

US 20150259810A1

(19) **United States**

(12) **Patent Application Publication**
Lewis et al.

(10) **Pub. No.: US 2015/0259810 A1**

(43) **Pub. Date: Sep. 17, 2015**

(54) **HYDROGEN EVOLUTION REACTION
CATALYSIS**

Publication Classification

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(51) **Int. Cl.**

C25B 11/04 (2006.01)

C25B 1/02 (2006.01)

(52) **U.S. Cl.**

CPC **C25B 11/0415** (2013.01); **C25B 1/02**
(2013.01); **C25B 11/0426** (2013.01)

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(57)

ABSTRACT

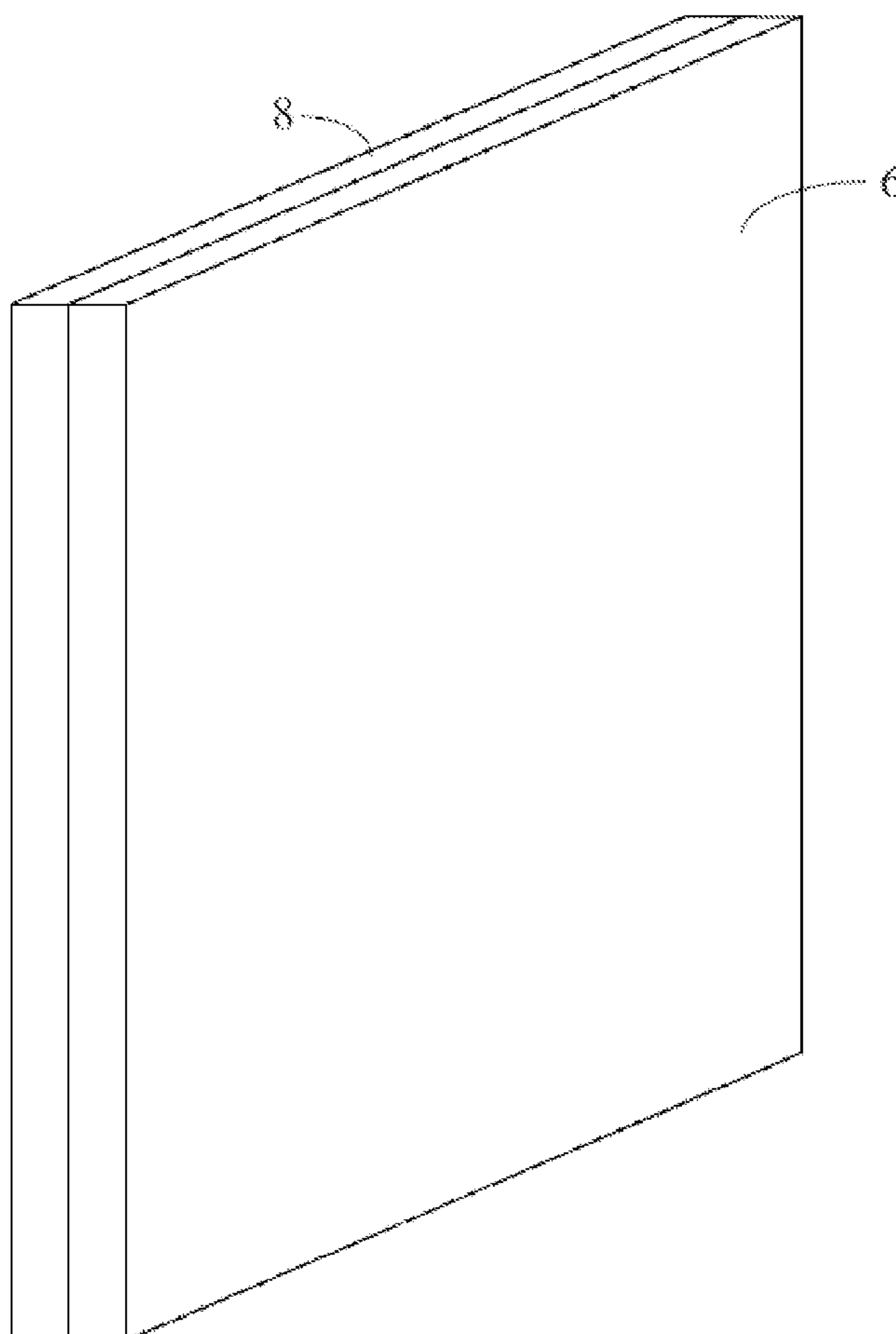
(21) Appl. No.: **14/660,699**

(22) Filed: **Mar. 17, 2015**

Related U.S. Application Data

(60) Provisional application No. 61/954,367, filed on Mar.
17, 2014.

A Hydrogen Evolution Reaction (HER) catalyst includes at least one component selected from a group consisting of transition metal phosphides and first row transition metal sulfides. The catalyst can be included in nanoparticles. In some instances, the catalyst is included in a hydrogen evolution reaction electrode. In one example, the catalyst is cobalt phosphide.



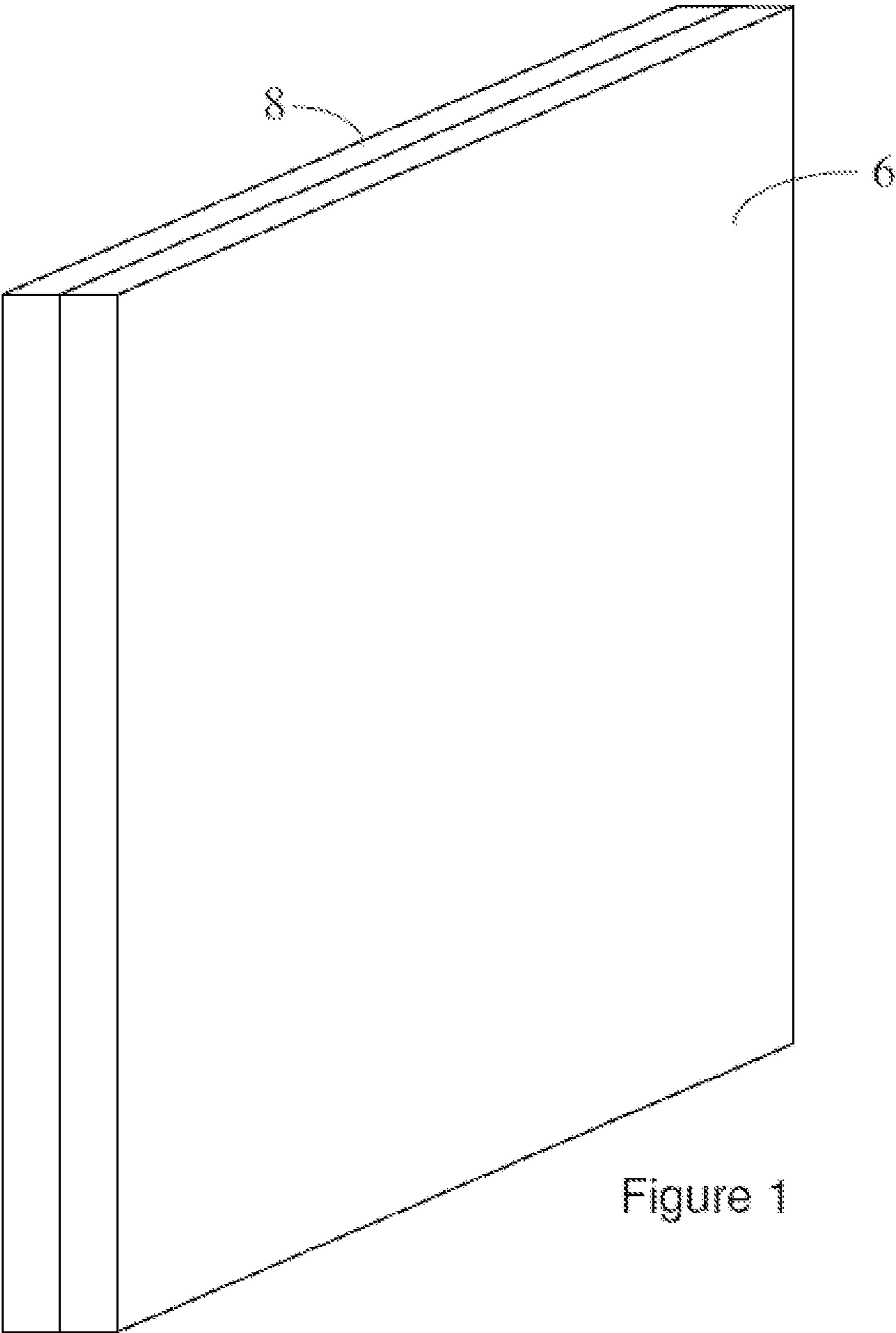


Figure 1

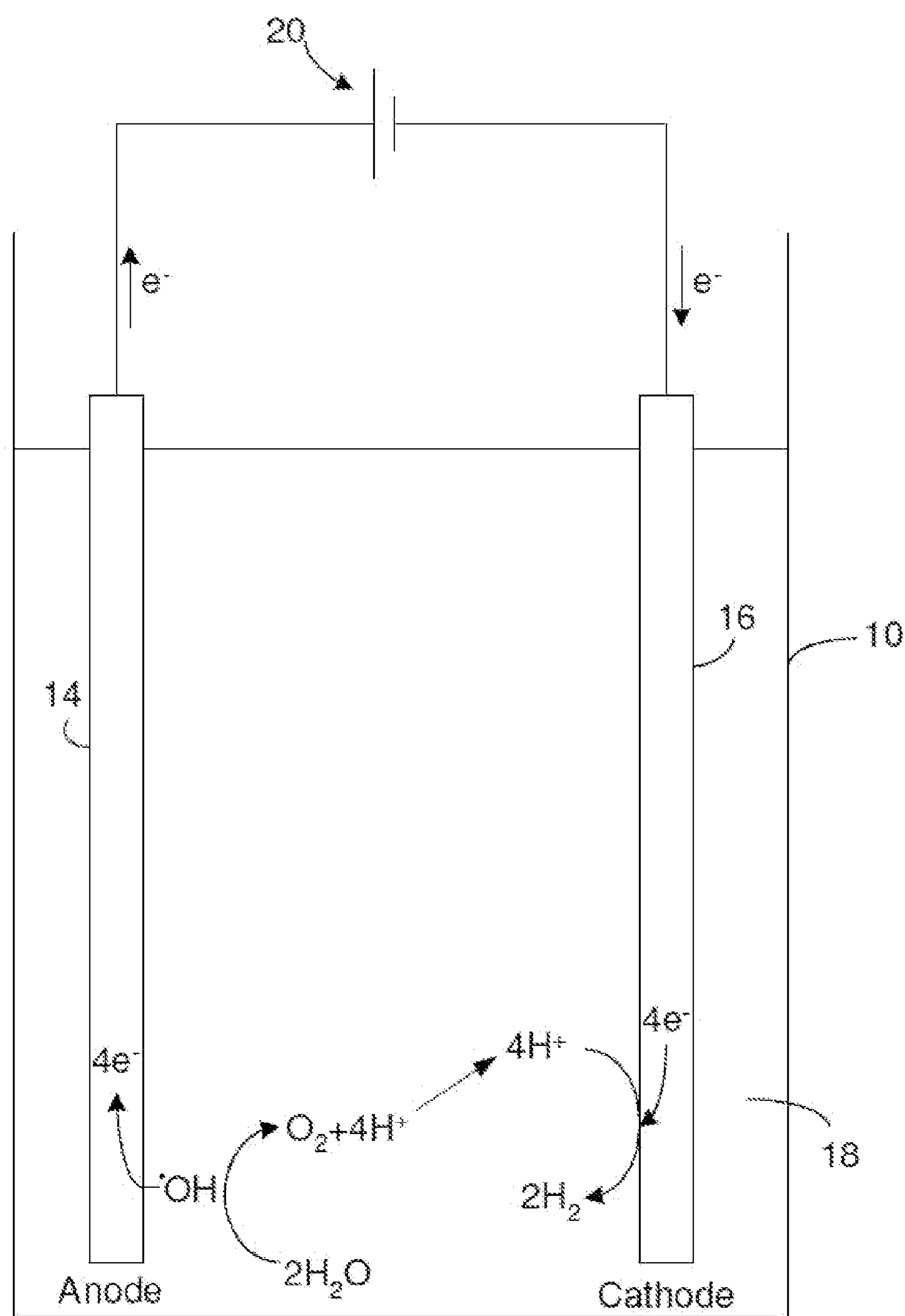


Figure 2

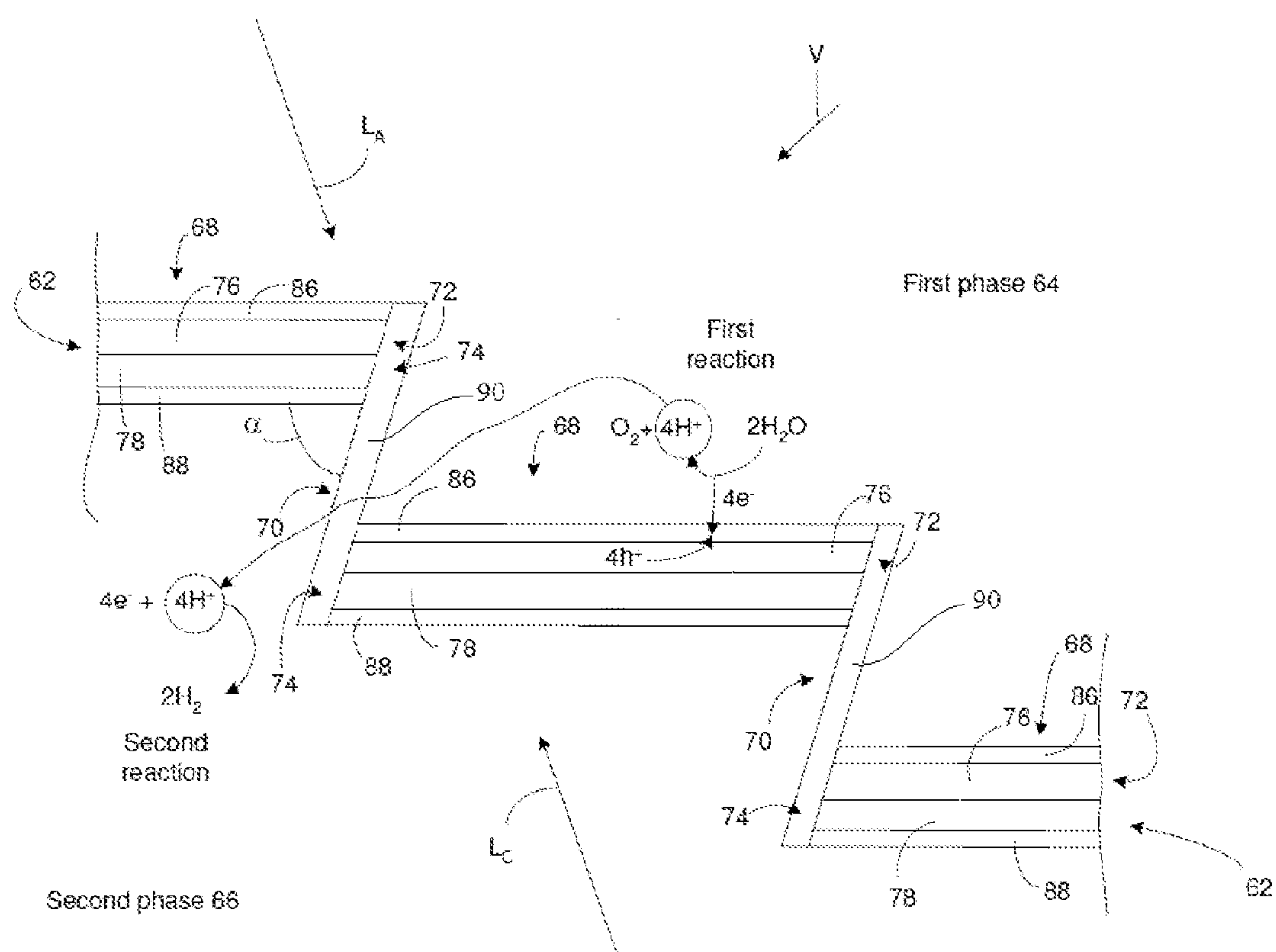


Figure 3A

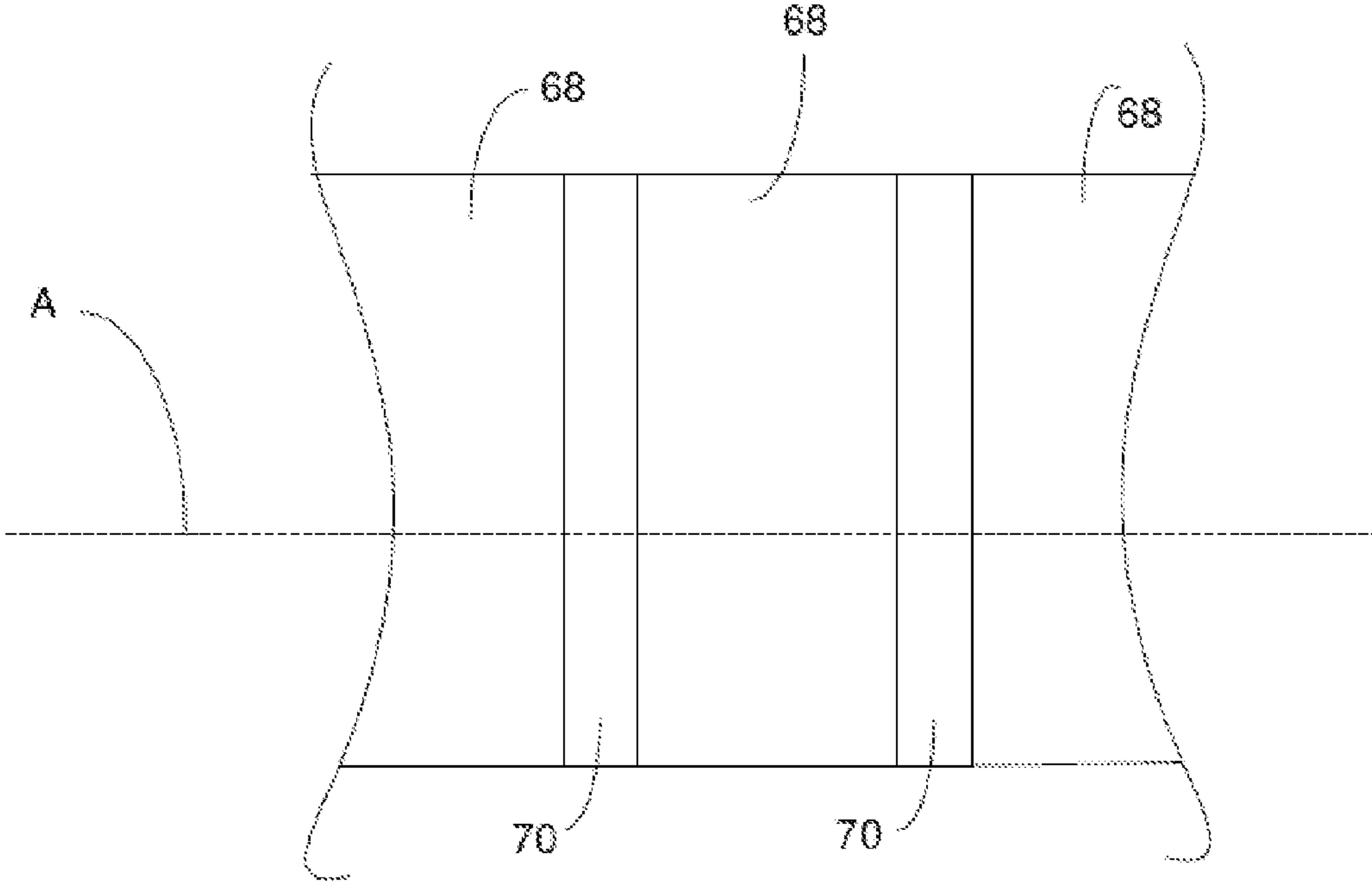


Figure 3B

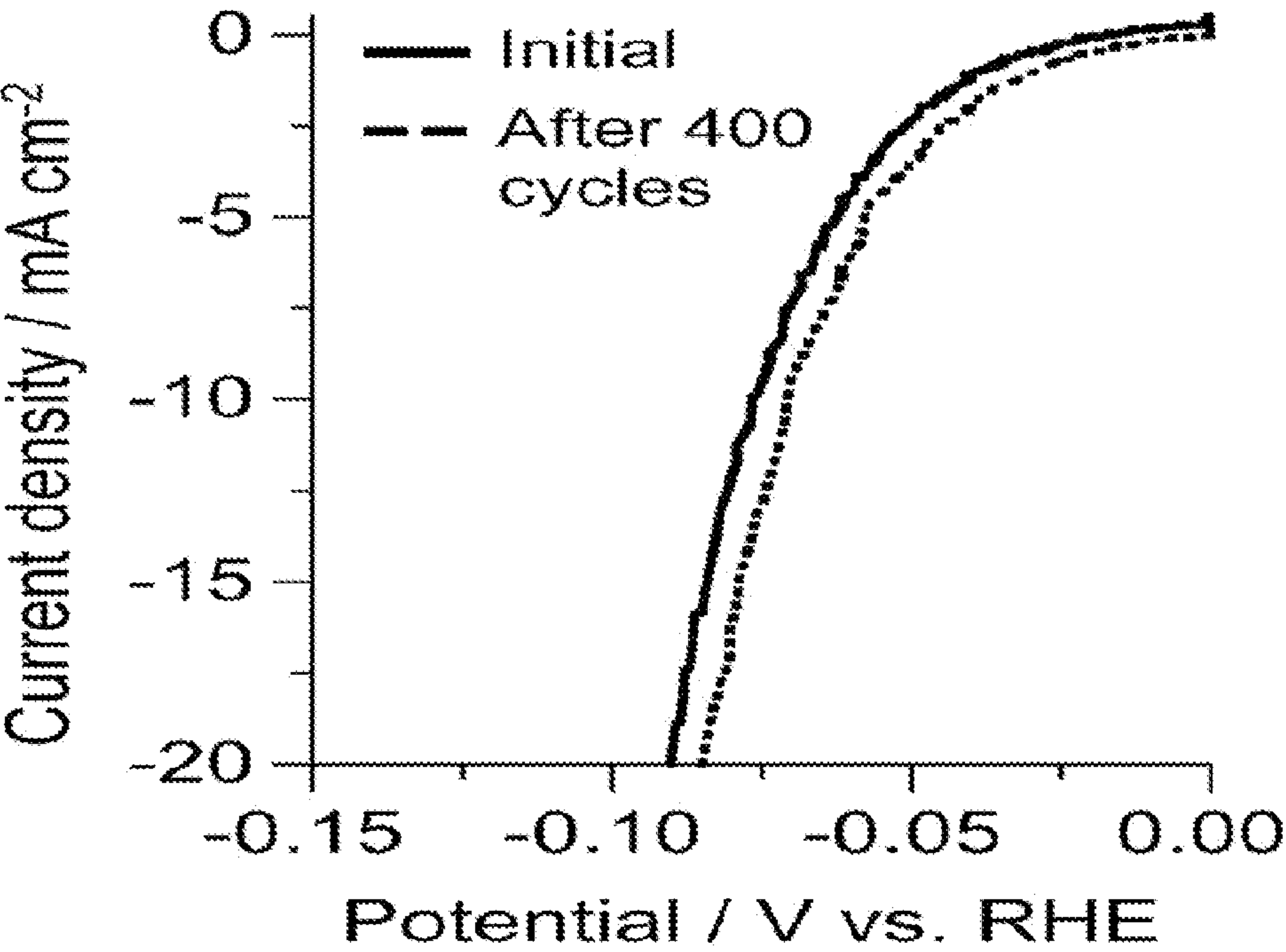


Figure 4

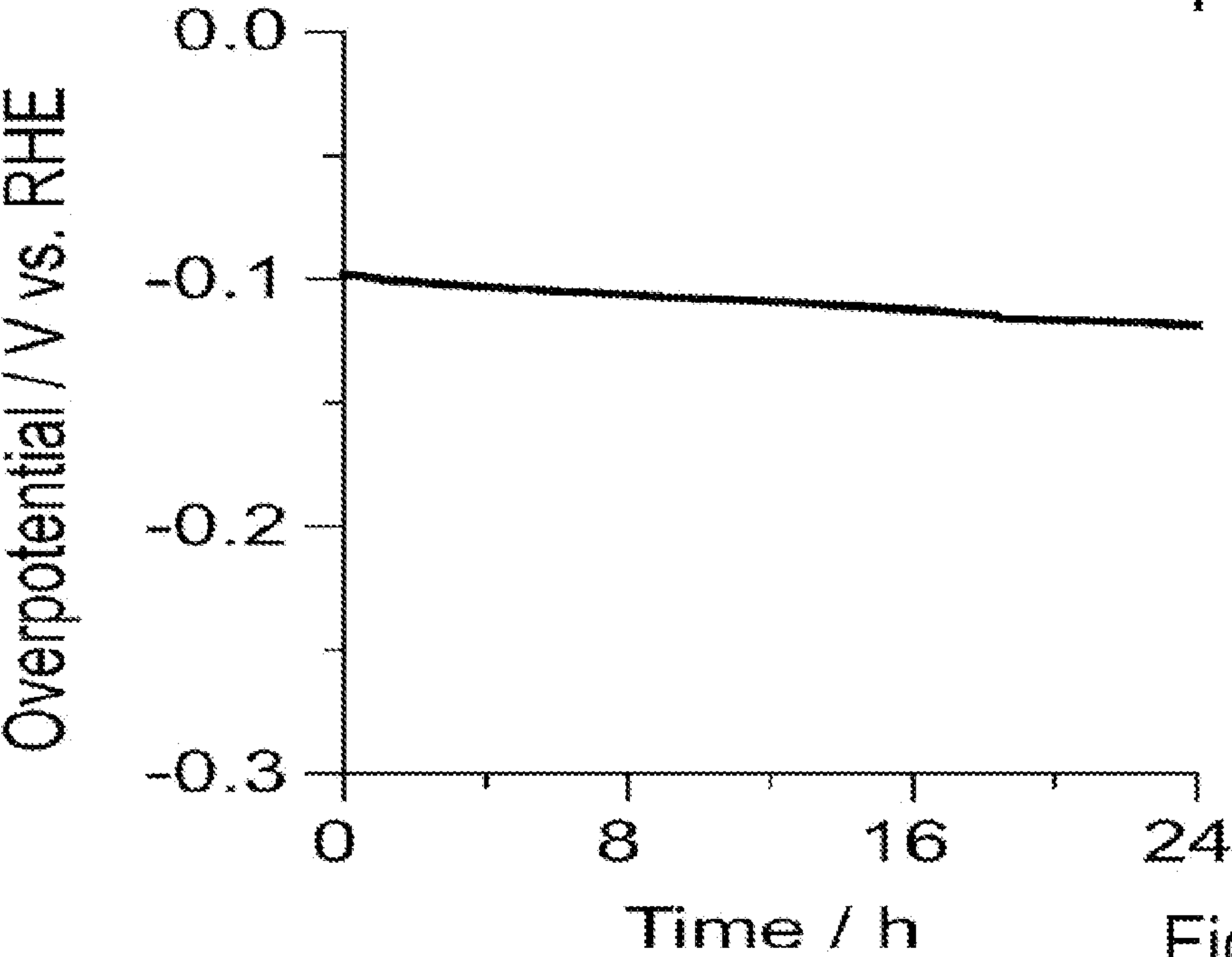


Figure 5

HYDROGEN EVOLUTION REACTION CATALYSIS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/954,367, filed on Mar. 17, 2014, and incorporated herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under grant numbers CHE1305124 and CHE0802907 awarded by the National Science Foundation and grant number DE-SC0004993 awarded by the Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The invention relates to catalysts, and more particularly, to electrocatalysts.

BACKGROUND

[0004] A variety of different applications make use of the Hydrogen Evolution Reaction (HER). Examples of these applications include solar fuels generation and water electrolysis. In applications such as solar fuels generation, the overpotential that can be applied to the electrodes where the hydrogen evolution reaction occurs is often limited to the photovoltage that can be achieved as a result of light being incident on semiconductors. Because of this limited photovoltage, it is desirable to have a catalyst that is effective at low overpotentials. In other applications, a low overpotential is desirable for minimizing electrical expenses. Many of the current electrocatalysts for the Hydrogen Evolution Reaction do not provide the desired level of performance for low overpotential applications and/or do not tolerate the acidic conditions that may be necessary for efficiently driving the HER. Additionally, these catalysts often make use of components that are expensive and/or are not present in the earth in sufficient levels for effective use on an industrial scale. Accordingly, there is a need for improved Hydrogen Evolution Reaction (HER) catalysts.

SUMMARY

[0005] A Hydrogen Evolution Reaction (HER) catalyst includes at least one component selected from a group consisting of transition metal phosphides, first row transition metal sulfides, and transition metal arsenides. In some instances, the transition metal phosphides include or consist of phosphorous and one or more transition metals selected from the group consisting of cobalt, tungsten, nickel, iron, titanium, vanadium, chromium, manganese, niobium, and molybdenum. In some instances, the first row transition metal sulfides include or consist of sulfur and one or more first row transition metals selected from the group consisting of vanadium, chromium, manganese, nickel, copper, iron and titanium. In some instances, the transition metal arsenides include or consist of arsenic and one or more transition metals selected from the group consisting of titanium, chromium, iron, cobalt, nickel, molybdenum, and tungsten.

[0006] The above catalysts can be an electrocatalyst included in an electrode. The electrode can optionally be

included in a hydrogen evolution system such that the HER occurs at the electrode during the operation of the system. In some instances, the electrode is positioned in an environment having a pH less than 6 or 3 during operation of the system.

BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 is a perspective view of an electrode that can include a hydrogen evolution catalyst.

[0008] FIG. 2 illustrates a hydrogen evolution system for water electrolysis.

[0009] FIG. 3A is a cross section of a solar fuels generator.

[0010] FIG. 3B is a sideview of the solar fuels generator shown in FIG. 3A taken looking in the direction of the arrow labeled V in FIG. 3A. The cross section shown in FIG. 3A can be taken along the line labeled A in FIG. 1B.

[0011] FIG. 4 illustrates current density versus potential results for accelerated degradation testing performed on an electrode including a hydrogen evolution catalyst.

[0012] FIG. 5 provides overpotential versus time results for water electrolysis performed using an electrode including a hydrogen evolution catalyst.

DESCRIPTION

[0013] As used herein and in the appended claims, the singular forms “a,” “and,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a catalyst” includes a plurality of such catalysts and reference to “the electrode” includes reference to one or more electrodes and so forth.

[0014] Also, the use of “or” means “and/or” unless stated otherwise. Similarly, “comprise,” “comprises,” “comprising” “include,” “includes,” and “including” are interchangeable and not intended to be limiting.

[0015] It is to be further understood that where descriptions of various embodiments use the term “comprising,” those skilled in the art would understand that in some specific instances, an embodiment can be alternatively described using language “consisting essentially of” or “consisting of.”

[0016] All publications mentioned throughout the disclosure are incorporated herein by reference in full for the purpose of describing and disclosing the methodologies, which are described in the publications, which might be used in connection with the description herein. The publications discussed throughout the text are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior disclosure. Moreover, with respect to similar or identical terms found in the incorporated references and terms expressly defined in this disclosure, the term definitions provided in this disclosure will control in all respects.

[0017] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art. Although there are many methods and reagents similar or equivalent to those described herein, the exemplary methods and materials are presented herein.

[0018] The disclosure describes a class of catalysts that are effective at low overpotentials. The catalysts include metal phosphides, metal sulfides, and metal arsenides. The catalysts and electrodes that include the catalyst have proven to be surprisingly tolerant of highly acidic environments. For instance, water electrolysis was performed with a working

electrode positioned in a 0.5 M H_2SO_4 solution. The working electrode had a cobalt phosphide catalyst coated on a titanium current collector. Accelerated degradation studies were performed by applying 400 cyclic voltammetry sweeps from +5 mV to 140 mV (versus reversible hydrogen electrode potential). After these sweeps, the catalyst surprisingly showed little measurable loss in catalytic activity. Additionally, an overpotential of ~ -0.95 mV was originally needed to achieve a current density of -20 mA/cm². This overpotential dropped to ~ -0.90 mV after the 400 cycles showing an unexpected stability in the highly acidic environment. Additionally, galvanostatic measurements showed that at a current density of -20 mA/cm², the overpotential increased only slightly over 24 hours (24 mV). Further, inspection of the electrode during these experiments showed the catalyst was not obviously becoming detached from the current collector. Additionally, the catalysts show an unexpectedly high adherence to suitable current collectors even under acidic conditions. As a further advantage, the materials for these catalysts are earth abundant making these catalysts suitable for scaling to industrial levels at reasonable costs.

[0019] The catalyst can include or consist of phosphides. The phosphides can include or consist of phosphorous and one or more transition metals. In some instances, the phosphides include or consist of phosphorous and one or more transition metals selected from the group consisting of cobalt, tungsten, nickel, iron, titanium, vanadium, chromium, manganese, niobium, and molybdenum. Examples of suitable metal phosphides include, but are not limited to, cobalt phosphide, tungsten phosphide, dinickel phosphide (Ni_2P), iron phosphide, titanium phosphide, vanadium phosphide, chromium phosphide, manganese phosphide, niobium phosphide, and molybdenum phosphide. The phosphides can be binary, ternary or higher order phosphides.

[0020] In some instance, the phosphide is represented by $\text{M1}_x\text{P}_y$, where M1 represents one or more metals, at least one of the metals represented by M1 is a transition metal, x has value greater than or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4. In some instances, at least one of the metals represented by M1 is selected from a group consisting of cobalt, tungsten, nickel, iron, titanium, vanadium, chromium, manganese, niobium, and molybdenum.

[0021] The catalyst can include or consist of sulfides. The sulfides can include or consist of sulfur and one or more first row transition metals. In some instances, the sulfides include or consist of sulfur and one or more first row transition metals selected from the group consisting of vanadium, chromium, manganese, nickel, copper, iron and titanium. Examples of metal sulfides include, but are not limited to, vanadium sulfide, chromium sulfide, manganese sulfide, nickel sulfide, copper sulfide, iron sulfide and titanium sulfide. The sulfides can be binary, ternary or higher order sulfides.

[0022] In some instance, the sulfide is represented by $\text{M2}_x\text{S}_y$, where M2 represents one or more metals, at least one of the metals represented by M2 is a first row transition metal, x has value greater than or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4. In some instances, at least one of the metals represented by M2 is selected from the group consisting of vanadium, chromium, manganese, nickel, copper, iron and titanium.

[0023] The catalyst can include or consist of arsenides. The arsenides can include or consist of arsenic and one or more

transition metals. In some instances, the arsenide includes or consists of arsenic and one or more transition metals selected from the group consisting of titanium, chromium, iron, cobalt, nickel, molybdenum, and tungsten. Examples of suitable metal arsenides include, but are not limited to, titanium arsenide, chromium arsenide, iron arsenide, cobalt arsenide, nickel arsenide, molybdenum arsenide, tungsten arsenide. The arsenides can be binary, ternary or higher order arsenides.

[0024] In some instance, the arsenide is represented by $\text{M3}_x\text{S}_y$, where M3 represents one or more metals, at least one of the metals represented by M3 is a transition metal, x has value greater than or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4. In some instances, at least one of the metals represented by M3 is selected from the group consisting of titanium, chromium, iron, cobalt, nickel, molybdenum, and tungsten.

[0025] A particular example of the catalyst is cobalt phosphide. In some instance, the cobalt phosphide is represented by Co_xP_y , wherein x has value greater than or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4. In one example, the catalyst is CoP.

[0026] The catalyst can catalyze a variety of reactions such as the Hydrogen Evolution Reaction, hydrodesulfurization, halide oxidation, and carbon dioxide reduction. In particular, the catalysts can catalyze the Hydrogen Evolution Reaction (HER). One example of the hydrogen evolution reaction is the reduction of protons represented by: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$.

[0027] The catalyst can be an electrocatalyst. For instance, the catalyst can have one, two or three features selected from the group consisting of functioning at the surface of an electrode, defining the surface of the electrode, or interacting with one or more components of the environment in which the electrode is positioned. In some instances, the catalyst catalyzes hydrogen evolution at the surface of an electrode and/or reduces protons present in the environment in which the electrode is positioned.

[0028] In some instances, nanoparticles include, consist of, or consist essentially of the catalyst. Suitable nanoparticles include, but are not limited to, nanoparticles with an average diameter greater than 1 nm, 100 nm, or 2500 nm and/or less than 100 nm, 2500 nm, or 10,000 nm. The nanoparticles can be hollow or solid in shape and crystalline or amorphous in structure. In instances where the nanoparticles include components in addition to the one or more catalysts, the nanoparticles can include binders or ionomers.

[0029] FIG. 1 is a perspective view of an electrode that includes the catalyst. The electrode includes a catalytic layer 6 on an electrode base 8. The catalytic layer 6 includes, consists of, or consists essentially of one or more of the catalysts. The catalytic layer 6 can include components in addition to the one or more catalysts. For instance, the catalytic layer 6 can include one or more components selected from the group consisting of binders, polymers, membranes, electrical conductors, ionic conductors, solid electrolytes, porous materials, and inert support materials. The electrode base 8 represents the portion of the electrode having a traditional electrode construction. Alternately, the electrode base 8 represents the portion of the electrode having a traditional electrode construction but with a prior catalytic layer removed from the electrode. Accordingly, the catalytic layer 6 can be added to a prior art electrode or can replace a catalytic layer 6 on a prior art electrode.

[0030] The electrode base **8** can be a current collector such as a metal foil or sheet, mesh, or conducting fabric. As will become evident from the below illustration of a solar fuels generator, the electrode base **8** can be or include a semiconductor layer. Although the electrode base **8** is shown as a single layer of material, the electrode base **8** can include multiple layers of material. For instance, the electrode base **8** can include one or more layers of active material on a current collector. In instance where the electrode is employed to reduce protons, the electrode operates as a cathode. During fabrication of the electrode, in some instances, the electrode base serves as the support for the catalyst. Accordingly, the catalyst can be formed directly on the electrode base.

[0031] Although the catalytic layer **6** is illustrated as being located on one side of the electrode base **8**, the catalytic layer **6** can be located on both sides of the electrode base. Additionally or alternately, FIG. 1 illustrates the catalytic layer **6** being located on the electrode base **8**; however, the electrode base **8** can be embedded in the catalytic layer **6**. For instance, electrode base **8** can be a mesh that is embedded in the catalytic layer **6**. Although FIG. 1 illustrates the catalytic layer **6** as a continuous layer of material, the catalytic layer **6** can be patterned so there are openings through the catalytic layer **6** and/or so there are regions of the catalytic layer **6** that are not continuous with one another such as would occur when the catalytic layer **6** is arranged in islands on the electrode base.

[0032] In the illustration of FIG. 1, the face of the catalytic layer **6** is illustrated as being substantially planar. However, the surface area of the catalytic layer **6** can be increased beyond what can be achieved with the planar face. In some instances, the surface area of the catalytic layer **6** can increase the catalytic current for a given overpotential. A variety of methods can be employed to increase the surface area of the catalytic layer **6**. For instance, the catalytic layer can include, consist of, or consist essentially of nanoparticles that include, consist of, or consist essentially of one or more of the catalysts. Suitable average diameters for the nanoparticles include, but are not limited to, average diameters greater than 1 nm, 100 nm, or 2500 nm and/or less than 100 nm, 2500 nm, or 10,000 nm. The nanoparticles can be hollow or solid in shape and crystalline or amorphous in structure. In instances where the nanoparticles include components in addition to the one or more catalysts, the nanoparticles can include binders or ionomers. Another possible technique for increasing the surface area of the catalyst layer is for the catalytic layer to be porous and/or microstructured using techniques such as mesoscale self-assembly, soft lithography, anodic etching, or other methods known to the art. In some instances, the catalytic layer includes, consists of, or consists essentially of nanoparticles and is also porous in that an environment in which the electrode is positioned can occupy spaces between adjacent nanoparticles. In some instances, the catalytic layer is constructed such that the specific surface area of the catalytic layer is much greater than the geometric area of the electrode. This can be expressed as a surface roughness factor (specific surface area/geometric area of the surface area of a planar electrode covered by the catalytic layer). A non-porous catalyst layer with a smooth surface would have a surface roughness factor of 1. The catalytic layer may have surface roughness factors greater than 1, 10, 100 or 1000.

[0033] The electrode can be employed in a hydrogen evolution system where the HER is catalyzed at one or more electrodes included in the system. Examples of these systems

include, but are not limited to, water electrolysis systems, solar fuels generators, energy storage systems, electrorefining, and/or electrolyzers. FIG. 2 provides an example of a water electrolysis system. The system includes a vessel **10** having a reservoir. Anodes **14** and cathodes **16** are positioned in the reservoir such that anodes **14** and cathodes **16** alternate with one another. The anodes **14** and cathodes **16** are parallel or substantially parallel with one another. A medium **18** is positioned in the reservoir such that anodes **14** and the cathodes **16** are in contact with the medium **18**. The medium **18** can be a liquid, gel, solid, a gas, or a combination thereof. The cathode can be constructed as described above in the context of FIG. 1. For instance, the catalytic layer **6** can include or consist of one or more of the catalysts such as cobalt phosphide and the electrode base **8** can be a conductive metal or non-metal, a suitable light absorbing semiconductor, or a combination thereof.

[0034] In some instances, the anode(s) **14** can have a catalytic layer **6** and base **8** arranged as disclosed in the context of FIG. 1. When an anode **14** is constructed according to FIG. 1, the electrode base **8** can be a current collector such as a metal foil or sheet, mesh, or conducting fabric.

[0035] When an anode **14** is constructed according to FIG. 1, the catalytic layer **6** can include, consist of, or consist essentially of one or more oxidation catalysts. The catalytic layer **6** can include components in addition to the one or more oxidation catalysts. For instance, the catalytic layer **6** can include one or more components selected from the group consisting of binders, polymers, membranes, electrical conductors, ionic conductors, solid electrolytes, porous materials, and inert support materials.

[0036] Suitable oxidation catalysts include metal oxides that include, consist of, or consist essentially of oxygen and one, two, three, four or five metals selected from the group consisting of Ir, Mn, Co, Ta, Sn, and Sb or the group consisting of Mn, Co, Ta, and Sb. In some instances, the metal oxide can be represented by $(\text{Ir}_u\text{Mn}_v\text{Co}_w\text{Ta}_y\text{Sb}_z)\text{O}_x$ or $(\text{Mn}_v\text{Co}_w\text{Ta}_y\text{Sb}_z)\text{O}_x$ where $u+v+w+y+z=1$, u is greater than or equal to 0 and less than 1, v is greater than or equal to 0 and less than 1, w is greater than or equal to 0 and less than 1, y is greater than or equal to 0 and less than 1, and z is greater than or equal to 0 and less than 1, and at least one, two, three or four of the variables selected from the group consisting of v , w , y , and z are greater than zero. In some instances where the catalyst includes Ta and/or Sb, the catalysts have the Ta in an amount that is less than or equal to 15 molar % of the metals in the catalyst and/or the Sb in an amount that is less than or equal to 25 molar % of the metals in the catalyst. The metal oxides in this class having at least two, three or four of the variables selected from the group consisting of v , w , y , and z are greater than zero have been shown to have a desirable level of catalytic activity for the oxygen evolution reaction. Additionally, these catalysts are also tolerant of the highly acidic environment such as environments with a pH less than 3, 1, or 0. Iridium oxide and ruthenium oxide are other examples of suitable oxidation catalysts. In some instances when an anode **14** is constructed according to FIG. 1, the catalytic layer **6** excludes iridium oxide and ruthenium oxide.

[0037] In one example of an anode **14** constructed according to FIG. 1, the catalytic layer **6** includes or consist of IrO_x as an oxidation catalyst and the electrode base **8** is a fluorine doped tin oxide film on glass, a light absorbing semiconductor, or a titanium foil current collector.

[0038] The cathode **16** and anode **14** are shown connected to a voltage source **20** that is sufficient to apply the overpotential needed to cause chemical reactions at the anode and/or cathode. For instance, when the hydrogen evolution system is used for water electrolysis, the voltage source **20** can apply the overpotential needed to cause the reactions illustrated in FIG. **2**. The voltage source can be any voltage source such as a photovoltaic voltage source, battery or other electronics. When the potential applied by the voltage source **20** can be controlled, the voltage source **20** can optionally apply the overpotential needed to generate a particular current density. However, when the level of the applied voltage cannot be controlled as often occurs in the case of a photovoltaic voltage source, it may not be possible to maintain a particular current density. The hydrogen gas and/or oxygen gas generated as a result of the reactions shown in FIG. **2** can be stored for later use as a fuel.

[0039] FIG. **3A** is a cross section of a solar fuels generator. FIG. **3B** is a sideview of the solar fuels generator shown in FIG. **3A** taken looking in the direction of the arrow labeled **V** in FIG. **3A**. The cross section shown in FIG. **3A** can be taken along the line labeled **A** in FIG. **3B**.

[0040] The solar fuels generator includes a barrier **62** between a first phase **64** and a second phase **66**. The barrier **62** includes or consists of one or more reaction components **68** and one or more separator components **70**. FIG. **3A** illustrates the reaction components **68** linked with separator components **70** so as to form the barrier **62** between the first phase **64** and the second phase **66**. The reaction components **68** are alternated with the separator components **70**. Each reaction component **68** contacts both the first phase **64** and the second phase **66** and each separator component **70** contacts both the first phase **64** and the second phase **66**. The barrier **62** is formed such that the first phase **64** can be maintained at a different chemical composition than the second phase **66**. For instance, the barrier **62** can be impermeable or substantially impermeable to nonionic atoms and/or nonionic compounds.

[0041] The reaction components **68** include anodes **72** and cathodes **74**. As illustrated by the arrow labeled L_A and L_C , light is incident on the anodes **72** and/or cathodes **74** during operation of the solar fuels generator. The anodes **72** and cathodes **74** convert the received light into excited electron-hole pairs that drive a chemical reaction such as electrolysis of water. The anodes **72** include an anode light absorber **76** selected to absorb light at a wavelength to which the anodes **72** will be exposed during operation of the solar fuels generator. Additionally, the cathodes **74** include a cathode light absorber **78** selected to absorb light at a wavelength to which the cathodes will be exposed during operation of the solar fuels generator.

[0042] Suitable materials for the anode light absorbers **76** and the cathode light absorbers **78** include, but are not limited to, semiconductors. In some instances, the anode light absorbers **76** include or consist of a semiconductor and/or the cathode light absorbers **78** include or consist of a semiconductor. The bandgap of the semiconductors included in the anode light absorbers **76** can be larger than the bandgap of the semiconductors included in the cathode light absorbers **78**. Suitable semiconductors for the anode light absorbers **76** include, but are not limited to, metal oxides, oxynitrides, sulfides, and phosphides that are stable in an oxidizing environment such as WO_3 , TiO_2 , and TaON. Suitable semicon-

ductors for the cathode light absorbers **78** include, but are not limited to, p-type silicon, InP, Cu_2O , GaP, CdTe, MoS_2 , and WSe_2 .

[0043] In some instances, the anode light absorbers **76** and/or the cathode light absorbers **78** are doped. The doping can be done to form one or more pn junctions within the anode light absorbers **76** and the cathode light absorbers **78**. For instance, the anode light absorber **76** can be an n-type semiconductor while the cathode light absorber **78** can be a p-type semiconductor. A pn junction can also be present within either the cathode light absorbers **78** or the anode light absorber **76** or both, and is arranged so that electrons flow from the cathode light absorber **78** to a reduction catalyst (discussed below) and holes flow from the anode light absorber **76** to an oxidation catalyst (discussed below).

[0044] The dashed lines at the interface of the anode light absorber **76** and the cathode light absorber **78** illustrate an interface between the materials of the anode light absorber **76** and the cathode light absorber **78**. However, the anode light absorber **76** and the cathode light absorber **78** can be the same material and/or include the same dopant. As a result, an anode light absorber **76** and the interfaced cathode light absorber **78** can be a continuous block of material. In these instances, the dashed lines shown in FIG. **3A** may represent a feature that is not discernable in the solar fuels generator. One example of a material that can serve as both the anode light absorber **76** and the cathode light absorber **78** is p-type silicon, which can function as the absorber on both the anode and cathode. In particular, p-type silicon is a candidate for the cathode material because it is cathodically stable under illumination in acidic aqueous media and in conjunction with various metal catalysts can evolve $H_2(g)$ from H_2O .

[0045] Other possible choices for the light anode light absorber **76** and/or the cathode light absorber **78** include semiconductors having wider bandgaps than silicon that are stable in a water vapor medium such as oxide semiconductors. Some of the oxide semiconductors that can be used as a light absorber include, but are not limited to: tandem structure anodes, including tungsten oxide (WO_3), bismuth vanadium oxide ($BiVO_4$), tantalumoxynitride (TaON), and titanium oxide (TiO_2); tandem structure cathodes, including silicon (Si), cuprous oxide (Cu_2O), gallium phosphide (GaP), gallium arsenide (GaAs), and indium phosphide (InP); single material electrodes, including strontium titanate ($SrTiO_3$), strontium niobate ($SrNbO_3$), and titanium oxide (TiO_2); multifunction photovoltaics, including triple junction amorphous silicon (a-Si), and vertically stacked epitaxially grown III-V semiconductors with tunnel junctions; and series connected photovoltaics, including silicon (Si) cells, gallium arsenide (GaAs) cells, cadmium telluride (CdTe) cells, and Copper Indium Gallium Selenide (CIGS) thin film cells.

[0046] The absorption of light by the cathode light absorber **78** and the anode light absorber **76** generates the photovoltage that drive a reaction such as water electrolysis. When semiconductors are used for the cathode light absorber **78** and the anode light absorber **76**, the achievable voltage depends on the choice of semiconductor materials, the associated bandgaps, and doping arrangements as is known in the solar cell arts. Accordingly, the material selections and arrangements can be selected to provide the desired voltage levels. For instance, tandem and multijunction structures in which two or more semiconductors in series add their voltages together can be used in order to achieve elevated voltages.

[0047] The anodes **72** include one or more oxidation catalyst layers **86** that each include or consist of one or more oxidation catalysts. One or more oxidation catalyst layers **86** can be in direct physical contact with the anode light absorber **76**. As is evident from FIG. 3A, when light is to be incident on the anode, the light passes through one or more oxidation catalyst layers **86** before reaching the anode light absorber **76**. As a result, the one or more oxidation catalyst layers **86** can be transparent and/or thin enough that the one or more oxidation catalyst layers **86** do not absorb an undesirably high level of the incoming light. A suitable thickness for an oxidation catalyst layer **86** includes, but is not limited to, a thickness less than 10 nm to a few micrometers.

[0048] The oxidation catalyst layer **86** can include, consist of, or consist essentially of an oxidation catalyst. Examples of suitable oxidation catalysts include, but are not limited to, the oxidation catalysts disclosed in the context of FIG. 2. For instance, suitable oxidation catalysts include metal oxides that include, consist of, or consist essentially of oxygen and one, two, three, four or five metals selected from the group consisting of Ir, Mn, Co, Ta, Sn, and Sb or the group consisting of Mn, Co, Ta, and Sb. In some instances, the metal oxide can be represented by $(\text{Ir}_u\text{Mn}_v\text{Co}_w\text{Ta}_y\text{Sb}_z)\text{O}_x$ or $(\text{Mn}_v\text{Co}_w\text{Ta}_y\text{Sb}_z)\text{O}_x$ where $u+v+w+y+z=1$, u is greater than or equal to 0 and less than 1, v is greater than or equal to 0 and less than 1, w is greater than or equal to 0 and less than 1, y is greater than or equal to 0 and less than 1, and z is greater than or equal to 0 and less than 1, and at least one, two, three or four of the variables selected from the group consisting of v , w , y , and z are greater than zero.

[0049] The cathodes **74** include one or more reduction catalyst layers **88** that each includes or consists of one or more reduction catalysts. One or more reduction catalyst layers **88** can be in direct physical contact with the cathode light absorber **78** as is shown in FIG. 3A. As is evident from FIG. 3A, when light is to be incident on the cathode, the light passes through one or more reduction catalyst layers **88** before reaching the cathode light absorber **78**. As a result, the one or more reduction catalyst layers **88** can be transparent and/or thin enough that the one or more reduction catalyst layers **88** do not absorb an undesirably high level of the incoming light. A suitable thickness for a reduction catalyst layer **88** includes, but is not limited to, a thickness of about 1 nm to 10 μm . In some instances, the catalyst layer **88** does not need to be transparent. For instance, the catalyst layer **88** need not be transparent if it is facing down (i.e., is away from the incident light source) or if the underlying substrate is structured to minimize light absorption by the catalyst.

[0050] The reduction catalyst layers **88** and/or the reduction catalyst can include, consist of, or consist essentially of the catalysts described above or the catalytic layer described above in the context of FIG. 1. For instance, the catalytic layer **6** described in the context of FIG. 1 can serve as the reduction catalyst layers **88** and/or the catalysts described above can serve as a reduction catalyst. As an example, the one or more reductions can be metal phosphides such as the transition metal phosphides or metal sulfides such first row transition metal sulfides. In one example, the reduction catalyst layers **88** include, consist of, or consist essentially of CoP. As another example, FeP, MoP, or Ni_2P is suitable for use as a reduction catalyst because it exhibits a high level of catalytic activity at low overpotentials.

[0051] The one or more reduction catalyst layers **88** are positioned on a surface of the cathode light absorber **78** such

that a line that is perpendicular to the surface extends from the surface through one or more of the reduction catalyst layers **88** before extending through the second phase **66**. The one or more reduction catalyst layers **88** can be positioned such that the one or more reduction catalyst layers **88** are on more than 10%, 30%, 50%, 75%, or 90% of the surface of the cathode light absorber **78**.

[0052] The separator components **70** include or consist of a separator **90** located between the first phase **64** and the second phase **66**. The separator **90** is ionically conductive. In some instances, the separator **90** is cationically conductive while concurrently being sufficiently nonconductive to the other components of the first phase **64** and the second phase **66** that the first phase **64** and the second phase **66** remain separated from one another. For instance, in some instances, the separator **90** is cationically conductive and non-conductive or substantially non-conductive to nonionic atoms and/or non-ionic compounds. In some instances, the separator **90** is cationically conductive while being non-conductive or substantially non-conductive to nonionic atoms and/or nonionic compounds and also to anions. Accordingly, the separator **90** can provide a pathway along which cations can travel from the first phase **64** to the second phase **66** without providing a pathway or a substantial pathway from the first phase **64** to the second phase **66** to one, two, or three entities selected from a group consisting of anions, nonionic atoms or nonionic compounds. In some instances, it may be desirable for the separator **90** to conduct both anions and cations. For instance, when the first phase **64** and/or the second phase **66** has elevated pH levels a separator **90** that conducts both anions and cations may be used. As a result, in some instances, the separator **90** conducts cations and anions but not nonionic atoms or nonionic compounds.

[0053] Additionally, the separator **90** should be able to exchange ions sufficiently to prevent the buildup of a pH gradient, and separate the reaction products sufficiently to prevent them from re-combining. A suitable separator **90** can be a single layer or material or multiple layers of material. Suitable materials for the separator **90** include, but are not limited to, ionomers and mixtures of ionomers. Ionomers are polymers that include electrically neutral repeating units and ionized repeating units. Suitable ionomers include copolymers of a substituted or unsubstituted alkylene and an acid such as sulfonic acid. In one example, the ionomer is a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxo-4-methyl-7-octene-sulfonic acid. A suitable material having a structure according to Formula I is sold under the trademark NAFION®. NAFION® is an example of a material that is cationically conductive of cations but is not conductive of anions or nonionic atoms or nonionic compounds. Another suitable separator **90** includes NAFION® functionalized with one or more components selected from a group consisting of dimethylpiperazinium cationic groups, glass frits, asbestos fibers, block copolymer formulated layers, and poly (arylene ether sulfone) with quaternary ammonium groups.

[0054] During operation, the solar fuels generator is exposed to light such as sunlight, terrestrial solar illumination, AM1 solar radiation, or similar illumination having approximately 1 kilowatt per square meter of incident energy or less. These light sources can be unconcentrated or can be concentrated using known light concentration devices and techniques. In some instances, the solar fuels generator is oriented such that the light travels through the anodes before reaching the cathodes. When the anode light absorber **76** has

a larger bandgap than the cathode light absorber **78**, the anodes absorb higher energy (shorter wavelength) light and allow lower energy (longer wavelength) light to pass through to the cathodes. The cathodes can then absorb the longer wavelengths. Alternately, the light can be incident on both the anodes and the cathodes or can be incident on the cathodes before reaching the anodes.

[0055] The absorption of light by an anode light absorber **76** generates hole-electron pairs within the anode light absorber **76**. The presence of an n-type anode light absorber **76** in the first phase **64** produces an electrical field that causes the holes to move to the surface of the anode light absorber **76** and then the surface of the oxidation catalyst layer **86** where the oxidation of water occurs as illustrated by the first reaction in FIG. 3A. The electrons generated in the anode light absorber **76** move toward the cathode light absorber **78** as a result of the electrical field.

[0056] The protons generated in the first reaction move from the oxidation catalyst layer **86** into the first phase **64**. Since the separator **90** is cationically conductive, the protons move from the first phase **64** to the second phase **66** through the separator **90**. As a result, the pathlength for the protons is reduced to the thickness of the separator **90**. A suitable thickness for the separator **90** is a thickness of about 100 nm to 1 μ m or more.

[0057] The absorption of light by the cathode light absorber **78** generates hole-electron pairs within the cathode light absorber **78**. The presence of a p-type cathode light absorber **78** in the second phase **66** produces an electrical field that causes the electrons within the cathode light absorber **78** to move to the surface of the cathode light absorber **78** and then the surface of the reduction catalyst layers **88** where they react with the protons to form hydrogen gas as illustrated by the second reaction in FIG. 3A. The generated fuel can enter the second phase **66** and can be stored for later use. The holes generated in the cathode light absorber **78** by the absorption of light move from the cathode light absorber **78** toward the anode light absorber **76** as a result of the electrical field and can recombine with the electrons from the anode light absorber **76**.

[0058] The first phase **64** is generally different from the second phase **66**. For instance, the first phase **64** generally has a different chemical composition than the second phase **66**. The first phase **64** and the second phase can both be a liquid. For instance, the first phase **64** can be a standing, ionically conductive liquid such as water. In some instances, the first phase and/or the second phase are acidic. For instance, the first phase and/or the second phase can have a pH less than 7, 3, or 1.

[0059] The one or more oxidation catalyst layers **86** illustrated in FIG. 3A can include materials in addition to the oxidation catalyst. For instance, an oxidation catalyst layer **86** can include one or more components selected from a group consisting of electrically conductive fillers, electrically conductive materials, diluents, and/or binders. The one or more reduction catalyst layers **88** illustrated in FIG. 3A can include materials in addition to the one or more reduction catalysts. For instance, a reduction catalyst layer **88** can include one or more components selected from a group consisting of electrically conductive fillers, electrically conductive materials, diluents, and/or binders.

[0060] A suitable method for forming oxidation catalyst layers **86** on the anode light absorber **76** includes, but is not limited to, electrodeposition, sputtering, electroless deposi-

tion, spray pyrolysis, and atomic layer deposition. Alternately, the catalyst layer **86** can be a catalytic layer formed directly on the anode light absorber **76** as described below. A suitable method for forming reduction catalyst layers **88** on the cathode light absorber **78** and/or an electrode base **8** includes, but is not limited to, traditional chemical synthesis, electrodeposition, sputtering, electroless deposition, spray pyrolysis, and atomic layer deposition. A suitable method for attaching the separator **90** to the anodes **72** and/or cathodes **74** includes, but is not limited to, clamping, lamination, sealing with epoxy or glue and the like.

EXAMPLES

Example 1

[0061] Solid CoP nanoparticles were synthesized using octacarbonyl dicobalt [stabilized with 1-5% hexane, $\text{Co}_2(\text{CO})_8$], oleic acid [tech. 90%, $\text{C}_{18}\text{H}_{34}\text{O}_2$] nonanoic acid [97%, $\text{C}_9\text{H}_{18}\text{O}_2$] (Alfa-Aesar), 1-octadecene [tech. 90%, $\text{C}_{18}\text{H}_{36}$], oleylamine [tech. 70%, $\text{C}_{18}\text{H}_{37}\text{N}$], trioctylphosphine [97%, $(\text{C}_8\text{H}_{17})_3\text{P}$]. The 1-octadecene (10 mL, 31.3 mmol), oleylamine (6 mL, 18.2 mmol), and nonanoic acid (2 mL, 11.3 mmol) were added to a 100 mL three-necked round bottom flask containing a polytetrafluoroethylene-coated magnetic stir bar. The flask was then placed in a heating mantle. A thermometer adapter, thermometer, Liebig condenser, and rubber septum were also connected to the flask. The reaction mixture was vigorously stirred and heated to 120° C. for 1 h under vacuum, to remove residual low-boiling solvents, including water. Following degassing, the mixture was heated to 230° C. under Ar. Meanwhile, in an Ar-filled septum-capped vial, octacarbonyl dicobalt (100 mg, 0.29 mmol) was suspended in 1-octadecene (4.5 mL, 14.1 mmol). Following solvation via sonication, the cobalt solution was slowly injected into the reaction flask. After injection of the Co solution, the reaction was held at -230° C. for 10 min, followed by rapid injection of degassed oleic acid (2 mL, 6.3 mmol). The reaction was maintained at -230° C. for 10 additional min until the contents were allowed to cool by removal of the heating mantle. The resulting cobalt nanoparticle sample was cleaned by adding isopropyl alcohol to the reaction mixture, followed by centrifugation at 9000 rpm for 5 min. Following centrifugation, the precipitate was resuspended in hexanes, followed by addition of isopropyl alcohol and subsequent centrifugation. The resulting pellet was suspended in hexanes, for characterization purposes, or was suspended in trioctylphosphine for conversion to CoP.

Example 2

[0062] Hollow CoP nanoparticles were synthesized using 1-octadecene [tech. 90%, $\text{C}_{18}\text{H}_{36}$], oleylamine [tech. 70%, $\text{C}_{18}\text{H}_{37}\text{N}$], and trioctylphosphine [97%, $(\text{C}_8\text{H}_{17})_3\text{P}$]. The 1-octadecene (5 mL, 15.7 mmol), oleylamine (5 mL, 15.2 mmol), and trioctylphosphine (5 mL, 11.2 mmol) were added to a 100 mL three-necked round-bottom flask that contained a borosilicate stir bar. The flask was also equipped with a thermometer adapter, thermometer, Liebig condenser, and rubber septum and placed in a heating mantle. The reaction mixture was degassed at 120° C. for 1 h under vacuum to remove water and other low boiling impurities from the system. The reaction mixture was then heated to -320° C., and allowed to equilibrate for 10 min. Following temperature equilibration, a pre-made suspension of cobalt nanoparticles

in degassed trioctylphosphine (2 mL, 4.5 mmol) was slowly injected into the reaction mixture. The resulting mixture was held at 320° C. for 1 h. The reaction mixture was allowed to cool to room temperature by removal of the heating mantle. The resulting CoP nanoparticles were cleaned by addition of the isopropyl alcohol to the reaction mixture. Precipitation of the CoP nanoparticles was performed via centrifugation at 9000 rpm for 5 min. The precipitate was resuspended using hexanes, followed by ethanol to promote flocculation and then centrifugation. This process was then repeated, and for later use the resulting CoP nanoparticles were suspended in hexanes.

Example 3

[0063] An electrode constructed according to FIG. 2 was generated. A solution of CoP nanoparticles at 5 mg/mL in hexanes was prepared according to Example 1. In 5-10 μ L increments, 36 μ L of the nanoparticle solution was deposited onto 0.2 cm² samples of Ti foil [99.7%, 0.25 mm thickness] to achieve 0.9 mg/cm² mass loading, or 80 μ L was deposited to achieve the 2 mg/cm² mass loading. Following deposition of CoP and drying, the CoP-coated Ti foils were annealed at 450° C. under 5% H₂/Ar (Air Liquide). The foils were affixed with Ag paint to a polyvinylchloride-coated copper wire that had been threaded through a 6-mm diameter glass capillary. Two-part epoxy [McMaster-Carr, HYSOL 9460] was used to cover all surfaces except the CoP-coated side of the Ti electrode.

Example 4

[0064] Electrochemical Measurements were taken using a Gamry Instruments Reference 600 potentiostat. The measurements were performed in high-purity 0.50 M sulfuric acid. Data were collected using a three-electrode single-compartment cell that contained a working electrode constructed according to example 3, a mercury/mercury sulfate (Hg/Hg₂SO₄) reference electrode and a graphite rod counter electrode.

[0065] Polarization data were collected at a sweep rate of 5 mV/s, and rapid stirring from a magnetic stir bar was used to agitate the solution. The current-interrupt method was used to account for any uncompensated resistance (R=2 ohms, leading to an iR correction of about 8 mV at 20 mA/cm²). Constant bubbling of research-grade H₂ at ~1 atm was used to maintain a constant potential for the RHE, with the RHE potential determined by measuring the open-circuit potential of a platinum electrode that was tested following investigation of the behavior of the CoP nanoparticle-coated electrode.

[0066] Long-term electrochemical stability measurements were made through the use of accelerated degradation studies. These studies included cyclic voltammetric cycling from +0.005 V to -0.140 V without accounting for any uncompensated resistance. The current density versus potential results for the first cycle are set forth in FIG. 4. The current density versus potential results for the 400th cycle are also set forth in FIG. 4. As is evident in FIG. 4, the CoP catalyst shows almost no measurable loss in catalytic activity over the 400 cycles. The production of a current density of -20 mA/cm² initially required an overpotential of ~-0.95 mV. The required overpotential changed to ~-0.90 mV after the 400 cycles showing an unexpected level of stability in highly acidic environments.

[0067] Short-term electrochemical stability was measured without correcting for uncompensated resistance by galvanostatically maintaining for 24 h a current density of -20 mA/cm². The overpotential versus time results are presented in FIG. 5. At a current density of -20 mA/cm², the overpotential increased only slightly (25 mV) over 24 hours of continuous operation. Some particle desorption from the Ti foil may have reduced the mass loading of the electrode and accordingly been the source of the increasing overpotential evident in FIG. 5.

[0068] Although the hydrogen evolution reaction catalyst is disclosed above in the context of nanoparticles, the catalyst can exist in other forms. For instance, the catalyst can exist in particles larger than nanoparticles or amorphous powders and films, nanopowders, or as individual molecules. Similarly, the form of the catalyst in an electrode can exist as the nanoparticles but are can also exist in particles larger than nanoparticles or amorphous powders and films, nanopowders, or as individual molecules.

1. A device, comprising:
a hydrogen evolution reaction catalyst, the catalyst including at least one component selected from a group consisting of transition metal phosphides, first row transition metal sulfides, and transition metal arsenides.
2. The device of claim 1, wherein the catalyst is included in nanoparticles.
3. The device of claim 2, wherein the nanoparticles have an average diameter greater than 1 nm and less than 10,000 nm.
4. The device of claim 1, wherein the catalyst is a phosphide that includes phosphorous and one or more transition metals selected from the group consisting of cobalt, tungsten, nickel, iron, titanium, vanadium, chromium, manganese, niobium, and molybdenum.
5. The device of claim 1, wherein the catalyst is a sulfide that includes sulfur and one or more first row transition metals selected from the group consisting of vanadium, chromium, manganese, nickel, copper, iron and titanium.
6. The device of claim 1, wherein the catalyst is an arsenide that includes arsenic and one or more transition metals selected from the group consisting of titanium, chromium, iron, cobalt, nickel, molybdenum, and tungsten.
7. The device of claim 1, wherein the catalyst is cobalt phosphide.
8. The device of claim 7, wherein the cobalt phosphide is represented by Co_xP_y, wherein x has value greater than or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4.
9. An electrode at which a hydrogen evolution reaction occurs, comprising:
a hydrogen evolution reaction catalyst, the catalyst including at least one component selected from a group consisting of transition metal phosphides and first row transition metal sulfides.
10. The electrode of claim 9, wherein the nanoparticles have an average diameter greater than 1 nm and less than 10,000 nm.
11. The electrode of claim 9, wherein the catalyst is selected from the group consisting of cobalt phosphide, tungsten phosphide, dinickel phosphide (Ni₂P), iron phosphide, and molybdenum phosphide.
12. The electrode of claim 9, wherein the catalyst is cobalt phosphide.
13. The electrode of claim 12, wherein the cobalt phosphide is represented by CoP wherein x has value greater than

or equal to 1 and less than or equal to 4 and y has a value greater than or equal to 1 and less than or equal to 4.

14. The electrode of claim **13**, wherein the cobalt phosphide is represented by CoP.

15. The electrode of claim **9**, wherein the catalyst is exposed to an environment with a pH less than 6.

16. A system, comprising:

an electrode at which a hydrogen evolution reaction occurs,
the electrode including a hydrogen evolution reaction catalyst, the catalyst including at least one component selected from a group consisting of transition metal phosphides and first row transition metal sulfides.

17. The system of claim **16**, wherein the catalyst is selected from the group consisting of cobalt phosphide, tungsten phosphide, dinickel phosphide (Ni_2P), iron phosphide, and molybdenum phosphide.

18. The system of claim **16**, wherein the catalyst is cobalt phosphide.

19. The system of claim **16**, wherein the electrode is positioned in an environment with a pH less than 6.

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