(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 September 2026 (24.09.2026)

WIPO | PCT

(10) International Publication Number
WO 2026/198612 A1

(51) International Patent Classification:
C25D 5/10 (2006.01) *C25B 11/061* (2021.01)
C25D 3/12 (2006.01) *C02F 1/461* (2023.01)
C25B 1/04 (2021.01)

(21) International Application Number:
PCT/US2026/019656

(22) International Filing Date:
18 March 2026 (18.03.2026)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/775,468 21 March 2025 (21.03.2025) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UY, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MU, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: CATHODES FOR ELECTROLYSIS

(57) Abstract: The present disclosure relates to electrodes comprising cobalt and nickel, systems comprising the same, and methods for use thereof.

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CATHODES FOR ELECTROLYSIS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Application No. 63/775,468, filed March 21, 2025, the contents of which are herein incorporated by reference in their entirety.

BACKGROUND

Seawater electrolysis for green hydrogen production and simultaneous CO_2 mineralization is a promising approach to mitigate climate change. However, the presence of various cations (*e.g.*, Ca^{2+}, Mg^{2+}), anions (*e.g.*, Cl^-, Br^-), bacteria/microbes, and other impurities in seawater leads to high overpotentials for H_2/O_2 production at the cathode/anode. To reduce overpotentials and energy consumption, there is an urgent need for negative electrocatalysts (i.e., cathodes) that can selectively and efficiently produce H_2 via the electrolysis of seawater.

SUMMARY OF THE INVENTION

In certain aspects, provided herein are negative electrodes (e.g., cathodes) comprising an outer layer comprising Co and Ni. In further aspects, provided herein are systems comprising negative electrodes comprising an outer layer comprising Co and Ni. In yet further aspects, provided herein are methods of producing H_2 comprising contacting an aqueous solution with a negative electrode comprising an outer layer comprising Co and Ni and passing a current through the aqueous solution and negative electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A shows schematic representation of an exemplary method for preparing a negative electrode comprising an outer layer comprising CoNi or CoNiMo.

Figure 1B shows images of an exemplary negative electrode of the disclosure.

Figure 2 is a plot of measured electrical potential values (top line, values given in V) and resistance values (bottom line, values given in Ω), at varying current densities (in A/m^2), for an exemplary negative electrode comprising an outer layer comprising CoNiMo.

Figure 3A is a graph comparing measured electrical potential values for various negative electrodes during a standardized seawater electrolysis experiment, at a current density of 300 A/m^2.

Figure 3B is a graph showing measured electrical potential values for an exemplary negative electrode comprising an outer layer comprising CoNiMo over a 6000 s time period. These data demonstrate that the exemplary electrode is stable under conditions of seawater electrolysis at a current density of 300 A/m^2 for at least 6000 s.

Figure 4 shows an exemplary voltage-versus-time plot for three electrodes with increasing surface areas: bare Ti felt, CoNi coated Ti felt (10 min electrodeposition), and CoNi coated Ti felt (30 min electrodeposition).

DETAILED DESCRIPTION OF THE INVENTION

Electrode Compositions

The current state-of-the-art Pt electrocatalyst used as a cathode in the electrolyzer is exceedingly rare (~0.005 parts Pt per million parts of other metals on earth) and costly. For large-scale seawater electrolysis, cheap, earth-abundant, and durable cathode electrocatalysts are needed that are capable of operating at hydrogen evolution reaction (HER) overpotentials competitive with Pt electrodes. Some non-platinum group transition metals and their alloys, such as Co, Co-Mo, CoNiFe, CoW, Fe, FeMo. NiCo, MoS, NiMo have been investigated for HER, though these still face challenges with durability and/or performance.

In certain aspects, provided herein are electrodes comprising:

a substrate; and

an outer layer disposed on the substrate;

wherein:

the substrate comprises a conductive or semi-conductive material; and

the outer layer comprises Co and Ni.

In certain embodiments, the substrate is conductive. In certain embodiments, the substrate is semi-conductive. In certain embodiments, the substrate comprises a metal. In further embodiments, the substrate is selected from metal oxide, metal silicate, metal carbonate, metal phosphide, metal sulfide, and metal selenide, or a combination thereof. In certain preferred embodiments, the substrate comprises titanium. In yet further embodiments, the substrate is carbon-based. In certain such embodiments, the substrate is selected from graphite, graphene, carbon nanotubes, and glassy carbon.

In certain embodiments, the substrate is solid. In certain such embodiments, the substrate is nonporous. In other embodiments, the substrate is porous. In some embodiments, the substrate is a plate, mesh, felt, foam, fiber, and particle, or a combination thereof. In some

embodiments, the substrate is a plate. In certain embodiments, the substrate is a mesh. In some embodiments, the substrate is a felt. In some embodiments, the substrate is a foam. In some embodiments, the substrate is a fiber. In some embodiments, the substrate is a particle. In some embodiments, the substrate is a combination of a plate, mesh, felt, foam, fiber, or particle.

In certain embodiments, the outer layer further comprises Mo. In certain such embodiments, the outer layer comprises Co, Ni, and Mo. In certain embodiments, the outer layer comprises Co oxide. In some embodiments, the outer layer comprises Ni oxide. In certain embodiments, the outer layer comprises Mo oxide.

In certain embodiments, a system comprises an electrolyzer, wherein the electrolyzer comprises any one of the electrodes described above. As will be appreciated, the preparation of non platinum-group metal (PGM) cathodes (*e.g.* comprising CoNi, CoNiMo) on high porosity, etched Ti felts affords a number of advantages, including significant reduction in costs (by replacing Pt with cheaper, earth-abundant metals) and energy consumptions (by lowering the cell voltage required to generate desired products) during seawater electrolysis. While not wishing to be bound by theory, the improved performance of CoNi and CoNiMo may be related to high electrochemical surface areas (ECSA) and Brunauer, Emmett and Teller (BET) surface areas, availability of large number of active sites for adsorption and desorption of reaction intermediates, and advantageous binding energy of reaction intermediates. At the cathode, water molecules split into adsorbed hydrogen (H*) and hydroxide ions (OH^-) via the Volmer step ($H_2O + e^- \rightarrow H^* + OH^-$), followed by H* combining to form H_2 gas (Heyrovsky/Tafel step: $H^* + H_2O + e^- \rightarrow H_2 + OH^-$ or $2H^* \rightarrow H_2$). The CoNiMo catalyst, according to certain embodiments of this disclosure, lowers the energy barrier for these steps, enabling efficient H_2 production in chloride-rich seawater. A combination of electrodeposition conditions (time, temperature, current density) and the composition of electrodeposition solutions (number and types of cations/anions in solution, pH and conductivity of the solution) is used to improve electrocatalyst performance. In some embodiments, as will be appreciated by one of ordinary skill in the art, the physical characteristics of the electrodes, *e.g.,* surface area, may be measured using standard measurement techniques known in the art including, for example, the Brunauer, Emmett and Teller (BET) method for obtaining the specific surface area (hereinafter "surface area"). In general, as will be appreciated by one of ordinary skill in the art, electrodes having higher surface area are generally more active in electrocatalytic applications (*e.g.,* exhibiting

HER at lower applied potentials) than electrodes of a similar composition having a lower surface area.

Production of H_2 from Aqueous Solutions

In certain aspects, provided herein are methods of producing H_2, comprising:

(a) in an anodic chamber of an electrochemical cell, performing an acidic process comprising:

acidifying a first solution by:

contacting the first solution with a positive electrode disposed inside the anodic chamber; and

passing a current through the first aqueous solution, thereby forming an acidic solution; and

(b) in a cathodic chamber, performing an alkaline process comprising:

alkalinizing a second aqueous solution by:

contacting the second aqueous solution with a negative electrode disposed inside of the cathodic chamber; and

passing a current through the second aqueous solution, thereby forming an alkaline solution and H_2;

wherein:

the anodic chamber and the cathodic chamber are in ionic communication; and

the acidic process and the alkaline process are performed simultaneously or sequentially.

As will be appreciated, saline water (*e.g.*, seawater) alkalization can be induced at overpotentials that yields locally-produced alkalinity (*e.g.*, OH^- ions) at the cathode as a result of the hydrogen evolution reaction (HER):

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$

(1)

The reaction not only produces hydrogen that can be collected as a clean fuel, it also produces alkalinity that can then react with atmospheric or concentrated CO_2 (*e.g.*, 400 ppm to 100%):

$$CO_2 + OH^- \rightarrow HCO_3^-$$

(2)

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

(3)

Strategies and conditions (e.g., direct hydroxide carbonation) for the formation of calcium and magnesium carbonates and hydroxycarbonates, *e.g.,* calcite ($CaCO_3$), aragonite ($CaCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$), and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) can also be exploited, thereby resulting in solid CO_2 mineralization. In other embodiments, carbon species are trapped in the dissolved (i.e., HCO_3^-/CO_3^{2-} ions) form, whereby less alkalinity (OH^-) is needed for every mole of CO_2 mineralized. These conditions can be achieved by equilibrating the alkalinized saline water with air (i.e., 400 ppm CO_2) or concentrated CO_2 streams (400 ppm to 100%), yielding two limiting cases: (1) solid carbonate/hydroxycarbonates production (i.e., 100% solid CO_2 sequestration), and (2) aqueous CO_2 sequestration. Following the former, 1 mol of CO_2 is captured by 2 mol of hydroxyl ions (OH^-) to produce 1 mol $CaCO_3$, $MgCO_3$ or other alkali metal (*e.g.,* Na, K, etc.) carbonates. In case of the latter, every mol of hydroxide ions (OH-) leads to the absorption of 1-2 mol of CO_2 to form aqueous HCO_3^-/CO_3^{2-} ions. The CO_2 immobilization can be implemented by using carbonation reactors, or by deploying the alkaline products (solids and solutions) on land and/or ocean allowing for atmospheric CO_2 drawdown. In any case, products from CO_2 immobilization should fall within the two limiting cases and yield a combination of solid and aqueous carbonate species.

In certain aspects, a system comprises:

an electrolyzer, wherein the electrolyzer comprises:

a cathodic chamber comprising:

a negative electrode comprising:

a substrate; and

an outer layer disposed on the substrate;

wherein the substrate comprises a conductive or semi-conductive material; and the outer layer comprises Co and Ni; and

an anodic chamber comprising a positive electrode;

wherein the cathodic chamber and the anodic chamber are in ionic communication.

In certain embodiments, the substrate is conductive. In certain embodiments, the substrate is semi-conductive. In further embodiments, the substrate comprises a metal. In yet further embodiments, the substrate is selected from metal oxide, metal silicate, metal carbonate, metal phosphide, metal sulfide, and metal selenide, or a combination thereof. In certain preferred embodiments, the substrate comprises titanium. In certain embodiments, the substrate is carbon-based. In certain such embodiments, the substrate is selected from graphite, graphene, carbon nanotubes, and glassy carbon.

In certain embodiments, the substrate is solid. In certain such embodiments, the substrate is nonporous. In other embodiments, the substrate is porous. In further embodiments, the substrate is a plate, mesh, felt, foam, fiber, or particle, or a combination thereof.

In certain embodiments, the outer layer further comprises Mo. In certain such embodiments, the outer layer comprises Co, Ni, and Mo. In certain embodiments, the outer layer comprises Co oxide. In some embodiments, the outer layer comprises Ni oxide. In certain embodiments, the outer layer comprises Mo oxide.

In certain embodiments, the cathodic chamber and the anodic chamber are separated by a semi-permeable barrier having a plurality of pores. In certain such embodiments, the semi-permeable barrier is a semi-permeable membrane, e.g., a membrane made of ion exchange materials, for example, Nafion. In certain other embodiments, the semi-permeable membrane is a hydrophilic ceramic membrane or plate, e.g., formed from aluminum oxide, zirconium oxide, silicon dioxide, asbestos, hydrous aluminum phyllosilicates, clay, or any combination thereof. In certain embodiments, the semi-permeable membrane is a polymer. In certain such embodiments, the polymer is cellulose, polyvinyl chloride, organic rubber, polyolefin, polyethylene, polypropylene, polyvinylidene fluoride, polytetrafluoroethylene, epoxy resin, silicone, or any combination thereof. In certain embodiments, the semi-permeable membrane is a ceramic-polymer composite.

In certain embodiments, the plurality of pores has a median pore diameter from about 0.1 nm to about 500 nm. In some embodiments, the semi-permeable barrier has a thickness of from about 5 μm to about 5 mm.

In certain aspects, provided herein is a method of producing hydrogen from an aqueous solution, comprising contacting the aqueous solution with the positive electrode and the negative electrode of any one of the systems described above and passing a current through the aqueous solution, thereby forming H_2 and/or OH^- ions at the negative electrode.

In certain aspects, a method of producing H_2 is provided herein, comprising:

(a) in an anodic chamber of an electrochemical cell, performing an acidic process comprising:

acidifying a first solution by:

contacting the first solution with a positive electrode disposed inside the anodic chamber; and

passing a current through the first aqueous solution, thereby forming an acidic solution; and

(b) in a cathodic chamber, performing an alkaline process comprising:

alkalinizing a second aqueous solution by:

contacting the second aqueous solution with a negative electrode disposed inside of the cathodic chamber; and

passing a current through the second aqueous solution, thereby forming an alkaline solution and H_2;

wherein:

the anodic chamber and the cathodic chamber are in ionic communication; and

the acidic process and the alkaline process are performed simultaneously or sequentially.

In certain embodiments, the alkaline process and acidic process are performed simultaneously.

In certain embodiments, the method further comprises contacting the alkaline solution with a CO_2 source, thereby forming a carbonated solution comprising a mixture of ionic compounds, wherein the ionic compounds comprise CO_3^{2-} or HCO_3^-.

In certain embodiments, the CO_2 source comprises from about 400 ppm to about 100% CO_2, preferably about 400 ppm. In certain embodiments, the CO_2 source is ambient air. In other embodiments, the CO_2 source has a higher CO_2 concentration than ambient air. In certain such embodiments the CO_2 concentration is that of gaseous effluent from an industrial process. In those embodiments, the industrial process may be oil and gas production, power generation, cement production, or steel production. In some embodiments, the concentrated CO_2 is derived from direct air capture processes. In certain such embodiments, the direct air capture process produces nearly pure or pure CO_2.

In certain embodiments, the first solution is selected from seawater, desalination brine, industrial brine, and natural brine. In certain embodiments, the second solution is selected from seawater, desalination brine, industrial brine, and natural brine. In certain such embodiments, the first solution and the second solution originate from the same source solution.

In certain embodiments, the alkaline process and the acidic process occur in vessels separated by a semi-permeable barrier having a plurality of pores. In certain embodiments, the semi-permeable barrier is a semi-permeable membrane. In such embodiments, the semi-permeable membrane is a membrane made of ion exchange materials, such as perfluorosulfonic acid (PFSA)/polytetrafluoroethylene (PTFE) copolymers (e.g., Nafion™). In certain embodiments, the semi-permeable membrane is a hydrophilic ceramic membrane

or plate, e.g., aluminum oxide, zirconium oxide, silicon dioxide, asbestos, hydrous aluminum phyllosilicates, clay, or any combination thereof. In certain embodiments, the semi-permeable membrane is a polymer, for example, cellulose, polyvinyl chloride, organic rubber, polyolefin, polyethylene, polypropylene, polyvinylidene fluoride, polytetrafluoroethylene, epoxy resin, silicone, or any combination thereof. In certain embodiments, the semi-permeable membrane is a ceramic-polymer composite.

In certain embodiments, the plurality of pores has a median pore diameter from about 0.1 nm to about 500 nm. In some embodiments, the semi-permeable barrier has a thickness of from about 5 μm to about 5 mm.

In certain embodiments, the alkaline solution has a pH from about 7 to about 14. In further embodiments, the alkaline solution has a pH from about 10 to about 11. In certain preferred embodiments, the alkaline solution has a pH of about 10.5. In certain embodiments, the acidic solution has a pH from about 0.1 to about 7. In certain such embodiments, the acidic solution has a pH from about 0.5 to 1.5. In certain preferred embodiments, the acidic solution has a pH of about 1.

In certain aspects, a method of making the electrode as described above comprises:

immersing the substrate in an acidic solution;

applying a first electrical potential across the substrate, thereby removing an oxidized surface of the substrate;

immersing the substrate in a plating solution; and

applying a second electrical potential across the substrate, thereby electrodepositing the outer layer on the substrate;

wherein the plating solution comprises Co and Ni ions.

In certain aspects, a method of making an electrode comprises:

immersing a substrate in an acidic solution;

applying a first electrical potential across the substrate, thereby removing an oxidized surface of the substrate;

immersing the substrate in a plating solution; and

applying a second electrical potential across the substrate, thereby electrodepositing an outer layer on the substrate;

wherein the plating solution comprises Co and Ni cations.

In certain embodiments, the plating solution comprises Co^{2+} and Ni^{2+} ions. In further embodiments, the plating solution further comprises Mo cations, e.g., Mo^{6+} ions.

In certain embodiments, the plating solution further comprises an electrolyte, optionally $(NH_4)_2SO_4$ and NH_4OH.

In certain embodiments, the acidic solution comprises H_2SO_4. In certain such embodiments, the concentration of H_2SO_4 is about 9 M.

In certain embodiments, the first electrical potential is applied across the substrate at about 80 °C. In certain embodiments, the outer layer comprises Co, Ni, and Mo. In certain embodiments, the second electrical potential is applied across the substrate at a current of about 50 mA/cm^2. In certain embodiments, the second electrical potential is applied across the substrate for about 120 min.

In certain aspects, an electrode is prepared according to any one of the methods above, comprising:

the substrate; and

the outer layer disposed on the substrate;

wherein:

the substrate comprises a conductive or semi-conductive material; and

the outer layer comprises Co and Ni.

In certain embodiments, the outer layer further comprises Mo.

In certain embodiments, the electrode as described above is prepared according to any one of the methods described above.

Definitions

Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art. Generally, nomenclature used in connection with, and techniques of, chemistry, chemical engineering, electrical engineering and civil engineering described herein, are those well-known and commonly used in the art.

The methods and techniques of the present disclosure are generally performed, unless otherwise indicated, according to conventional methods well known in the art and as described in various general and more specific references that are cited and discussed throughout this specification.

Chemistry terms used herein, unless otherwise defined herein, are used according to conventional usage in the art, as exemplified by "The McGraw-Hill Dictionary of Chemical Terms", Parker S., Ed., McGraw-Hill, San Francisco, C.A. (1985).

All publications, patents and published patent applications referred to in this application are specifically incorporated by reference herein. In case of conflict, the present specification, including its specific definitions, will control.

As used herein, the terms "optional" or "optionally" mean that the subsequently described event or circumstance may occur or may not occur, and that the description includes instances where the event or circumstance occurs as well as instances in which it does not. For example, "optionally substituted alkyl" refers to the alkyl may be substituted as well as where the alkyl is not substituted.

The term "alkalinizing" as used herein refers to a process of increasing the pH of a given solution, *e.g.*, alkalinizing the first solution to prepare an alkaline solution with a higher pH.

The term "ionic communication" as used herein refers to the ability for ions to freely flow between two objects or regions of an object, *e.g.*, between the cathodic chamber and anodic chamber of an electrochemical cell, in accordance with local chemical gradients. Non-limiting examples of such gradients include flow of ions from an area of high electrical potential to low electrical potential, from high ion concentration to low ion concentration, and from high chemical potential to low chemical potential. In certain embodiments, two objects or regions may be physically separated by a semi-permeable barrier (*e.g.*, not in fluid communication) but still be in ionic communication, *e.g.*, by virtue of ion diffusion or transport through the barrier.

As used herein, the term "selectivity" refers to the degree to which a certain process or electrode favors the formation of a particular product over other products. As will be understood by a person of ordinary skill in the art, the selectivity may be a function of process steps, parameters, and conditions (e.g., temperature, reaction times, pre-treatment steps, etc.), and/or may be the result of intrinsic properties of system components (e.g., as a result of using electrodes that are selective for the formation of oxygen). A selectivity value may refer to a proportion of the product(s) of interest compared to other product(s) produced, or may refer to the proportion of other product(s) produced compared to the product(s) of interest. A person of ordinary skill in the art will appreciate how to select suitable methods for testing, calculating, and comparing selectivity values relevant to the present disclosure. For example, in certain embodiments, electrodes disclosed herein are at greater than 99% selective for Oxygen Evolution Reactions (OER) and less than 1% selective for Chlorine Evolution Reactions

(ClER), while a platinum electrode used as a non-oxygen-selective benchmark exhibits a selectivity from about 20% to about 40% for OER and from about 60% to about 80% for ClER.

As used herein, the term "simulated seawater" is mixture of water and certain salts that mimics the composition of natural seawater (*e.g.*, for use in testing electrodes disclosed herein). For example, "simulated seawater" as used herein may refer to a solution which meets the American Society for Testing and Materials (ASTM International) standard ASTM D1141-52, Formula a, Table 1, Section 4 and the updated Standard ASTM D1141-98 (2013) Formula a, Table x1.1, Section 6.

As used herein, the term "current density" refers to an amount of charge flowing per unit time (i.e., current) through a unit area. For example, current density may be expressed as current (*e.g.*, in Amperes) flowing through a unit area (*e.g.*, in m^2) of the surface of an anode of the disclosure using the unit A/m^2. Those of skill in the art are familiar with means of measuring and adjusting current density in electrical circuits relevant to the present disclosure.

As used herein, the terms "semiconductive," "electrically semiconductive," "semiconductor," and other grammatical variants thereof refer to any material having semiconductive properties, including, *e.g.*, a non-zero band gap between the valence band and conduction band of the material, and/or an electrical conductivity that increases as temperature increases. Such materials include, as non-limiting examples: Si, SiC, SiGe, SiGeC, Si alloys, Ge, Ge alloys, GaAs, InAs, InP. "Doped" semiconductors, comprising both n- and p-type dopants are also expressly contemplated.

As used herein, the terms "conductive," "electrically conductive," and other grammatical variants thereof describe any electrically conductive material, *e.g.*, metals, which have a high electrical conductivity and low electrical resistivity and which have properties common to conductors (*e.g.*, an electrical conductivity that decreases as temperature increases). For example, a material described herein as "conductive" may comprise a material having an electrical conductivity of about 58 MS/m (the International Annealed Copper Standard).

The phrase "a combination thereof," as used herein with reference to a list or group (*e.g.*, "wherein the dopant is selected from Sn, Fe, W, In, F, Si, and *a combination thereof*"), expressly contemplates any combination of any number of the group members. For example, in certain embodiments of the present disclosure, "a combination thereof" is used in reference to the group Sn, Fe, W, In, F, and Si. In such embodiments, the present disclosure expressly contemplates each and every combination of any two elements, any three elements, any four

elements, any five elements, and all six elements of the group, *e.g.*, the combination of Sn and Fe (two elements), and the combination of Sn, Fe, W, In, F, and Si (all six elements).

EXAMPLES

The invention now being generally described, it will be more readily understood by reference to the following examples which are included merely for purposes of illustration of certain aspects and embodiments of the present invention, and are not intended to limit the invention.

Example 1: Preparation of Exemplary Electrodes

Figure 1A shows a schematic representation of the general procedure used for cathode fabrication. Ti was used as a substrate for electrodeposition due to its stability over a wide pH range. Ti does not dissolve in acidic solutions (e.g. 5% HNO_3) under atmospheric conditions, in contrast to the mostly used Ni substrates. However, the presence of native oxide-layer (TiO_2) present on Ti under atmospheric conditions presents problems such as poor adhesion of the electrodeposit on the substrate. Accordingly, electrochemical etching of Ti felt in 9M H_2SO_4 at 80 °C was used to remove the native oxide-layer and to increase the roughness of the substrate. The substrate was washed with ethanol and DI water, each for 5 minutes. Immediately after washing, electrodeposition of Ti was carried out in a two-electrode electrochemical bath, containing ~36 cm^2 platinized Ti counter electrode (anode) and ~25 cm^2 etched Ti working electrode (cathode), and 500 mL solution mixture of 0.08M $CoSO_4$, 0.02M $NiSO_4$, 0.01M Na_2MoO_4, 1M $NaSO_4$, 0.7M NaOH (100mL each). $(NH_4)_2SO_4$ and NH_4OH were added to the solution to improve the conductivity and maintain the pH of the solution during electrodeposition. Electrodeposition was carried out for 120 minutes at a constant current of 50 mA/cm^2. The distance between the anode and cathode was about 4 cm. The electrodeposited sample was left in the electrodeposition solution overnight and washed under DI water the next day. As shown in Figure 1B, an electrode comprising a uniform and strongly adherent electrodeposited outer layer was obtained.

Example 2: Performance Testing of Exemplary Electrodes

Figure 2 shows the voltage and resistance data at different current densities. The current was varied between 0 A/m^2 and 500 A/m^2 and the voltage and resistance values were recorded. A voltage of around 2.3 V is required to obtain a current density at 100 A/m^2, and a voltage of around 3.2 V is required to achieve a current density of 300 A/m^2. The experiment was conducted in a two-electrode setup, using an oxygen selective anode, PFSA membrane

separator, and CoNiMo coated on Ti felt as the cathode. Suitable oxygen selective anodes may be found in, for example, U.S. Patent Application Pub. No. 2024/0254640 A1, the contents of which are herein incorporated by reference in their entirety. The resistance values shown in Figure 2 were obtained from electrochemical impedance spectroscopy measurements and vary between 1.2 ohm to 1.4 ohm.

Figure 3A shows a comparison of the voltages required to electrolyze seawater at a constant current density of 300 A/m^2 using CoNiMo, Pt, Ti and CoNi cathodes. The CoNiMo cathode gives the lowest cell voltage of 3.18 V for a period of 30 min. The platinized Ti operates at an average cell voltage of 3.31 V, more than 100 mV higher than the newly developed CoNiMo cathode. A CoNi cathode, also prepared in-house using the same procedure as for CoNiMo cathode, operates at 3.29 V. Ti felt (uncoated) as cathode showed the highest cell voltage of 3.84 V. The CoNiMo cathode showed great improvement over other cathodes during seawater electrolysis at 300 A/m^2 and operated at 3.19 V during second run (Figure 1B). Similar to Pt cathode, the pH of the anolyte and catholyte effluents using CoNiMo cathode during electrolysis at 300 A/m^2 was about 1.4 and 10.3, respectively.

Figure 4 shows an exemplary voltage-versus-time plot for three electrodes with increasing surface areas: bare Ti felt, CoNi coated Ti felt (10 min electrodeposition), and CoNi coated Ti felt (30 min electrodeposition). Higher surface area cathodes, resulting from longer electrodeposition time, show lower cell voltage during seawater electrolysis, while maintaining a constant current density of 300 A/m^2. This opposing relationship between surface area and voltage suggests improved electrocatalytic activity, likely stemming from enhanced reactive sites and better accessibility for ion transport. As the CoNi deposition time increases from 10 to 30 minutes, the BET surface area increases (3.3 m^2/g to 10.3 m^2/g), and the electrolysis voltage decreases (~3.6 V to ~3.3 V). Consequently, the extended CoNi electrodeposition confers superior performance compared to the bare Ti felt, illustrating that strategic electrode engineering can optimize electrochemical seawater splitting by reducing energy losses.

INCORPORATION BY REFERENCE

All publications and patents mentioned herein are hereby incorporated by reference in their entirety as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

EQUIVALENTS

While specific embodiments of the subject invention have been discussed, the above specification is illustrative and not restrictive. Many variations of the invention will become apparent to those skilled in the art upon review of this specification and the claims below. The full scope of the invention should be determined by reference to the claims, along with their full scope of equivalents, and the specification, along with such variations.

We claim:

1. An electrode comprising:
a substrate; and
an outer layer disposed on the substrate;
wherein:
the substrate comprises a conductive or semi-conductive material; and
the outer layer comprises Co and Ni.

2. The electrode of claim 1, wherein the substrate is conductive.

3. The electrode of claim 1, wherein the substrate is semi-conductive.

4. The electrode of any one of claims 1-3, wherein the substrate comprises a metal.

5. The electrode of any one of claims 1-4, wherein the substrate is selected from metal oxide, metal silicate, metal carbonate, metal phosphide, metal sulfide, and metal selenide, or a combination thereof.

6. The electrode of any one of claims 1-5, wherein the substrate comprises titanium.

7. The electrode of claim 1 or 3, wherein the substrate is carbon-based.

8. The electrode of claim 7, wherein the substrate is selected from graphite, graphene, carbon nanotubes, and glassy carbon.

9. The electrode of any one of claims 1-8, wherein the substrate is solid (*e.g.*, non-porous).

10. The electrode of any one of claims 1-8, wherein the substrate is porous.

11. The electrode of any one of claims 1-10, wherein the substrate is a plate, mesh, felt, foam, fiber, or particle, or a combination thereof.

12. The electrode of any one of claims 1-11, wherein the outer layer further comprises Mo.

13. The electrode of any one of claims 1-12, wherein the outer layer comprises Co, Ni, and Mo.

14. The electrode of any one of claims 1-13, wherein the outer layer comprises Co oxide.

15. The electrode of any one of claims 1-14, wherein the outer layer comprises Ni oxide.

16. The electrode of any one of claims 1-15, wherein the outer layer comprises Mo oxide.

17. A system comprising an electrolyzer, wherein the electrolyzer comprises the electrode of any one of claims 1-16.

18. A system comprising:
an electrolyzer, wherein the electrolyzer comprises:
a cathodic chamber comprising:
a negative electrode comprising:
a substrate; and
an outer layer disposed on the substrate;
wherein the substrate comprises a conductive or semi-conductive material; and the outer layer comprises Co and Ni; and
an anodic chamber comprising a positive electrode;
wherein the cathodic chamber and the anodic chamber are in ionic communication.

19. The system of claim 18, wherein the substrate is conductive.

20. The system of claim 18, wherein the substrate is semi-conductive.

21. The system of any one of claims 18-20, wherein the substrate comprises a metal.

22. The system of any one of claims 18-21, wherein the substrate is selected from metal oxide, metal silicate, metal carbonate, metal phosphide, metal sulfide, and metal selenide, or a combination thereof.

23. The system of any one of claims 18-22, wherein the substrate comprises titanium.

24. The system of claim 18 or 20, wherein the substrate is carbon-based.

25. The system of claim 24, wherein the substrate is selected from graphite, graphene, carbon nanotubes, and glassy carbon.

26. The system of any one of claims 18-25, wherein the substrate is solid (*e.g.*, non-porous).

27. The system of any one of claims 18-25, wherein the substrate is porous.

28. The system of any one of claims 18-27, wherein the substrate is a plate, mesh, felt, foam, fiber, or particle, or a combination thereof.

29. The system of any one of claims 18-28, wherein the outer layer further comprises Mo.

30. The system of any one of claims 18-29, wherein the outer layer comprises Co, Ni, and Mo.

31. The system of any one of claims 18-30, wherein the outer layer comprises Co oxide.

32. The system of any one of claims 18-31, wherein the outer layer comprises Ni oxide.

33. The system of any one of claims 18-32, wherein the outer layer comprises Mo oxide.

34. The system of any one of claims 18-33, wherein the cathodic chamber and the anodic chamber are separated by a semi-permeable barrier having a plurality of pores.

35. The system of claim 34, wherein the semi-permeable barrier is a semi-permeable membrane (*e.g.*, a membrane made of ion exchange materials (*e.g.*, Nafion), hydrophilic ceramic membrane or plate (*e.g.*, aluminum oxide, zirconium oxide, silicon dioxide, asbestos, hydrous aluminum phyllosilicates, clay, or any combination thereof), polymer (*e.g.*, cellulose, polyvinyl chloride, organic rubber, polyolefin, polyethylene, polypropylene, polyvinylidene fluoride, polytetrafluoroethylene, epoxy resin, silicone, or any combination thereof), or ceramic-polymer composites).

36. The system of claim 34 or 35, wherein the plurality of pores has a median pore diameter from about 0.1 nm to about 500 nm.

37. The system of any one of claims 34-36, wherein the semi-permeable barrier has a thickness of from about 5 μm to about 5 mm.

38. A method of producing hydrogen from an aqueous solution, comprising contacting the aqueous solution with the positive electrode and the negative electrode of the system of any one of claims 18-37 and passing a current through the aqueous solution, thereby forming H_2 and/or OH^- ions at the negative electrode.

39. A method of producing H_2, comprising:

(a) in an anodic chamber of an electrochemical cell, performing an acidic process comprising:

acidifying a first solution by:

contacting the first solution with a positive electrode disposed inside the anodic chamber; and

passing a current through the first aqueous solution, thereby forming an acidic solution; and

(b) in a cathodic chamber, performing an alkaline process comprising:

alkalinizing a second aqueous solution by:

contacting the second aqueous solution with a negative electrode disposed inside of the cathodic chamber; and

passing a current through the second aqueous solution, thereby forming an alkaline solution and H_2;

wherein:

the anodic chamber and the cathodic chamber are in ionic communication; and
the acidic process and the alkaline process are performed simultaneously or sequentially.

40. The method of claim 39, wherein the alkaline process and acidic process are performed simultaneously.

41. The method of claim 39 or 40, wherein the method further comprises contacting the alkaline solution with a CO_2 source, thereby forming a carbonated solution comprising a mixture of ionic compounds, wherein the ionic compounds comprise CO_3^{2-} or HCO_3^-;

42. The method of claim 41, wherein the CO_2 source comprises from about 400 ppm to about 100% CO_2, preferably about 400 ppm.

43. The method of claim 41 or 42, wherein the CO_2 source is ambient air.

44. The method of any one of claims 41-43, wherein the CO_2 source has a higher CO_2 concentration than ambient air, such as gaseous effluent from an industrial process (*e.g.*, oil and gas production, power generation, cement production, or steel production), or concentrated CO_2 from direct air capture processes (*e.g.*, nearly pure or pure-CO_2).

45. The method of any one of claims 39-44, wherein the first solution is selected from seawater, desalination brine, industrial brine, and natural brine.

46. The method of any one of claims 39-45, wherein the second solution is selected from seawater, desalination brine, industrial brine, and natural brine.

47. The method of any one of claims 39-46, wherein the first solution and the second solution originate from the same source solution.

48. The method of any one of claims 39-47, wherein the alkaline process and acidic process occur in spaces separated by a semi-permeable barrier having a plurality of pores.

49. The method of claim 48, wherein the semi-permeable barrier is a semi-permeable membrane (*e.g.*, a membrane made of ion exchange materials (*e.g.*, Nafion), hydrophilic

ceramic membrane or plate (*e.g.*, aluminum oxide, zirconium oxide, silicon dioxide, asbestos, hydrous aluminum phyllosilicates, clay, or any combination thereof), polymer (*e.g.*, cellulose, polyvinyl chloride, organic rubber, polyolefin, polyethylene, polypropylene, polyvinylidene fluoride, polytetrafluoroethylene, epoxy resin, silicone, or any combination thereof), or ceramic-polymer composites).

50. The method of claim 48 or 49, wherein the plurality of pores has a median pore diameter from about 0.1 nm to about 500 nm.

51. The method of any one of claims 48-50, wherein the semi-permeable barrier has a thickness of from about 5 μm to about 5 mm.

52. The method of any one of claims 48-51, wherein the alkaline solution has a pH from about 7 to about 14.

53. The method of any one of claims 39-52, wherein the alkaline solution has a pH from about 10 to about 11.

54. The method of any one of claims 39-53, wherein the alkaline solution has a pH of about 10.5.

55. The method of any one of claims 39-54, wherein the acidic solution has a pH from about 0.1 to about 7.

56. The method of any one of claims 39-55, wherein the acidic solution has a pH from about 0.5 to 1.5.

57. The method of any one of claims 39-56, wherein the acidic solution has a pH of about 1.

58. A method of making the electrode of any one of claims 1-16, comprising:
immersing the substrate in an acidic solution;
applying a first electrical potential across the substrate, thereby removing an oxidized surface of the substrate;

immersing the substrate in a plating solution; and

applying a second electrical potential across the substrate, thereby electrodepositing the outer layer on the substrate;

wherein the plating solution comprises Co and Ni ions.

59. A method of making an electrode comprising:

immersing a substrate in an acidic solution;

applying a first electrical potential across the substrate, thereby removing an oxidized surface of the substrate;

immersing the substrate in a plating solution; and

applying a second electrical potential across the substrate, thereby electrodepositing an outer layer on the substrate;

wherein the plating solution comprises Co and Ni cations.

60. The method of claim 58 or 59, wherein the plating solution comprises Co^{2+} and Ni^{2+} ions.

61. The method of any one of claims 58-60, wherein the plating solution further comprises Mo cations.

62. The method of any one of claims 58-61, wherein the plating solution further comprises Mo^{6+} ions.

63. The method of any one of claims 58-62, wherein the plating solution further comprises an electrolyte.

64. The method of any one of claims 58-63, wherein the plating solution further comprises $(NH_4)_2SO_4$ and NH_4OH.

65. The method of any one of claims 58-64, wherein the acidic solution comprises H_2SO_4.

66. The method of claim 65, wherein the concentration of H_2SO_4 is about 9 M.

67. The method of any one of claims 58-66, wherein the first electrical potential is applied across the substrate at about 80 °C.

68. The method of any one of claims 59-67, wherein the outer layer comprises Co, Ni, and Mo.

69. The method of any one of claims 58-68, wherein the second electrical potential is applied across the substrate at a current of about 50 mA/cm^2.

70. The method of any one of claims 58-69, wherein the second electrical potential is applied across the substrate for about 120 min.

71. An electrode prepared according to any one of claims 59-70, comprising:
the substrate; and
the outer layer disposed on the substrate;
wherein:
the substrate comprises a conductive or semi-conductive material; and
the outer layer comprises Co and Ni.

72. The electrode of claim 71, wherein the outer layer further comprises Mo.

73. The electrode of any one of claims 1-16, prepared according to the method of any one of claims 59-70.

FIGURE 1A

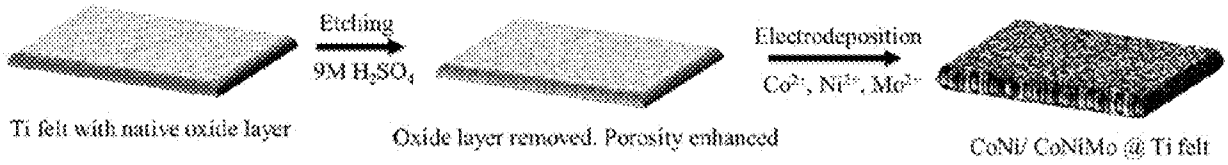


FIGURE 1B

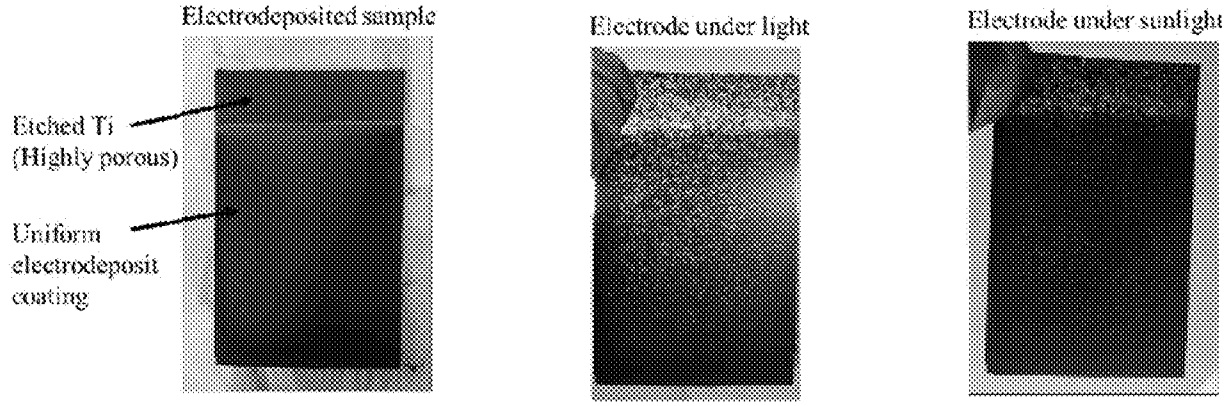


FIGURE 2

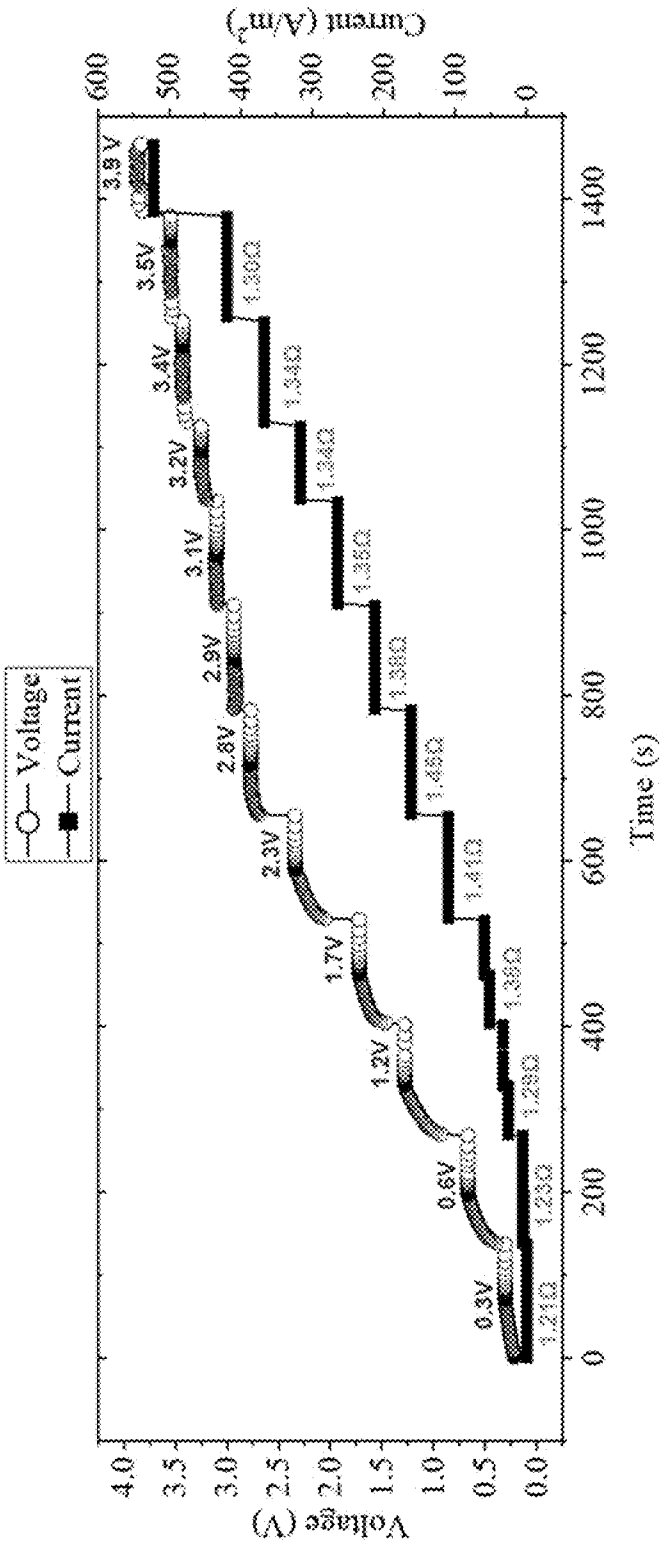

Voltage
Current
Voltage (V)
Current (A/m²)
Time (s)
0.3V
0.6V
1.2V
1.7V
2.3V
2.8V
2.9V
3.1V
3.2V
3.4V
3.5V
3.8 V
1.210
1.230
1.260
1.380
1.410
1.450
1.380
1.360
1.340
1.320
1.300

FIGURE 3A

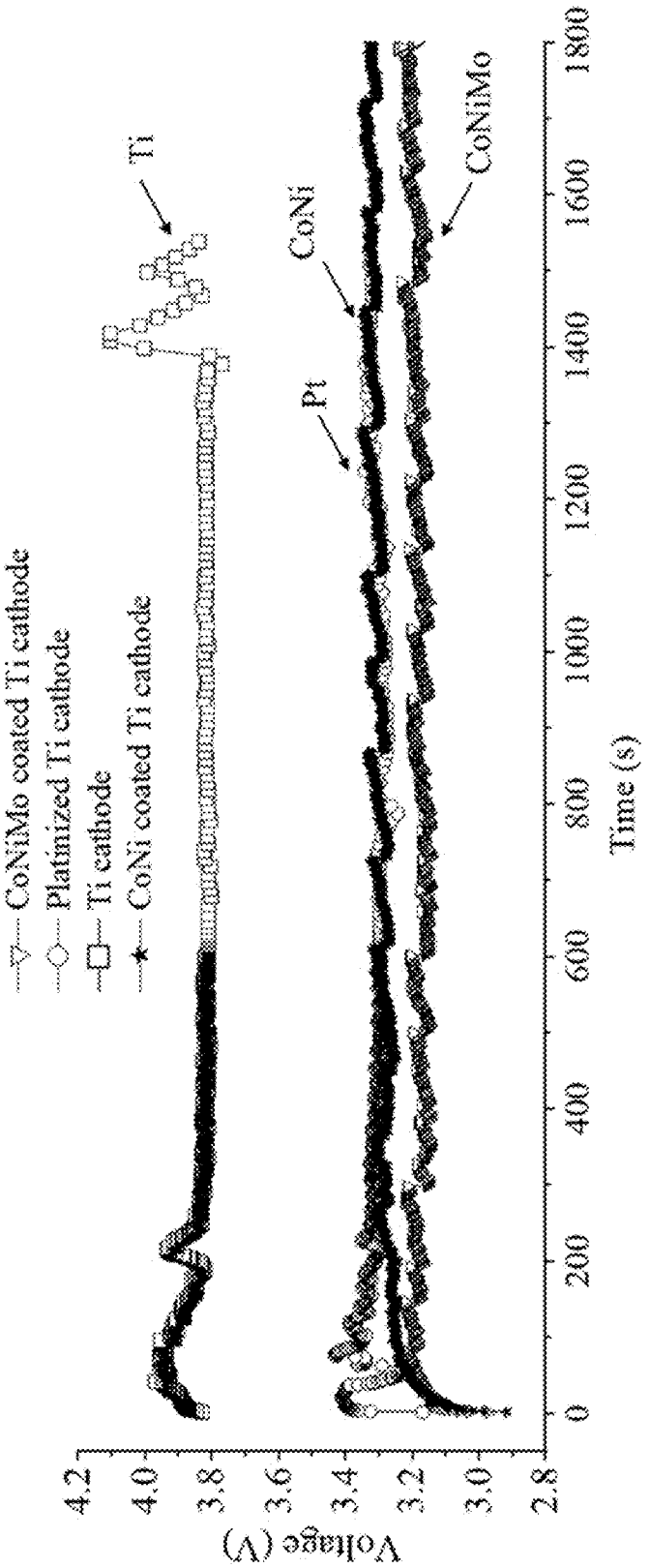

CoNiMo coated Ti cathode
Platinized Ti cathode
Ti cathode
CoNi coated Ti cathode
Ti
CoNi
Pt
CoNiMo
Voltage (V)
Time (s)
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
0
200
400
600
800
1000
1200
1400
1600
1800

FIGURE 3B

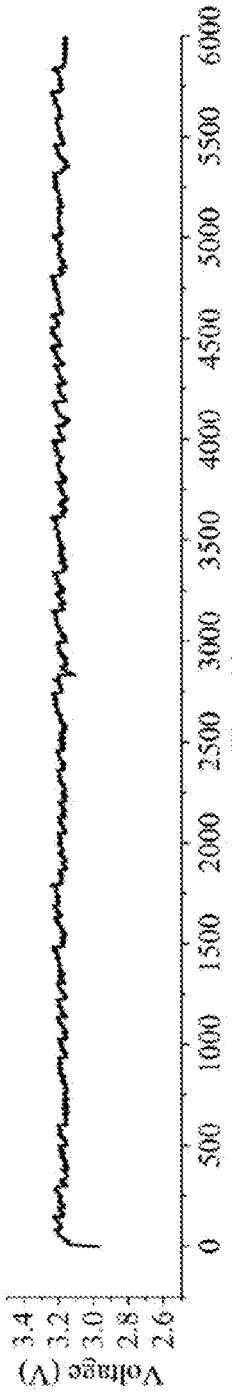
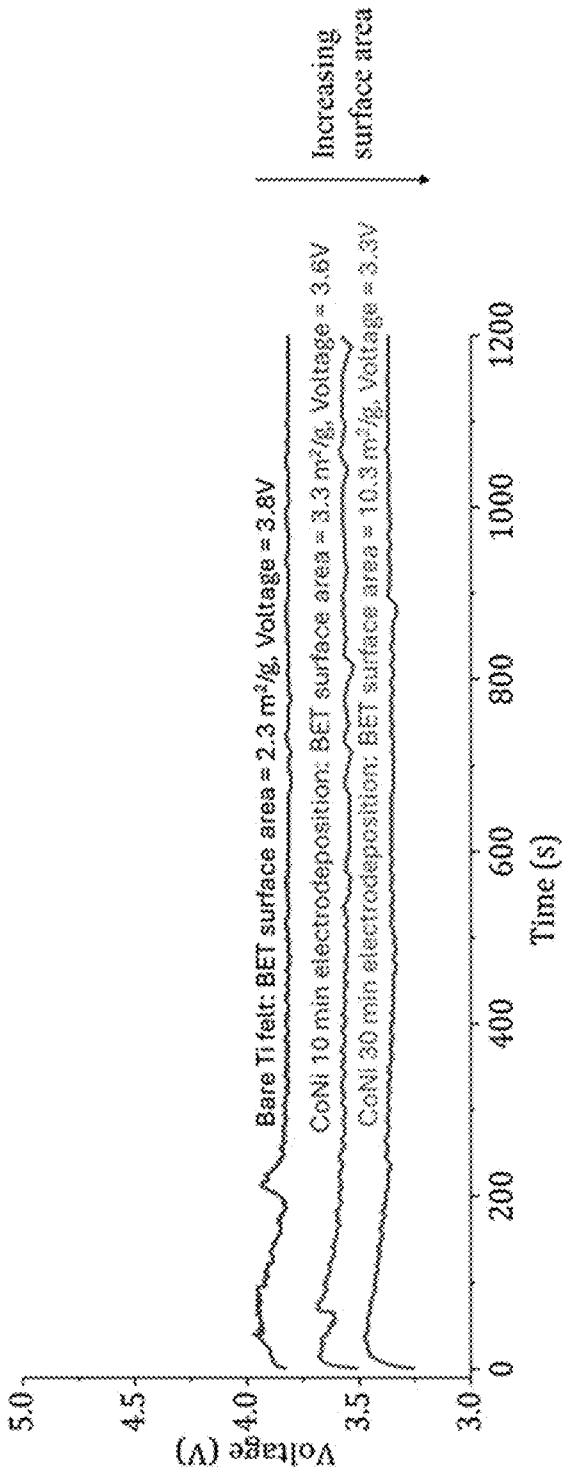

Voltage (V)
3.4
3.2
3.0
2.8
2.6
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
Time (s)

FIGURE 4


Increasing surface area
Bare Ti felt: BET surface area = 2.3 m²/g, Voltage = 3.8V
CoNi 10 min electrodeposition: BET surface area = 3.3 m²/g, Voltage = 3.6V
CoNi 30 min electrodeposition: BET surface area = 10.3 m²/g, Voltage = 3.3V
Voltage (V)
5.0
4.5
4.0
3.5
3.0
0
200
400
600
800
1000
1200
Time (s)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2026/019656

A. CLASSIFICATION OF SUBJECT MATTER

C25D 5/10(2026.01)i; ***C25D 3/12***(2026.01)i; ***C25B 1/04***(2026.01)i; ***C25B 11/061***(2026.01)i; ***C02F 1/461***(2026.01)i
CPC:C25D 5/10; C25D 3/12; C25B 1/04; C25B 11/061; C02F 1/461; C02F 2201/461

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)

C25D 5/10; C25D 3/12; C25B 1/04; C25B 11/061; C02F 1/461
CPC:C25D 5/10; C25D 3/12; C25B 1/04; C25B 11/061; C02F 1/461; C02F 2201/461

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

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

Databases consulted: Esp@cenet, Google Patents, Google Scholar, AI based search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 2019169762 A1 (HITACHI SHIPBUILDING ENG CO [JP]) 06 June 2019 (2019-06-06)	
X	the whole document	1-5,8,9,11,17-22, 25,26,28,38,58-60,65-67,69-71,73
Y		23,24,27,29-37
	CN 118176328 A (MAXTERRIER INC) 11 June 2024 (2024-06-11)	
X	the whole document	1-16,58-64,68,71-73
Y		23,24,27,29-33
	US 6527940 B1 (PERMELEC ELECTRODE LTD [JP]) 04 March 2003 (2003-03-04)	
X	the whole document	39-57
Y		34-37

☐ 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	Date of mailing of the international search report
09 July 2026	**12 July 2026**

Name and mailing address of the ISA/IL	Authorized officer
Israel Patent Office **Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel** **Israel** Telephone No. **972-73-3927109** Email: **pctoffice@justice.gov.il**	**KATZ Nina** Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2026/019656

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US 2019169762 A1	06 June 2019	US 2019169762 A1	06 June 2019
		EP 3498888 A1	19 June 2019
		EP 3498888 A4	08 April 2020
		JP 2018024925 A	15 February 2018
		WO 2018029967 A1	15 February 2018
CN 118176328 A	11 June 2024	CN 118176328 A	11 June 2024
		AU 2022291934 A1	01 February 2024
		AU 2022292751 A1	01 February 2024
		AU 2022292752 A1	01 February 2024
		AU 2022293579 A1	01 February 2024
		CA 3224552 A1	22 December 2022
		CA 3224554 A1	22 December 2022
		CA 3224559 A1	22 December 2022
		CA 3224563 A1	22 December 2022
		CN 118202091 A	14 June 2024
		CN 118202092 A	14 June 2024
		CN 118215752 A	18 June 2024
		EP 4355924 A1	24 April 2024
		EP 4355924 A4	01 April 2026
		EP 4355933 A1	24 April 2024
		EP 4355933 A4	07 January 2026
		EP 4355934 A1	24 April 2024
		EP 4355934 A4	12 November 2025
		EP 4355935 A1	24 April 2024
		EP 4355935 A4	12 November 2025
		JP 2024527497 A	25 July 2024
		JP 2024527498 A	25 July 2024
		JP 2024528420 A	30 July 2024
		JP 2024528422 A	30 July 2024
		KR 20240093442 A	24 June 2024
		KR 20240093443 A	24 June 2024
		KR 20240093444 A	24 June 2024
		KR 20240093445 A	24 June 2024
		US 2023151831 A1	18 May 2023
		US 12163208 B2	10 December 2024
		US 2023143308 A1	11 May 2023
		US 12359289 B2	15 July 2025
		US 2023142535 A1	11 May 2023
		US 12516403 B2	06 January 2026
		US 2023138199 A1	04 May 2023
		US 2023145335 A1	11 May 2023
		US 2023147807 A1	11 May 2023
		US 2023151505 A1	18 May 2023
		US 2023151871 A1	18 May 2023
		US 2024368767 A1	07 November 2024
		US 2024368793 A1	07 November 2024
		US 2024410072 A1	12 December 2024
		US 2024410073 A1	12 December 2024
		US 2025263820 A1	21 August 2025
		WO 2022266528 A1	22 December 2022

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2026/019656

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
		WO 2022266529 A1	22 December 2022
		WO 2022266532 A1	22 December 2022
		WO 2022266533 A1	22 December 2022
US 6527940 B1	04 March 2003	US 6527940 B1	04 March 2003
		JP H09262583 A	07 October 1997
		JP 3785219 B2	14 June 2006