

Title of Invention: Oxyhydroxide Catalysts, Pre-Catalysts And Methods of Preparation Thereof**Technical Field**

The present disclosure generally refers to catalysts and pre-catalysts for alkaline oxygen evolution reactions, and methods of preparing the same, in particular, oxyhydroxide catalysts and their pre-catalysts for alkaline oxygen evolution reactions, and methods of preparing the same.

Background Art

The utilization of hydrogen as a clean energy carrier has long been proposed as a solution to the inconsistent and unreliable supply of renewable energy sources. However, the efficiency and costs of current electrolyzer technologies still impose limitations on the production of hydrogen using renewable energy sources. A significant obstacle lies in the development of affordable and durable catalysts for the oxygen evolution reaction (OER), which accounts for substantial energy losses in water electrolysis. The proton exchange membrane (PEM) electrolyser, which typically employs noble metal-based catalysts, are usually expensive due to the costs of the catalyst materials. Also, PEM electrolyzers utilize acidic OER, which requires substantial maintenance costs in the long run. Conversely, alkaline water electrolyzers (AWEs) and anion exchange membrane (AEM) water electrolyzers are slightly more cost-effective alternatives. Notably, catalysts based on 3d-transition metals (such as Fe, Co, and Ni) demonstrate promising potential for hydrogen production.

It is known that cobalt-based oxyhydroxide catalysts exhibit high activity in alkaline OER. The exceptional intrinsic activity of these catalysts may be attributed to the presence of di- μ -oxo bridged motifs within the oxyhydroxide structure, which becomes active oxygen ligands upon deprotonation. However, such Co-based catalysts require costly and complicated synthesis methods. On top of that, some of the methods require harsh conditions, e.g., sol-gel, hydrothermal and/or solvothermal methods. As such, the presently known methods can hardly be scaled-up to manufacture anodes for commercial-scale applications.

Hence, there is a need to find new methods of synthesizing catalysts for alkaline OER that overcome one or more of the problems mentioned above.

Summary

In an aspect of the present disclosure, there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst.

The catalyst and/or pre-catalyst of the present invention do not require prior synthesis steps, nor do they require additional preparation steps, e.g., sol-gel, hydrothermal, solvothermal, chemical precipitation, mechanical alloying, etc.. The pre-catalyst may be easily prepared from its starting materials, and may be easily converted (via electrochemical reconstruction/activation) to the active oxyhydroxide catalyst, and

may thus be easily, cheaply and reliably produced in a large scale for industrial applications. The pre-catalyst of the present invention may also be easily electrochemically converted to the active oxyhydroxide catalyst species without requiring any costly and/or complicated material synthesis, and thus the pre-catalysts and catalysts may be advantageously cheaper and easier to produce as compared to known catalysts.

In another aspect of the present disclosure, there is provided an oxyhydroxide catalyst prepared by electrochemically oxidizing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride.

The presently disclosed oxyhydroxide catalysts may be highly porous and exhibit high specific surface area, and may advantageously exhibit high catalytic activity.

In a further aspect of the present disclosure, there is provided a pre-catalyst for preparing an oxyhydroxide catalyst, wherein:

- the pre-catalyst comprises cobalt(II) chloride and iron(III) chloride;
- the pre-catalyst is applied on a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
- the pre-catalyst does not contain oxyhydroxide.

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 described herein, are those well-known and commonly used in the art.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

As used herein, the term “pre-catalyst” refers to a substance that does not exhibit any catalytic activity and requires further activation to become an active catalyst species. The activation of the pre-catalyst may occur via electrochemical activation and/or electrochemical reconstruction.

As used herein, the term “oxyhydroxides” refer to compounds containing a mixture of oxides and hydroxides.

As used herein, the term “di- μ -oxo motif” refers to a specific structural feature where two oxygen atoms bridge two metal centers (usually transition metals) through μ -oxo bridges.

As used herein, the term “amorphous” refers to a solid form of a nanoparticle, molecule, atom, salt, mixture and/or ions that is not crystalline. In particular, when a nanoparticle is not crystalline, the nanoparticle lacks a crystalline structure that is uniformly present throughout the nanoparticle,

As used herein, the term “sol-gel process” refers to a process where the starting materials are dissolved in a solvent to form a solution, following which the starting materials undergo hydrolysis at temperatures ranging from 70 °C to 100 °C. In a “sol-gel” process, gelling agents, e.g., propylene oxide, are also added to initiate gelling.

As used herein, the term “hydrothermal process” refers to a process where the starting materials are dissolved in water, and subjected to heating under high pressure, typically in autoclaves. Typically in a hydrothermal process, pressures range from at least 0.1 MPa to about 500 MPa, while temperatures range from at least 100 °C to 1000 °C.

As used herein, the term “solvothermal process” refers to a process where the starting materials are dissolved in a solvent other than water, and subjected to heating under high pressure, typically in autoclaves. Typically in a solvothermal process, pressures range from at least 0.1 MPa to about 500 MPa, while temperatures range from at least 100 °C to 1000 °C.

As used herein, the term “ambient” or “ambient conditions”, refer to conditions at room temperature and pressure, i.e., about 25 °C to about 30 °C, and at about 0.1 MPa.

As used herein, the term “cyclic voltammetry waveform” or “reversible cyclic voltammetry waveform” refers to a potential waveform where the potential is swept, over time, from an initial potential to a final potential, and then back to the initial potential. The sweep from the initial potential to the final potential is typically termed “a forward scan”, while the sweep from the final potential to the initial potential is termed “the reverse scan”. The waveform may take various shapes, e.g., triangular, sinusoidal, staircase, square-wave, etc., as long as the waveform is sweeping between two potentials.

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

As used herein in the specification and in the claims, the phrase “at least,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and

at least one, optionally including more than one, B (and optionally including other elements); etc.

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

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Brief Description of Drawings

The accompanying drawings illustrate disclosed embodiments and serve to explain the principles of the disclosed embodiments. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1a

Fig. 1b is a schematic showing the fabrication of an exemplary electrode having Co(Fe)Cl_x pre-catalyst on top of a carbon support.

Fig. 1b

Fig. 1b is an image showing an exemplary di- μ -oxo motif found in oxyhydroxides.

Fig. 2a

Fig. 2a is a graph showing the Oxygen Evolution Reaction (OER) Cyclic Voltammetry (CV) spectrum of Co(Fe)Cl_x pre-catalyst as the anode over 20 cycles.

Fig. 2b

Fig. 2b is a CV profile showing the pseudocapacitive behavior of the Co(Fe)Cl_x pre-catalyst over 20 cycles, before OER.

Fig. 3a

Fig. 3a is a High-Resolution Transmission Electron Microscopy (HRTEM) image showing the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst at low magnification.

Fig. 3b

Fig. 3b is a High-Resolution Transmission Electron Microscopy (HRTEM) image showing the interface region of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst at high magnification.

Fig. 3c

Fig. 3c is a graph showing the X-Ray Diffraction (XRD) pattern of the Co(Fe)Cl_x pre-catalyst prior to electrochemical reconstruction.

Fig. 4a

Fig. 4a is a graph showing the Co K-edge X-ray Absorption Near Edge Spectroscopy (XANES) spectrum of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst, with standard Co(OH)_2 and CoOOH spectra added for comparison.

Fig. 4b

Fig. 4b is a graph showing the Co K-edge Extended X-ray absorption fine structure (EXAFS) spectrum of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst, with standard Co(OH)_2 and CoOOH spectra added for comparison.

Fig. 5a

Fig. 5a is a graph showing the OER CV spectrum of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst on commercial carbon supports.

Fig. 5b

Fig. 5b is a CV spectrum showing the pseudocapacitive behaviour of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst on commercial carbon supports, before OER.

Fig. 6

Fig. 6 is a graph showing the OER CV spectra of catalysts prepared from cobalt(II) and iron (III) (i) chlorides, (ii) sulphates and (iii) nitrates.

Fig. 7a

Fig. 7a is a graph showing the OER CV spectrum of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst and a hydrothermal synthesised $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst.

Fig. 7b

Fig. 7b is a CV spectrum showing the pseudocapacitive behaviour before OER, of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst and a hydrothermal synthesised $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst.

Detailed Disclosure of Drawings

Referring to Fig. 1a, the preparation of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst first started with the preparation of a Co(Fe)Cl_x pre-catalyst (not shown). To do so, CoCl_2 and FeCl_3 were dissolved, along with a binder, in a suitable solvent, e.g., isopropanol/water 1:4 to form a Co(Fe)Cl_x mixture. A carbon support, dissolved in a prior solvent, was first drop-casted onto an electrode. The electrode was then dried under ambient conditions, following which the Co(Fe)Cl_x mixture was then drop-casted on the electrode. This electrode was dried again under ambient conditions to form the coated electrode coated with the Co(Fe)Cl_x pre-catalyst ready for electrochemical reconstruction. To perform the electrochemical reconstruction, the coated electrode was used as an anode, and cyclic voltammetry (CV) was performed on the electrode, e.g., for up to 20 cycles, to afford the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst.

Detailed Disclosure of Embodiments

Conventional Co-based catalysts require costly and complicated synthesis methods. On top of that, some of the methods require harsh conditions, e.g., hydrothermal and/or solvothermal methods. As such, the presently known methods can hardly be scaled-up to manufacture anodes for commercial-scale applications. In this regard, there is demand for new catalysts that may be easily, cheaply and reliably produced in a large scale for industrial applications, in particular, industrial hydrogen production.

Additionally, as the surface area of the electrode channels in membrane electrolyzers are limited, it is further desirable to manufacture catalysts that possess nano or sub-nano structures that translate to high specific surface area, in order to increase the amount of active catalytic sites on the catalyst surface.

In the present invention, the inventors have surprisingly discovered a Co(Fe)Cl_x pre-catalyst that may be easily converted into an active CoFeO_xH_y catalyst species simply by applying a voltage, e.g., a voltage having a cyclic voltammetry (CV) voltage waveform. Direct synthesis of catalysts from the starting materials is often costly and difficult, and the inventors have instead discovered a Co(Fe)Cl_x pre-catalyst that is easily prepared from its starting materials, and is easily converted (via electrochemical reconstruction/activation) to the active catalyst species.

The catalyst and/or pre-catalyst of the present invention do not require prior synthesis steps, nor does it require additional preparation steps, e.g., sol-gel, hydrothermal, solvothermal, chemical precipitation, mechanical alloying, etc. The pre-catalyst of the present invention can also be easily electrochemically converted to the active oxyhydroxide catalyst species without requiring any costly and/or complicated material synthesis.

The pre-catalyst (and consequently the active catalyst) of the present invention is also cheaper compared to catalysts synthesised via traditional methods. The presently disclosed Co(Fe)Cl_x pre-catalyst only consists of 3d-transition metals that are inexpensive and earth-abundant. The pre-catalyst also does not need to undergo harsh treatment conditions like solvothermal or hydrothermal methods, nor does it require additional reagents or solvents to be converted to the active catalyst, e.g., chemical precipitation, sol-gel,

etc.. The carbon black support used in the present invention is also cheap and low in cost, and thus can greatly reduce the cost of anode fabrication.

The $\text{Co(Fe)O}_x\text{H}_y$ catalyst produced by the present invention shows sub-nanometer particle sizes, and have extremely high specific surface area, thus delivering high geometric Oxygen Evolution Reaction (OER) activity.

In one aspect is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst.

The method disclosed in the present invention has several advantages over traditional synthesis of nano-sized electrocatalysts. Typically, the chemical synthesis of nano-sized electrocatalysts takes a long-time in the ageing process to help form smaller particle sizes, and often also require the use of costly surfactants. Compared to such traditional methods, method disclosed in the present invention avoids the use of such surfactants. The presently disclosed method is also simple and reliable, and is easily scalable to manufacture anodes for commercial electrolyzers and in electrochemical applications.

The method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.

In some embodiments, the method further discloses before step (ii), a step (i-a):

- (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions.

In some embodiments, the pre-catalyst in step (i), (i-a) and/or (ii) does not comprise a colloid and/or a polymer.

In some embodiments, the pre-catalyst in step (i) and/or step (i-a) do not undergo further treatment prior to electrochemical reconstruction, e.g., treatment by sol-gel, solvothermal, hydrothermal, mechanical alloying, etc.. In some embodiments, the pre-catalyst is chemically unchanged after step (i) and/or (i-a). In some other embodiments, the pre-catalyst in step (i) and/or step (i-a) remains as an admixture of Co salts and Fe salts while it has yet to undergo electrochemical reconstruction. In some embodiments, the pre-catalyst in step (i) and/or step (i-a) does not contain oxyhydroxides.

In some embodiments, the pre-catalyst is applied on the conductive substrate with a mass loading in a range of at least about 0.03 mg/cm^2 , at least about 0.05 mg/cm^2 ; or from about 0.03 mg/cm^2 to about 0.08 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.075 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.07 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.065 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.06 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.055 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.05 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.045 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.04 mg/cm^2 , from about 0.03 mg/cm^2 to about 0.035 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.08 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.075 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.07 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.065 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.06 mg/cm^2 , from about 0.05 mg/cm^2 to about 0.055 mg/cm^2 ;

or from about 0.03 mg/cm² to about 0.08 mg/cm², from about 0.035 mg/cm² to about 0.08 mg/cm², from about 0.04 mg/cm² to about 0.08 mg/cm², from about 0.045 mg/cm² to about 0.08 mg/cm², from about 0.05 mg/cm² to about 0.08 mg/cm², from about 0.055 mg/cm² to about 0.08 mg/cm², from about 0.06 mg/cm² to about 0.08 mg/cm², from about 0.065 mg/cm² to about 0.08 mg/cm², from about 0.07 mg/cm² to about 0.08 mg/cm², from about 0.075 mg/cm² to about 0.08 mg/cm², from about 0.03 mg/cm² to about 0.05 mg/cm², from about 0.035 mg/cm² to about 0.05 mg/cm², from about 0.04 mg/cm² to about 0.05 mg/cm², from about 0.045 mg/cm² to about 0.05 mg/cm²; or at most about 0.05 mg/cm², at most about 0.08 mg/cm²; or about 0.03 mg/cm², about 0.035 mg/cm², about 0.04 mg/cm², about 0.045 mg/cm², about 0.05 mg/cm², about 0.055 mg/cm², about 0.06 mg/cm², about 0.065 mg/cm², about 0.07 mg/cm², about 0.075 mg/cm², about 0.08 mg/cm², or any ranges or values therebetween.

In some embodiments, the conductive substrate is coated on an electrode.

In some embodiments, the conductive substrate is a carbon black powder. In some embodiments the conductive substrate comprises 99% Super P® Conductive, acetylene black, Vulcan XC72, Ketjenblack EC-600JD and/or combinations and mixtures thereof.

In some embodiments, the conductive substrate has a Brunauer, Emmett and Teller (BET) surface area in a range of at least about 50 m²/g, at least about 62 m²/g, at least about 90 m²/g, at least about 130 m²/g, at least about 223 m²/g, at least about 1270 m²/g; or from about 50 m²/g to about 1500 m²/g, from about 50 m²/g to about 1400 m²/g, from about 50 m²/g to about 1300 m²/g, from about 50 m²/g to about 1270 m²/g, from about 50 m²/g to about 1250 m²/g, from about 50 m²/g to about 1000 m²/g, from about 50 m²/g to about 750 m²/g, from about 50 m²/g to about 500 m²/g, from about 50 m²/g to about 400 m²/g, from about 50 m²/g to about 300 m²/g, from about 50 m²/g to about 275 m²/g, from about 50 m²/g to about 250 m²/g, from about 50 m²/g to about 225 m²/g, from about 50 m²/g to about 223 m²/g, from about 50 m²/g to about 200 m²/g, from about 50 m²/g to about 175 m²/g, from about 50 m²/g to about 150 m²/g, from about 50 m²/g to about 130 m²/g, from about 50 m²/g to about 125 m²/g, from about 50 m²/g to about 123 m²/g, from about 50 m²/g to about 100 m²/g, from about 50 m²/g to about 90 m²/g, from about 50 m²/g to about 75 m²/g, from about 50 m²/g to about 62 m²/g, from about 62 m²/g to about 1500 m²/g, from about 62 m²/g to about 1400 m²/g, from about 62 m²/g to about 1300 m²/g, from about 62 m²/g to about 1270 m²/g, from about 62 m²/g to about 1250 m²/g, from about 62 m²/g to about 1000 m²/g, from about 62 m²/g to about 750 m²/g, from about 62 m²/g to about 500 m²/g, from about 62 m²/g to about 400 m²/g, from about 62 m²/g to about 300 m²/g, from about 62 m²/g to about 275 m²/g, from about 62 m²/g to about 250 m²/g, from about 62 m²/g to about 225 m²/g, from about 62 m²/g to about 223 m²/g, from about 62 m²/g to about 200 m²/g, from about 62 m²/g to about 175 m²/g, from about 62 m²/g to about 150 m²/g, from about 62 m²/g to about 130 m²/g, from about 62 m²/g to about 125 m²/g, from about 62 m²/g to about 123 m²/g, from about 62 m²/g to about 100 m²/g, from about 62 m²/g to about 90 m²/g, from about 62 m²/g to about 75 m²/g, from about 90 m²/g to about 1500 m²/g, from about 90 m²/g to about 1400 m²/g, from about 90 m²/g to about 1300 m²/g, from about 90 m²/g to about 1270 m²/g, from about 90 m²/g to about 1250 m²/g, from about 90 m²/g to about 1000 m²/g, from about 90 m²/g to about 750 m²/g, from about 90 m²/g to about 500 m²/g, from about 90 m²/g to about 400 m²/g, from about 90 m²/g to about 300 m²/g, from about 90 m²/g to about 275 m²/g, from about 90 m²/g to about 250 m²/g, from about 90 m²/g to about 225 m²/g, from about 90 m²/g to about 223 m²/g, from about 90 m²/g to about 200 m²/g, from about 90 m²/g to about 175 m²/g, from about 90 m²/g to about 150 m²/g, from about 90 m²/g to about 130 m²/g, from about 90 m²/g to about 125 m²/g, from about 90 m²/g to about 123 m²/g, from about 90 m²/g to about 100 m²/g, from about 90 m²/g to about 90 m²/g.

[illegible]

m^2/g , about $1500 \text{ m}^2/\text{g}$, or any ranges or values therebetween.

In some embodiments, the conductive substrate has an electrical conductivity in a range of at least about 0.05 S cm^{-1} , at least about 0.1 S cm^{-1} , at least about 0.505 S cm^{-1} , at least about 0.6 S cm^{-1} , at least about 2.77 S cm^{-1} ; or from about 0.05 S cm^{-1} to about 3 S cm^{-1} , from about 0.05 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.05 S cm^{-1} to about 2.5 S cm^{-1} , from about 0.05 S cm^{-1} to about 2 S cm^{-1} , from about 0.05 S cm^{-1} to about 1.5 S cm^{-1} , from about 0.05 S cm^{-1} to about 1 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.75 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.5 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.25 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.1 S cm^{-1} , from about 0.1 S cm^{-1} to about 3 S cm^{-1} , from about 0.1 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.1 S cm^{-1} to about 2.5 S cm^{-1} , from about 0.1 S cm^{-1} to about 2 S cm^{-1} , from about 0.1 S cm^{-1} to about 1.5 S cm^{-1} , from about 0.1 S cm^{-1} to about 1 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.75 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.5 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.25 S cm^{-1} , from about 0.505 S cm^{-1} to about 3 S cm^{-1} , from about 0.505 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.505 S cm^{-1} to about 2.5 S cm^{-1} , from about 0.505 S cm^{-1} to about 2 S cm^{-1} , from about 0.505 S cm^{-1} to about 1.5 S cm^{-1} , from about 0.505 S cm^{-1} to about 1 S cm^{-1} , from about 0.505 S cm^{-1} to about 0.75 S cm^{-1} , from about 0.505 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.6 S cm^{-1} to about 3 S cm^{-1} , from about 0.6 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.6 S cm^{-1} to about 2.5 S cm^{-1} , from about 0.6 S cm^{-1} to about 2 S cm^{-1} , from about 0.6 S cm^{-1} to about 1.5 S cm^{-1} , from about 0.6 S cm^{-1} to about 1 S cm^{-1} , from about 0.6 S cm^{-1} to about 0.75 S cm^{-1} , from about 2.77 S cm^{-1} to about 3 S cm^{-1} ; or from about 0.05 S cm^{-1} to about 3 S cm^{-1} , from about 0.1 S cm^{-1} to about 3 S cm^{-1} , from about 0.25 S cm^{-1} to about 3 S cm^{-1} , from about 0.5 S cm^{-1} to about 3 S cm^{-1} , from about 0.505 S cm^{-1} to about 3 S cm^{-1} , from about 0.6 S cm^{-1} to about 3 S cm^{-1} , from about 0.75 S cm^{-1} to about 3 S cm^{-1} , from about 1 S cm^{-1} to about 3 S cm^{-1} , from about 1.5 S cm^{-1} to about 3 S cm^{-1} , from about 2 S cm^{-1} to about 3 S cm^{-1} , from about 2.5 S cm^{-1} to about 3 S cm^{-1} , from about 2.77 S cm^{-1} to about 3 S cm^{-1} , from about 0.05 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.1 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.25 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.5 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.505 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.6 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.75 S cm^{-1} to about 2.77 S cm^{-1} , from about 1 S cm^{-1} to about 2.77 S cm^{-1} , from about 1.5 S cm^{-1} to about 2.77 S cm^{-1} , from about 2 S cm^{-1} to about 2.77 S cm^{-1} , from about 2.5 S cm^{-1} to about 2.77 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.25 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.5 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.505 S cm^{-1} to about 0.6 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.1 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.25 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.5 S cm^{-1} to about 0.505 S cm^{-1} , from about 0.05 S cm^{-1} to about 0.1 S cm^{-1} ; or at most about 0.1 S cm^{-1} , at most about 0.505 S cm^{-1} , at most about 0.6 S cm^{-1} , at most about 2.77 S cm^{-1} , at most about 3 S cm^{-1} ; or about 0.05 S cm^{-1} , about 0.1 S cm^{-1} , about 0.25 S cm^{-1} , about 0.5 S cm^{-1} , about 0.505 S cm^{-1} , about 0.6 S cm^{-1} , about 0.75 S cm^{-1} , about 1 S cm^{-1} , about 1.5 S cm^{-1} , about 2 S cm^{-1} , about 2.5 S cm^{-1} , about 2.77 S cm^{-1} , about 3 S cm^{-1} , or any ranges or values therebetween.

In some embodiments, step (ii) comprises applying a voltage to the pre-catalyst. In some embodiments, the voltage is applied to the pre-catalyst in the presence of an electrolyte. The electrolyte may be KOH, NaOH, LiOH, CsOH, or mixtures and combinations thereof.

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In some embodiments, the pH of the electrolyte may be in a range of at least about 10; or from about 10 to about 14, from about 10 to about 13.5, from about 10 to about 13, from about 10 to about 12.5, from about 10 to about 12, from about 10 to about 11.5, from about 10 to about 11, from about 10 to about 10.5; or from about 10 to about 14, from about 10.5 to about 14, from about 11 to about 14, from about 11.5 to about 14, from about 12 to about 14, from about 12.5 to about 14, from about 13 to about 14, from about 13.5 to about 14; or at most about 14; or about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, about 13, about 13.5, about 14, or any other ranges or values therebetween.

In the present invention, electrochemical reconstruction/activation of the pre-catalyst to form the active catalyst was performed by applying cyclic voltammetry to the pre-catalyst as the anode. A cyclic voltammetry waveform, comprising both a forward scan (of increasing potential) and a backward scan (of decreasing potential) as the forward scan is required to activate the Co and Fe species to the active state, while the back scan allows for the re-deposition of the active Co and Fe species as active solid species. Typically, such a CV scan would start at a positive potential but below the $\text{Co}^{3+}/\text{Co}^{2+}$ redox potential of +1.15 V vs. RHE. The voltage is then gradually increased, past the $\text{Co}^{3+}/\text{Co}^{2+}$ redox potential, to a pre-determined voltage, at which point the voltage is then gradually decreased, past the $\text{Co}^{3+}/\text{Co}^{2+}$ redox potential, to the initial starting voltage.

In some embodiments, the voltage follows a cyclic voltammetry waveform. In some embodiments, the voltage follows a reversible cyclic voltammetry waveform, e.g., in a loop. In some embodiments, the waveform resembles a triangular waveform, sinusoidal waveform, staircase waveform, and/or combinations thereof.

In some embodiments, the initial voltage, vs. RHE, in the waveform loop may be in a range of at least about +0.8 V, at least about +0.95 V; or from about +0.8 V to about +1 V, from about +0.8 V to about +0.975 V, from about +0.8 V to about +0.95 V, from about +0.8 V to about +0.925 V, from about +0.8 V to about +0.9 V, from about +0.8 V to about +0.875 V, from about +0.8 V to about +0.85 V, from about +0.8 V to about +0.825 V, from about +0.95 V to about +1 V, from about +0.95 V to about +0.975 V, from about +0.975 V to about +1 V; or from about +0.8 V to about +1 V, from about +0.825 V to about +1 V, from about +0.85 V to about +1 V, from about +0.875 V to about +1 V, from about +0.9 V to about +1 V, from about +0.925 V to about +1 V, from about +0.95 V to about +1 V, from about +0.975 V to about +1 V, from about +0.8 V to about +0.95 V, from about +0.825 V to about +0.95 V, from about +0.85 V to about +0.95 V, from about +0.875 V to about +0.95 V, from about +0.9 V to about +0.95 V, from about +0.925 V to about +0.95 V; or at most about +0.95 V, at most about +1 V; or about +0.8 V, about +0.825 V, about +0.85 V, about +0.875 V, about +0.9 V, about +0.925 V, about +0.95 V, about +0.975 V, about +1 V, or any ranges or values therebetween.

In some embodiments, the lowest voltage, vs. RHE, in the waveform loop may be in a range of at least about +0.8 V, at least about +0.9 V; or from about +0.8 V to about +1 V, from about +0.8 V to about +0.975 V, from about +0.8 V to about +0.95 V, from about +0.8 V to about +0.925 V, from about +0.8 V to about +0.9 V, from about +0.8 V to about +0.875 V, from about +0.8 V to about +0.85 V, from about +0.8 V to about +0.825 V, from about +0.9 V to about +1 V, from about +0.9 V to about +0.975 V, from about +0.9 V to about +0.95 V, from about +0.9 V to about +0.925 V; or from about +0.8 V to about +1

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V, from about +0.825 V to about +1 V, from about +0.85 V to about +1 V, from about +0.875 V to about +1 V, from about +0.9 V to about +1 V, from about +0.925 V to about +1 V, from about +0.95 V to about +1 V, from about +0.975 V to about +1 V, from about +0.8 V to about +0.9 V, from about +0.825 V to about +0.9 V, from about +0.85 V to about +0.9 V, from about +0.875 V to about +0.9 V; or at most about +0.9 V, at most about +1 V; or about +0.8 V, about +0.825 V, about +0.85 V, about +0.875 V, about +0.9 V, about +0.925 V, about +0.95 V, about +0.975 V, about +1 V, or any ranges or values therebetween.

In some embodiments, the highest voltage, vs. RHE, in the waveform loop may be in a range of at least about +1.4 V, at least about +1.58 V; or from about +1.4 V to about +2.0 V, from about +1.4 V to about +1.8 V, from about +1.4 V to about +1.7 V, from about +1.4 V to about +1.65 V, from about +1.4 V to about +1.625 V, from about +1.4 V to about +1.6 V, from about +1.4 V to about +1.58 V, from about +1.4 V to about +1.575 V, from about +1.4 V to about +1.55 V, from about +1.4 V to about +1.525 V, from about +1.4 V to about +1.5 V, from about +1.4 V to about +1.475 V, from about +1.4 V to about +1.45 V, from about +1.4 V to about +1.425 V, from about +1.58 V to about +2.0 V, from about +1.58 V to about +1.8 V, from about +1.58 V to about +1.7 V, from about +1.58 V to about +1.65 V, from about +1.58 V to about +1.625 V, from about +1.58 V to about +1.6 V; or from about +1.4 V to about +2.0 V, from about +1.425 V to about +2.0 V, from about +1.45 V to about +2.0 V, from about +1.475 V to about +2.0 V, from about +1.5 V to about +2.0 V, from about +1.525 V to about +2.0 V, from about +1.55 V to about +2.0 V, from about +1.575 V to about +2.0 V, from about +1.58 V to about +2.0 V, from about +1.6 V to about +2.0 V, from about +1.625 V to about +2.0 V, from about +1.65 V to about +2.0 V, from about +1.7 V to about +2.0 V, from about +1.8 V to about +2.0 V, from about +1.4 V to about +1.58 V, from about +1.425 V to about +1.58 V, from about +1.45 V to about +1.58 V, from about +1.475 V to about +1.58 V, from about +1.5 V to about +1.58 V, from about +1.525 V to about +1.58 V, from about +1.55 V to about +1.58 V, from about +1.575 V to about +1.58 V; or at most about +1.58 V, at most about +2.0 V; or about +1.4 V, about +1.425 V, about +1.45 V, about +1.475 V, about +1.5 V, about +1.525 V, about +1.55 V, about +1.575 V, about +1.58 V, about +1.6 V, about +1.625 V, about +1.65 V, about +1.7 V, about +1.8 V, about +2.0 V, or any ranges or values therebetween.

In some embodiments, the voltage follows a reversible cyclic voltammetry waveform, where the voltage starts at +0.95 V, then increases to +1.58 V, decreases to +0.9 V and increases to +0.9 V, all vs. RHE, in a loop.

In some embodiments, the cyclic voltammetry is performed in a range of at least about 10 cycles, at least about 20 cycles; or from about 10 cycles to about 30 cycles, from about 10 cycles to about 28 cycles, from about 10 cycles to about 26 cycles, from about 10 cycles to about 25 cycles, from about 10 cycles to about 24 cycles, from about 10 cycles to about 22 cycles, from about 10 cycles to about 20 cycles, from about 10 cycles to about 18 cycles, from about 10 cycles to about 16 cycles, from about 10 cycles to about 15 cycles, from about 10 cycles to about 14 cycles, from about 10 cycles to about 12 cycles, from about 20 cycles to about 30 cycles, from about 20 cycles to about 28 cycles, from about 20 cycles to about 26 cycles, from about 20 cycles to about 25 cycles, from about 20 cycles to about 24 cycles, from about 20 cycles to about 22 cycles; or from about 10 cycles to about 30 cycles, from about 12 cycles to about 30 cycles, from about 14 cycles to about 30 cycles, from about 15 cycles to about 30 cycles, from about 16 cycles to about 30 cycles, from about 18 cycles to about 30 cycles, from about 20 cycles to about 30 cycles, from about

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22 cycles to about 30 cycles, from about 24 cycles to about 30 cycles, from about 25 cycles to about 30 cycles, from about 26 cycles to about 30 cycles, from about 28 cycles to about 30 cycles, from about 10 cycles to about 20 cycles, from about 12 cycles to about 20 cycles, from about 14 cycles to about 20 cycles, from about 15 cycles to about 20 cycles, from about 16 cycles to about 20 cycles, from about 18 cycles to about 20 cycles; or at most about 20 cycles, at most about 30 cycles; or about 10 cycles, about 12 cycles, about 14 cycles, about 15 cycles, about 16 cycles, about 18 cycles, about 20 cycles, about 22 cycles, about 24 cycles, about 25 cycles, about 26 cycles, about 28 cycles, about 30 cycles, or any ranges or values therebetween.

In some embodiments, the pre-catalyst comprises cobalt(II) chloride hexahydrate and iron(III) chloride hexahydrate.

In some embodiments, the molar ratio of cobalt to iron in the pre-catalyst is in a range of at least about 3:1, at least about 4:1; or from about 3:1 to about 5:1, from about 3:1 to about 4.8:1, from about 3:1 to about 4.6:1, from about 3:1 to about 4.5:1, from about 3:1 to about 4.4:1, from about 3:1 to about 4.2:1, from about 3:1 to about 4:1, from about 3:1 to about 3.8:1, from about 3:1 to about 3.6:1, from about 3:1 to about 3.5:1, from about 3:1 to about 3.4:1, from about 3:1 to about 3.2:1, from about 4:1 to about 5:1, from about 4:1 to about 4.8:1, from about 4:1 to about 4.6:1, from about 4:1 to about 4.5:1, from about 4:1 to about 4.4:1, from about 4:1 to about 4.2:1; or from about 3:1 to about 5:1, from about 3.2:1 to about 5:1, from about 3.4:1 to about 5:1, from about 3.5:1 to about 5:1, from about 3.6:1 to about 5:1, from about 3.8:1 to about 5:1, from about 4:1 to about 5:1, from about 4.2:1 to about 5:1, from about 4.4:1 to about 5:1, from about 4.5:1 to about 5:1, from about 4.6:1 to about 5:1, from about 4.8:1 to about 5:1, from about 3:1 to about 4:1, from about 3.2:1 to about 4:1, from about 3.4:1 to about 4:1, from about 3.5:1 to about 4:1, from about 3.6:1 to about 4:1, from about 3.8:1 to about 4:1; or at most about 4:1, at most about 5:1; or about 3:1, about 3.2:1, about 3.4:1, about 3.5:1, about 3.6:1, about 3.8:1, about 4:1, about 4.2:1, about 4.4:1, about 4.5:1, about 4.6:1, about 4.8:1, about 5:1, or any ranges or values therebetween.

In some embodiments, the pre-catalyst further comprises a solvent. Any solvent capable of dissolving the cobalt and iron salts may be used in the present invention. Exemplary solvents may include water, alcohols, lactones, lactams, amides, ketones, and/or combinations thereof. In some other embodiments, the solvent comprises water, alcohols, ketones, ethers, and mixtures thereof. In some embodiments, the ketone comprises acetone, butanone, and/or combinations and mixtures thereof. In other embodiments, the ether comprises tetrahydrofuran, methyl-THF, and/or combinations thereof. In some other embodiments, the alcohol comprises ethanol, methanol, isopropanol, butanol, isobutanol, t-butanol, pentanol, isopentanol, t-pentanol, and/or combinations and mixtures thereof. In some embodiments, the solvent comprises isopropanol and water. In some other embodiments, the solvent comprises isopropanol and water in a 1:4 ratio.

In some embodiments, the pre-catalyst further comprises a binder. In some embodiments, the binder comprises Na⁺-exchanged Nafion, polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (SCMC), poly(tetrafluoroethylene) (PTFE) and/or combinations and mixtures thereof.

In some embodiments, the pre-catalyst does not comprise a colloid and/or a polymer.

In some embodiments, the oxyhydroxide catalyst comprises oxyhydroxides having a di- μ -oxo motif.

During electrochemical reconstruction, the pre-catalyst undergoes significant changes in its physical and crystalline structure. The metal cations will be hydroxylated under alkaline condition and undergo electrochemical dehydrogenation to form the oxyhydroxide species. In some embodiments, the oxyhydroxide catalyst does not contain Cl. In some embodiments, the oxyhydroxide catalyst does not contain propylene oxide.

In some embodiments, the oxyhydroxide catalyst is amorphous or generally not crystalline.

In some embodiments, the oxyhydroxide catalyst comprises $\text{Co}(\text{Fe})\text{O}_x\text{H}_y$, $\text{Co}_2\text{O}_2(\text{OH})$, $\text{CoO}(\text{OH})$, and/or $\text{FeO}(\text{OH})$, wherein x is an integer in the range of 1 to 3 and y is an integer in the range of 0 to 1. The oxyhydroxide catalyst may nominally be CoOOH and FeOOH , however as they are amorphous and may have structural defects, the derived oxyhydroxide catalyst may be described as $\text{Co}(\text{Fe})\text{O}_x\text{H}_y$. The derived catalyst may also be described as $\text{Co}_a\text{Fe}_b\text{O}_x\text{H}_y$, wherein x is between 1 to 3 and y is between 0 to 1, and a and b are any of the ratios of Co:Fe described in the present application, e.g., a is 4 and b is 1. In other embodiments, the oxyhydroxide catalyst comprises Co^{3+} , Fe^{3+} , O^{2-} and OH^- ions.

In some embodiments, x may be in a range of at least about 1; or from about 1 to about 3, from about 1 to about 2.8, from about 1 to about 2.6, from about 1 to about 2.4, from about 1 to about 2.2, from about 1 to about 2, from about 1 to about 1.8, from about 1 to about 1.6, from about 1 to about 1.4, from about 1 to about 1.2; or from about 1 to about 3, from about 1.2 to about 3, from about 1.4 to about 3, from about 1.6 to about 3, from about 1.8 to about 3, from about 2 to about 3, from about 2.2 to about 3, from about 2.4 to about 3, from about 2.6 to about 3, from about 2.8 to about 3; or at most about 3; or about 1, about 1.2, about 1.4, about 1.6, about 1.8, about 2, about 2.2, about 2.4, about 2.6, about 2.8, about 3, or any ranges or values therebetween.

In some embodiments, y may be in a range of at least 0, at least about 0.1; or from 0 to about 1, from 0 to about 0.9, from 0 to about 0.8, from 0 to about 0.7, from 0 to about 0.6, from 0 to about 0.5, from 0 to about 0.4, from 0 to about 0.3, from 0 to about 0.2, from 0 to about 0.1; or from 0 to about 1, from about 0.1 to about 1, from about 0.2 to about 1, from about 0.3 to about 1, from about 0.4 to about 1, from about 0.5 to about 1, from about 0.6 to about 1, from about 0.7 to about 1, from about 0.8 to about 1, from about 0.9 to about 1; or at most about 1; or about 0, about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1, or any ranges or values therebetween.

The catalyst may have a particle size in a range of at least about 2 nm; or from about 2 nm to about 5 nm, from about 2 nm to about 4.5 nm, from about 2 nm to about 4 nm, from about 2 nm to about 3.5 nm, from about 2 nm to about 3 nm, from about 2 nm to about 2.5 nm; or from about 2 nm to about 5 nm, from about 2.5 nm to about 5 nm, from about 3 nm to about 5 nm, from about 3.5 nm to about 5 nm, from about 4 nm to about 5 nm, from about 4.5 nm to about 5 nm; or at most about 5 nm; or about 2 nm, about 2.5 nm, about 3 nm, about 3.5 nm, about 4 nm, about 4.5 nm, about 5 nm, or any ranges or values therebetween.

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In some embodiments, the substrate may be first applied onto an electrode. In some embodiments, the electrode is a glass carbon electrode.

In an aspect is provided an oxyhydroxide catalyst prepared by chemically reducing and/or electrochemically oxidizing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride.

The oxyhydroxide catalyst is not prepared via a sol-gel process, a hydrothermal process, and/or a solvothermal process.

The amorphous nanostructure of the catalyst may provide a large specific surface area for the $\text{Co(Fe)O}_x\text{H}_y$ species, which may lead to high current density in the oxygen evolution reaction. The derived $\text{Co(Fe)O}_x\text{H}_y$ on carbon is mostly oxyhydroxide species, with the di- μ -oxo bridged motif in oxyhydroxide species being identified as a highly active motif for oxygen evolution reaction.

In some embodiments, the pre-catalyst does not need to undergo further treatment prior to electrochemical reconstruction, e.g., treatment by sol-gel, solvothermal, hydrothermal, mechanical alloying, etc.. In some embodiments, the pre-catalyst does not undergo further treatment prior to electrochemical reconstruction, e.g., treatment by sol-gel, solvothermal, hydrothermal, mechanical alloying, etc.. In some embodiments, the pre-catalyst is chemically unchanged before electrochemical reconstruction. In some other embodiments, the pre-catalyst remains as an admixture of Co salts and Fe salts while it has yet to undergo electrochemical reconstruction. In some embodiments, the pre-catalyst does not contain oxyhydroxides.

In an aspect is provided a pre-catalyst for preparing an oxyhydroxide catalyst, wherein:

the pre-catalyst comprises cobalt(II) chloride and iron(III) chloride;

the pre-catalyst is applied on a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and

the pre-catalyst does not contain oxyhydroxide.

The pre-catalyst is not involved in a sol-gel process, a hydrothermal process, and/or a solvothermal process.

In one embodiment there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst,

wherein the method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.

In one embodiment there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride;
- (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst.

In one embodiment there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride;
- (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst,

wherein the method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.

In one embodiment there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride;
- (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst,

wherein the pre-catalyst in step (i) and step (i-a) does not contain oxyhydroxides.

In one embodiment there is provided a method of preparing an oxyhydroxide catalyst, the method comprising:

- (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride;
- (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
- (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst,

wherein the pre-catalyst in step (i) and step (i-a) does not contain oxyhydroxides, and

wherein the method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.

Statements of Invention

1. A method of preparing an oxyhydroxide catalyst, the method comprising:
 - (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride; and
 - (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst.
2. The method of statement 1, wherein the method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.
3. The method of statement 1 or 2, further comprising, before step (ii):
 - (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions.
4. The method of any one of statements 1 to 3, wherein the pre-catalyst in step (i) and step (i-a) does not contain oxyhydroxides.

5. The method of statement 3 or 4, wherein the pre-catalyst is applied on the conductive substrate with a mass loading of about 0.03 to about 0.08 mg/cm².
6. The method of any one of statements 3 to 5, wherein the conductive substrate is coated on an electrode.
7. The method of any one of statements 3 to 6, wherein the conductive substrate has a BET surface area of about 50 m²/g to about 1500 m²/g.
8. The method of any one of statements 3 to 7, wherein the conductive substrate has an electrical conductivity of about 0.05 S cm⁻¹ to about 3 S cm⁻¹.
9. The method of any one of statements 3 to 8, wherein the conductive substrate is selected from the group consisting of carbon black and acetylene black.
10. The method of any one of statements 1 to 9, wherein step (ii) comprises applying a voltage to the pre-catalyst.
11. The method of statement 10, wherein the voltage follows a reversible cyclic voltammetry waveform.
12. The method of statement 11, wherein the reversible cyclic voltammetry is performed for about 10 to about 30 cycles.
13. The method of any one of statements 1 to 12, wherein the pre-catalyst comprises cobalt(II) chloride hexahydrate and iron(III) chloride hexahydrate.
14. The method of any one of statements 1 to 13, wherein the molar ratio of cobalt to iron in the pre-catalyst is about 3:1 to about 5:1.
15. The method of any one of statements 1 to 14, wherein the pre-catalyst further comprises a solvent selected from the group consisting of water, alcohols, ethers, ketones, and mixtures thereof.
16. The method of any one of statements 1 to 15, wherein the pre-catalyst further comprises a binder.
17. The method of any one of statements 1 to 16, wherein the pre-catalyst does not comprise a polymer.
18. The method of any one of statements 1 to 17, wherein the oxyhydroxide catalyst comprises oxyhydroxides having a di-μ-oxo motif.
19. The method of any one of statements 1 to 18, wherein the oxyhydroxide catalyst does not contain Cl.

20. The method of any one of statements 1 to 19, wherein the oxyhydroxide catalyst is amorphous or generally not crystalline.
21. The method of any one of statements 1 to 20, wherein the oxyhydroxide catalyst comprises $\text{Co(Fe)O}_x\text{H}_y$, $\text{Co}_2\text{O}_3(\text{OH})$, $\text{CoO}(\text{OH})$, and/or $\text{FeO}(\text{OH})$, wherein x is between 1 to 3 and y is between 0 to 1.
22. An oxyhydroxide catalyst prepared by electrochemically oxidizing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride.
23. The oxyhydroxide catalyst of statement 22, wherein the oxyhydroxide catalyst is not prepared via a sol-gel process, a hydrothermal process, and/or a solvothermal process.
24. The oxyhydroxide catalyst of statement 22 or 23, wherein the pre-catalyst does not contain oxyhydroxides.
25. A pre-catalyst for preparing an oxyhydroxide catalyst, wherein:
the pre-catalyst comprises cobalt(II) chloride and iron(III) chloride;
the pre-catalyst is applied on a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
the pre-catalyst does not contain oxyhydroxides.
26. The pre-catalyst of statement 25, wherein the pre-catalyst is not involved in a sol-gel process, a hydrothermal process, and/or a solvothermal process.

Examples

Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Pre-catalyst Preparation

The Co(Fe)Cl_x pre-catalyst was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at a molar ratio of 4:1 in a solvent of isopropanol/water (vol/vol = 1:4), following which Na^+ -exchanged Nafion was added as a binder. The pre-catalyst is typically made up to 1 mg ml^{-1} , but can differ depending on the volume to be drop-casted onto the electrode.

Example 2: Electrode Preparation

A schematic showing the fabrication of an exemplary electrode having Co(Fe)Cl_x pre-catalyst on top of a carbon support is illustrated in Fig. 1a.

Acetylene black (AB), as the substrate material, was first drop-casted on a glassy carbon electrode at a mass loading of 0.05 mg cm^{-2} . The Co(Fe)Cl_x pre-catalyst solution was subsequently drop-casted onto the substrate-coated electrode while maintaining the overall Co and Fe metal loading at $\sim 0.05 \text{ mg cm}^{-2}$. The coated electrode was dried under ambient conditions and used in the subsequent electrochemical conversion step without further modification.

Example 3: Electrochemical Reconstruction of Pre-catalyst to Form Oxyhydroxide Catalyst

The electrochemical reconstruction of the pre-catalyst was carried out by performing cyclic voltammetry (CV) for 20 cycles in a three-electrode electrolysis cell. 1 M KOH was used as the electrolyte, a platinum plate ($1 \text{ cm}^2 \times 2 \text{ cm}^2$) was used as the counter electrode and a Hg/HgO electrode (O_2 -saturated 1 M KOH) was used as the reference electrode.

The CV and the pseudocapacitive electrochemical behaviour of the Co(Fe)Cl_x pre-catalyst for Oxygen Evolution Reaction (OER) over 20 cycles are shown in Figs. 2a and 2b respectively.

It is noted from Fig. 2a that the OER current density showed a notable increment from the 1st to the 20th cycle, indicating that the Co(Fe)Cl_x was electrochemically reconstructed to the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst species.

The electrochemical reconstruction also showed notable pseudocapacitive behaviour that may be indicated by the irreversible oxidative current. This irreversible oxidation was the most notable in the 1st cycle, only reaching a steady CV profile after around 20 cycles.

In steady CV, the $\text{Co}^{2+}/\text{Co}^{3+}$ redox may be assigned to the oxidation state transition between the $\text{Co}^{\text{II}}(\text{Fe})(\text{OH})_2$ and $\text{Co}^{\text{III}}(\text{Fe})(\text{O})\text{OH}$ species, which indicated the electrochemical reconstruction was completed and a stable catalytic surface having a carbon/ $\text{Co(Fe)O}_x\text{H}_y$ configuration was reached.

Example 4: Characterisation of Active $\text{Co(Fe)O}_x\text{H}_y$ Catalyst

After electrochemical reconstruction, the active carbon/ $\text{Co(Fe)O}_x\text{H}_y$ catalyst was observed under high-resolution TEM (HR-TEM). High-Resolution Transmission Electron Microscopy (HRTEM) images showing the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst at both low and high magnifications are shown in Figs. 3a and 3b respectively.

At low magnification (Fig. 3a), the morphology of carbon black (acetylene black) is clearly identified. At high magnification (Fig. 3b), the observed low-crystalline (or amorphous) clusters correspond to the active $\text{Co(Fe)O}_x\text{H}_y$ reconstructed from Co(Fe)Cl_x . The $\text{Co(Fe)O}_x\text{H}_y$ clusters were further observed to have a particle size of about 2 nm to about 5 nm. The amorphous nanostructure provides a large specific surface area of the $\text{Co(Fe)O}_x\text{H}_y$ species, thus leading to a high current density during the oxygen evolution reaction.

X-ray diffraction of the Co(Fe)Cl_x pre-catalyst was performed in order to confirm that no oxyhydroxides

were present in the pre-catalyst prior to electrochemical reconstruction. The obtained pattern is shown in Fig. 3c. From Fig. 3c, it was observed that the XRD pattern of the pre-catalyst follows the pattern of a standard CoCl_2 well, indicating that the Co in the pre-catalyst was present predominantly as CoCl_2 .

The low-crystalline structure of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst presents a challenge when characterizing the catalyst using usual X-ray diffraction techniques. Hence, X-ray absorption fine structure (XAFS) spectroscopy and X-ray absorption near-edge spectroscopy (XANES) were performed to measure the local atomic structures around different atomics species in the activated $\text{Co(Fe)O}_x\text{H}_y$ catalyst.

Fig. 4a shows the Co K-edge XANES spectra of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst, the spectra of standard Co(OH)_2 and Co(O)OH have been added as references. The near-edge feature indicated that the oxidation state of Co in the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst was close to that of standard Co(O)OH , which thus suggests that Co^{III} , instead of Co^{II} , was the predominant form in $\text{Co(Fe)O}_x\text{H}_y$.

Fig. 4b shows the Co K-edge extended EXAFS spectra of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst, with standard Co(OH)_2 and Co(O)OH spectra added as reference. According to the EXAFS spectra, the Co-O and Co-Co features in $\text{Co(Fe)O}_x\text{H}_y$ are consistent with that in Co(O)OH . Therefore, the oxyhydroxide species predominates in the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst, and the di- μ -oxo bridged motif in oxyhydroxide species was identified as the highly active motif for oxygen evolution reaction.

Example 5: Carbon Support

The BET surface areas of carbon black supports (Super P® Conductive, 99+, Acetylene Black, Vulcan XC72 and Ketjenblack EC-600JD) are given in Table 1.

Table 1: BET Surface Area and Electrical Conductivity of Tested Carbon Supports

Carbon Supports	BET surface area	Typical Electrical Conductivity
<i>Super P® Conductive, 99+%</i>	62 m ² g ⁻¹	0.505 S cm ⁻¹
<i>Acetylene Black</i>	90 m ² g ⁻¹	0.6 S cm ⁻¹
<i>Vulcan XC72</i>	223 m ² g ⁻¹	2.77 S cm ⁻¹
<i>Ketjenblack EC-600JD</i>	1270 m ² g ⁻¹	0.1 S cm ⁻¹

Fig. 5a shows the steady CVs of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst species on various carbon supports during OER. In the CVs shown in Fig. 5a, the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst exhibited electrochemical activity with all tested catalysts. In particular, the OER activity of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst paired with an Acetylene Black support ($\text{AB@Co(Fe)O}_x\text{H}_y$) showed the highest OER activity, while the same catalyst showed a comparatively lower activity when paired with the Ketjenblack EC-600JD as the carbon support ($\text{KJB@Co(Fe)O}_x\text{H}_y$).

Fig. 5b further shows the pseudocapacitive charge in CVs of the active $\text{Co(Fe)O}_x\text{H}_y$ catalysts on different carbon supports before OER. The $\text{KJB@Co(Fe)O}_x\text{H}_y$ delivered the highest capacitance, indicating that it possessed the largest electrochemical surface area and the most abundant active sites during the electrochemical reaction. The $\text{KJB@Co(Fe)O}_x\text{H}_y$ even showed the lowest onset potential for OER as

compared to other carbon supports tested. However, the comparatively lower activity of the catalyst when paired with this substrate may be due to the lower electrical conductivity, resulting in a higher overpotential greatly compromising its OER activity. Despite the above, acetylene black was identified as the best support for the $\text{Co(Fe)O}_x\text{H}_y$ catalyst of the present invention.

Comparative Examples

Comparative Example 1: Comparison of Cl^- against other Counter-ions

The effects of the cobalt and iron counterions on the activity of the final $\text{Co(Fe)O}_x\text{H}_y$ catalyst species was examined. Chlorides, sulphates, and nitrates were compared.

Pre-catalysts were prepared according to Example 1, except that the chlorides were replaced with sulphates and nitrates. The Co and Fe salts were mixed in isopropanol/water (vol/vol = 1:4) to maintain a molar ratio of Co:Fe = 4:1, reaching a total concentration of 1 mg ml^{-1} . The reagents used and the pre-catalysts prepared are detailed in Table 2.

Table 2: Pre-catalysts Prepared From Different Salts

Sample	Pre-catalyst	Co salt used	Fe salt used
6a	Co(Fe)Cl_x	CoCl_2	FeCl_3
6b	$\text{Co(Fe)(NO}_3)_x$	$\text{Co(NO}_3)_2$	$\text{Fe(NO}_3)_3$
6c	$\text{Co(Fe)(SO}_4)_x$	CoSO_4	$\text{Fe}_3(\text{SO}_4)_2$

The other two pre-catalysts (Samples 6b and 6c) were also applied to and electrochemically activated on electrodes using the same procedure as detailed in Examples 2 and 3.

CV spectrums of the three pre-catalysts during OER are shown in Fig. 6. From Fig. 6, it was observed that $\text{Co(Fe)(NO}_3)_x$ (Sample 6b) had the lowest activity among the three samples tested. While Co(Fe)Cl_x (Sample 6a) and $\text{Co(Fe)(SO}_4)_x$ (Sample 6c) had similar activity, the Cl^- in Sample 6a would undergo oxidation and be removed as Cl_2 gas, while the SO_4^{2-} ion in Sample 6c would remain in the final catalyst as it is challenging to remove electrochemically.

As shown above, the pre-catalyst of the present invention, prepared from cobalt(II) and iron(III) chlorides, was re-constructed into a catalyst that had far higher electrochemical activity than a catalyst prepared from cobalt (II) and iron(III) nitrates instead.

While the catalysts prepared from chlorides (Sample 6a) and sulphates (Sample 6c) were observed to have similar activity, the presence of sulphates may affect the activity and efficiency of the catalyst. Further, such sulphate ions may precipitate out in the presence of Ca^{2+} or Mg^{2+} ions in the electrolyte and poison the catalyst surface, further reducing electrochemical activity of the catalyst. Sea water and hard water, among others, are examples of water sources that have high concentrations of Ca^{2+} and Mg^{2+} and other ions. Advantageously, the catalysts of the present invention contain only cobalt(III) and iron(III) oxyhydroxides and do not contain any additional counterions or only in trace amounts (as the Cl^- ions

undergo oxidation and are removed as Cl_2 gas) that may affect the activity of the catalyst in electrochemical applications.

Comparative Example 2: Comparison of Present Synthesis Method Against Hydrothermal Process

The activity of the $\text{Co(Fe)O}_x\text{H}_y$ catalyst of the present invention was compared against a $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst chemically synthesised via a hydrothermal process.

Briefly, $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ was synthesised using a hydrothermal method. CoSO_4 and FeCl_3 were mixed in a molar ratio of Co:Fe (4:1) and dissolved in 30 ml H_2O . The total amount of metal cations (Co^{2+} and Fe^{3+}) was limited to 3 mmol. Urea (7.5 mmol) was then added to the mixture, and the mixture further stirred until it became clear. The mixture was transferred to a 50 ml stainless-steel Teflon-lined autoclave and heated and 90 °C for 24 hours to produce the $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst. The as-synthesised $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ was then cooled back to room temperature and rinsed with DI water and ethanol successfully, following which it was vacuum-dried at 60 °C for 12 hours. The $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ was then loaded onto a glassy carbon electrode at a mass loading of about 0.25 mg cm^{-2} .

The graph showing the CV spectrum of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst (on acetylene black) and a hydrothermal synthesised $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst is shown in Fig. 7a, while the CV spectrum showing the pseudocapacitive behaviour of the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst and a hydrothermal synthesised $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst, before OER, is shown in Fig. 7b.

From Fig. 7a, the active $\text{Co(Fe)O}_x\text{H}_y$ catalyst was observed to outperform the $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$, even at a much lower loading of Co and Fe in $\text{Co(Fe)O}_x\text{H}_y$ as (about 0.05 mg cm^{-2}) compared to $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ (about 0.25 mg cm^{-2}). Fig. 7b further indicated the $\text{Co}^{2+}/\text{Co}^{3+}$ redox peaks in $\text{Co(Fe)O}_x\text{H}_y$ were much smaller as compared to $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$, further confirming the higher catalytic activity of the $\text{Co(Fe)O}_x\text{H}_y$ catalyst of the present invention over $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ synthesised using a conventional hydrothermal method.

From the above, the inventors have shown that the present invention produces a catalyst that is far more electrochemically active than a $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst produced via a conventional hydrothermal method. This is evidenced by the catalyst of the present invention showing higher electrochemical activity as compared to the other comparative catalyst, despite a lower catalyst loading on the electrode (0.05 mg cm^{-2} as compared to 0.25 mg cm^{-2}).

The present catalyst is comparatively easier to prepare from the pre-catalyst, requiring only *in situ* electrochemical reconstruction, as compared to the comparative $\text{Co}_{0.8}\text{Fe}_{0.2}\text{OOH}$ catalyst requiring a harsh hydrothermal process (at elevated pressures and at 90 °C for over 24 hours). As such the present invention is far easier to use in preparing oxyhydroxide catalysts as compared to conventional methods.

Industrial Applicability

The present invention relates to oxyhydroxide pre-catalysts, catalysts and methods of preparation. The pre-catalysts of the present invention require simple preparation steps, and can be easily converted via

electrochemical activation to the active catalyst species. The pre-catalysts and catalysts of the present invention also avoids expensive metals, reagents, surfactants, and harsh conditions, and can be easily scaled up to industrial-scale production. Thus, this invention is capable of industrial applicability.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

1. A method of preparing an oxyhydroxide catalyst, the method comprising:
 - (i) preparing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride; and
 - (ii) electrochemically oxidizing the pre-catalyst to form the oxyhydroxide catalyst.
2. The method of claim 1, wherein the method does not comprise a sol-gel process, a hydrothermal process, and/or a solvothermal process.
3. The method of claim 1 or 2, further comprising, before step (ii):
 - (i-a) applying the pre-catalyst to a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions.
4. The method of any one of claims 1 to 3, wherein the pre-catalyst in step (i) and step (i-a) does not contain oxyhydroxides.
5. The method of claim 3 or 4, wherein the pre-catalyst is applied on the conductive substrate with a mass loading of about 0.03 to about 0.08 mg/cm².
6. The method of any one of claims 3 to 5, wherein the conductive substrate is coated on an electrode.
7. The method of any one of claims 3 to 6, wherein the conductive substrate has a BET surface area of about 50 m²/g to about 1500 m²/g.
8. The method of any one of claims 3 to 7, wherein the conductive substrate has an electrical conductivity of about 0.05 S cm⁻¹ to about 3 S cm⁻¹.
9. The method of any one of claims 3 to 8, wherein the conductive substrate is selected from the group consisting of carbon black and acetylene black.
10. The method of any one of claims 1 to 9, wherein step (ii) comprises applying a voltage to the pre-catalyst.
11. The method of claim 10, wherein the voltage follows a reversible cyclic voltammetry waveform.
12. The method of claim 11, wherein the reversible cyclic voltammetry is performed for about 10 to about 30 cycles.
13. The method of any one of claims 1 to 12, wherein the pre-catalyst comprises cobalt(II) chloride hexahydrate and iron(III) chloride hexahydrate.
14. The method of any one of claims 1 to 13, wherein the molar ratio of cobalt to iron in the pre-catalyst is about 3:1 to about 5:1.

15. The method of any one of claims 1 to 14, wherein the pre-catalyst further comprises a solvent selected from the group consisting of water, alcohols, ethers, ketones, and mixtures thereof.
16. The method of any one of claims 1 to 15, wherein the pre-catalyst further comprises a binder.
17. The method of any one of claims 1 to 16, wherein the pre-catalyst does not comprise a polymer.
18. The method of any one of claims 1 to 17, wherein the oxyhydroxide catalyst comprises oxyhydroxides having a di- μ -oxo motif.
19. The method of any one of claims 1 to 18, wherein the oxyhydroxide catalyst does not contain Cl.
20. The method of any one of claims 1 to 19, wherein the oxyhydroxide catalyst is amorphous or generally not crystalline.
21. The method of any one of claims 1 to 20, wherein the oxyhydroxide catalyst comprises $\text{Co(Fe)O}_x\text{H}_y$, $\text{Co}_2\text{O}_2(\text{OH})$, $\text{CoO}(\text{OH})$, and/or $\text{FeO}(\text{OH})$, wherein x is an integer in the range of 1 to 3 and y is an integer in the range of 0 to 1.
22. An oxyhydroxide catalyst prepared by electrochemically oxidizing a pre-catalyst comprising cobalt(II) chloride and iron(III) chloride.
23. The oxyhydroxide catalyst of claim 22, wherein the oxyhydroxide catalyst is not prepared via a sol-gel process, a hydrothermal process, and/or a solvothermal process.
24. The oxyhydroxide catalyst of claim 22 or 23, wherein the pre-catalyst does not contain oxyhydroxides.
25. A pre-catalyst for preparing an oxyhydroxide catalyst, wherein:
 - the pre-catalyst comprises cobalt(II) chloride and iron(III) chloride;
 - the pre-catalyst is applied on a conductive substrate, wherein the pre-catalyst is allowed to dry on the conductive substrate under ambient conditions; and
 - the pre-catalyst does not contain oxyhydroxides.
26. The pre-catalyst of claim 25, wherein the pre-catalyst is not involved in a sol-gel process, a hydrothermal process, and/or a solvothermal process.