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(71) Applicants: PANI CLEAN, INC. [US/US]; 2350 Flintshire View, Coralville, Iowa 52241 (US). **UNIVERSITY OF IOWA RESEARCH FOUNDATION** [US/US]; 2660 University Capitol Centre, 200 South Capitol Street, Iowa City, Iowa 52242 (US).

(72) Inventors: LEE, Joun; 2350 Flintshire View, Coralville, Iowa 52241 (US). **JAWAHAR HUSSAINI, Syed Mubeen**; 2350 Flintshire View, Coralville, Iowa 52241 (US). **CWIERTNY, David**; 2350 Flintshire View, Coralville, Iowa 52241 (US). **AL SAEDI, Abdulsattar**; 706 Carriage Hill, Apt#3, Iowa City, Iowa 52246 (US). **YOUNG, Timothy**; 2000 El Camino de al Luz, Santa Barbara, California 93109 (US).

(74) Agent: CHRISTENSON, Logan B. et al.; Workman Nydegger, 60 East South Temple, Suite 1000, Salt Lake City, Utah 84111 (US).

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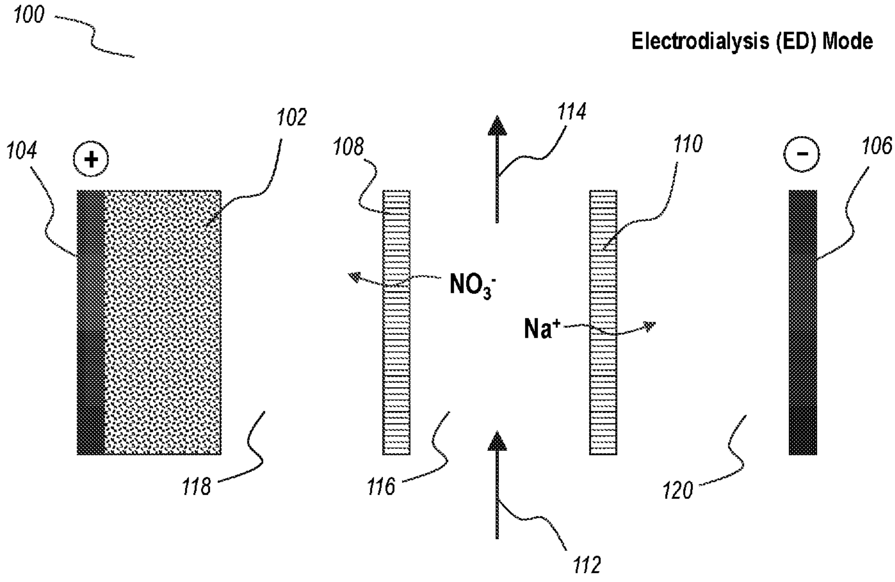

FIG. 1A

(57) Abstract: Disclosed are systems and processes for the removal and conversion of pollutants in water. A system includes a set of electrodes with at least one electrode having an integrated catalyst material. The system is operatable in a first, electrodialysis mode in which one or more pollutants are separated from a feedwater stream, and a second electrolysis mode in which the separated pollutant(s) are catalytically converted into benign products by way of the catalyst material of the electrode. Electrodialysis and electrolysis are therefore carried out using the same unit.

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HYBRID ELECTRODIALYSIS AND ELECTROLYSIS SYSTEMS AND PROCESSES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of United States Provisional Patent Application Serial No. 63/038,625, filed June 12, 2020, the entirety of which is incorporated herein by this reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under grant no. 2019-33610-29769 awarded by the United States Department of Agriculture, National Institute of Food and Agriculture. The government has certain rights in the invention.

BACKGROUND

[0003] Removal of pollutants from waters presents unique scientific, environmental and economic challenges. In the case of nitrate, currently, the US Environmental Protection Agency (EPA) lists ion-exchange resin (IX), reverse osmosis (RO) and electrodialysis (ED) as the state-of-the-art technologies for removal from waters. All the foregoing technologies produce highly concentrated brine residuals and are limited by expensive brine disposal and management requirements. Current options for brine disposal and management include evaporation in aeration ponds, deep well injection, direct release to sewers, and piping into oceans.

[0004] Brine disposal adds extra costs to the process of treating drinking water. For example, evaporation ponds for holding brines require substantially high maintenance costs and land usage. Injection wells can be a lower cost option, but their use raises environmental concerns. Moreover, environmental concerns are leading to tighter restrictions on surface and ocean releases of brine, and disposal costs are expected to rise accordingly.

[0005] Currently, IX and RO are the most common approaches for nitrate removal. However, for IX technologies, the possibility of competitive adsorption and the inefficient and energy-intensive regeneration processes have limited wide-spread adoption. For example, concentrated brine solutions used to regenerate spent resins are disposed after a single use, requiring ~6 g of salt per gallon of water treated. Such salt use can represent more than 70% of the financial burden, and more than 83% of the environmental impact, of adsorption-based processes.

[0006] For RO, a major limitation is the freshwater recovery rate. Typically, the freshwater recovery rate is approximately 50%-65%. In other words, 35%-50% of the output is concentrated brine. ED, on the other hand, offers higher water recovery rates (>85%). However, ED processes are limited by high capital and energy costs.

[0007] All the foregoing technologies suffer from brine disposal issues. For inland areas in particular, where cost-effective concentrate management options are not available, safe disposal of large volumes of concentrated brines impacts operation costs significantly. Biological denitrification, on the other hand, avoids brine management issues. However, current biological denitrification processes are limited by long start-up times, long recovery times, required post-treatment processes to remove biological sludge, high relative temperature sensitivity, and high physical footprint requirements.

[0008] Accordingly, there remains an ongoing need for systems and methods capable of effectively removing unwanted pollutants, such as nitrate, from water while minimizing or avoiding brine management issues associated with the current state of the art.

SUMMARY

[0009] Embodiments described herein include systems and processes for the removal of pollutants from water and their conversion to less harmful products. Certain embodiments are directed to systems configured to provide bi-functional operation in which (1) a first polarity provides an electrodialysis mode for removing one or more target pollutants from a feedwater stream, and (2) a second, reversed polarity provides an electrolysis mode for converting concentrated pollutant(s) to environmentally benign, less harmful, and/or value-added products. The electrodialysis and electrolysis modes are provided by the same system, thereby minimizing or negating the need for a separate, independent electrolysis system of other conversion system downstream of the electrodialysis system.

[0010] By reducing the need for separate, independent systems, the embodiments described herein beneficially provide increased operational and space efficiencies. Moreover, the electrodialysis mode functions to concentrate target pollutants at the active sites where effective conversion can occur during the subsequent electrolysis mode, thereby further increasing overall operational efficiencies.

[0011] In one embodiment, a system configured to provide both electrodialysis and electrolysis of a feedwater comprises a first electrode including a catalyst material associated therewith, a second electrode disposed opposite the first electrode, and one or

more ion exchange membranes disposed between the first and second electrodes. The one or more ion exchange membranes are arranged to define: (i) a feedwater compartment through which a feedwater flows during operation of the system, and (ii) a first ion concentration compartment, the first ion concentration compartment being adjacent to the first electrode such that during operation of the system an ion-concentrated stream contacts the first electrode.

[0012] The one or more ion exchange membranes may comprise at least one anion exchange membrane and at least one cation exchange membrane. In such embodiments, the feedwater compartment is disposed between the anion exchange membrane and the cation exchange membrane, an anion concentration compartment is disposed between the anion exchange membrane and whichever electrode has a positive charge during electrodialysis mode, and a cation concentration compartment is disposed between the cation exchange membrane and whichever electrode has a negative charge during electrodialysis mode.

[0013] In the example of nitrate treatment, the ion exchange membranes are arranged so that the anion concentration compartment is adjacent the first electrode, and the first electrode is operated with a positive charge during electrodialysis mode to attract and concentrate nitrate ions into the anion concentration compartment. During electrolysis mode, the polarity of the electrodes is reversed so that the first electrode now carries a negative charge. The negative charge enables the catalyst material of the first electrode to catalyze the conversion of concentrated nitrate into environmentally benign, less harmful, and/or value-added products (such as nitrogen gas).

[0014] In some embodiments, the second electrode can also include an integrated catalyst material. In such embodiments, both cation and anion contaminants can be removed from the feedwater and then converted in the subsequent electrolysis mode.

[0015] A method for removing one or more contaminants from a feedwater via electrodialysis and converting the one or more contaminants via electrolysis comprises the steps of: providing an electrodialysis and electrolysis system such as described above; operating the system in an electrodialysis mode by providing a first polarity across the first and second electrodes while passing the feedwater through the feedwater channel to thereby generate an ion-concentrated stream in the first ion concentration compartment; and operating the system in an electrolysis mode by reversing the polarity across the first and second electrodes, wherein the catalyst material, under the reversed polarity, catalyzes conversion of one or more ions concentrated in the first ion concentration compartment.

[0016] In some embodiments, the feedwater comprises nitrate, and the nitrate is removed from the feedwater and concentrated in the first ion concentration compartment during the electrodialysis mode. Subsequently, at least a portion of the concentrated nitrate is reduced to nitrogen gas upon reversing polarity during the electrolysis mode. In this example, the first electrode is operated with a positive charge during the electrodialysis mode and with a negative charge during the electrolysis mode.

[0017] This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the detailed description. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used as an indication of the scope of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Various objects, features, characteristics, and advantages of the invention will become apparent and more readily appreciated from the following description of the embodiments, taken in conjunction with the accompanying drawings and the appended claims, all of which form a part of this specification. In the Drawings, like reference numerals may be utilized to designate corresponding or similar parts in the various Figures, and the various elements depicted are not necessarily drawn to scale, wherein:

[0019] Figure 1A illustrates a system configured for removing one or more pollutants (nitrate, in this example) from a feedwater stream and converting the one or more pollutants to environmentally benign, less harmful, and/or value-added products, showing the system in an electrodialysis mode, with a first polarity setting, that functions to remove the pollutant(s) from the feedwater stream and concentrate the pollutant(s) at corresponding electrodes;

[0020] Figure 1B illustrates the system of Figure 1A in an electrolysis mode, with a reversed polarity setting, that functions to convert the concentrated pollutant(s) to environmentally benign, less harmful, and/or value-added products (converting nitrate to nitrogen gas, in this example);

[0021] Figure 1C illustrates an alternative embodiment in which both electrodes are associated with a catalyst portion, the system therefore being capable of removing different pollutants of opposite charge and using the electrodes to convert the different pollutants;

[0022] Figures 2A-2C illustrate results from electrochemical impedance spectroscopy (EIS) testing, showing series resistance results for different carbon materials (Figure 2A), charge transfer resistances for the tested carbon materials (Figure 2B), and electrochemically active surface area of the tested carbon materials (Figure 2C);

[0023] Figure 2D compares the desalination performance over time of a "3D" carbon foam electrode to a conventional platinum (Pt) planar electrode, showing that the 3D electrode achieved 86% desalination efficiency (DE) [(initial concentration – final concentration)/initial concentration] in 85 min, reached a target drinking water level, and had a 93% water recovery rate as compared to the planar electrode which achieved 33% demineralization efficiency without reaching the target drinking water level;

[0024] Figures 3A and 3B illustrate scanning electron microscope (SEM) images of Pd-Cu nanoparticles deposited on a carbon foam substrate using a co-electrodeposition method, with particle sizes ranging from about 100 nm to about 300 nm;

[0025] Figures 4A and 4B illustrate SEM images of palladium (Pd) nanoparticles deposited on copper (Cu) using a galvanic displacement method;

[0026] Figure 5A compares polarization curves of Pd-Cu electrocatalysts in different electrolytes (NaOH, NO_2, and NO_3);

[0027] Figure 5B compares polarization curves showing NO_3 reduction for different catalyst systems (Cu-Pd, Cu, and Pd);

[0028] Figure 6A illustrates results of a nitrate conversion test, showing operation of Pd-Cu nanoparticles at 3.2 V for over 100 hours; and

[0029] Figure 6B illustrates the proportions of products obtained in the nitrate conversion test for different catalysts utilized, showing that a Pd-Cu system had effective nitrate-to-nitrogen selectivity.

DETAILED DESCRIPTION

Overview of Electrodialysis/Electrolysis Systems

[0030] Embodiments described herein include systems and processes for the removal of pollutants from water and their conversion to less harmful products. Certain embodiments are directed to systems configured to provide bi-functional operation in which (1) a first polarity provides an electrodialysis mode for removing one or more target pollutants from a feedwater stream, and (2) a second, reversed polarity provides an electrolysis mode for converting concentrated pollutant(s) to environmentally benign, less harmful, and/or value-added products. The electrodialysis and electrolysis modes are provided by the same system, thereby minimizing or negating the need for a separate, independent electrolysis system of other conversion system downstream of the electrodialysis system.

[0031] Figures 1A and 1B illustrate an exemplary hybrid electrodialysis and electrolysis system 100. The illustrated system 100 includes a first electrode 104 and an opposing second electrode 106. At least one anion exchange membrane 108 and at least one cation exchange membrane 110 are disposed between the electrodes 104 and 106. Although only a single anion exchange membrane 108 and a single cation exchange membrane 110 are illustrated here, it will be understood that alternative embodiments may include multiples of either or both type of ion exchange membrane. Ion exchange membranes and other electrodialysis components as known in the art may be utilized, such as membranes components sold under the trade name NEOSEPTA (Astom Corp.) and components sold by PCCell Gmbh.

[0032] The ion exchange membranes 108 and 110 are spaced such that a feedwater compartment 116 in formed therebetween. The feedwater compartment 116 is configured to receive an inlet stream 112 (with high relative concentration of pollutant(s)) and to output an outlet stream 114 (with lowered concentration of pollutant(s)). The anion exchange membrane 108 and the first electrode 104 define an anion concentration compartment 118 formed therebetween. The cation exchange membrane 110 and the second electrode 106 define a cation concentration compartment 120 formed therebetween.

[0033] In electrodialysis mode operation (Figure 1A), one or more ions pass from the feedwater compartment 116 toward their respective electrodes of opposite charge. In the illustrated example, the first electrode 104 is provided with a positive charge and the second electrode 106 is provided with a negative charge. Referring to nitrate (a negatively charged ion) as an example pollutant targeted for removal, the nitrate passes from the feedwater compartment 116, through the anion exchange membrane 108, and into the anion concentration compartment 118, which is disposed adjacent to the first electrode 104. One or more types of cations (e.g., sodium ions) can pass from the feedwater compartment 116, through the cation exchange membrane 110, and into the cation concentration compartment 120, which is disposed adjacent the second electrode 106.

[0034] After the system 100 has operated in the electrodialysis mode for a first time period, the polarities of the electrodes 104 and 106 are reversed and the system 100 transitions to the electrolysis mode. Figure 1B illustrates the system 100 under operation in electrolysis mode. As shown, the polarities of electrodes 104 and 106 are reversed such that the first electrode is now negatively charged and the second electrode 106 is now positively charged.

[0035] As shown, the first electrode 104 includes a catalyst portion 102 connected and/or integrated thereto. The catalyst portion 102 incorporates one or more catalysts configured to provide conversion of the pollutant(s) that concentrate in the anion concentration compartment 118 to environmentally benign, less harmful, and/or value-added products. Continuing with the example of nitrate, nitrate concentrated in the anion concentration compartment 118 is reduced to less harmful nitrogen products such as nitrite, ammonia/ammonium, and/or (preferably) nitrogen gas. Corresponding oxidation reactions may occur at the second electrode 106 (e.g., water splitting).

[0036] A hybrid electrodialysis and electrolysis system such as illustrated beneficially combines the functions of pollutant removal and pollutant conversion into a single unit/system. This improves operational and space efficiencies as compared to using a dedicated electrodialysis system and a separate, downstream electrolysis system for denitrification. Moreover, because electrolytic energy efficiency and electrolytic rates are proportional to the localized concentration of the target pollutant, the pre-concentration of the pollutant in the direct vicinity of the catalyst portion 102 beneficially enables effective and efficient conversion within the same unit/system.

[0037] Figure 1C illustrates another embodiment of a hybrid electrodialysis and electrolysis system 200. The system 200 is similar in many respects to the hybrid electrodialysis and electrolysis system 100, and similarly includes first and second electrodes 204 and 206, an anion exchange membrane 208, and a cation exchange membrane 210. As with the system 100, these components are arranged to form a feedwater compartment 216 through which an inlet stream 212 and outlet stream 214 pass, an anion concentration compartment 218, and a cation concentration compartment 220. In this embodiment, both the first electrode 204 and the second electrode 206 are associated with respective catalyst portions 202 and 205. The system 200 is therefore capable of removing different pollutants of opposite charge (in electrodialysis mode) and then using both electrodes to convert the different pollutants to environmentally benign, less harmful, and/or value-added products (in electrolysis mode).

Additional Electrode & Catalyst Details

[0038] The following features can be incorporated individually or in combination with one or more of the other features into the hybrid electrodialysis and electrolysis systems described herein (including system 100 and/or system 200).

[0039] Various substrates may be utilized to form one or both electrodes of the hybrid electrodialysis and electrolysis system. Suitable electrode substate materials include graphite, nickel, copper, iron, polytetrafluoroethylene (PTFE) membrane materials, carbon (e.g., activated carbon, carbon nanotubes), transparent conductive oxides, and combinations thereof. The form of the substrate is preferably configured to provide a high surface area. For example, the substrate may be configured as a mesh, felt, foamed structure, or other porous material. In systems where only one electrode includes a catalytic portion, the counter electrode may be formed from a simple conductive material such as stainless steel.

[0040] Where a porous substrate is utilized, the pores preferably have an average diameter of about 100 μm to about 1 mm, or more preferably about 200 μm to about 800 μm, or about 300 μm to about 700 μm, or about 350 μm to about 650 μm, or about 400 μm to about 600 μm, such as about 500 μm, or within a range having any two of the foregoing values as endpoints. A porous electrode substrate with an average pore diameter within the foregoing values was found to optimally balance sufficient charge transfer capabilities with high surface areas and ability to effectively integrate catalyst material therein.

[0041] Further, when a porous substrate is utilized, the substrate is preferably configured with a pore density of about 20 to about 200 pores per square inch (ppi), or more preferably about 25 ppi to about 150 ppi, or about 30 ppi to about 120 ppi, or about 35 ppi to about 100 ppi, or about 40 ppi to about 80 ppi, or about 50 ppi to about 70 ppi, such as about 60 ppi, or a pore density within a range defined by any two of the foregoing values. A substrate with a pore density within the foregoing values was found to provide sufficiently low charge transfer resistance while also providing sufficiently high electrochemically active surface area.

[0042] The catalyst associated with one or more of the electrodes to form the catalyst portion(s) may be provided as nanoparticles that are embedded or otherwise incorporated into the corresponding electrodes. For example, where the electrode substrate is formed as a porous material, catalyst nanoparticles may be distributed and embedded within the porous surfaces of the substrate to take advantage of the increased surface area provided by the porous structure.

[0043] Suitable catalyst materials for nitrate reduction (but which may be additionally or alternatively used for other pollutants) include Cu, Pd-Cu, Ni, Zn-Cu, Pt, Rh, Pt-Rh, Pd-Cu, Pt-Cu, Rh-Cu, Ir-Cu, Sn-Pt, Sn-Pd-Au, Pd-Sn, Pd-Cu, Pd-In, Fe-Ni, Pd, Ag, Au, Ru, Ir, metal oxides, metal hydroxides, and combinations thereof.

[0044] Exemplary electrode substrates and catalysts, and certain exemplary combinations of electrode substrates and catalysts that may be utilized together in a hybrid electrodialysis and electrolysis system, are provided below in Table 1:

Table 1

Substrate material	**Catalyst**
Graphite	Cu and Pd-Cu
Ni	Ni particles
	Zn-Cu Alloy
Cu	Cu
PTFE Membrane	Pt
PTFE Membrane	Rh
PTFE Membrane	Pt-Rh alloy
Activated Carbon	Pd-Cu, Pt-Cu, Rh-Cu, and Ir-Cu
	Sn-Pt, and Sn-Pd-Au
Graphite	Pt
Ni	Cu
Cu	Cu
Ni Foam	Cu
ITO	Pd-Sn
Carbon Nanotube (CNT)	Pd-Cu
CNT-TiO2	Pd-Cu
Lignocellulose	Pd-In
Activated Carbon felt	Pd-Cu
Fe	Fe
Fe	Pd
Fe	Ag

[0045] Catalyst nanoparticles may be loaded onto the electrode substrate using a variety of integration or deposition methods known in the art. In some embodiments, electrodeposition is utilized to deposit the catalyst nanoparticles. In some embodiments where a multi-metallic catalyst is utilized, each metal may be electrodeposited using a co-electrodeposition technique. Alternatively, a galvanic displacement technique may be utilized wherein a base metal (having a relatively higher oxidation potential) is first deposited on the substrate, and subsequently a second metal (having a relatively lower oxidation potential) is introduced to galvanically displace the first metal. The mass loading of catalyst nanoparticles to the electrode substrate may range from about 0.05 $mg_{catalyst}/cm^2$ to about 0.25 or up to about 0.5 $mg_{catalyst}/cm^2$.

[0046] The size of the catalyst nanoparticles integrated with the electrode substrate may vary according to particular application needs. Catalyst nanoparticles may range in average size from about 2 nm to about 500 nm, more typically about 10 nm to about 300 nm, or about 15 nm to about 200 nm, or about 20 nm to about 100 nm, or may have an average size within a range with endpoints defined by any two of the foregoing values. Systems utilizing catalyst nanoparticles within the foregoing size ranges were found to provide effective surface area and catalytic activity while also balancing the ability to effectively integrate the nanoparticles into the pores of the electrode substrate.

Exemplary Water Treatment Applications

[0047] The hybrid electrodialysis and electrolysis systems described herein may be utilized in a variety of water treatment applications. For nitrate removal and conversion applications, such systems can be installed as an edge-of-field installation for fields that are drained using tiles. The systems can then treat nitrate-laden waters prior to discharge from the field into surface waters. Systems can also be utilized to treat community water systems or to treat private water supplies (e.g., private groundwater wells). Presently, in the U.S., there are over 1,700 community drinking water systems with nitrate levels higher than 10 mg/L. Many private wells have nitrate levels above recommended health advisory levels, particularly in agricultural areas.

[0048] Although many of the examples described herein relate to nitrate removal and conversion, the components and principles described herein may also be utilized for the removal and conversion of a wide variety of other chemical and/or biological contaminants/pollutants. A non-exhaustive list of such chemical contaminants includes nitrogen, bleach, salts, pesticides, metals, toxins produced by bacteria, nitrate (NO3), chloride (Cl), chromium-6 (Cr-6), chromium-3 (Cr-6), copper (Cu), fluoride (F), iron (Fe), selenium (VI), boron, lithium (Li), sodium (Na), calcium (Ca), magnesium (Mg), zinc (Zn), arsenic (As), uranium (U), strontium (Sr), cadmium (Cd), cyanide (CN), nitrite (NO2), phosphate, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), 1,1-dichloroethane, acetochlor, methyl bromide (bromomethane), metolachlor, nitrobenzene, 1,4-Dioxane, 1,2,3-trichloropropane, and chloroamine.

[0049] A non-exhaustive list of medicinal pollutants that may be removed from feedwater and converted using the systems described herein includes aspirin, codeine, cyclophosphamide, galaxolide, pentoxifylline, tonalide, triclosan, etofibrate, etofyllinclofibrat, flurbiprofen, ketoprofen, nadolol, tolfenamic acid, carbamazepine, diazepam, ibuprofen, paracetamol, phenazone, bezafibrate, clofibrate, diclofenac, fenoprofen, fenofibrate, femfibrozil, indomethacine, iopromide, mefenamic acid, metoprolol, naproxen, propranolol, propyphenazone, roxithromycin, salbutamol, sulfamethoxazole, doxycycline, estrone, hydrochlorothiazide, iopamidol, metronidazole, ofloxacin, enalapril, furazolidone, ifosfamide, ketorolac, methicillin, nafcillin, erythromycin, furosemide, iomeprol, lincomycin, methotrexate, norfloxacin, oleandomycin, simvastatin, sotalol, omeprazole, oxacillin, oxytetracycline, penicillin, pindolol, piroxicam, ranitidine, ronidazole, spiramycin, sulfacetamide, sulfadiazine, sulfadiamethoxine, sulfadimidine, sulfafuanidine, sulfamethazine, sulfamethazine, sulfapyridine, sulfasalazine, sulfathiazine, tamoxifen, terbutaline, tetracycline, tilmicosin, trimethoprim, tylosin, virginiamycin, 17α-ethinylestradiol, 17β-estradiol, acetyl-sulfamethoxazole, amidotrizoic acid, aminopyridine, amoxycillin, anhydro-erythromycin, atenolol, bisoprolol, chloramphenicol, chlortetracycline, ciprofloxacin, clarithromycin, clenbuterol, cloxacillin, cyclophosphamide, dapsone, dimethyl diazepam, dextropropoxyphene, dicloxacillin, acetaminophen, and carbamazepine.

[0050] A non-exhaustive list of biological contaminants/pollutants that may be removed from feedwater and optionally destroyed using the systems described herein includes pathogenic microorganisms (viruses, bacteria, fungi, protozoa) and DNA and RNA contaminants. Common feedwater pathogens of concern include adenoviruses, caliciviruses, *Campylobacter jejuni*, enteroviruses, *Escherichia coli*, *Helicobacter pylori*, hepatitis A virus, *Legionella pneumophila*, *Mycobacterium avium*, *Naegleria fowleri*, and *Salmonella enterica*.

[0051] Table 2 provides a particular list of example contaminants that can be removed using the systems described herein, along with the present maximum contaminant level (MCL) as established by the U.S. Environmental Protection Agency (EPA), potential negative health effects associated with the contaminant, and common sources of the contaminant:

Table 2

Contaminants	MCL (mg/L)	Potential health effects	Common source
Nitrate (NO3-)	10	Infants could become seriously ill and, if untreated, may die. (blue-baby syndrome)	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits

Chloride (Cl)	4	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Chromium-6 (Cr-6)	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Chromium-3 (Cr-6	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper (Cu)	1.3	Short-term exposure: Gastrointestinal distress. Long-term exposure: Liver or kidney damage	Corrosion of household plumbing systems; erosion of natural deposits
Fluoride (F)	4	Bone disease (pain and tenderness of the bones); children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Iron (Fe)	0.3		
Selenium (VI)	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum and metal refineries; erosion of natural deposits; discharge from mines
Boron	0.5		
Lithium			
Sodium (Na)	200 (WHO limit)		
Calcium			
Magnesium			
Zinc	5		
Arsenic (As)	0.01	Skin damage or problems with circulatory systems, increased risk of cancer	Erosion of natural deposits; runoff from orchards; runoff from glass & electronics production wastes
Uranium	30 µg/L	Increased risk of cancer, kidney toxicity	Erosion of natural deposits
Strontium			
Cadmium	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Cyanide	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories
Nitrite (NO_2^-)	1	Similar to risks of nitrate	Runoff from fertilizer use; leaching from septic tanks,

			sewage; erosion of natural deposits
Phosphate			Runoff from fertilizer use; erosion of natural deposits

Examples

Example 1: Electrode Substrate Testing

[0052] Various carbon supports (carbon foam, carbon cloth, carbon felt; available from vendor Fuel Cell Store), and their electroactivity (charge transfer resistance) was characterized using AC EIS. The EIS for these carbon supports was recorded in 0.1M H_2SO_4 at the open-circuit voltage in the frequency range of 1 MHz to 1 Hz with a 10-mV peak-to-peak sinusoidal potential perturbation. Saturated silver/silver chloride was used as the reference electrode and Pt wire as the counter electrode.

[0053] All carbon materials showed similar uncompensated series resistances (from 1.4 to 4.4-ohm cm^2) as measured from the EIS, indicating the robustness of the measurement set-up (Figure 2A). We then determined the charge transfer resistances from EIS for the carbon materials tested (Figure 2B). Lower charge transfer resistance corresponds to a faster electron transfer rate (faster reaction rate), a key attribute for electrocatalysis. Our target was to achieve charge transfer resistances <100-ohm cm^2, suitable for effective electrolysis applications. Carbon felt and carbon foam with 60 ppi met this criterion. Another important characteristic of electroactive support is its electrochemically active surface area. For typical electrolysis applications, this value is preferred to be >10 when normalized with its geometric area. Carbon felt and carbon foam with 60 and 100 ppi met this criterion (Figure 2C).

Example 2: Comparison of Porous Carbon Electrode to Planar Platinum Electrode

[0054] A porous carbon electrode was also compared to a planar Pt electrode. Figure 2D compares the desalination performance over time of a “3D” carbon foam electrode to a conventional planar Pt electrode, showing that the 3D electrode achieved 86% desalination efficiency (DE) [(initial concentration – final concentration)/initial concentration] in 85 min, reached a target drinking water level, and had a 93% water recovery rate as compared to the planar electrode which achieved 33% demineralization efficiency without reaching the target drinking water level. The comparison was conducted using a flow rate of 400 ml/min and a voltage of 2.6 V.

Example 3: Integration of Catalyst Material with Electrode Substrate

[0055] We developed various synthetic routes to deposit catalysts (Pd, Cu, and Pd-Cu bimetallic systems) on carbon substrates. Pd and Cu were selected as most likely to have high selectivity for nitrate reduction. Electrodeposition allows the synthesis of catalysts directly on the most accessible electroactive sites of the support substrate, thereby increasing catalyst utilization efficiency.

[0056] For bimetallic systems, two synthetic techniques were employed. The first technique utilized the co-electrodeposition of both metals in one single step. In the second technique, a base metal was first electrodeposited (Cu), which was then galvanically displaced by the second metal (Pd) having a lower oxidation potential than the displaced metal (Cu). While co-electrodeposition benefits from simplicity, electrodeposition followed by galvanic displacement enables good spatial for the deposition of the second metal. All synthesized catalysts were characterized for their morphology and elemental composition using SEM and energy dispersive spectroscopy (EDS).

[0057] Figures 3A and 3B illustrate SEM images of Pd-Cu nanoparticles deposited on a carbon foam substrate using the co-electrodeposition method, with particle sizes ranging from about 100 nm to about 300 nm. Figures 4A and 4B illustrate SEM images of Pd nanoparticles deposited on copper Cu using the galvanic displacement method.

Example 4: Nitrate Reduction Using Different Catalyst Systems

[0058] Nitrate reduction studies were conducted in 30 mM $NaNO_3$ in 0.1M NaOH electrolyte using a half-cell two-compartment electrochemical set-up. For control, electrochemical reduction studies were also carried out in 0.1M NaOH electrolyte and 0.1M NaOH with 30 mM $NaNO_2$ electrolyte.

[0059] The catalytic activity of the Pd-Cu electrocatalyst for nitrate reduction was evaluated by linear sweep voltammetry measurements at 5 mV/s in N_2-saturated 0.1M NaOH electrolyte with 30 mM NaNO3 electrolyte, and the data are compared in the absence of nitrate ion concentration. Nitrogen was purged to minimize currents originating from the reduction of dissolved oxygen. As seen in Figure 5A, a clear increase in reduction reaction currents was observed in the presence of nitrate ion concentration as the potential was scanned from -0.2V to -1.0 V vs. mercury/mercury oxide reference electrode. Potentials more negative than -1.0 V were not chosen to minimize hydrogen evolution due to water reduction reaction. The Pd-Cu system also showed an increase in reduction currents in the presence of nitrite ions. Interestingly, higher activity was obtained for nitrate reduction compared to nitrite reduction for potentials more negative than -0.8 V.

[0060] Figure 5B shows the effect of the catalytic system on nitrate reduction. Three different catalytic systems were compared: Pd; Cu; and Pd-Cu. Although both Pd and Cu showed some nitrate reduction currents, the Pd-Cu system provided the greatest effects, showing that a bifunctional/bimetallic catalyst can provide efficient electrochemical reduction of nitrates.

Example 5: Nitrate Reduction Conversion Efficiency

[0061] The Pd-Cu catalyst was then integrated into a half-cell configuration and tested for its stability for nitrate conversion under accelerated testing conditions (1 kA/m^2 = 100 mA/cm^2). Testing was conducted in 0.1 M $NaNO_3$ neutral electrolyte using an in-house half-cell two-compartment electrochemical set-up. Figure 6A shows operation of the Pd-Cu nanoparticles at 3.2 V for over 100 hours. This voltage was chosen so the obtained currents are greater than 100 mA/cm^2. After 100 hours of operation, we tested the products obtained from different catalyst materials synthesized (Figure 6B). Pd and Cu showed about 40% selectivity for N_2 production and produced nitrite and hydrogen as the co-products. In contrast, Pd-Cu nanoparticles showed very effective nitrate-to-nitrogen selectivity, reaching a nitrogen conversion efficiency of 84% after 100 hours of operation.

Example 6: Nitrate Removal from Different Feedwaters

[0062] We assessed the performance of the electrode assembly described in the previous Examples in different feed water sources listed in Table 3. For each feedwater chemistry, nitrate removal in electrodialysis mode, nitrate-to-nitrogen conversion in electrolysis mode, and freshwater recovery were experimentally determined. The initial nitrate concentration was 1000 mg/L and the temperature was maintained at 26°C.

Table 3

Feed	Sodium	Bicarbonate	Sulfate	Nitrate removal from ED	Nitrate Conversion	Fresh water recovery
1	500	500	100	97	84	94
2	2000	2000	500	98	82	97
3	5000	5000	1000	97	79	93
	Caclium	Sulfate	Na+Mg	Nitrate removal from ED	Nitrate Conversion	Fresh water recovery
4	500	500	100	95	82	92
5	2000	2000	500	98	88	91
6	5000	5000	1000	95	79	90
	Sodium	Chloride		Nitrate removal from ED	Nitrate Conversion	Fresh water recovery
7	500	500		97	86	96
8	2000	2000		98	83	97
9	5000	5000		89	74	95
	Silica	Sodium+Chloride		Nitrate removal from ED	Nitrate Conversion	Fresh water recovery
7	0.5	1000		94	80	95
8	1	2000		98	78	93
9	2.5	5000		89	71	95

[0063] Table 3 shows that for all different feed water chemistries tested, we were able to achieve freshwater recovery of 85% and higher. We were also able to achieve nitrate-to-nitrogen conversion efficiencies >75% for all feed water chemistries, the only exception being feedwaters with chloride ion concentration equal to 5000 mg/L.

Additional Terms & Definitions

[0064] While certain embodiments of the present disclosure have been described in detail, with reference to specific configurations, parameters, components, elements, etcetera, the descriptions are illustrative and are not to be construed as limiting the scope of the claimed invention.

[0065] Furthermore, it should be understood that for any given element of component of a described embodiment, any of the possible alternatives listed for that element or component may generally be used individually or in combination with one another, unless implicitly or explicitly stated otherwise.

[0066] In addition, unless otherwise indicated, numbers expressing quantities, constituents, distances, or other measurements used in the specification and claims are to be understood as optionally being modified by the term “about” or its synonyms. When the terms “about,” “approximately,” “substantially,” or the like are used in conjunction with a stated amount, value, or condition, it may be taken to mean an amount, value or condition that deviates by less than 20%, less than 10%, less than 5%, less than 1%, less than 0.1%, or less than 0.01% of the stated amount, value, or condition. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0067] Any headings and subheadings used herein are for organizational purposes only and are not meant to be used to limit the scope of the description or the claims.

[0068] It will also be noted that, as used in this specification and the appended claims, the singular forms “a,” “an” and “the” do not exclude plural referents unless the context clearly dictates otherwise. Thus, for example, an embodiment referencing a singular referent (e.g., “widget”) may also include two or more such referents.

[0069] It will also be appreciated that embodiments described herein may also include properties and/or features (e.g., ingredients, components, members, elements, parts, and/or portions) described in one or more separate embodiments and are not necessarily limited strictly to the features expressly described for that particular embodiment. Accordingly, the various features of a given embodiment can be combined with and/or incorporated into other embodiments of the present disclosure. Thus, disclosure of certain features relative to a specific embodiment of the present disclosure should not be construed as limiting application or inclusion of said features to the specific embodiment. Rather, it will be appreciated that other embodiments can also include such features.

CLAIMS

1. A system configured to provide both electrodialysis and electrolysis of a feedwater, the system comprising:

a first electrode including a catalyst material associated therewith;

a second electrode disposed opposite the first electrode;

one or more ion exchange membranes disposed between the first and second electrodes so as to define:

a feedwater compartment through which a feedwater flows during operation of the system, and

a first ion concentration compartment, the first ion concentration compartment being adjacent to the first electrode such that during operation of the system an ion-concentrated stream contacts the first electrode.

2. The electrodialysis and electrolysis system of claim 1, wherein the one or more ion exchange membranes comprises at least one anion exchange membrane and at least one cation exchange membrane.

3. The electrodialysis and electrolysis system of claim 2, wherein the feedwater compartment is disposed between the anion exchange membrane and the cation exchange membrane.

4. The electrodialysis and electrolysis system of claim 3, wherein the first ion concentration compartment is an anion concentration compartment and is disposed between the anion exchange membrane and the first electrode.

5. The electrodialysis and electrolysis system of claim 4, further comprising a second ion concentration compartment disposed between the cation exchange membrane and the second electrode, wherein the second ion concentration compartment is a cation concentration compartment.

6. The electrodialysis and electrolysis system of claim 5, wherein the second electrode also includes a catalyst material associated therewith.

7. The electrodialysis and electrolysis system of claim 3, wherein the first ion concentration compartment is a cation concentration compartment and is disposed between the cation exchange membrane and the first electrode.

8. The electrodialysis and electrolysis system of claim 6, further comprising a second ion concentration compartment disposed between the anion exchange membrane and the second electrode, wherein the second ion concentration compartment is an anion concentration compartment.

9. The electrodialysis and electrolysis system of claim 8, wherein the second electrode also includes a catalyst material associated therewith.

10. The electrodialysis and electrolysis system of any one of claims 1-9, wherein the first electrode is formed from a porous substrate.

11. The electrodialysis and electrolysis system of claim 10, wherein the porous substrate is carbon.

12. The electrodialysis and electrolysis system of claim 10 or claim 11, wherein pores of the porous substrate have an average diameter of about 100 μm to about 1 mm.

13. The electrodialysis and electrolysis system of any one of claims 10-12, wherein the porous substrate has a pore density of about 20 to about 200 pores per square inch (ppi).

14. The electrodialysis and electrolysis system of any one of claims 1-13, wherein the catalyst material comprises one or more of Cu, Pd-Cu, Ni, Zn-Cu, Pt, Rh, Pt-Rh, Pd-Cu, Pt-Cu, Rh-Cu, Ir-Cu, Sn-Pt, Sn-Pd-Au, Pd-Sn, Pd-Cu, Pd-In, Fe-Ni, Pd, Ag, Au, Ru, Ir, metal oxides, metal hydroxides, or combinations thereof.

15. The electrodialysis and electrolysis system of any one of claims 1-14, wherein the catalyst material comprises catalyst nanoparticles deposited on surfaces of the first electrode.

16. A method of removing one or more contaminants from a feedwater via electrodialysis and converting the one or more contaminants via electrolysis, the method comprising:

providing an electrodialysis and electrolysis system that includes

a first electrode including a catalyst material associated therewith;

a second electrode disposed opposite the first electrode; and

one or more ion exchange membranes disposed between the first and second electrodes so as to define (i) a feedwater compartment, and (ii) a first ion concentration compartment, the first ion concentration compartment being adjacent to the first electrode;

operating the system in an electrodialysis mode by providing a first polarity across the first and second electrodes while passing the feedwater through the feedwater channel to thereby generate an ion-concentrated stream in the first ion concentration compartment; and

operating the system in an electrolysis mode by reversing the polarity across the first and second electrodes, wherein the catalyst material, under the reversed polarity, catalyzes conversion of one or more ions concentrated in the first ion concentration compartment.

17. The method of claim 16, wherein the one or more contaminants comprise one or more of nitrogen, bleach, salts, pesticides, metals, toxins produced by bacteria, nitrate (NO3), chloride (Cl), chromium-6 (Cr-6), chromium-3 (Cr-6), copper (Cu), fluoride (F), iron (Fe), selenium (VI), boron, lithium (Li), sodium (Na), calcium (Ca), magnesium (Mg), zinc (Zn), arsenic (As), uranium (U), strontium (Sr), cadmium (Cd), cyanide (CN), nitrite (NO2), phosphate, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), 1,1-dichloroethane, acetochlor, methyl bromide (bromomethane), metolachlor, nitrobenzene, 1,4-Dioxane, 1,2,3-trichloropropane, or chloroamine.

18. The method of claim 16 or claim 17, wherein the one or more contaminants comprise one or more of aspirin, codeine, cyclophosphamide, galaxolide, pentoxifylline, tonalide, triclosan, etofibrate, etofyllinclofibrat, flurbiprofen, ketoprofen, nadolol, tolfenamic acid, carbamazepine, diazepam, ibuprofen, paracetamol, phenazone, bezafibrate, clofibrate, diclofenac, fenoprofen, fenofibrate, femfibrozil, indomethacine, iopromide, mefenamic acid, metoprolol, naproxen, propranolol, propyphenazone, roxithromycin, salbutamol, sulfamethoxazole, doxycycline, estrone, hydrochlorothiazide, iopamidol, metronidazole, ofloxacin, enalapril, furazolidone, ifosfamide, ketorolac, methicillin, nafcillin, erythromycin, furosemide, iomeprol, lincomycin, methotrexate, norfloxacin, oleandomycin, simvastatin, sotalol, omeprazole, oxacillin, oxytetracycline, penicillin, pindolol, piroxicam, ranitidine, ronidazole, spiramycin, sulfacetamide, sulfadiazine, sulfadiamethoxine, sulfadimidine, sulfafuanidine, sulfamethazine, sulfamethazine, sulfapyridine, sulfasalazine, sulfathiazine, tamoxifen, terbutaline, tetracycline, tilmicosin, trimethoprim, tylosin, virginiamycin, 17α-ethinylestradiol, 17β-estradiol, acetyl-sulfamethoxazole, amidotrizoic acid, aminopyridine, amoxycillin, anhydro-erythromycin, atenolol, bisoprolol, chloramphenicol, chlortetracycline, ciprofloxacin, clarithromycin, clenbuterol, cloxacillin, cyclophosphamide, dapsone, dimethyl diazepam, dextropropoxyphene, dicloxacillin, acetaminophen, or carbamazepine.

19. The method of any one of claims 16-18, wherein the one or more contaminants comprise one or more of viruses, bacteria, fungi, protozoa, or DNA or RNA contaminants.

20. The method of claim 19, wherein the one or more contaminants comprise one or more of adenovirus, caliciviruses, *Campylobacter jejuni*, enterovirus, *Escherichia coli*,

Helicobacter pylori, hepatitis A virus, *Legionella pneumophila*, *Mycobacterium avium*, *Naegleria fowleri*, and *Salmonella enterica*.

21. The method of any one of claims 16-20, wherein the electrodialysis and electrolysis system is a system as in any one of claims 1-15.

22. The method of any one of claims 16-21, wherein the first polarity during the electrodialysis mode provides a positive charge to the first electrode to thereby attract negative ions thereto.

23. The method of claim 22, wherein the feedwater comprises nitrate, and wherein nitrate is removed from the feedwater and concentrated in the first ion concentration compartment during the electrodialysis mode and subsequently at least a portion of the concentrated nitrate is then reduced to nitrogen gas upon reversing polarity during the electrolysis mode.

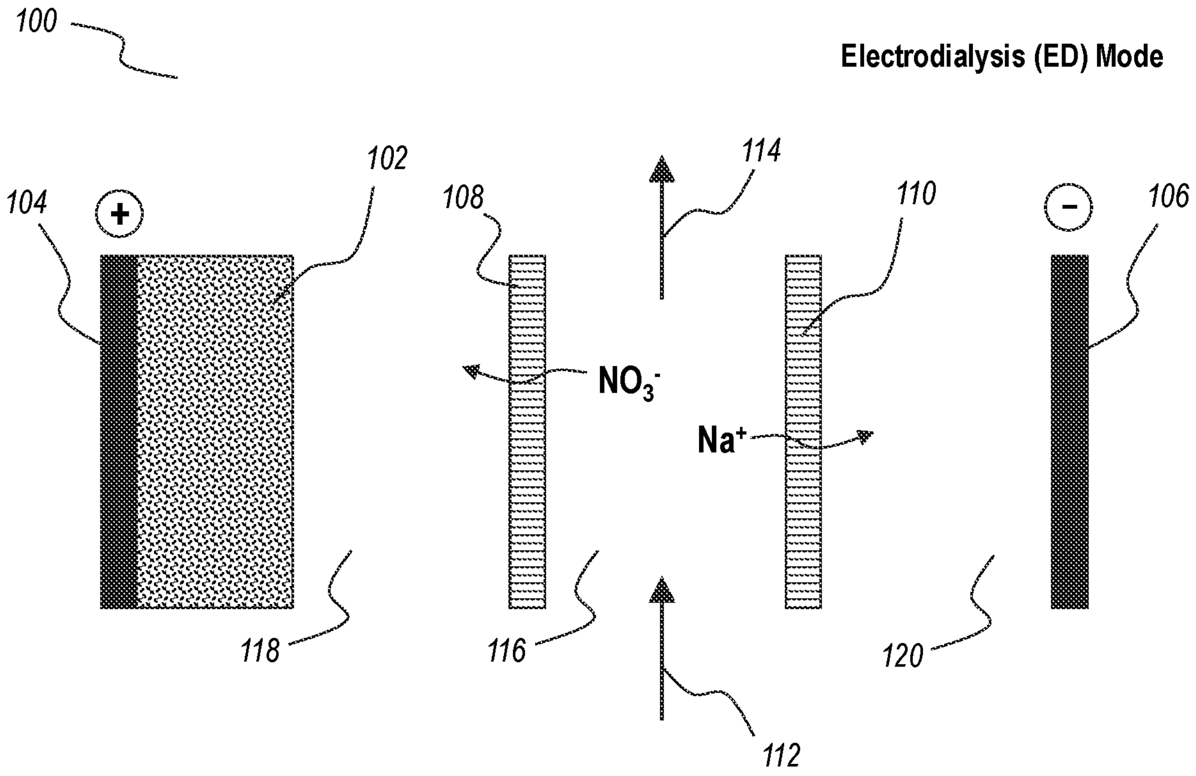

100
Electrodialysis (ED) Mode
104
+
102
108
114
110
−
106
NO_3^-
Na^+
118
116
120
112

FIG. 1A

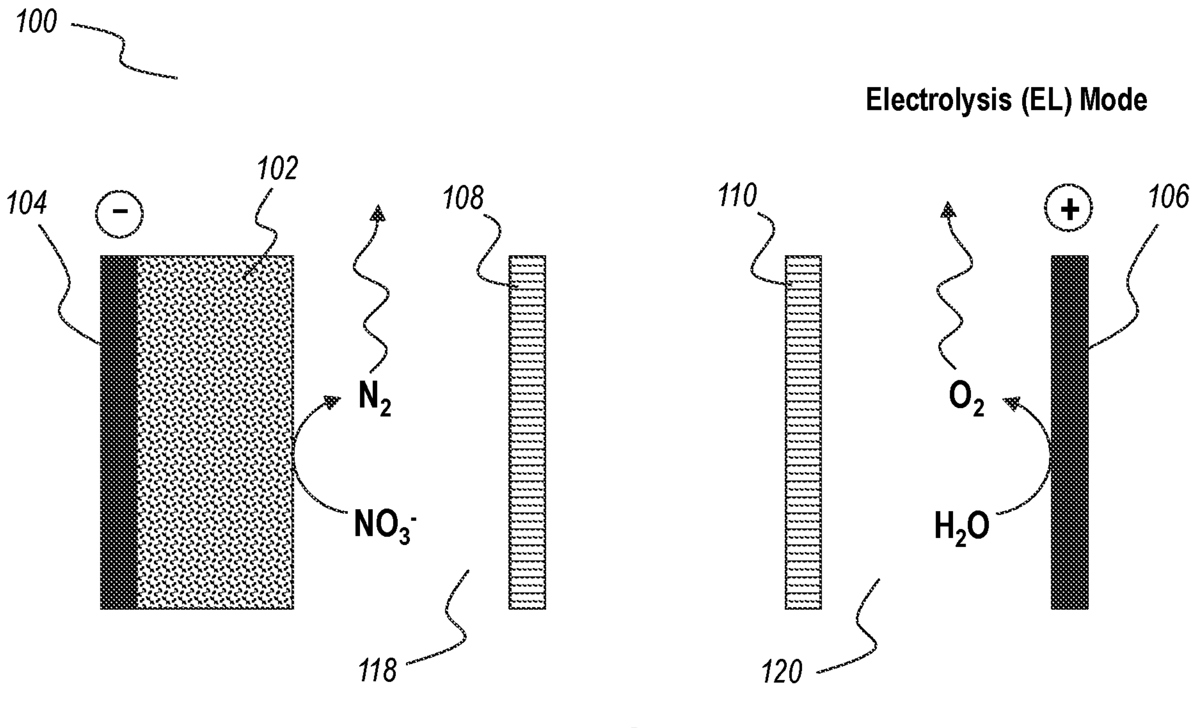

100
Electrolysis (EL) Mode
104
−
102
108
110
+
106
N_2
O_2
NO_3^-
H_2O
118
120

FIG. 1B

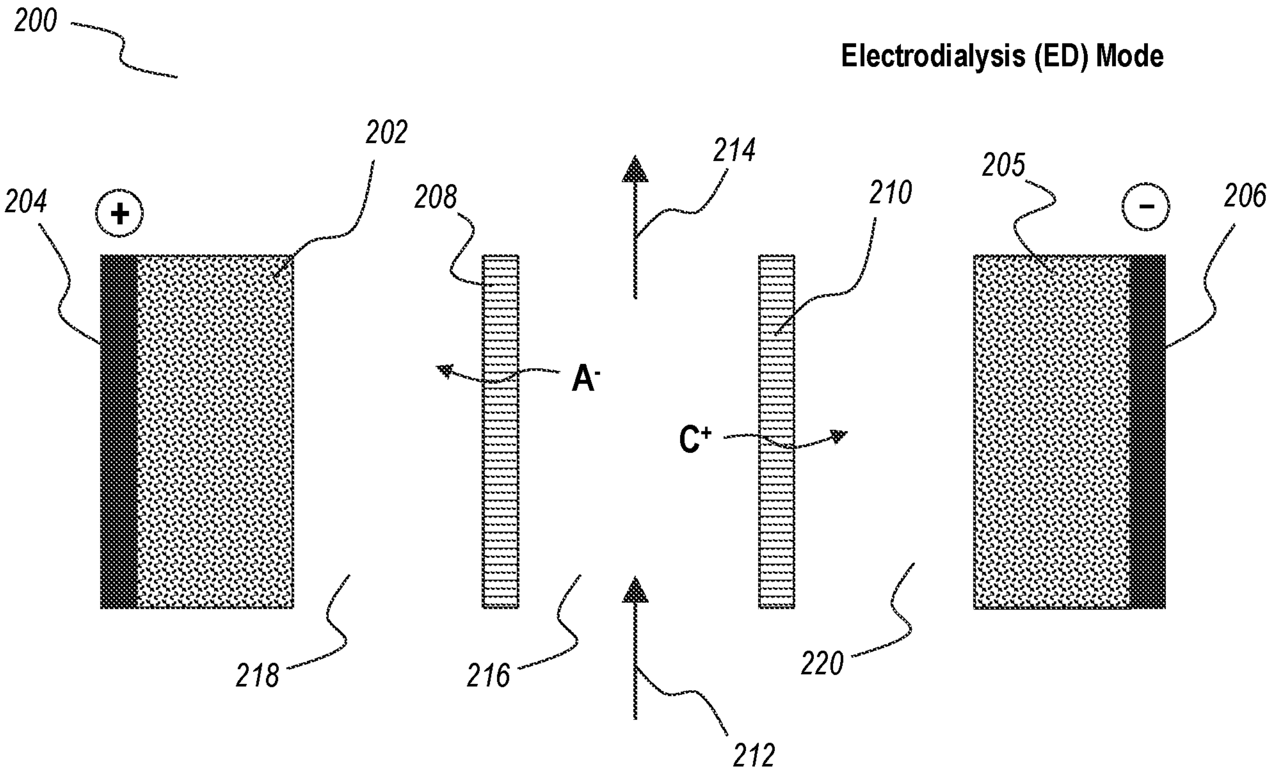

200
Electrodialysis (ED) Mode
202
214
204
208
210
205
206
A^-
C^+
218
216
220
212

FIG. 1C

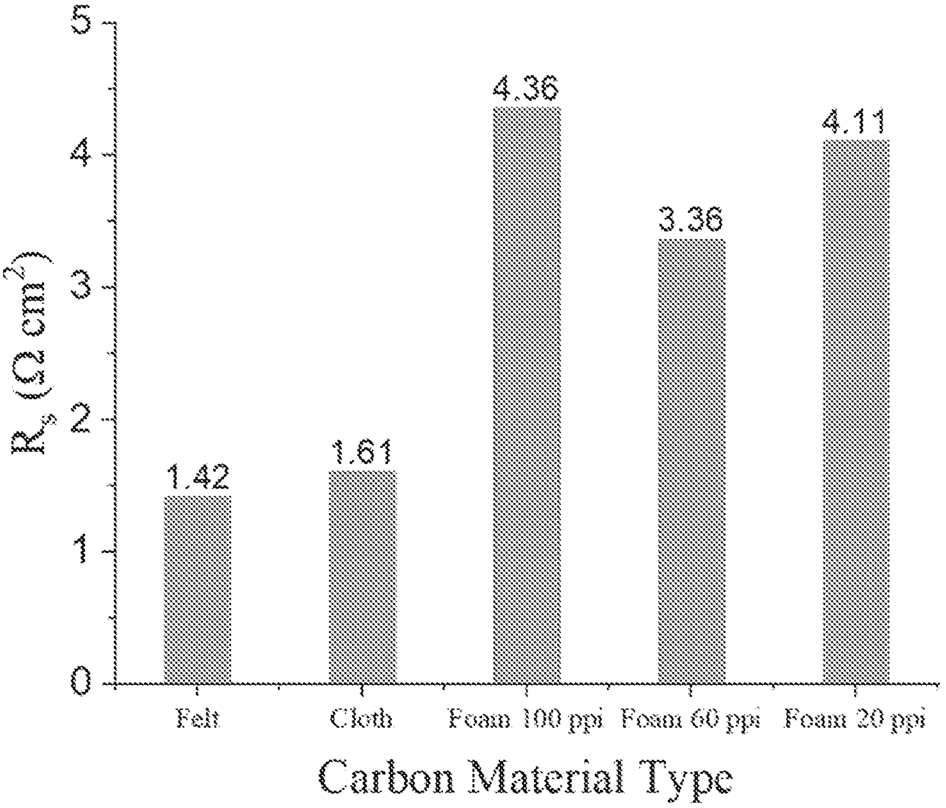

5
4
3
2
1
0
R_s (Ω cm^2)
1.42
1.61
4.36
3.36
4.11
Felt
Cloth
Foam 100 ppi
Foam 60 ppi
Foam 20 ppi
Carbon Material Type

FIG. 2A

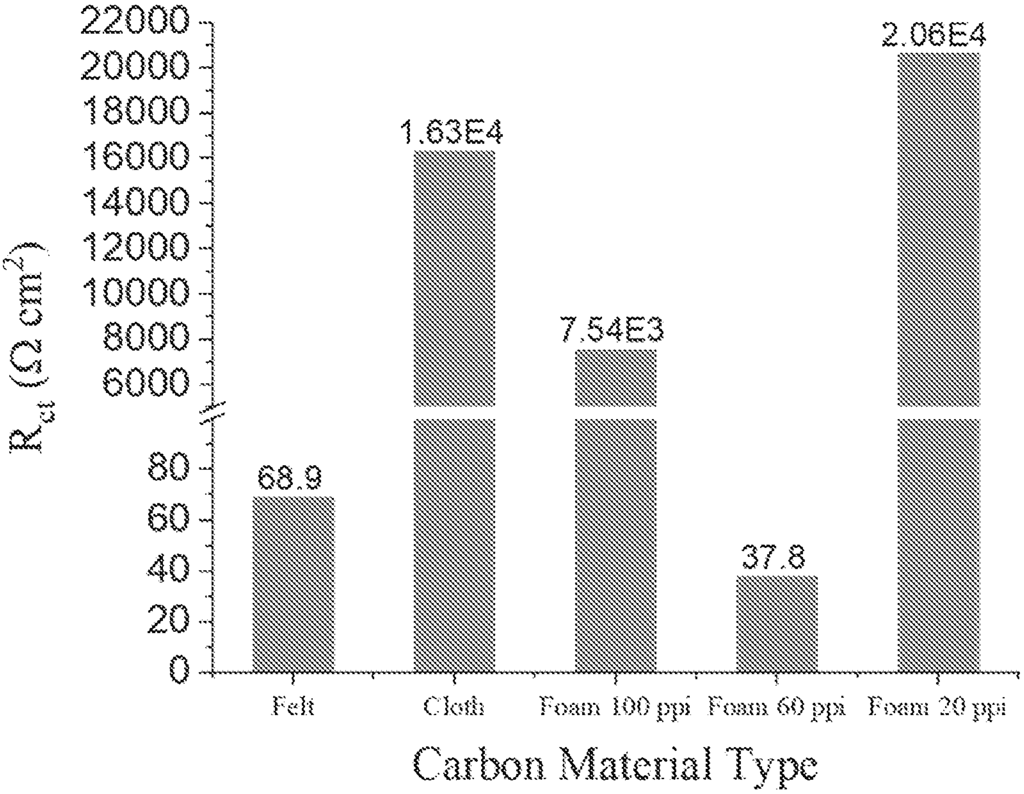

22000
20000
18000
16000
14000
12000
10000
8000
6000
80
60
40
20
0
R_{ct} (Ω cm^2)
68.9
1.63E4
7.54E3
37.8
2.06E4
Felt
Cloth
Foam 100 ppi
Foam 60 ppi
Foam 20 ppi
Carbon Material Type

FIG. 2B

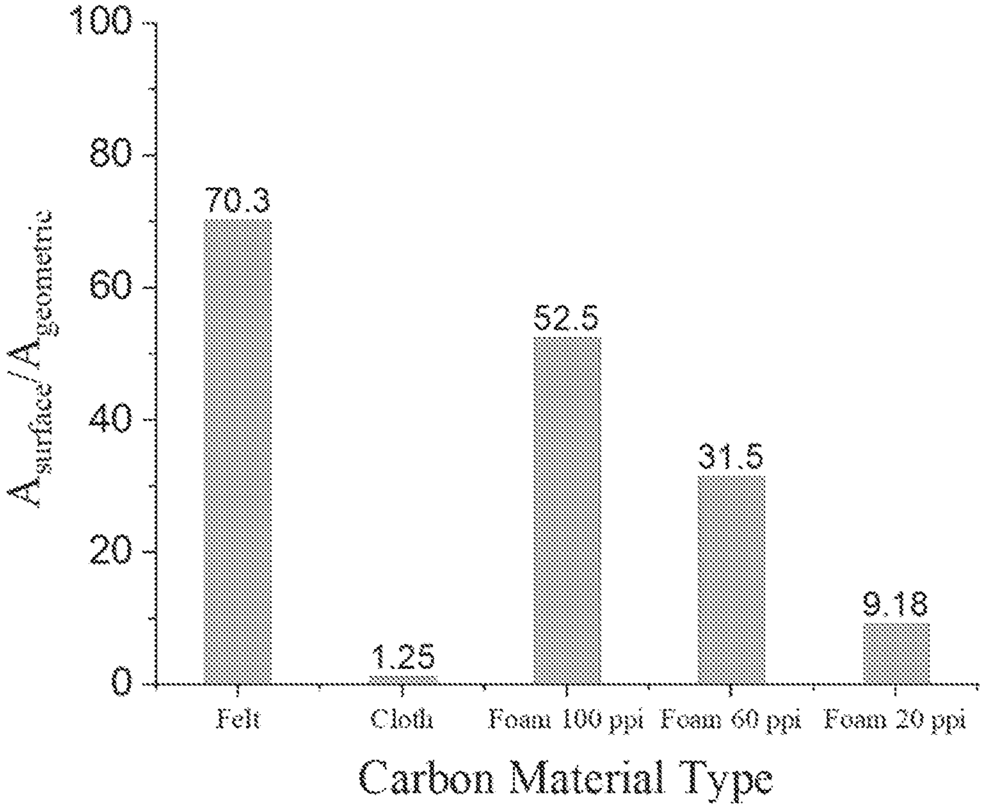

100
80
60
40
20
0
$A_{surface}/A_{geometric}$
70.3
1.25
52.5
31.5
9.18
Felt
Cloth
Foam 100 ppi
Foam 60 ppi
Foam 20 ppi
Carbon Material Type

FIG. 2C

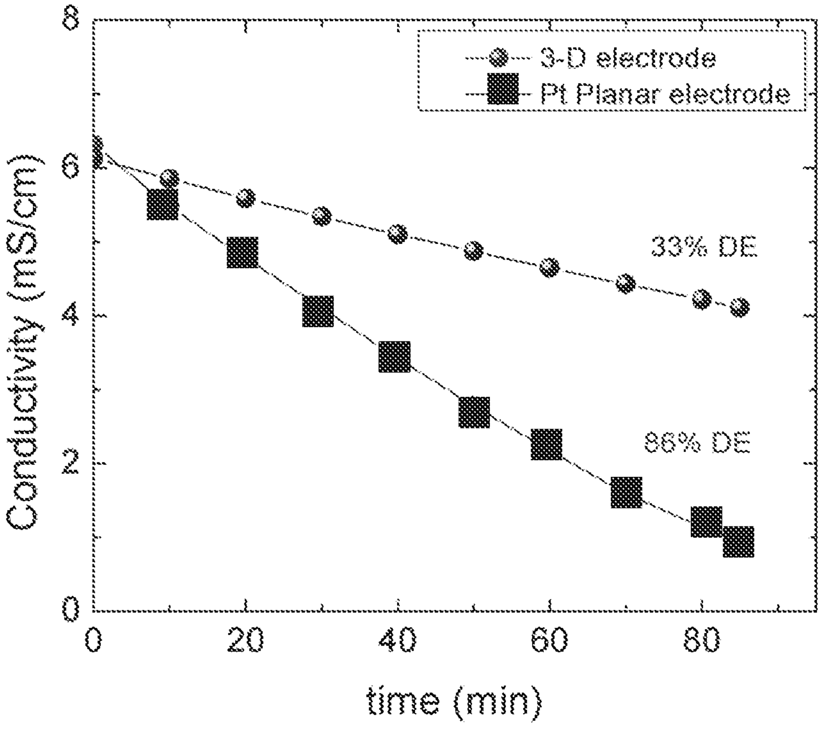

3-D electrode
Pt Planar electrode
33% DE
86% DE
Conductivity (mS/cm)
0
2
4
6
8
0
20
40
60
80
time (min)

FIG. 2D

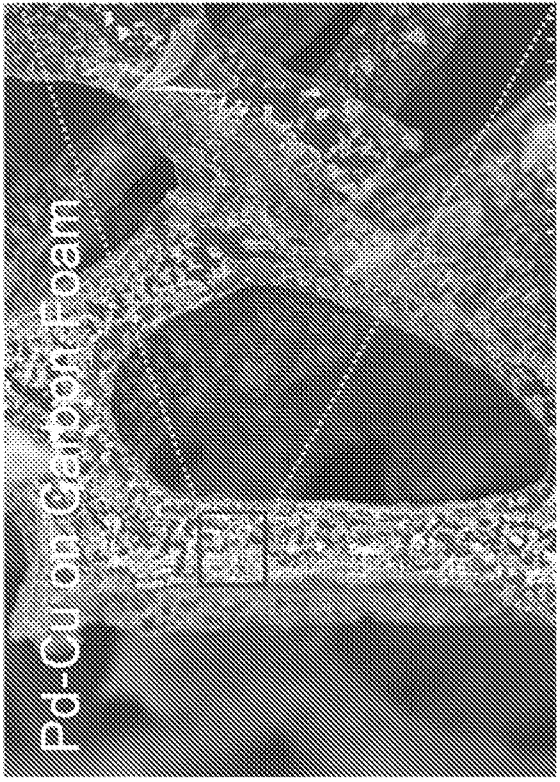


FIG. 3A

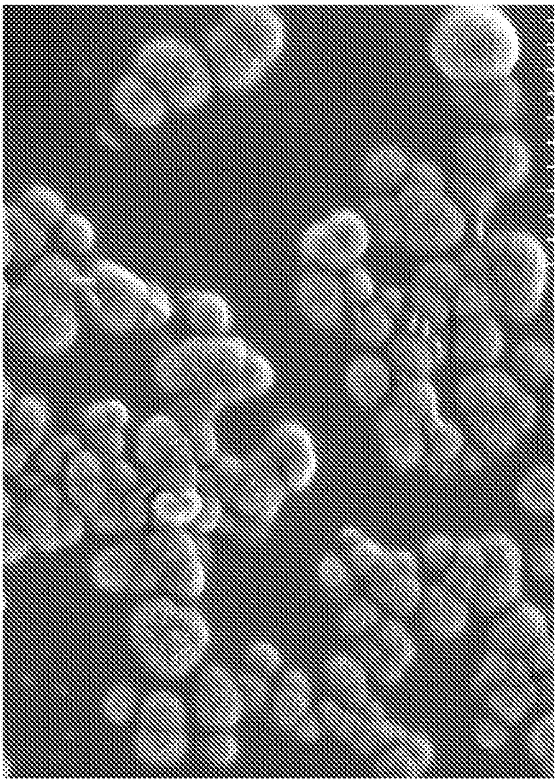


FIG. 3B

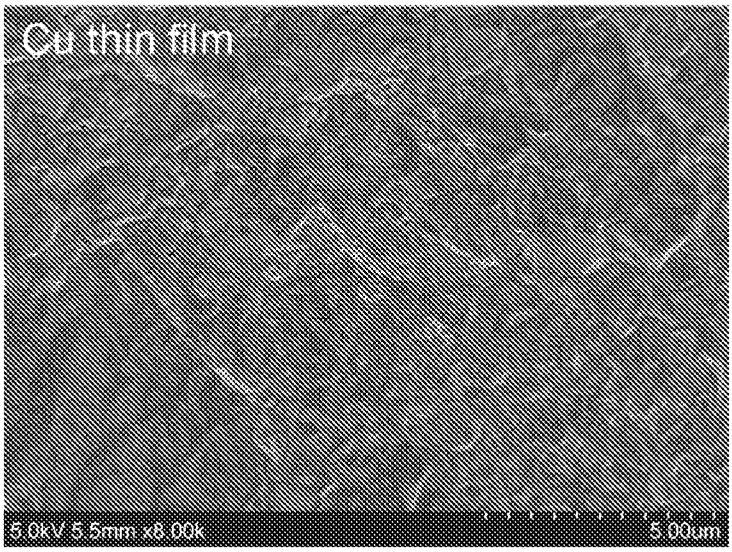

Cu thin film
5.0kV 5.5mm x8.00k
5.00um

FIG. 4A

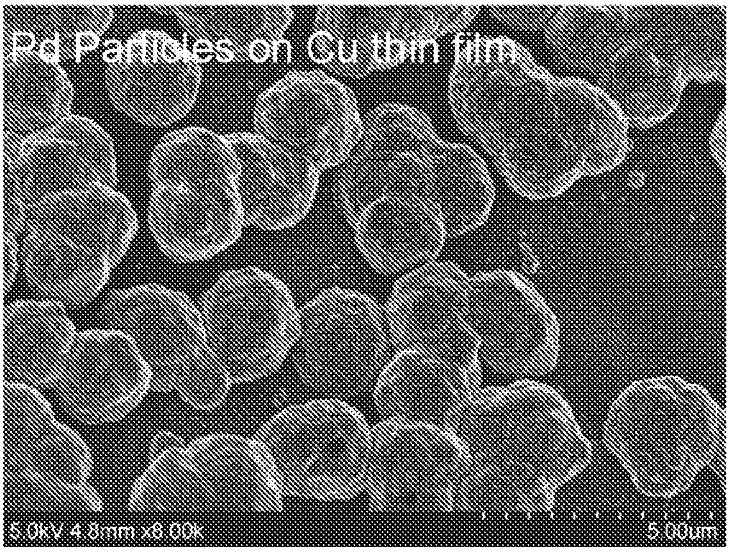
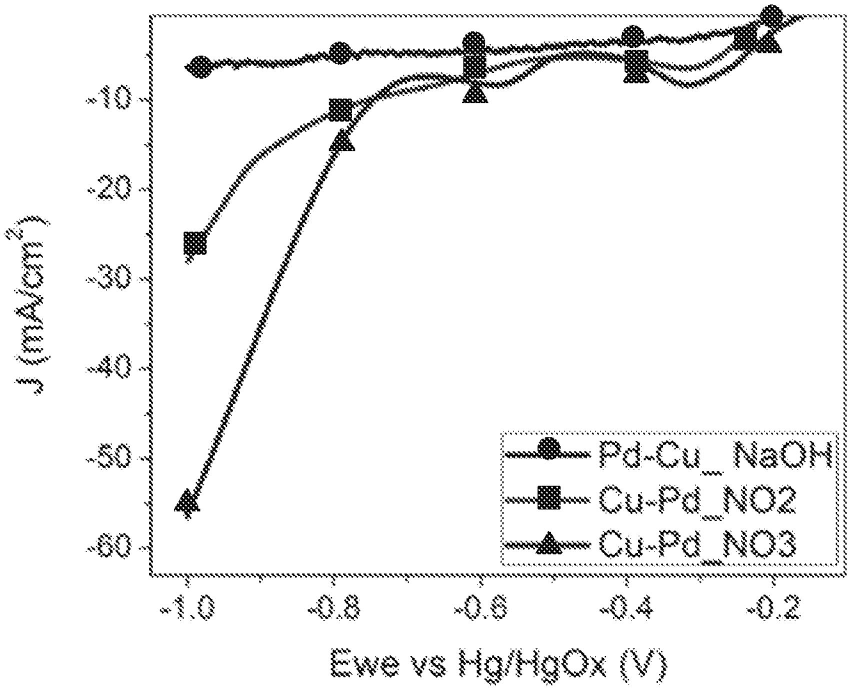
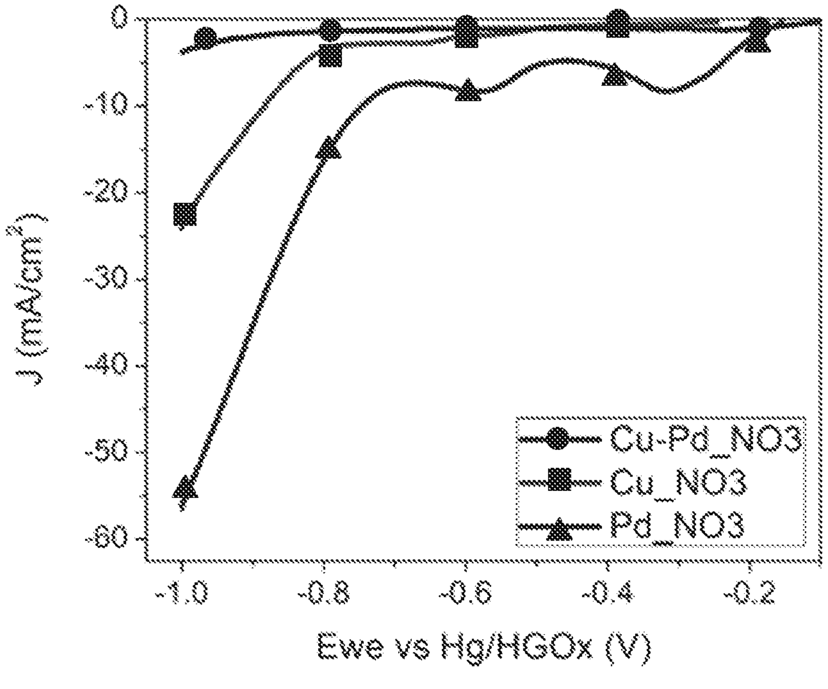

Pd Particles on Cu thin film
5.0kV 4.8mm x8.00k
5.00um

FIG. 4B



J (mA/cm^2)
-10
-20
-30
-40
-50
-60
-1.0
-0.8
-0.6
-0.4
-0.2
Ewe vs Hg/HgOx (V)
Pd-Cu_ NaOH
Cu-Pd_NO2
Cu-Pd_NO3

FIG. 5A



J (mA/cm^2)
0
-10
-20
-30
-40
-50
-60
-1.0
-0.8
-0.6
-0.4
-0.2
Ewe vs Hg/HGOx (V)
Cu-Pd_NO3
Cu_NO3
Pd_NO3

FIG. 5B

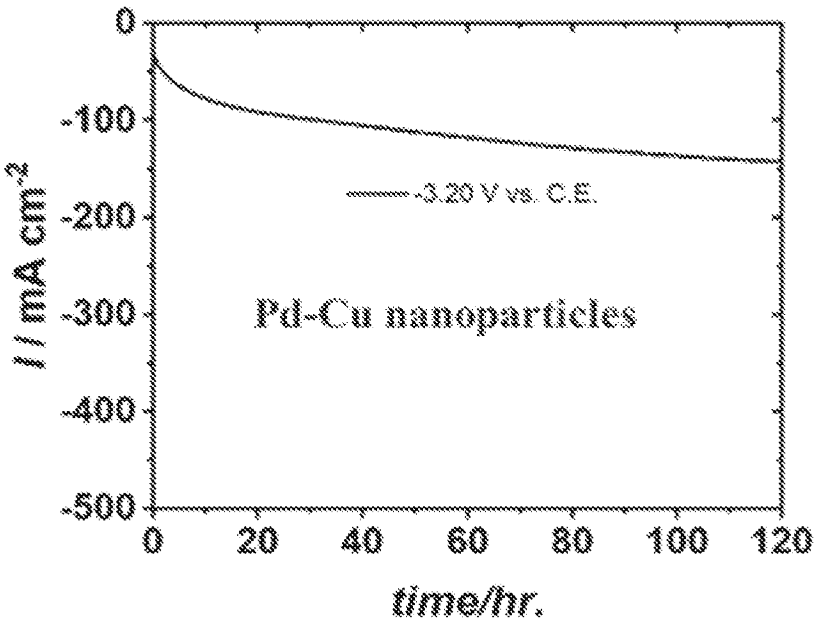

0
-100
-200
-300
-400
-500
I / mA cm^{-2}
0
20
40
60
80
100
120
time/hr.
-3.20 V vs. C.E.
Pd-Cu nanoparticles

FIG. 6A

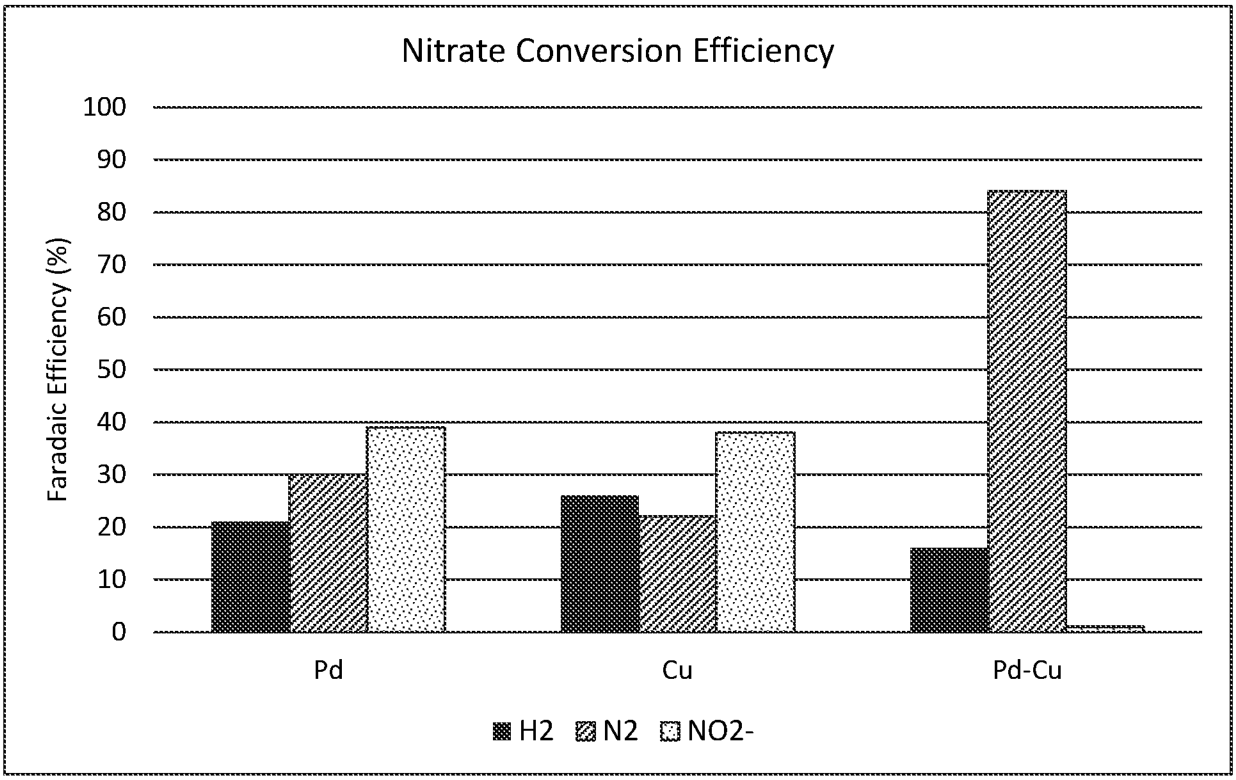

Nitrate Conversion Efficiency
Faradaic Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
Pd
Cu
Pd-Cu
■ H2
▨ N2
□ NO2-

FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 21/37105

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C25B 1/00, C02F 1/46, B01D 61/42 (2021.01)

CPC - B01D 61/44, C02F 1/461, C02F 1/4693, C25B 1/04, B01D 2313/345, B01D 61/48, C02F 2001/46161, C02F 2001/46138

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 2011/0117395 A1 (Roodenburg) 19 May 2011 (19.05.2011); the entire document, and more specifically: para [0010]-[0015], [0022], [0037]-[0038], [0040]-[0042]; figures 1-3; abstract	1-9 --------- 10-11
Y	US 2011/0042219 A1 (WEI et al.) 24 February 2011 (24.02.2011); the entire document, and more specifically: para [0008], [0018], [0022]-[0023]; figure 2-3; abstract	10-11
A	US 2009/0159460 A1 (DU et al.) 25 June 2009 (25.06.2009); the entire document	1-11
A	US 8,491,771 B2 (SANO) 23 July 2013 (23.07.2013); the entire document	1-11
A	US 9,340,437 B2 (ANDERSEN) 17 May 2016 (17.05.2016); the entire document	1-11
A	PENG et al., "Recovery of copper and water from copper-electroplating wastewater by the combination process of electrolysis and electrodialysis"; Volume 189, Issue 3 (May 2011), pg 814-820 (the entire document)	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 6 October 2021 (06.10.2021)	Date of mailing of the international search report NOV 23 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 12-15 and 19-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: claims 1-11, directed to a system configured to provide both electrodialysis and electrolysis of a feedwater.

Group II: claims 16-18, directed to a method of removing one or more contaminants from a feedwater via electrodialysis and converting the one or more contaminants via electrolysis.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

please see the continuation at the end of this form

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-11

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

**continuation of Box III (Lack of Unity) **

Special Technical Features:

Group I requires that the first ion concentration compartment being adjacent to the first electrode such that during operation of the system an ion-concentrated stream contacts the first electrode, not required by group II.

Group II requires a method of removing one or more contaminants from a feedwater via electrodialysis and converting the one or more contaminants via electrolysis; operating the system in an electrodialysis mode by providing a first polarity across the first and second electrodes; and operating the system in an electrolysis mode by reversing the polarity across the first and second electrodes, not required by group I.

Common Technical Features:

Groups I and II share the technical feature of electrodialysis and electrolysis of a feedwater; a first electrode including a catalyst material associated therewith; a second electrode disposed opposite the first electrode; and one or more ion exchange membranes disposed between the first and second electrodes so as to define a feedwater compartment, and a first ion concentration compartment, the first ion concentration compartment being adjacent to the first electrode; passing/flowing the feedwater. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by US 2011/0117395 A1 (Roodenburg).

Roodenburg teaches electrodialysis and electrolysis of a feedwater (para [0010]-[0013], [0015], [0042]; figures 2-3; This object is achieved with the device according to the invention for performing a reverse electrodialysis process, comprising: a first compartment provided with at least a first and a second electrode; a second compartment separated from the first compartment and provided with at least a first and a second electrode; and a switching element for switching between a first mode and a second mode. Further, during the first mode of the cell the first electrode pair is thus active, i.e. the anode in the first (anode) compartment and the cathode in the second (cathode) compartment are mutually connected. After switching of the flow direction in the second mode, the first compartment functions as cathode compartment and the second compartment as anode compartment. In addition, figures 2 and 3 show the first and the second mode respectively. Figures 2 and 3 also show the flow of seawater 12 and river water 14. Please also see instant specification, instant para [0013]: In the example of nitrate treatment, the ion exchange membranes are arranged so that the anion concentration compartment is adjacent the first electrode, and the first electrode is operated with a positive charge during electrodialysis mode to attract and concentrate nitrate ions into the anion concentration compartment. During electrolysis mode, the polarity of the electrodes is reversed so that the first electrode now carries a negative charge.); a first electrode including a catalyst material associated therewith (para [0040]-[0041], [0022]; figures 2-3; Here, cathode 6 can be thought as the first electrode. The cathode preferably comprises a cover layer of ruthenium/iridium or platinum.); a second electrode disposed opposite the first electrode (para [0040]-[0041]; figure 2; Here, anode 4 can be thought as the second electrode. Further, as seen in figures 2, anode 4 and cathode 6 are disposed opposite of each other.); and one or more ion exchange membranes disposed between the first and second electrodes so as to define a feedwater compartment (para [0014], [0042]; figure 2; At least one cation exchange membrane and anion exchange membrane, which are placed alternately between the first and second compartment. As seen in figure 2, a plurality of membranes 8 and 10 are disposed between cathode 6 (first electrode) and anode 4 (second electrodes). In addition, as seen in figures 2-3, seawater 12 and river water 14 flow through and around the membranes 8 and 10.); and a first ion concentration compartment, the first ion concentration compartment being adjacent to the first electrode (para [0040]-[0041]; figures 2-3; As seen in figure 2, Na+ ions permeate through the membrane 10 towards cathode 6 (first electrode), concentrating the area adjacent to cathode 6 (first electrode). Thus, here, the first ion compartment can be thought as the space between cathode 6 (first electrode) and the most left hand side membrane 10.); passing/flowing the feedwater (para [0037]; figures 2-3; Electrolyte compartments are formed between anion exchange membranes 8 and cation exchange membranes 10, wherein a flow of seawater 12 and river water 14 flow alternately through adjacent compartments.).

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

Note: claims 12-15 and 19-23 are unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).