exchange membrane **M3** can reject the transport of multivalent anions and all the cations. Additionally, divalent cations can transport from stream **C** to stream **B** but are blocked by normal anion exchange membrane **M2**. Finally, nutrients are removed from stream **C** to stream **B**. Then the effluent from dilute chamber (stream **C2**) can be transferred for the further treatment, and the effluent from concentrate chamber stream **B2** can be transferred for further treatment to cultivate plants. The use of the monovalent selective anion

exchange membrane **M3** can enhance the concentration of monovalent anions. The design of two mediation chambers **130** can block the transport of cations from stream **B** to cathode chamber **110**, which can prevent the electrode scaling.

[0086] Enhancing Resource (e.g., Nutrients) Recovery

[0087] Ammonium and phosphate recovery from wastewater without ammonium loss and electrode scaling can be realized by the electrodialysis stack in **FIG. 3A** to **FIG. 3C**. the stream **B** can be stripping solution such as tap water for nutrients concentration, and the stream **C** can be wastewater like dewatering centrate to provide nutrients. Then ammonium can transport from wastewater stream **C** to stream **B**. At the same time, most of phosphate can transport from wastewater to stream **B** although a small amount of phosphate would transport from wastewater to salt stream **A**. Additionally, divalent cations and organic matters can be retained in wastewater solution (stream **C2**). Finally, ammonium and phosphate can be recovered from wastewater without ammonium loss and electrode scaling. If the ED stack is designed as the configuration in **FIG. 4A** and **FIG. 4B**, the phosphate loss can be further decreased since the use of monovalent selective anion exchange membrane **M3** can reject the transport of multivalent anions.

[0088] Experiments

[0089] Experiments were conducted using lab scale prototypes of the proposed ED stack including: one cathode chamber, two mediation chambers, two concentrate chambers, two dilute chambers, and one anode chamber divided by two normal cation exchange membranes, three anion exchange membranes, and two monovalent selective cation exchange membranes. No spacer was used. Both electrodes were made of titanium with ruthenium coating with an effective area of 7 cm². Peristaltic pumps were used to pump electrode solution, salt solution, concentrate solution, and dilute solution with flow rate at 400 mL/min. All these streams were recirculating during electrodialysis operation.

[0090] 4L of dewatering centrate from a wastewater plant was used as the treated wastewater to provide ammonium and phosphate. 200 mL Tap water was used as the stripping solution and recirculated in the concentrate chamber. 400 mL 0.1 M NaCl was used as the mediating solution and recirculated in the mediation chambers. 400 mL 0.3 M Na₂SO₄ was used as the electrode solution and

recirculated in the electrode chamber. The applied current was 35 mA. The results are shown in **FIG. 5** to **FIG. 9**.

[0091] **FIG. 5** shows the concentration of $\text{NH}_4^+\text{-N}$ in each stream during electrodialysis. As shown in **FIG. 5**, the initial concentration of $\text{NH}_4^+\text{-N}$ in dewatering centrate (dilute stream) is 0.698 g/L, but the concentration of $\text{NH}_4^+\text{-N}$ in the product (the final effluent of concentrate stream) reached 6.133 g/L after 60 h. $\text{NH}_4^+\text{-N}$ was not detected in mediating stream and electrode stream, indicating there was no ammonium leakage.

[0092] **FIG. 6** shows the concentration of phosphate in each stream during electrodialysis. As shown in **FIG. 6**, the initial concentration of phosphate in the dewatering centrate (dilute stream) is 0.362 g/L, but the concentration of phosphate in the product (the final effluent of concentrate stream) reached 0.850 g/L after 60 h. The concentration of phosphate in mediating solution stream reached 0.335 g/L, indicating a small amount of phosphate can transport from dilute stream to mediating solution stream. Since there were only two electrodialysis cell pairs used in this lab scale experiment and the number of electrodialysis cell pairs can be more than one hundred in large scales, the phosphate loss can be reduced to a minimal level during electrodialysis in pilot scale.

[0093] **FIG. 7** shows the concentration of Mg^{2+} in each stream during electrodialysis. **FIG. 8** shows the concentration of Ca^{2+} in each stream during electrodialysis. As shown in **FIG. 7** and **FIG. 8**, the concentration of divalent cations in concentrate stream increased in the initial stage, which suggests the monovalent selective cation exchange membrane cannot fully reject the transport of divalent cations. No divalent cations were observed in mediating solution stream and electrode stream, indicating that the passage for most of divalent cations were blocked by the anion exchange membrane. The blocking effect prevented the formation of electrode scaling during ED.

[0094] **FIG. 9** shows the TOC in each stream during electrodialysis. As shown in **FIG. 9**, the TOC of dilute stream (dewatering centrate) was at a stable level during electrodialysis. At the same time, the TOC of concentrate stream, mediating solution stream, and electrode stream were nearly 0, suggesting that organic

matters were retained in the dilute stream (dewatering centrate) and the product solution with concentrated nutrients has high purity without organic contaminants.

[0095] Benefits

[0096] The present disclosure describes a method to prevent electrode scaling during electrodialysis by introducing two mediation chambers.

[0097] One mediation chamber is near the cathode chamber, and the other mediation chamber is near the anode chamber. The mediation chambers can help prevent the transport of divalent cations into electrode chambers and mitigate scaling in electrode chambers. For the case of using cation exchange membranes to form the electrode chambers, since an anion exchange membrane is paired with the cation exchange membrane to form this mediation chamber, the anion exchange membrane prevents the transport of divalent cations from the adjacent dilute chamber to the mediation chamber and eventually minimize the divalent cations transporting into electrode chamber, which can prevent scaling formation on cathode and in electrode chamber. For the case of using anion exchange membranes to form the electrode chambers, the anion exchange membranes prevent the cations transporting into electrode chambers and thus mitigate scaling.

[0098] The mediation chambers also prevent the monovalent cations from both dilute and concentration chambers transporting into the mediating solution and thus prevent their leakage into electrode chamber, which increases the enrichment efficiency of monovalent ions in concentrate chamber.

[0099] The selective anion exchange membranes can also be used in the stack which can block the transport of multi-valent anions or anions with large sizes, which can mitigate scaling and fouling in concentrate chamber and/or on the ion exchange membranes.

[00100] By further introducing monovalent selective cation exchange membranes, the transport of most of divalent cations from the feed solution into concentrate chambers is blocked and therefore, the monovalent ion concentration factor can be further increased.

[00101] By using a clean stripping solution flowing through the concentrate chamber, highly purified ions are enriched in the stripping solution effluent where uncharged species, such as organic compounds and pharmaceuticals, can be

removed. When selective ion exchange membranes are used in the stack, the multiple valent cations and/or anions (such as Ca^{2+} , Mg^{2+} , heavy metal ions, sulphate ions, phosphate ions, etc.) as well as charged organics with large sizes are also removed and not present in the stripping solution.

[00102] As described above, the proposed ED stack can provide separate flow paths for mediating solutions, stripping (concentrate) solutions and feed (dilute) solutions, and integrate different types of ion exchange membranes.

[00103] Electrodialysis Setup and IEMs

[00104] A further study was conducted based on the laboratory scale ED stack as shown in **FIG. 10**. The ED stack comprises six chambers (1 anode, 1 cathode, 2 concentrate, and 2 dilute chambers) between the cathode and the anode. Each chamber had a spacer to fix the chamber thickness to 1 mm. Anion exchange membranes (AEMs), denoted as CJMA-4, and cation exchange membranes (CEMs), denoted as CJMC-4, were provided by Hefei ChemJoy Polymers Co., Ltd., China. Membrane properties, including membrane thickness, ion exchange capacity, water volume fraction, limiting current density, and electric area resistance, are listed in Table 1. The effective area of each membrane was 189 cm^2 .

Table 1. Membrane Properties^a

Membrane name	Thickness (μm) ^b	IEC (meq/g) ^c	Water volume fraction ^d	Limiting current density (mA/cm^2) ^e	Electric area resistance ($\Omega \text{ cm}^2$) ^f
CEM (CJMC-4)	66±6	1.52±0.05	0.327±0.003	17.7±0.3	1.25±0.07
AEM (CJMA-4)	55±6	1.08±0.11	0.178±0.014	18.7±2	1.41±0.14

a: Data measured in this work show the mean and standard error of at least three replications.

b: Wet thickness (after in contact with 0.5 M NaCl) measured by micrometer.

c: Ion exchange capacity (IEC) was measured according to method provided by Galama, A. H.; Post, J. W.; Cohen Stuart, M. A.; Biesheuvel, P. M., Validity of the Boltzmann equation to describe Donnan equilibrium at the membrane–solution interface. *Journal of Membrane Science* **2013**, 442, 131-139.

d: Measured according to method provided by Kingsbury, R. S.; Zhu, S.; Flotron, S.; Coronell, O., Microstructure Determines Water and Salt Permeation in Commercial Ion-Exchange Membranes. *ACS Appl Mater Interfaces* **2018**, *10*, (46), 39745-39756.

e: Measured in 0.1M NaCl solution.

f: Measured in 0.5M NaCl solution.

[00105] ED Desalination Experiments

[00106] All of the ED experiments were performed in batch mode (**FIG. 10**). The major aim of this study is to unveil the evolution of scaling during ED desalination of a stream containing divalent cations and to elucidate associated mechanisms. Thus, seawater, which contains divalent cations (Mg^{2+} and Ca^{2+}), was chosen as the model solution in this work. ED scaling was analyzed during the desalination of synthetic seawater (SW) containing divalent cations (Mg^{2+} and Ca^{2+}) and other major ions in SW. The composition of the SW is listed in Table 2.

Table 2. The composition of model seawater

Chemical	Concentration (g/L)
NaCl	24.53
MgCl ₂	5.2
Na ₂ SO ₄	4.09
CaCl ₂	1.16
NaHCO ₃	0.201

[00107] At the beginning of each ED test, 2 L of original SW was stored in both the dilute solution (DS) tank and the CS tank. During each test, the SW from the DS tank was recirculated through the diluted chamber, and that from the CS tank was recirculated through the concentrate chamber, respectively. Both the CS and DS were recirculated by a dual-head peristaltic pump (Lead Fluid, BT-600L-2 × YT15, China) with the same flow rate of 432 mL/min and a corresponding crossflow velocity of 4 cm/s through ED chambers. The NaCl solution with the same conductivity of the SW (51.5 mS/cm) was used as a scaling free baseline solution for comparison. 0.3 M Na₂SO₄ solution with an initial volume of 2 L was used as ES

and was circulated in anode and cathode chambers at a flow rate of 432 mL/min per chamber (i.e., equivalent to a crossflow velocity of 8 cm/s).

[00108] The ED experiments were operated under constant-current mode with a current density at 14 mA/cm² using a direct current supply (A-BF SS-L603SPD, China) and were stopped when the conductivity of DS reached 12 mS/cm. All the experiments were replicated at least twice.

[00109] Scaling Characterization and ED Performance Analysis

[00110] During each experiment, the current and stack voltage were recorded every minute on a laptop using PowerDC software, and the conductivities of the DS and that of the CS were recorded by conductivity meters (Thermo Scientific Orion star A212, USA) every 3 min. The pHs of the DS, CS, ES, and effluents of both electrode chambers were measured every hour by a portable pH meter (Mettler Toledo Seven2Go pH/Ion meter S8, Singapore). Samples of 0.5 mL were collected every hour from DS, CS, and ES, respectively, during the ED tests to analyze the transport of divalent cations (Mg²⁺ and Ca²⁺) which are scaling precursors. The concentrations of divalent cations in each sample were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Avio 550Max, PerkinElmer). Membrane morphology and elementary analysis were characterized by field-emission scanning electron microscopy (FESEM, JEOL-7200F, Japan) and energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments Aztec Standard X-max 50, UK), respectively. Powdered precipitates around the cathode (i.e., scaling on cathode surface and spacer in cathode chamber, as well as precipitates in electrode streams) were collected after ED scaling tests. The precipitate powders, pristine CEM, and CEM1 (i.e., the CEM near cathode chamber) after ED desalination tests were characterized by X-ray diffraction (XRD, Bruker D8).

[00111] The desalination performance of ED experiments was evaluated by DE, which was calculated by equation (1).

$$DE = \left(1 - \frac{\text{conductivity of diluate at time } t}{\text{initial conductivity of dilute}} \right) \times 100\% \quad (1)$$

[00112] The system electrical was calculated according to Ohm's Law. The value of SER (Ω) at time t was calculated using equation (2).

$$SER = \frac{U}{I} \quad (2)$$

where U and I are the stack voltage (**FIG. 11**) and current at time t, respectively.

[00113] Performance Decline during SW Desalination.

[00114] **FIG. 13A** shows that during ED testing, the ED desalination efficiencies (DEs) based on conductivity measurement for both NaCl solution and SW increased with increasing desalination duration. However, DE for SW was slightly lower than that for the NaCl solution, and the gap of DE between the two solutions became increasingly large with the progress of desalination. A possible reason for this is the greater water transport from dilute to concentrated solution during ED desalination of SW, as shown in **FIG. 12**. This is due to greater hydration number of divalent cations in SW, which can decrease the volume of DS and lead to the DE losses. Another possible explanation lies in the occurrence of severe scaling within the ED stack, resulting in a reduction of the effective salt ion flux when water splitting occurred, which will be confirmed and discussed in the following section.

[00115] **FIG. 13B** shows the system electrical resistance (SER) as a function of the desalination efficiency (DE) during ED. SER for NaCl gradually increased with experiment time. This can be explained by the increase in the resistance of dilute chamber due to desalination. SER for SW experienced a sharp increase from the start to DE at around 5%, and then remained stable at $\sim 1.27 \Omega$. After that, the SER for SW increased from $\sim 1.27 \Omega$ at DE = $\sim 40\%$ to 1.36Ω at DE = $\sim 76\%$. It can be found that the SER for SW was higher than that for NaCl through the whole ED process. Since the effects of dilute chamber resistance and concentrate chamber resistance on the SER were excluded at the same DE, the gap of SER between SW and NaCl (**FIG. 13B**) can be ascribed to the increase in the resistance of both ion exchange membranes and electrode systems, which is likely caused by the scaling during ED desalination of SW. Coincidentally, it was previously observed that the scaling could significantly increase the stack electrical resistance. The following sections will conduct a systematic analysis of scaling during ED desalination at different locations of the entire ED stack.

[00116] Characterization of Scaling Formed at Different Parts of the ED Stack

[00117] After ED desalination tests, IEMs, electrodes, and spacers in the ED stack were autopsied to characterize scaling at different parts of the ED stack.

[00118] A significant amount of precipitates were observed on the cathode (FIG. 14A), spacer (FIG. 14B), and the surface of CEM1 facing the cathode side (FIG. 14C) after ED desalination tests. Besides, the extent of scaling was more severe on the cathode at outlet than at inlet. Similarly, the presence of scaling was observed only in the region of the CEM1 surface near the outlet of the cathode solution chamber. SEM and EDX elemental analyses were used to analyze these precipitates on membrane surface. Compared with the pristine CEM (FIG. 14D), the CEM1 facing cathode side after ED (FIG. 14E1) had a layer of crystals. The wide distribution of Mg on the surface of CEM1 facing cathode (FIG. 14E2) indicates that magnesium is a major component of the crystals formed on the membrane. The results of EDX elemental analysis in FIG. 14E3 show that fluorine, sulfur, and sodium were detected in the pristine CEM (FIG. 15C) due to its functional groups disappeared in the surface of CEM1 facing the cathode side after ED desalination of SW. Besides, the atomic percentage of carbon decreased sharply from 70.6% in the surface of pristine CEM to 8.5% in the membrane surface after ED. The element changes also suggest a layer of scales formed on the same side of CEM1. In addition, the presence of a great amount of magnesium and oxygen (FIG. 14E3) was observed on the CEM1 surface after ED, suggesting the high compositions of Mg and O in scaling. In sum, the different morphologies and compositions of the surfaces of electrodes and CEM1 surface before (FIG. 15A and FIG. 14D, respectively) and after (FIG. 14A, FIG. 14E1, respectively) ED indicate severe scaling formed in the cathode chamber during ED desalination of SW.

[00119] XRD analysis was also performed to identify the type of scaling (FIG. 14F). Compared to the diffractogram of a pristine CEM, the peak occurs between 15 and 25° (2 θ) for the CEM with scales shifted to lower 2 θ , and a series of peaks (in the following 2 θ range) characterizing magnesium hydroxide in brucite crystal form were observed on the surface of CEM1 facing the cathode chamber. This is consistent with the high concentration of magnesium during the elementary analysis (FIG. 14E3). The peak shift suggests the formation of scaling may cause the disruption of membrane. It is interesting to note that a little Ca(OH)₂ in the portlandite form and CaCO₃ in the aragonite form were observed on the fouled CEM by XRD, but the atomic percentage of calcium was 0.2% according to the EDX

result. The possible reason is the penetration depths for XRD (a few tens of micrometers) and EDX (1~5 μm), which led to this difference when the distribution of scaling was uneven. In the diffractogram of precipitate powders collected from the cathode chamber and electrode streams, peaks corresponding to brucite, portlandite, and CaCO_3 in the aragonite crystal form were observed. The formation of a trace amount of CaCO_3 mainly arises from the generation of CO_3^{2-} through the transformation of HCO_3^- in the basic cathode solution. The presence of HCO_3^- in the ES was possibly due to the HCO_3^- leakage from SW and the dissolution of carbon dioxide from the atmosphere. The above XRD results suggest that the formed scaling during ED consists of a large amount of $\text{Mg}(\text{OH})_2$ and small amounts of $\text{Ca}(\text{OH})_2$ and CaCO_3 .

[00120] Mild scaling on the surface of CEM1 and AEM1 facing dilute chamber adjacent to the cathode chamber was observed. Fewer precipitates could be observed on the surfaces of the CEM1 and the AEM1 facing the dilute chamber (chamber 2 in FIG. 10, i.e., the chamber near the cathode chamber) after ED desalination, as shown in FIG. 16A and FIG. 16B, which indicates the extent of scaling was less significant than that on the CEM1 surface facing the cathode chamber. The SEM images of the surface of CEM1 and AEM1 facing chamber 2 (FIG. 17A1 to FIG. 17B3) also show the particles on them, which indicates the scaling also formed on the surface of the CEM1 and AEM1 facing dilute chamber during ED desalination of SW. The elemental mapping of Mg distribution shows that the Mg element can only be visualized on the membrane surface where the precipitates deposited (FIG. 17A2). Compared with the membrane surface facing cathode chamber (FIG. 14E3), a lower level of magnesium and oxygen, as well as higher atomic percentages of carbon, sulfur, and fluorine, was detected on the surface of CEM1 facing the dilute solution (DS) (FIG. 17A3), which is in agreement with the lower extent of scaling and thinner scaling layer formed on the surface of CEM1 facing the DS. That again indicates that the scaling formation on CEM1 facing the DS was less significant compared with that on the surface facing the cathode chamber. Compared with the pristine AEM (FIG. 18A and FIG. 18B), a trace level of magnesium presented on the surface of AEM1 near dilute side as shown in FIG. 17B2 and FIG. 17B3, which indicates little scaling containing Mg was

formed on the surface of AEM1 facing dilute chamber. There was no calcium carbonate observed on the surfaces of membranes facing the dilute chamber adjacent to the cathode chamber (i.e., chamber 2 in **FIG. 10**). The possible reason for the composition of scaling can be attributed to the low concentration of bicarbonate ions (negatively charged), which led to the low partition (adsorption) of them in the AEM1 and none of them near the negatively charged CEM1.

[00121] No scaling was detected on the surface of membranes away from the cathode. No precipitate was observed on both surfaces of the CEM near the anode (CEM2, **FIGs. 19A/19B** and **FIGs. 20A/20B**) and the CEM in the center (CEM3, **FIGs. 21A/21B** and **FIGs. 22A/22B**) after ED desalination, but trace amounts of both sodium and magnesium were detected on them. This can be ascribed to the electrostatic attraction of these counterions by the negatively charged function groups in the CEM. In addition, none of divalent cations were observed on the surface of AEM1 facing the concentrate chamber (**FIGs. 23A/23B**) and both surfaces of the AEM2 (**FIGs. 24A/24B** and **FIGs. 25A/25B**). These observations suggest that no scaling formed on them during ED desalination. In other words, although scaling was observed on the membrane surfaces facing the dilute chamber near cathode chamber, the formation of scaling did not occur on the membrane surfaces facing dilute chamber 4 as shown in **FIG. 10**. This suggests that the scaling in the dilute chamber was not dominated by the carbonate alkalinity in the initial stage of ED desalination. Thus, the analysis of the carbonate alkalinity is not included in this work.

[00122] In summary, scaling mainly formed around the cathode (including cathode surface and cathode spacer) and on the surface of CEM1 facing the cathode chamber during ED desalination of seawater. In addition, scaling can be observed on two membrane surfaces (CEM1 and AEM1) facing dilute chamber 2, but no scaling formed on the surfaces of CEM2, CEM3, and AEM2.

[00123] Mechanisms of Scaling in ED

[00124] Electrode scaling is due to the synergistic effects of divalent cation accumulation and water electrolysis in electrode chamber. Accumulation of divalent cations in electrode chambers were observed. To better understand the scaling formation mechanisms during the ED desalination of SW, the concentrations of

Mg²⁺ and Ca²⁺ in each stream during ED were monitored with the progress of ED desalination. As shown in **FIGs. 26A** and **26B**, the concentration of both divalent cations in the DS decreased with increasing desalination efficiency (DE) and nearly depleted at the end of the ED desalination test. However, their concentration only slightly increased in the concentrate solution (CS). It is worth noting that both divalent cations accumulated in the electrode solution (ES) during the ED operation (**FIGs. 27A** and **27B**).

[00125] This can be explained by the competitive transport between monovalent and divalent cations. Specifically, divalent cations in the seawater could transport from the dilute chamber to the cathode chamber. However, it is difficult for them to transport out from the anode chamber across the adjacent CEM to the concentrate chamber, since the CEM is more selective to monovalent cations (especially H⁺) than divalent cations. Eventually, divalent cations accumulate and enrich in the ES that circulates in both the cathode and anode chambers.

[00126] **FIG. 26C/26D** shows the pH changes in the cathode effluent (CE) with the progression of ED desalination of NaCl and SW, respectively. Initially, an increase in the pH of CE was observed for both solutions (**FIG. 26C**). The pH of CE for NaCl increased from the initial 5.99 ± 0.41 to 11.67 ± 0.04 when DE was ~14%, while the pH of CE for SW increased from the initial 5.66 ± 0.46 to 10.52 ± 0.18 when DE was ~12%. The increase in the pH of CE can be attributed to water electrolysis (Table 3), which occurred at electrodes during the ED desalination process for the transmission between ionic current and electronic current.

Table 3. Electrode reactions for the electrode system with Na₂SO₄ as the electrolyte in the electrode solution.

Electrode	Electrode reactions	Label
Cathode	Acidic media: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	Route 1
	Basic media: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	Route 2
Anode	Acidic media: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	Route 3
	Basic media: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	Route 4

[00127] At the cathode, the reduction of water (Route 2 in Table 3) produces hydroxide ions (OH^-) which leads to the pH increase in the CE. The high concentration of OH^- in the cathode solution increases the tendency of scaling during the ED desalination of SW with the accumulation of divalent cations in the cathode solution.

[00128] Based on the above-mentioned results, the formation and evolution of scaling during ED desalination of SW are via 3 phases, as illustrated in **FIG. 28**. Phase 1 serves as the prerequisite for scaling formation. In phase 1, divalent cations transported from the dilute chamber to the cathode chamber and started to accumulate in the electrode solution (ES) due to the competitive transport (**FIGs. 26A and 26B**). It is worth noting that the selective transport of cations through the CEM1 could lead to the concentration polarization, resulting in the high concentration of divalent cations on the CEM1 surface contacting the cathode solution (**FIG. 28**). At the same time, water electrolysis occurred at the cathode through Route 2 (Table 3), which leads to the generation of OH^- near the cathode surface (**FIG. 26C**). In the electric field, OH^- transported toward the anode, but its transport was rejected by the CEM1, leading to the accumulation of OH^- at the interface between the cathode solution and the CEM1 surface.

[00129] In phase 2, crystals formed on the cathode surface, spacer, and surface of CEM1 facing the cathode chamber. The high concentration of OH^- generated during electrolysis near the surface of the cathode allowed the reactions between OH^- and the divalent cations (Mg^{2+} and Ca^{2+}) and HCO_3^- accumulated in the cathode chamber, resulting in the occurrence of scaling on the cathode surface (**FIG. 14A**). On the CEM1 surface, the concentrated Mg^{2+} , Ca^{2+} , and OH^- also contributed to the formation of scaling (**FIG. 14C**). Moreover, the accumulated Mg^{2+} , Ca^{2+} , and OH^- in the bulk ES in the cathode chamber facilitated the formation of crystals in the ES and around the spacer (**FIG. 14B**). The formation of scaling was supported by the continuous loss of divalent cations during ED (**FIGs. 27C and 27D**), i.e., the continuous formation of scaling contributed to the increase in the consumption of divalent cations. Besides, the number of divalent cations (in the units of moles) in the ES increased with increasing DE at a decreased rate (**FIGs.**

27A and 27B). The possible reason for the decrease in the rate is the consumption of divalent cations due to cathode scaling.

[00130] The occurrence and evolution of scaling in the cathode chamber were also reflected by the pH changes in the CE as shown in **FIG. 26C**. Due to water electrolysis in the electrode chamber, the pH of the CE for both cases of NaCl desalination and SW desalination increased with increasing DE during the initial stage of ED desalination until DE was ~14%. Despite this, the extent of the pH increase in CE was different for cases of NaCl and SW. During ED desalination of SW, the pH of CE increased to 10.52 ± 0.18 when DE was around 12%. This pH increase was lower than that for NaCl ($\text{pH} = 11.67 \pm 0.04$ at $\text{DE} = \sim 14\%$). Due to the identical stack arrangement and the use of the same type of membranes, the major reason for the lower pH increase during the initial stage of SW desalination than NaCl is due to the more complex ionic composition of SW. Specifically, the HCO_3^- , Mg^{2+} , and Ca^{2+} ions from SW transported into the electrode chamber, which leads to the consumption of OH^- . During the initial stage of SW desalination, the accumulated scaling precursor ions Mg^{2+} and Ca^{2+} ions were still at a relatively low concentration, and thus, the consumption of OH^- was at a low rate.

[00131] Consequently, the pH was still increasing despite being slightly lower than NaCl desalination. With the progress of ED desalination, when the DE was higher than 14%, the pH of CE for NaCl still maintained a relatively stable level (~ 11.65), whereas a sharp decrease of pH was observed for SW desalination, and the pH decreased continuously to ~ 5.51 at $\text{DE} = \sim 54\%$. This is primarily caused by the severe scaling with the continuous enrichment of scaling precursor ions (Mg^{2+} and Ca^{2+}) in the electrode chamber. At a relatively higher concentration, increasingly larger crystals formed, and the precipitation rate increased significantly in the electrode chamber from a kinetic point of view. This substantially increased the consumption of OH^- and the decrease of pH in the CE. In addition, pH changes in the AE, the mixed ES from CE and AE, the DS, and the CS were observed. Apart from scaling, the pH changes in these solutions are caused by a variety of other factors and their combined effects such as oxidation reactions in the anode chamber, ion competitive transport through IEMs, and imperfect permselectivity.

[00132] The low pH of the ES (i.e., cathode solution at the inlet) promoted the dissolution of scaling at the inlet. However, both the consumption of H^+ in acidic media (Route 1) and the generation of OH^- in basic media (Route 2) led to an increase in the pH of the cathode solution. Consequently, the concentration of OH^- in the cathode chamber increased along the flowing direction, and its concentration on the cathode surface was sufficiently high to facilitate the scaling formation, thereby resulting in more severe scaling at the outlet than at the inlet of the cathode chamber (**FIGs. 14A** and **14C**). The visual evidence of scaling on the cathode surface after ED desalination (**FIG. 14A**) and the continuous decrease in the pH of the CE (**FIG. 26C**) strongly imply that the formation of scaling prevailed over its dissolution in the cathode chamber.

[00133] On the scaling-enhanced scaling on CEM, most of the precipitates were blocked by the spacer in the cathode chamber and could not be flushed off. The crystals formed on the surface of CEM1 facing the cathode chamber reduced the effective area of CEM1 and blocked the transport of ions. For the typical operation mode with a fixed current (i.e., fixed apparent current density) during desalination with the occurrence of scaling, the local ion flux across the membrane areas with no deposited crystal must increase accordingly to carry the required ionic current, which results in an increase in the local current density. With the increase in DE, the concentration of ions in the dilute chamber decreased to a low level and the limiting current density (LCD) decreased accordingly. Under this circumstance, the ions with reduced concentration at the DS were not sufficient to carry the required current during ED, which led to the occurrence of water splitting for the generation of OH^- and H^+ to carry current. This is phase 3 (**FIG. 28**) during which the local current density was higher than the LCD. In this phase, when water splitting occurs on the local membrane surface, H^+ ions migrated across CEM1, while OH^- ions are distributed in the dilute chamber. As shown in **Figure 5D**, the pH for the dilute stream increased when DE increased from ~54% to ~76%.

[00134] The high concentration of OH^- on the local surface of CEM1 could react with the divalent cations to form precipitates, which resulted in the scaling on the surface of CEM1 and AEM1 facing the dilute chamber (**FIGs. 17A** to **17B3**). This indicates that the scaling formed in the cathode chamber further enhances the

occurrence of scaling on the CEM, i.e., a phenomenon of scaling-enhanced scaling. The scaling-enhanced scaling phenomenon was also supported by the change in the concentrations of divalent cations. Since the scaling-enhanced scaling formed in the dilute chamber, the transport of divalent cations from the dilute chamber to the cathode chamber decreased. As shown in **FIGs. 26A** and **26B**, the concentration of divalent cations in the DS decreased, while that in the CS and the ES nearly remained stable when DE increased from ~54% to ~76%. Besides, the amount of change of divalent cations in the electrode stream at the end of the test was nearly the same as that at DE = ~54% (**FIGs. 27A** and **27B**), which indicates there was nearly no increase in the number of divalent cations in the ES after DE was higher than 54%. This suggests the consumption of divalent cations in the dilute chamber. In addition, the decrease in the transport of divalent cations from the dilute chamber to the cathode chamber further decreased the consumption of OH⁻ in the cathode chamber. Thus, there was an increase in the pH of CE when DE increased from ~54 to ~76%.

[00135] The pH of the DS only slightly increased from 6.88 ± 0.16 to 7.22 ± 0.82 when DE increased from ~54% to ~76%. The possible reason is that scaling-enhanced scaling consumed the hydroxide ions generated from water splitting on the surface of CEM1 facing dilute chamber 2. After the consumption of hydroxide ions in this dilute chamber, the pH of the DS was lower than the pH required to form mineral precipitates (pH = 10.5 for Mg(OH)₂ with $K_{sp} = 1.8 \times 10^{-11}$, and pH = 12.4 for Ca(OH)₂ with $K_{sp} = 6 \times 10^{-6}$ at 25 °C³¹). This is consistent with the results that no scaling was observed on the membrane surfaces facing another dilute chamber (i.e., chamber 4). No scaling on other membrane surfaces also suggests that water splitting did not occur on membrane surfaces facing dilute chamber 4, which indicates the current density used in this study did not exceed the limiting current density of the membranes without scaling. Thus, the scaling on the surfaces of CEM1 and AEM1 facing dilute chamber 2 was induced by the scaling formed in the cathode chamber, i.e., scaling enhanced scaling.

[00136] Comparison

[00137] Further experiments were conducted in which the proposed ED stack was compared against various other ED stacks. **FIG. 29A** to **FIG. 29C** provide a

graphical summary of the scaling mechanism occurring in conventional ED, BED, and SED stacks and, in contrast, the **FIG. 29A** is a schematic diagram showing scaling formation during conventional electrodialysis, e.g., as a result of precipitation of divalent cations in electrodialysis (ED) stacks. The precipitation of multivalent cations particularly in the cathode chamber is found to be one of the critical issues limiting the desalination efficiency and increasing the energy consumption and operating cost during ED. **FIG. 29B** schematically illustrates an ED stack in which the cathode chamber is formed using a bipolar membrane (BPM) in place of a cation exchange membrane (CEM). As will be shown in greater in the following, the BED cannot prevent scaling formation in the cathode chamber. **FIG. 29C** schematically illustrates an ED stack in which the cathode chamber is formed using a monovalent selective cation exchange membrane (SCEM) in place of a CEM. Similar to the BED, the SED cannot prevent scaling formation in the cathode chamber.

[00138] **FIG. 30** schematically illustrates an embodiment of the proposed ED stack. As will be further described in the following, the proposed ED stack is capable of preventing scaling. The proposed ED stack includes a two mediating chambers bookending a series of alternating or interleaving dilute solution (DS) chambers and concentrate solution (CS) chambers. The solution in the mediating chambers may be referred to as the mediating solution.

[00139] **FIG. 31A to FIG. 31C** reveals the ion transport during ED desalination of high salinity solution in a conventional ED, BED, and SED stack, respectively. As shown in **FIG. 31A**, the accumulation of divalent cations and simultaneous hydroxide ions (OH^-) generation within the cathode chamber led to scaling around the cathode, which further contributed to scaling on the membrane surfaces facing the adjacent chamber. This mechanism suggests the efficient strategy to control cathode scaling during ED desalination is preventing the accumulation of divalent cations in the electrode solution, e.g., preventing the transport of divalent cations from the feed solution to the electrode solution.

[00140] **FIG. 31B** schematically illustrates an ED stack with BPM forming the cathode chamber (also referred to as “bipolar ED” or “BED”). Conventional thinking may believe that BPM can be used to hinder the transport of ions from the treated

solution to the cathode solution. BPMs are a category of ion exchange membranes consisting of a cation exchange layer (CEL) and an anion exchange layer (AEL), which are designed for water dissociation at the interface between the CEL and AEL and to prevent ion transport across it. Indeed, some utilized a BPM as a shielding membrane positioned at the cathode of a reverse electrodialysis (RED) stack, with the CEL and AEL oriented towards the feed solution and the cathode solution, respectively, and were able to mitigate inorganic scaling during the RED process. In this study, as shown in **FIG. 31B**, a BPM was placed near the cathode to form the cathode chamber, with its AEL facing cathode and CEL facing dilute chamber, to utilize the BPM for blocking the transport of divalent cations from the dilute solution (DS) to the cathode solution.

[00141] **FIG. 31C** schematically illustrates an ED stack with a monovalent selective cation exchange membrane (SCEM) forming the cathode chamber (also referred to as “selective ED” or “SED”). A SCEM typically involves a regular cation exchange membrane (CEM) serving as the substrate and a thin surface layer. The thin surface layer can either be highly dense or comprise strong positive charges, for repelling multivalent cations with larger sizes and greater charges, and to enhance monovalent cation selectivity. Previous studies employed the SCEM with its thin surface layer facing the dilute solution in the ED stack for lithium extraction from Salt Lake water containing both Mg^{2+} and Li^+ ions. In this study, as shown in **FIG. 31C**, a SCEM was positioned adjacent to the cathode within the ED stack, with the surface of the thin layer (denoted by the active surface) oriented towards the dilute solution, aiming to reduce the transport of divalent anions.

[00142] Although numerous studies have focused on the preparation of BPMs with minimized ion leakage and SCEMs with enhanced monovalent selectivity, it was found that undesired ion transport persists in the BPM and the SCEM.

[00143] It was also found that, in an ED stack arrangement, placing an anion exchange membrane (AEM) close to each electrode chamber can significantly decrease the transport of cations into the electrode solution. However, the transport of chloride ion through the AEM into the electrode solution led to the generation of Cl_2 and ClO^- , resulting in the contamination and corrosion.

[00144] **FIG. 31D** is another schematic illustration of the proposed ED stack with a mediating solution (MS) chamber adjacent to each electrode chamber (referred to herein as “EDM”). The proposed EDM does not necessitate alterations to the membrane or the membrane arrangement of the conventional ED stack. The proposed EDM involves the introduction of a mediating solution into the chamber adjacent to the electrode, and this was found to successfully impede the migration of divalent ions to the cathode.

[00145] **FIG. 31E** shows the ED setup for the ED stack of **FIG. 31B**. **FIG. 31E** shows the stack configuration of BED in which one BPM was placed near the cathode to form the cathode chamber, with its anion exchange layer (AEL) facing cathode and cation exchange layer (CEL) facing dilute chamber. Two anion exchange membranes (AEMs), and two CEMs were alternately placed between the BPM and anode. The arrangement for this BED stack formed flow channels for electrode solution (ES), dilute solution (DS), and concentrate solution (CS).

[00146] **FIG. 31F** shows the ED setup for the ED stack of **FIG. 31C** stack. **FIG. 31F** shows the stack configuration of SED. One SCEM, two AEMs, and two CEMs were placed between the cathode and anode. SCEM was placed near cathode, and its active surface was placed toward anode.

[00147] **FIG. 31G** shows the ED setup for the proposed ED stack of **FIG. 31D**, e.g., showing a circulation path configuration for the ES and DS. **FIG. 31G** shows the stack configuration of ED with mediating solution chambers (EDM). The EDM uses the same membranes and has the same solution chambers as those in conventional ED stacks except that the dilute chamber adjacent to the cathode chamber and the concentrate chamber adjacent to the anode chamber were filled with a separate mediating solution (MS) that has the same cation as that in the electrode solution (ES) but is free of divalent cations. The experimental results show that introducing two mediating chambers can separate the electrode solution from the treated solution (i.e., concentrate solution or dilute solution), and preventing the transport of multivalent cations from the treated solution to the electrode solution.

[00148] For example, in this study, Na_2SO_4 was used as the electrode solution (ES), and NaCl was chosen for MS. The effective area of each membrane in all the ED stacks (**FIG. 31B** to **FIG. 31G**) was 189 cm^2 , and spacers were used to fix the

thickness of each flow channel at 1 mm. Both the anode and cathode were fabricated from titanium coated with ruthenium. Seawater, a representative solution containing divalent cations such as Mg^{2+} and Ca^{2+} , was selected as the model solution for this study.

[00149] The desalination performance of each stack design was compared by evaluating their desalination efficiency and system electrical resistance. Moreover, the concentrations of divalent cations and the pH levels were monitored throughout the ED operation for different designs to elucidate the mechanisms of success or failure of scaling prevention for each design.

[00150] Materials

[00151] Unless otherwise specified, all the chemicals and agents used in this study were ACS grade. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), and sodium bicarbonate (NaHCO_3) were purchased from Sigma-Aldrich to prepare the synthetic seawater (SW) according to the composition of seawater in a previous study. The NaCl solution with the same conductivity of the synthetic SW (51.5 mS/cm) was also prepared and used in the non-scaling experiments for comparison. The bipolar membranes (BPMs, CJBPM-2 type), anion exchange membranes (AEMs, CJMA-4 type), and cation exchange membranes (CEMs, CJMC-4 type) used are available from Hefei ChemJoy Polymers Co., Ltd., China. Neosepta CXP-S monovalent-selective cation exchange membranes (SCEM) are available from ASTOM Corp., Japan.

[00152] Lab-Based Tests

[00153] All the ED tests were operated in the batch mode. The solutions used in different chambers during each test were listed in the table below:

Table 4. Feed Solutions Used in the Experiments

ED stack	Feed solution			
	CS	DS	ES	MS
BED	NaCl (51.5 mS/cm)	NaCl (51.5 mS/cm)		-
BED	SW	SW	0.3 M Na_2SO_4	-
SED	NaCl (51.5 mS/cm)	NaCl (51.5 mS/cm)		-
SED	SW	SW		-

EDM	NaCl (51.5 mS/cm)	NaCl (51.5 mS/cm)	0.1 M NaCl
EDM	SW	SW	0.1 M NaCl

[00154] The initial volume for each feed was 2 L. During each test, the dilute solution (DS) and the concentrate solution (CS) were recirculated through the diluted chamber and the concentrate chamber by a dual-head peristaltic pump (Lead Fluid, BT-600L-2×YT15, China) at a flow rate of 432 mL/min (i.e., equivalent to an apparent cross-flow velocity of 4 cm/s), respectively. The conductivities of the DS and the CS were recorded every three minutes by two conductivity meters (Thermo Scientific Orion star A212, USA), respectively. The ES was the same in all the tests. The ES was 0.3 M Na₂SO₄ solution and was recirculated in both cathode and anode chambers at a flow rate of 432 mL/min per chamber (equivalent to an apparent cross-flow velocity of 8 cm/s). During each EDM test, the mediating solution was recirculated by a peristaltic pump at a flow rate of 432 mL/min (i.e., equivalent to an apparent cross-flow velocity of 4 cm/s). The pH of CS, DS, ES, MS, and effluent of both anode and cathode chambers were measured every hour by two pH meters (Mettler Toledo SD20 pH meter, Singapore).

[00155] All the BED, SED, and EDM experiments were operated under constant current density of 14 mA/cm² by a direct current supply (A-BF SS-L603SPD, China). The voltage and the current during each test were recorded every minute by PowerDC software. Samples from CS, DS, ES, and MS, respectively, were collected every hour during each test and analyzed by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES, Avio 550Max, PerkinElmer) to determine the concentration of divalent cations (Mg²⁺ and Ca²⁺). The experiments were terminated upon the attainment of a DS conductivity of 12 mS/cm or the completion of a 6-hour testing duration. Upon the completion of each test, the volumes of the CS and the DS were measured using a graduated cylinder, and the average of the volume changes in the dilute solution and the concentrate solution was calculated as the water transport in each operation. After each test, the ED stack was cleaned by deionized water for 10 min to wash off soluble salts. Subsequently, the membrane near the cathode was taken out and dried using a freeze dryer (Martin Christ Alpha 2-4). The morphology and elementary analysis of the membrane near

the cathode were characterized by field-emission scanning electron microscopy (FESEM, JEOL-7200F, Japan) and energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments Aztec Standard X-max 50, UK), respectively. All the ED tests were replicated at least twice.

[00156] Desalination efficiency (DE) and system electrical resistance (SER) were used to evaluate the performance of each ED test, respectively. DE and SER were calculated using equations (1) and (2) as given above.

[00157] Results and discussion of scaling formation and characterization thereof

[00158] After each test with different stack configurations, the membranes near the cathode were examined via Field Emission Scanning Electron Microscopy (FSEM) and Energy Dispersive X-ray Spectroscopy (EDX) to detect scaling formation.

[00159] BED cannot prevent cathode scaling

[00160] **FIG. 32A** is an optical image of the cathode and **FIG. 32B** is an optical image of the spacer in the cathode chamber of the BED stack after ED desalination of SW. **FIG. 32C** and **FIG. 32D** are FSEM images of the bipolar membrane (BPM) facing the cathode and the dilute chamber in the BED stack after ED desalination of SW, respectively. **FIG. 32E** and **FIG. 32F** are EDX spectrum of surfaces shown in **FIG. 32C** and **FIG. 32D**, respectively. **FIG. 32G** is a SEM image of the cross section of the BPM. **FIG. 32H** is an EDX mapping of Mg element distribution in the cross section shown in **FIG. 32G**. In the FSEM images, At% refers to the atomic percentage.

[00161] **FIG. 32A** and **FIG. 32B** show the formation of scaling on both the cathode and the spacer within the cathode chamber in the BED stack after the ED desalination of SW, which suggests the use of a BPM cannot prevent scaling around cathode. Compared with the pristine BPM (**FIG. 32A1/32A2** and **FIG. 32B1/32B2**), it is evident that a distinct layer of crystalline structures has manifested on the surfaces of the BPM, as illustrated in **FIG. 32C** and **FIG. 32D**. This visual observation is consistent with the EDX spectra obtained from these surfaces **FIG. 32E** and **FIG. 32F**, which unveil conspicuous quantities of magnesium and oxygen, alongside a minor presence of calcium within the scaling composition.

[00162] The FSEM image of the cross section of BPM (**FIG. 32G**) also elucidates the occurrence of a distinct precipitate layer on the AEL surface. Additionally, compared to the pristine BPM (**FIG. 32C1/32C2**), the interface between the anion exchange layer (AEL) and the cation exchange layer (CEL) became apparent after BED treatment. Furthermore, the elemental distribution map featuring Mg element within the BPM cross-section (**FIG. 32H**) highlights a notable increase in magnesium content, particularly in the interface region. This observation strongly suggests the formation of scaling within the BPM, particularly at the interface between the AEL and the CEL.

[00163] SED cannot prevent cathode scaling.

[00164] **FIG. 33A** and **FIG. 33B** are respective optical images of the cathode and the spacer in the cathode chamber of the SED stack after ED desalination of SW. **FIG. 33C** and **FIG. 33E** are FSEM images of the monovalent selective cation exchange membrane (SCEM) facing the cathode and the dilute chamber in the SED stack after ED desalination of SW, respectively. **FIG. 33D** and **FIG. 33F** are EDX spectrum of surfaces shown in **FIG. 33C** and **FIG. 33E**, respectively. In the figures, BED: ED stack with a SCEM forming the cathode chamber. At%: the atomic percentage. In the FSEM images, At% refers to the atomic percentage.

[00165] **FIG. 33A** shows a layer of precipitates formed on the cathode of SED stack after ED desalination of SW, and white particles also present on the spacer in the cathode **FIG. 33B**. These observations suggest that the utilization of a monovalent selective cation exchange membrane (SCEM) did not prevent scaling on cathode during SW desalination.

[00166] **FIG. 33C** shows that a layer of crystals covered the SCEM surface facing the cathode after ED desalination of SW. The elemental analysis performed on this surface **FIG. 33D** revealed a substantial increase in the atomic percentages of magnesium and oxygen compared with the pristine back surface of the SCEM (i.e., the pristine surface of the substrate shown in **FIG. 33A1/33A2**). Additionally, the atomic percentage of carbon on the SCEM surface facing the cathode sharply decreased due to the occurrence of the crystal layer. These elemental changes also suggest that scaling containing magnesium and oxygen formed on the SCEM surface facing the cathode chamber during ED desalination.

[00167] Small particles were observed on the surface of SCEM facing the dilute chamber as shown in **FIG. 33E**, and its surface was less smooth than the pristine active surface of the SCEM (i.e., the pristine surface of the thin layer shown in **FIG. 33B1/33B2**). Compared with the elemental analysis of the pristine active surface **FIG. 33B1**, there were slight increases in the atomic percentages of magnesium, oxygen, and calcium **FIG. 33F** after ED desalination of SW. These changes in the membrane morphology and the element distribution indicate the formation of scaling on the SCEM surface facing the dilute chamber.

[00168] EDM can prevent cathode scaling

[00169] **FIG. 34A** and **FIG. 34B** are optical images of the cathode and the spacer in the cathode chamber of the EDM stack after ED desalination of SW, respectively, in which the EDM stack refers to one embodiment of the proposed ED stack having a mediating solution (MS) chamber adjacent to each electrode chamber. **FIG. 34C** and **FIG. 34E** are FSEM images of the regular cation exchange membrane (CEM) facing the cathode and the dilute chamber in the EDM stack after ED desalination of SW, respectively. **FIG. 34D** and **FIG. 34F** are EDX spectrum of surfaces shown in **FIG. 34C** and **FIG. 34E**, respectively. In each EDX spectrum, At% refers to the atomic percentage.

[00170] **FIG. 34A** and **FIG. 34B** show that the cathode surface was clear and that no precipitate was blocked by the spacer after SW desalination by EDM, respectively, indicating no scaling formation in EDM stack after ED desalination of SW. In addition, FSEM images **FIG. 34C** and **FIG. 34E** demonstrate that no particles were observed on both sides of the regular CEM near the cathode in EDM stack after ED desalination of SW. According to the results of elemental analysis as shown in **FIG. 34D** and **FIG. 34F**, the dominant elements detected in both surfaces of the CEM were carbon and fluorine, which can be attributed to the membrane polymer matrix being made of polyvinylidene fluoride (PVDF). Additionally, sulfur and oxygen were also detected, as the CEM contains sulfonate groups in its functional groups. The detection of elements from the backbone and charged groups on both surfaces of the membrane suggests that the membrane surfaces were not covered by other matters, thereby indicating the elimination of scaling formation by the EDM stack.

[00171] Desalination efficiency and system electrical resistance during ED desalination by different stack designs

[00172] **FIG. 35A** shows the desalination efficiency (DE) during ED desalination of different feed solutions (i.e., SW and NaCl) by different stack designs (i.e., BED stack, SED stack, and EDM stack). For all the stack designs, DE for NaCl treatment was higher than that for SW treatment, and DE for either desalination of NaCl or desalination of SW follows SED > EDM > BED. These differences can primarily be ascribed to the water transport (**FIG. 35B**).

[00173] The difference in the desalination efficiency (DE) can be mainly ascribed to the ion transport and water transport during each operation. Since the hydration numbers of divalent cations (Mg^{2+} and Ca^{2+} in SW) were higher than that of sodium ion², water transport during NaCl treatment was lower than that in SW desalination except the case BED (**FIG. 35B**). The abnormal trend in the water transport of BED can be explained by the formation of scaling at the BPM interface during BED desalination of SW (**FIG. 32G**). Scaling at the BPM interface block the transport path for water and decreased water splitting, which decreased the water transport for the case SW compared to the case NaCl during BED.

[00174] The water transport can mitigate the decrease in the apparent conductivity of dilute solution. This led to the lower DE for SW treatment in this work. Specifically, DEs were $66.1 \pm 0.2\%$ for NaCl treatment and $60.2 \pm 0.8\%$ for SW treatment under BED at 6 h, respectively. In other words, longer experiment time was required to reach the same DE for SW treatment. Under the case of SED, the experimental duration to attain a desalination efficiency of $76.5 \pm 0.1\%$ differed notably between NaCl treatment (4.95 hours) and SW treatment (5.3 hours), highlighting the prolonged timeframe required for the latter due to the higher water transport (i.e., 320 ± 1 mL for SW treatment > 303 ml for NaCl treatment, as shown in **FIG. 35B**). The required time for EDM (5.15 h and 5.65 h for NaCl and SW treatment, respectively) were slightly longer than that for SED due to the higher water transport in EDM (346 ± 6 ml and 374 ± 4 ml for NaCl and SW treatment, respectively). The possible reason may be the dense SCEM of the SED stack, which can decrease water transport through it. It can be found that DE under condition BED was the lowest. This is because the BPM contains both anion exchange layer (AEL) and

cation exchange layer (CEL). In general, AEL and CEL can block the transport of most of cations and anions, respectively. Thus, the transport of ions between the dilute chamber and the cathode chamber was substantially decreased in BED, which decreased the desalination efficiency.

[00175] The order of water transport ($\text{EDM} > \text{BED} > \text{SED}$) during SW desalination was consistent with the order of the amount of the divalent cation transport from the dilute to the concentrate solution (**FIG. 35C** and **FIG. 35D**) due to the higher hydration number of divalent cations as discussed above.

[00176] **FIG. 36A** to **FIG. 36C** illustrate the relationship between the system electrical resistance (SER) and desalination efficiency (DE) for ED desalination by different stack designs. Compared to the SER during ED desalination of NaCl by either the BED stack or the SED stack, the SER for SW treatment was higher due to the formation of scaling. Additionally, the SERs for NaCl treatment and SW treatment by the EDM stack were similar at the same DE, which is consistent with the phenomenon that no scaling was observed under ED desalination by the EDM stack. The SER for SW treatment at DE of ~60% follows: $\text{SED} > \text{BED} > \text{EDM}$.

[00177] The mechanism of scaling mitigation

[00178] The synergistic effects of the pH changes in the cathode effluent and the accumulation of divalent cations affect the formation of cathode scaling. As shown in **Fig. 39A**, the pH of cathode effluent increased for all cases in the early stage of ED due to the water reduction. Thus, it is important to avoid the transport of divalent cations from the treated solution to the cathode chamber to impede scaling.

[00179] The transport of divalent cations during ED desalination of SW

[00180] **FIG. 37A** and **FIG. 37B** show the concentration of magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}) respectively in different solutions during ED desalination of SW by different stack designs. **FIG. 37A** and **FIG. 37B** depict the dynamic evolution of divalent cation concentrations in each solution. It was found that the concentrations of both Mg^{2+} and Ca^{2+} in the dilute solution (DS) under all stack designs decreased with increasing desalination efficiency (DE). Under the EDM condition, a remarkable reduction in the concentrations of divalent cations in DS was attained, reaching the lowest level of 3.52 ± 0.14 mM for Mg^{2+} and 0.32 ± 0.02 mM for Ca^{2+} at DE of 76.5%. Simultaneously, the concentrations of divalent cations

in concentrate solution (CS) observed under the EDM condition was higher, in comparison to the other two stack designs. It can also be found that the concentrations of divalent cations in both the ES and the mediating solution (MS) were nearly zero.

[00181] The utilization of a monovalent selective cation exchange membrane (SCEM) in the SED stack can decrease the transport of divalent cations from the DS to the cathode solution, which contributed to the lowest decreases in the concentrations of Mg^{2+} (22.71 ± 1.69 mM at $DE = 76.5 \pm 0.1\%$) and Ca^{2+} (2.76 ± 0.09 mM at $DE = 76.5 \pm 0.1\%$) in the case of ED desalination by the SED stack. Similarly, employing a bipolar membrane (BPM) encompassing both cation exchange layer (CEL) and anion exchange layer (AEL) in the BED stack was observed to decrease the divalent cation transportation. The reduction in the divalent cation transport due to a BPM was lower than that due to a SCEM, i.e., the reductions in the concentrations of divalent cations in DS for BED were between that for SED and EDM.

[00182] When the desalination efficiency was lower than ~60%, the Mg^{2+} concentration in the concentrate solution (CS) during ED desalination by the BED stack was found to closely resemble that by the SED stack (**FIG. 37A**). Similarly, comparable concentrations of Ca^{2+} in CS were also observed between these two operations (**FIG. 37B**). Remarkably, the concentrations of both Mg^{2+} and Ca^{2+} in the electrode solution (ES) under ED operations using the BED stack and the SED stack increased with increasing desalination rate. These findings suggest that the utilization of SCEM and BPM cannot fully reject the transport of divalent cations from the dilute solution to the cathode solution. The low concentration in CS and the divalent cation accumulation in ES can be ascribed to the competitive transport between divalent cations and monovalent cations in the electrode chamber under conditions of BED and SED. In an ideal scenario, the transport of divalent cations from the anode chamber to the concentrate chamber should occur to compensate the ion transport from the dilute chamber to the cathode chamber. However, the CEM is more selective to the transport of monovalent cations (i.e., hydrogen ions and sodium ions in the anode solution in this work), which led to the accumulation of divalent cations in ES.

[00183] Scaling formation or mitigation during ED desalination of SW

[00184] **FIG. 38A** to **FIG. 38C** are schematic diagrams illustrating the cation transport through the BPM of the BED stack (**FIG. 38A**), the SCEM of the SED stack (**FIG. 38B**), and the mediating solution chambers of the EDM stack (**FIG. 38C**), respectively. The BED stack includes an ED stack with a bipolar membrane (BPM) forming the cathode chamber. The BPM includes an anion exchange layer (AEL) and a cation exchange layer (CEL). The SED stack includes an ED stack with a monovalent selective cation exchange membrane (SCEM) forming the cathode chamber. The active surface of the SCEM represents the surface of the thin layer which is configured to reject ions with larger sizes and greater charges.

[00185] The EDM stack includes one or more cation exchange membrane (CEM) and one or more anion exchange membrane (AEM), alternately disposed to define chambers for dilute solution (DS) and concentrate solution (CS). The EDM includes the ED stack with a mediating solution (MS) chamber adjacent to each electrode chamber. The mediating solution (MS) is provided in each of the two MS chambers. In this example, X represents monovalent cations, e.g., Na^+ and H^+ ions in the experiments conducted, and Y represents divalent cations, e.g., Mg^{2+} and Ca^{2+} in the experiments conducted. In other applications, the particular monovalent cations and multivalent cations (e.g., divalent cations, trivalent cations) may vary from case to case.

[00186] The conventional stack designs BED and SED seek to employ the bipolar membrane (BPM) and the selective monovalent cation exchange membrane (SCEM) to impede the transport of multivalent cations, respectively. **FIG. 38A** and **FIG. 38B** show the desired and undesired ion transport within the BPM and the SCEM during SW desalination. The CEL and AEL of the BPM were placed toward the dilute chamber and cathode chamber in the BED stack, respectively, and the active surface of the SCEM was orientated towards the dilute chamber. It is desired that the AEL of the BPM and the active surface of the SCEM can impede the transport of divalent cations. However, divalent cations were observed in the electrode solution for both BED and SED (**FIG. 37A** and **FIG. 37B**). This suggests that the AEL of BPM and the SCEM failed to completely or adequately prevent the transport of divalent cations from SW to the cathode chamber. In other words, there

was undesired multivalent cation transport within the BPM and the SCEM as shown in **FIG. 38A** and **FIG. 38B**.

[00187] The pH changes in each solution through the ED operations are also consistent with the scaling behavior. The increase in the pH of cathode solution (e.g., the generation of hydroxide ions) as a result of water reduction occurred in the initial period of the ED desalination of SW with the BED stack and the SED stack (**FIG. 39A** and **FIG. 39B**). More specifically, it was observed that, in ED operations using either the BED stack and the SED stack, an initial increase in the pH of the cathode effluent (CE) was observed for both NaCl treatment (**FIG. 39A**) and SW treatment (**FIG. 39B**) in the early stage ($DE < \sim 10\%$) due to the generation of hydroxide ions from the water reduction at cathode. The pH of CE then maintained a stable pH level until the end of the respective experiments for NaCl treatment, while it experienced a decrease during the following BED and SED operations for SW treatment. This different trend can be attributed to the formation of scaling, which consumed hydroxide ions.

[00188] For the EDM operations, the trends of the pH of CE for SW desalination (**FIG. 39B**) were the same as that for NaCl desalination (**FIG. 39A**) throughout the whole operations. This suggests there was no consumption of OH^- , i.e., no cathode scaling during the EDM operations for SW treatment.

[00189] The anode effluent (AE) pH for all stack designs sharply decreased to a relative low level in the initial stage ($DE < 15\%$) due to the oxidation of water at anode. Subsequently, the pH of AE during ED operation using the EDM stack exhibited the same trend (i.e., nearly kept stable) for both NaCl treatment and SW treatment, while that using the BED stack and the SED stack remained stable for SW treatment but slightly increased for NaCl treatment. The difference in the trends of the pH of AE during ED with the BED stack and the SED stack can be also attributed to the scaling formation. Besides, the electrode solution (ES) exhibited an alkaline state for NaCl treatment (**FIG. 39A**) and an acid state for SW treatment (**FIG. 39B**) for the ED operations with the BED stack and the SED stack, while the ES during ED desalination of both NaCl and SW with the EDM stack showed an alkaline state. This again indicates the OH^- consumption due to scaling formation during SW treatment using the BED stack and the SED stack.

[00190] Because of the oxidation of water at anode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$), the pH of anode effluent (AE) for all operations exhibited an acid state. According to ion transport behavior in the electric field, the competitive transport between counterions existed during each ED operation. There were hydrogen ions and other cations in the anode solution, and the CEM is more selective for the transport of hydrogen ions. At the same time, water reduction occurred at cathode ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$) and generated OH^- ions whose transport were nearly fully blocked by the membrane near the electrodes. When there was no scaling formation during NaCl treatment (i.e., no OH^- consumption due to scaling), the H^+ concentration in the anode solution was lower than the OH^- concentration in the cathode solution due to the transport of H^+ from the anode solution to the near solution (i.e., concentrate solution in BED and SED, mediating solution in EDM). Consequently, the mixed electrode solution (ES) exhibited an alkaline state, with the pH of ES at 8.15 ± 0.11 , 10.00 ± 0.14 , and 9.34 ± 0.94 at the end of BED, SED, and EDM, respectively. The increase in the pH of ES was fed as the feed of anode solution, which contributed to the slight increase in the pH for the cases using the BED stack and the SED stack. For the EDM case, the effluents of two mediating chambers were mixed and recirculated in these two mediating chambers, which allowed the transport of H^+ from the mediating solution to the cathode solution, thereby contributing the stable pH of AE. For the SW treatment, the trends of the pH in each solution for SW desalination were similar to that for NaCl desalination since there was no scaling formation during ED desalination of SW with the EDM stack. During ED operations using the BED stack and the SED stack, the formation of cathode scaling would consume the OH^- ions in the cathode solution, which was higher than the transport of H^+ from the anode solution to the near solution, thereby resulting in the higher concentration of H^+ than OH^- ions in the electrode solution. Thus, the electrode solution was acidic solution for the ED desalination of SW using the BED stack or the SED stack.

[00191] Both the transport of multivalent cations and the generation of hydroxide ions contributed to the formation of scaling (**FIG. 32A to FIG. 32H**, and **FIG. 33A to FIG. 33F****Error! Reference source not found.**). To sum up, the BED and SED configurations failed to prevent the formation of scaling.

[00192] Referring again to **FIG. 38C** which illustrates the transport of cations during ED desalination of SW with the EDM stack, in the EDM configuration, two mediating solution chambers were introduced and positioned near the cathode chamber and the anode chamber, respectively. 0.1 M NaCl solution was chosen as the mediating solution (MS) in this study, avoiding the existence of multivalent cations in the flow channel near cathode chamber. During ED desalination of SW by the EDM stack, cations can transport from the dilute solution (DS) to the concentrate solution (CS), and the transport of cations from CS to the MS was prevented by the AEM, thereby preventing the cation transport from CS to the cathode solution (**FIG. 38C**). This mechanism is supported by the findings indicating the absence of the leakage of divalent cations in the ES during ED desalination with the EDM stack (**FIG. 37A** and **FIG. 37B**). As discussed above, no scaling was detected in the EDM stack (**FIG. 34A** to **FIG. 34F**).

[00193] **FIG. 40A** and **FIG. 40B** show changes in the pH of DS, CS, and MS as a function of as a function of desalination efficiency (DE) during desalination for different treated solutions. The observed pH changes in each solution provide additional evidence of the lack of scaling formation during the ED desalination of SW by the EDM stack (as described in the foregoing).

[00194] It has therefore been experimentally demonstrated that the proposed EDM configuration can effectively impede the transport of divalent cations into the electrode solution and prevent the formation of scaling around cathode.

[00195] Benefits

[00196] The experiments described above demonstrated the viability and improved performance of the proposed EDM stack, especially with respect to the mitigation of scaling during the ED desalination of high salinity solution containing scaling precursor ions. It was found that ED with the stack employing mediating chambers (EDM) can effectively mitigate scaling around the cathode during seawater desalination, while ED with the BED stack (i.e., the stack using a bipolar membrane to form the cathode chamber) or the SED stack (i.e., the stack using a monovalent selective cation exchange membrane to form the cathode chamber) were inadequate in preventing scaling formation. During ED operations with the BED stack and the SED stack, the transport of divalent cations from the feed

solution to the electrode solution was not fully blocked, and the water electrolysis at the cathode increased the concentration of OH^- in the cathode solution at the same time. These facilitated the formation of scaling, suggesting the failure of scaling mitigation through both the BED and SED configurations. Under the EDM stack condition, two mediating solutions chambers were introduced to separate the flow chambers for the treated solution containing multivalent cations and the electrode chambers. This arrangement slightly increased the system electrical resistance but successfully blocked the transport of divalent cations from seawater to the cathode solution, and prevented the formation of cathode scaling.

[00197] According to various embodiments, an electrodialysis stack includes a cathode, an anode, and a membrane stack, in which the membrane stack includes a first mediation chamber and a second mediation chamber. The cathode is disposed in an electrode solution in a cathode chamber. The anode is disposed in the electrode solution in an anode chamber. The membrane stack includes a plurality of chambers defined by a corresponding plurality of membranes. The plurality of membranes are alternately disposed ones of one or more cation exchange membranes and one or more anion exchange membranes. The first mediation chamber is interposed between the cathode chamber and a first chamber of the plurality of chambers. A first membrane of the membrane stack is disposed between a first stream in the first chamber and a mediation solution in the first mediation chamber. A cathode chamber membrane is disposed between the first mediation chamber and the cathode chamber. The second mediation chamber is interposed between the anode chamber and a last chamber of the plurality of chambers. A last membrane of the membrane stack is disposed between a last stream in the last chamber and a mediation solution in the second mediation chamber. An anode chamber membrane is disposed between the second mediation chamber and the anode chamber.

[00198] According to some embodiments, the electrodialysis stack is configured with the mediation solution and the electrode solution being similar with respect to anions present in the mediation solution and the electrode solution.

[00199] In some embodiments, the anions consist of monovalent ions and/or divalent ions.

[00200] According to some embodiments, each of the first membrane and the last membrane may be selected to block selected ions from transporting into the first mediation chamber and the second mediation chamber, respectively. In some embodiments, the first membrane may be a cation exchange membrane selected to block the selected anions from transporting from the first mediation chamber into the first chamber. In some embodiments, the last membrane may be a cation exchange membrane selected to block the selected anions from transporting from the last chamber into the last mediation chamber. In some embodiments, the cathode chamber membrane may be an anion exchange membrane, the anion exchange membrane being selected to block the selected cations from transporting into the cathode chamber.

[00201] According to some embodiments, the first mediation chamber and the second mediation chamber may be configured as respective ones of a dilute chamber and a concentrate chamber. According to some embodiments, the dilute chamber is one of the first mediation chamber and the second mediation chamber, and the concentrate chamber is another of the first mediation chamber and the second mediation chamber. According to some embodiments, ion transport of one or more selected ions is permitted across adjacent ones of a mediation chamber (e.g., first mediation chamber and second mediation chamber) and an electrode chamber (e.g., cathode chamber or anode chamber) at one end of the membrane stack and ion transport of the one or more selected ions is blocked across adjacent ones of another mediation chamber and another electrode chamber of the ED stack.

[00202] According to some embodiments, the first membrane may be a cation exchange membrane selected to block the selected anions from transporting from the first mediation chamber into the first chamber. The last membrane may be a cation exchange membrane selected to block the selected anions from transporting from the last chamber into the last mediation chamber.

[00203] According to some embodiments, the cathode chamber membrane may be an anion exchange membrane. The anion exchange membrane may be selected to block the selected cations from transporting into the cathode chamber.

[00204] According to some embodiments, the electrodialysis stack may be characterized in that similar anions are present in the mediation solution and in the electrode solution.

[00205] According to some embodiments, the first membrane may be an anion exchange membrane selected to block the selected cations from transporting from the first chamber into the first mediation chamber. The last membrane may be an anion exchange membrane selected to block the selected cations from transporting from the last mediation chamber into the last chamber.

[00206] According to some embodiments, the cathode chamber membrane may be a cation exchange membrane. The cation exchange membrane may be selected to allow the selected cations from transporting into the cathode chamber and block the anions from transporting into the first mediation chamber.

[00207] According to some embodiments, the electrodialysis stack may be characterized in that similar cations are present in the mediation solution and in the electrode solution.

[00208] According to some embodiments, the cathode chamber membrane may be selected to block the selected ions from transporting between the first mediation chamber and the cathode chamber.

[00209] According to some embodiments, a transport path of the selected ions from any one of the first stream and the last stream to the electrode solution in the respective one of the cathode chamber and the anode chamber may traverse across the respective one of the first mediation chamber and the second mediation chamber. In some embodiments, the mediation solution is a recirculating stream distinct from any one of the concentrate stream and the dilute stream flowing through respective ones of the plurality of chambers. In some embodiments, the mediation solution is a recirculating stream distinct from any one of a concentrate stream and a dilute stream flowing through respective ones of the plurality of chambers. Concurrently, ion transport of similar ones of the selected ions into the cathode chamber and the anode chamber is blocked. According to some embodiments, the selected ions are retained in a concentrate stream.

[00210] According to some embodiments, the electrodialysis stack may further include one or more monovalent selective cation exchange membranes and one or

more anion exchange membranes alternately disposed between the plurality of chambers. All of the one or more monovalent selective cation exchange membranes and all of the one or more anion exchange membranes may be disposed between the first mediation chamber and the second mediation chamber.

[00211] According to some embodiments, the one or more monovalent selective cation exchange membranes may be selected to block a transport of multivalent cations therethrough.

[00212] According to some embodiments, the electrodialysis stack may further include one or more monovalent selective anion exchange membranes and one or more cation exchange membranes alternately disposed between the plurality of chambers. All of the one or more monovalent selective anion exchange membranes and all of the one or more cation exchange membranes may be disposed between the first mediation chamber and the second mediation chamber.

[00213] According to some embodiments, the one or more monovalent selective anion exchange membranes may be selected to block a transport of multivalent anions therethrough.

[00214] According to some embodiments, the multivalent ions may include divalent ions.

[00215] According to some embodiments, the first mediation chamber may be formed by an anion exchange membrane paired with a cation exchange membrane.

[00216] According to some embodiments, the first stream may be a concentrate stream, in which the anion exchange membrane is selected to deter a transport of cations from the concentrate stream to the first mediation chamber. In some embodiments, the first stream may be a concentrate stream and the first membrane may be an anion exchange membrane, in which the anion exchange membrane is selected to deter a transport of divalent ions from the dilute concentrate stream to the first mediation chamber.

[00217] According to some embodiments, the first stream may be a dilute stream, and wherein the first membrane is a monovalent selective cation exchange membrane selected to deter a transport of anions from the dilute stream to the first mediation chamber. In some examples, the first stream is a dilute stream and the first membrane is a monovalent selective cation exchange membrane, in which the

monovalent selective cation exchange membrane is selected to deter a transport of divalent ions from the concentrate dilute stream to the first mediation chamber.

[00218] According to some embodiments, the selected ions may include divalent cations, in which a transport of the divalent cations into any one or both of the first mediation chamber and the second mediation chamber is blocked by the first membrane and the last membrane, respectively.

[00219] According to some embodiments, selected ones of the plurality of chambers may be configured to be concentrate chambers, and in which a concentrate stream in each of the concentrate chambers may be configured to be enriched with the selected ions.

[00220] According to some embodiments, selected ones of the plurality of chambers may be configured to be concentrate chambers, and in which a clean stripping solution may be flowable through each of the concentrate chambers to provide a stripping solution effluent stream enriched in the selected ions.

[00221] According to some embodiments, the electrodialysis stack may include a plurality of selective ion exchange membranes disposed between the plurality of chambers, in which the stripping solution effluent stream is clean of target ions and/or charged organic molecules.

[00222] According to some embodiments, large species are prevented from transporting from the dilute chambers into respective adjacent ones of the concentrate chambers, the large species being any one or more selected from the group consisting of multivalent ions, organic compounds, microorganisms, virus, and pathogens.

[00223] According to some embodiments, the electrodialysis stack may further include separate flow paths for each one of a mediating solution, a stripping solution, and a feed solution, in which the stripping solution and the feed solution are fed to alternate ones of the plurality of chambers, and in which the mediating solution is fed solely to the first mediation chamber and the second mediation chamber.

[00224] As illustrated in the schematic diagram of **FIG. 41**, the proposed electrodialysis stack may be implemented in various embodiments (e.g., including but not limited to, a first configuration, a second configuration, ..., nth configuration,

etc.), with the transport of selected ions (e.g., divalent cations and Cl^-) from the first stream and the last stream into (the mediation chambers and then into) the electrode chambers being blocked or prevented. In the proposed electrodialysis stack, the electrode solution can be essentially kept free of selected ions and/or species generally found to enable/promote fouling. The proposed electrodialysis stack includes: a cathode, the cathode being disposed in an electrode solution in a cathode chamber; an anode, the anode being disposed in the electrode solution in an anode chamber; and a membrane stack. The membrane stack includes: a plurality of chambers defined by a corresponding plurality of membranes, the plurality of membranes being alternately disposed ones of one or more cation exchange membranes and one or more anion exchange membranes; a first mediation chamber interposed between the cathode chamber and a first chamber of the plurality of chambers, a first membrane of the membrane stack being disposed between a first stream in the first chamber and a mediation solution in the first mediation chamber, a cathode chamber membrane being disposed between the first mediation chamber and the cathode chamber; and a second mediation chamber interposed between the anode chamber and a last chamber of the plurality of chambers, a last membrane of the membrane stack being disposed between a last stream in the last chamber and a mediation solution in the second mediation chamber, an anode chamber membrane being disposed between the second mediation chamber and the anode chamber.

[00225] In the proposed electrodialysis stack, a transport path of the selected ions from any one of the first stream and the last stream to the electrode solution in a respective one of the cathode chamber and the anode chamber is blocked by a respective one of the first mediation chamber and the second mediation chamber, and wherein the mediation solution is a recirculating stream distinct from any one of a concentrate stream and a dilute stream, the concentrate stream and the dilute stream being respective streams flowing through respective ones of the plurality of chambers.

[00226] In the proposed electrodialysis stack, a selected ion transport from the membrane stack into the electrode solution is blocked from occurring across at least

one of the following: (i) the cathode chamber membrane and/or the anode chamber membrane, and (ii) the first membrane and/or the last membrane.

[00227] All examples described herein, whether of apparatus, methods, materials, or products, are presented for the purpose of illustration and to aid understanding, and are not intended to be limiting or exhaustive. Modifications not involving inventive effort may be made by one of ordinary skill in the art without departing from the scope of the claimed invention.

CLAIMS

1. An electrodialysis stack, comprising:
 - a cathode, the cathode being disposed in an electrode solution in a cathode chamber;
 - an anode, the anode being disposed in the electrode solution in an anode chamber; and
 - a membrane stack, the membrane stack including:
 - a plurality of chambers defined by a corresponding plurality of membranes, the plurality of membranes being alternately disposed ones of one or more cation exchange membranes and one or more anion exchange membranes;
 - a first mediation chamber interposed between the cathode chamber and a first chamber of the plurality of chambers, a first membrane of the membrane stack being disposed between a first stream in the first chamber and a mediation solution in the first mediation chamber, a cathode chamber membrane being disposed between the first mediation chamber and the cathode chamber; and
 - a second mediation chamber interposed between the anode chamber and a last chamber of the plurality of chambers, a last membrane of the membrane stack being disposed between a last stream in the last chamber and a mediation solution in the second mediation chamber, an anode chamber membrane being disposed between the second mediation chamber and the anode chamber.
2. The electrodialysis stack as recited in claim 1, wherein a transport path of the selected ions from any one of the first stream and the last stream to the electrode solution in a respective one of the cathode chamber and the anode chamber is blocked by a respective one of the first mediation chamber and the second mediation chamber, and wherein the mediation solution is a recirculating stream distinct from any one of a concentrate stream and a dilute stream, the

concentrate stream and the dilute stream being respective streams flowing through respective ones of the plurality of chambers.

3. The electrodialysis stack as recited in claim 1 or claim 2, wherein a selected ion transport from the membrane stack into the electrode solution is blocked from occurring across at least one of the following: (i) the cathode chamber membrane and/or the anode chamber membrane, and (ii) the first membrane and/or the last membrane.

4. The electrodialysis stack as recited in any one of claims 1 to 3, wherein the mediation solution and the electrode solution are similar with respect to anions present in the mediation solution and the electrode solution.

5. The electrodialysis stack as recited in claim 4, wherein the anions consist of monovalent ions and/or divalent ions.

6. The electrodialysis stack as recited in any one of claims 1 to 5, wherein each of the first membrane and the last membrane is selected to block selected ions from transporting into the first mediation chamber and the second mediation chamber, respectively.

7. The electrodialysis stack as recited in claim 6, wherein the first membrane is a cation exchange membrane selected to block the selected anions from transporting from the first mediation chamber into the first chamber.

8. The electrodialysis stack as recited in claim 7, wherein the last membrane is a cation exchange membrane selected to block the selected anions from transporting from the last chamber into the last mediation chamber.

9. The electrodialysis stack as recited in claim 7, wherein the cathode chamber membrane is an anion exchange membrane, the anion exchange membrane being selected to block the selected cations from transporting into the cathode chamber.

10. The electrodialysis stack as recited in any one of claims 1 to 3, wherein the first membrane is an anion exchange membrane selected to block the selected cations from transporting from the first chamber into the first mediation chamber.

11. The electrodialysis stack as recited in claim 10, wherein the last membrane is an anion exchange membrane selected to block the selected cations from transporting from the last mediation chamber into the last chamber.

12. The electrodialysis stack as recited in claim 10, wherein the cathode chamber membrane is a cation exchange membrane, the cation exchange membrane being selected to allow the selected cations from transporting into the cathode chamber and block the anions from transporting into the first mediation chamber.

13. The electrodialysis stack as recited in any one of claims 10 to 12, characterized in that similar cations are present in the mediation solution and in the electrode solution.

14. The electrodialysis stack as recited in claim 7 or claim 10, wherein the cathode chamber membrane is selected to block the selected ions from transporting between the first mediation chamber and the cathode chamber.

15. The electrodialysis stack as recited in any one of claims 2 to 14, wherein the mediation solution is a recirculating stream distinct from any one of the concentrate stream and the dilute stream flowing through respective ones of the plurality of chambers.

16. The electrodialysis stack as recited in claim 15, further comprising one or more monovalent selective cation exchange membranes and one or more anion exchange membranes alternately disposed between the plurality of chambers, wherein all of the one or more monovalent selective cation exchange membranes

and all of the one or more anion exchange membranes are disposed between the first mediation chamber and the second mediation chamber.

17. The electrodialysis stack as recited in claim 16, wherein the one or more monovalent selective cation exchange membranes are selected to block a transport of multivalent cations therethrough.

18. The electrodialysis stack as recited in any one of claims 15 or 16, further comprising one or more monovalent selective anion exchange membranes and one or more cation exchange membranes alternately disposed between the plurality of chambers, wherein all of the one or more monovalent selective anion exchange membranes and all of the one or more cation exchange membranes are disposed between the first mediation chamber and the second mediation chamber.

19. The electrodialysis stack as recited in any one of claims 15 or 16, wherein the one or more monovalent selective anion exchange membranes are selected to block a transport of multivalent anions therethrough.

20. The electrodialysis stack as recited in claim 17, wherein the multivalent ions comprise divalent ions.

21. The electrodialysis stack as recited in any one of claims 6 to 13, wherein the first mediation chamber is formed by an anion exchange membrane paired with a cation exchange membrane.

22. The electrodialysis stack as recited in any one of claims 15 to 20, wherein the first stream is a concentrate stream and the first membrane is an anion exchange membrane, and wherein the anion exchange membrane is selected to deter a transport of divalent ions from the concentrate stream to the first mediation chamber.

23. The electrodialysis stack as recited in any one of claims 15 to 20, wherein the first stream is a dilute stream and the first membrane is a monovalent selective cation exchange membrane, and wherein the monovalent selective cation exchange membrane is selected to deter a transport of divalent ions from the dilute stream to the first mediation chamber.

24. The electrodialysis stack as recited in any one of claims 4 to 9, wherein the selected ions comprise divalent cations, and wherein a transport of the divalent cations into any one or both of the first mediation chamber and the second mediation chamber is blocked by the first membrane and the last membrane, respectively.

25. The electrodialysis stack as recited in claim 24, wherein selected ones of the plurality of chambers are configured to be concentrate chambers, and wherein a concentrate stream in each of the concentrate chambers is configured to be enriched with the selected ions.

26. The electrodialysis stack as recited in any one of claims 6 to 25, wherein selected ones of the plurality of chambers are configured to be concentrate chambers, and wherein a clean stripping solution is flowable through each of the concentrate chambers to provide a stripping solution effluent stream enriched in the selected ions.

27. The electrodialysis stack as recited in claim 26, comprising a plurality of selective ion exchange membranes disposed between the plurality of chambers, wherein the stripping solution effluent stream is clean of target ions and/or charged organic molecules.

28. The electrodialysis stack as recited in claim 27, wherein large species are prevented from transporting from the dilute chambers into respective adjacent ones of the concentrate chambers, the large species being any one or more selected

from the group consisting of multivalent ions, organic compounds, microorganisms, virus, and pathogens.

29. The electrodialysis stack as recited in any one of claims 1 to 25, further comprising separate flow paths for each one of a mediating solution, a stripping solution, and a feed solution, wherein the stripping solution and the feed solution are fed to alternate ones of the plurality of chambers, and wherein the mediating solution is fed solely to the first mediation chamber and the second mediation chamber.