

Iridium Catalysts

Technical Field

5 The present disclosure generally relates to catalysts and their uses, and more particularly to iridium catalysts for producing hydrogen. The present disclosure also relates to a method of producing such catalysts, and their uses thereof.

Background Art

10 Taking full advantage of renewable energy is a viable path towards a sustainable future. To tackle the intermittent availability of renewable energies, large-scale implementation of energy conversion and storage facilities is a must. Converting electricity from renewable energy into hydrogen fuel for energy storage is promising. Such a renewable energy conversion and storage
15 process can be realized through electrochemical water splitting, which is a sustainable way of producing hydrogen without the emission of any carbon-related products. Electrochemical water splitting involves two half reactions: hydrogen evolution reaction and oxygen evolution reaction (OER). The latter, with a higher kinetic barrier, is often considered to determine the efficiency of water electrolysis.

20 Among the technologies for electrochemical water splitting, proton-exchange membrane (PEM) water electrolyzers seem to be the most suitable for pairing with renewable energy. However, the acidic and oxidizing conditions limit the choice of OER catalysts to iridium (Ir), which is one of the least abundant elements. To maximize the activity of Ir catalysts in OER by increasing the number
25 of available active Ir sites, the preparation of nano-sized Ir or IrO₂ with a high surface area is a general approach. A conventional method involves reducing Ir salts in a solvent. However, this method often requires multiple organic reagents, such as tetralin, dibenzyl ether, and oleylamine, which can be toxic and explosive. In addition, large-scale production of nano-catalysts using this strategy might be difficult due to the relatively low yield.

30 Therefore, there is a need to provide Ir catalysts that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

35 In an aspect of the present disclosure, there is provided a catalyst consisting essentially of IrO_xH_y, wherein X and Y fulfill an equation $4 + Y = 2X$.

40 In another aspect of the present disclosure, there is provided a method of preparing a catalyst consisting essentially of IrO_xH_y, wherein X and Y fulfill an equation $4 + Y = 2X$, the method comprising:

- (i) immersing Sr₄IrO₆ in acid to form a mixture; and
- (ii) subjecting the mixture of step (i) to agitation for more than 12 hours.

45 In a further aspect of the present disclosure, there is provided a catalyst obtained by the method as disclosed herein.

 In another aspect of the present disclosure, there is provided a use of the catalyst as disclosed herein to produce hydrogen.

Advantageously, the disclosed catalysts may exhibit higher activity as compared to other Ir catalysts. The disclosed catalysts may be amorphous, which intrinsically have higher activity as compared to crystalline catalysts. The disclosed amorphous catalysts may also be advantageously stable in OER conditions.

Further advantageously, the disclosed catalysts may be hierarchically porous. Hierarchically porous catalysts exhibit increased surface area, and enhanced mass transport when the catalyst is used as an anode. This allows the disclosed catalysts to advantageously exhibit superior electrochemical performance as compared to known Ir catalysts.

Also advantageously, the disclosed catalysts may be support-free, which allows them to be used in membrane electrode assemblies (MEAs) and water electrolyzers without a support material, reducing the costs of production and also the hydrogen production cost. Support materials used in OER conditions are also known to negatively impact the activity and stability of Ir catalysts, therefore the disclosed catalysts being support-free advantageously allow them to exhibit higher activity and stability over supported Ir catalysts.

Further advantageously, the disclosed catalysts may be highly stable in acidic media. This allows the catalysts to be used over a longer period, thus reducing the overall cost of the catalyst, and subsequently the hydrogen production cost.

Also advantageously, the disclosed methods may also provide a way for easy recycling of dissolved Ir during chemical leaching, specifically the loss/dissolution of Ir, which reduces the overall material cost of production of the catalyst, and addresses the high scarcity of Ir and its high cost. The disclosed methods are hence advantageously suitable for large scale production.

Further advantageously, the disclosed catalysts may be used to produce hydrogen in oxygen evolution reactions as the anodes of PEM water electrolyzers to provide an accelerated oxygen evolution reaction as compared to the commercially available catalysts.

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 phrase "consisting essentially of" refers to a catalyst whose only active component is the indicated active component, however other impurities that would not materially affect the characteristics of the catalyst may be present.

As used herein, the term "amorphous" refers to a substance that does not have any appreciable repeating crystalline structure.

As used herein, the term "hierarchically porous", or also sometimes referred to using the acronym "HP", refers to the presence of at least two different pore sizes, wherein the pores are macropores, mesopores, or micropores. Macropores are generally known as, and in accordance with the IUPAC nomenclature, pores with a diameter of greater than 50 nm, mesopores as pores having a diameter of greater than 2 nm and up to 50 nm, and micropores as pores with a diameter of up to 2 nm. The pore size distribution can be measured by methods known to a person skilled in the art, such as the Barrett-Joyner-Halenda (BJH) method.

As used herein, the term "support-free" refers to the absence of support material, such as a material which has been sprayed or impregnated with a solution of the active components or onto which the active components have been adhesively applied in another manner.

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 +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 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. 1

Fig. 1 is a series of diagrams showing the physical characteristics of a catalyst precursor Sr_4IrO_6 of the present invention, with (a) showing the crystal structure; (b) showing the Scanning Electron Microscope (SEM) image before acid-treatment; (c) showing the same images of (b) after acid treatment; (d) showing the X-ray photoelectron spectrum (XPS) of the catalyst precursor before and after acid treatment; (e) and (f) showing SEM images after acid treatment; (g) and (h) showing a TEM image of the catalyst precursor after acid treatment; and (i) is a graph showing the surface area of the catalyst precursor before and after acid treatment.

Fig. 2

Fig. 2 is an X-ray Diffraction (XRD) spectrum of a catalyst precursor (Sr_4IrO_6) of the present invention.

Fig. 3

Fig. 3 (a) is a spectrum showing X-ray absorption near the edge structure of a catalyst precursor (Sr_4IrO_6) of the present invention and a comparative example (rutile IrO_2); and (b) is a fine structure spectrum showing the k^3 -weighted Co K-edge extended X-ray absorption of the catalyst precursor (Sr_4IrO_6).

Fig. 4

Fig. 4 are SEM images of a catalyst precursor (Sr_4IrO_6) of the present invention before and after acid leaching (scale bar: 10 μm).

Fig. 5

Fig. 5 is an XRD spectrum of a catalyst precursor (Sr_4IrO_6) of the present invention after chemical leaching and calcination.

Fig. 6

Fig. 6 is a graph showing the physisorption isotherms of a catalyst precursor (Sr_4IrO_6) of the present invention after acid-treatment.

Fig. 7

Fig. 7 is a series of diagrams showing the physical characteristics of an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$), with (a) showing the XRD pattern; (b) showing the X-ray absorption fine structure spectrum; (c) showing the cyclic voltammetry curve; (d) showing the thermogravimetric profile; (e) and (f) showing kinetic barriers for the proposed dehydration of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units; (g) showing the optimized energy of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ systems; (h) showing the predicted and (i) showing the actual densification from a catalyst precursor (Sr_4IrO_6) of the present invention to an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$).

Fig. 8

Fig. 8 is a spectrum showing the X-ray absorption near edge structure of a catalyst precursor (Sr_4IrO_6) of the present invention after acid-treatment and a comparative example (rutile IrO_2).

5 **Fig. 9**

Fig. 9 is a graph showing the different CV curves from an embodiment of the present invention (f) and comparative embodiments ((a) to (e) and (g) to (k)).

Fig. 10

10 Fig. 10 is a graph showing the evolution of CV curves of a comparative example (Ir metal nano particles (20% Iridium supported on Vulcan XC-72)).

Fig. 11

15 Fig. 11 is a graph showing the phonon curves of Sr_4IrO_6 -type H_8IrO_6 .

Fig. 12

Fig. 12 is a diagram showing the initial (a) and optimized (b) structures of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra with two $-\text{OH}_2$ groups in a "head-to-head" arrangement.

20 **Fig. 13**

Fig. 13 is a graph showing the kinetic barriers for the second dehydration processes of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units with an $-\text{OH}$ group and an $-\text{OH}_2$ group in a "head to head" arrangement.

Fig. 14

25 Fig. 14 is a diagram showing the possible approaching behaviours between two isolated $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra with different intermolecular distances (IMD).

Fig. 15

30 Fig. 15 is a graph showing the physisorption isotherms of an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$ -ball milled (BM)).

Fig. 16

35 Fig. 16 is a graph showing the X-ray photoelectron spectroscopy signals of Ir_{4f} and O_{1s} from embodiments of the present invention ($\text{HP-IrO}_x\text{H}_y$ -BM and $\text{HP-IrO}_x\text{H}_y$).

Fig. 17

Fig. 17 is a graph showing the CV curve from an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$ -BM).

Fig. 18

40 Fig. 18 (above) is a graph showing the specific activities (activity normalized to Brunauer-Emmett-Teller (BET) surface area) of some embodiments of the present invention ($\text{HP-IrO}_x\text{H}_y$ -BM and $\text{HP-IrO}_x\text{H}_y$) and (below) is a graph showing the improvement factor of an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$ -BM) induced by the ball-milling at high potentials.

45 **Fig. 19**

Fig. 19 is a graph showing the mass activity of an embodiment of the present invention ($\text{HP-IrO}_x\text{H}_y$ -BM) and other comparative embodiments (IrO_2 nano (7 ± 2 nm), IrO_2 nano (1.7 ± 0.4 nm), IrO_2 nano-AA (Alfa-Aldrich), IrO_2 nano-JM (Johnson Matthey), IrO_2 nano (< 2 nm), Ir nano (2.1 ± 0.4 nm), and Ir nano-TKK). NREL: National Renewable Energy Laboratory.

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Fig. 20

Fig. 20(a) is a graph showing the polarization curves of an MEA with an anode comprising an embodiment of the present invention (HP-IrO_xH_y-BM) and MEAs with anodes comprising other comparative embodiments. Fig. 20(b) is Tafel plots of the HFR-free cell voltage in cells with anodes comprising a comparative embodiment (IrO_xH_y-AA) and an embodiment of the present invention (HP-IrO_xH_y-BM). Inset are the Tafel plots between 10-100 mA cm⁻², with the Tafel slopes obtained through linear fitting. Fig. 20(c) is a graph showing the calculated $\Delta\eta_m$ and $\Delta\eta_o$ at high current densities (≥ 1 A cm⁻²).

Fig. 21

Fig. 21 is a graph showing the measured HFRs of an embodiment of the present invention (HP-IrO_xH_y-BM) and a comparative embodiment (IrO_xH_y-AA).

Fig. 22

Fig. 22 is a series of SEM images showing (a) the top-view and (b) side-view of the anode catalyst layers of a comparative embodiment (IrO_xH_y-AA), and (c) the top-view and (d) side-view of the anode catalyst layers of an embodiment of the present invention (HP-IrO_xH_y-BM).

Fig. 23

Fig. 23 is a series of diagrams showing a stability test conducted on an MEA with an anode comprising an embodiment of the present invention (HP-IrO_xH_y-BM), with (a) showing the chronopotentiometric measurement for the MEA with an embodiment of the present invention (HP-IrO_xH_y-BM) as the anode (top) and the estimated S-number of said HP-IrO_xH_y-BM anode vs time, (b) showing an extracted power output profile from practical solar panels (circles) and applied power input profile (line), (c) showing the recorded cell voltage and current profiles of (b), and (d) showing the estimated D-number vs cycle number (profiles based on renewable energy).

Fig. 24

Fig. 24 is a graph showing the recorded OER potentials of a H-cell comprising an embodiment of the present invention (HP-IrO_xH_y-BM) as the anode.

Fig. 25

Fig. 25 is a graph showing the measured cell voltages and HFRs during the interval of each cycle of an MEA with an anode comprising an embodiment of the present invention (HP-IrO_xH_y-BM).

Detailed Description of Figures

Referring to Fig. 1, Fig. 1(a) is a diagram showing the crystal structure of a catalyst precursor of the present invention (Sr₄IrO₆) and the arrangement of IrO₆ octahedra that are isolated by Sr²⁺ in said catalyst precursor. Fig. 1(b) is a scanning electron microscope (SEM) image of particles of the catalyst precursor (scale bar: 10 μm). Fig. 1(c) are SEM images of particles of the catalyst precursor after acid-treatment (scale bar: 10 μm), and a formed surface slit in said catalyst precursor after acid-treatment (scale bar: 100 nm). Fig. 1(d) is a graph showing the X-ray Photoelectron Spectroscopy (XPS) signal of a catalyst precursor before and after chemical leaching has taken place. Figs. 1(e) and 1(f) are SEM images of a cross-sectional specimen of the catalyst precursor after acid-treatment prepared by focused ion beam (FIB) milling (scale bar: 500 nm). Figs. 1(g) and 1(h) are transmission electron microscope (TEM) images of the local structure of pores/channels within the bulk of the catalyst precursor after acid-treatment (scale bar: 500 nm in 1(g), 50 nm in 1(h)). Fig. 1(i) is a graph showing the surface areas of the catalyst precursor before and after acid-treatment. The upper limit of the surface area for the catalyst precursor before treatment is estimated using a spherical model, with

a diameter $>10\ \mu\text{m}$ (marked in the larger circle). The smaller circle represents the equivalent IrO_2 sphere for the acid-treated Sr_4IrO_6 , with a calculated diameter of $\sim 12.8\ \text{nm}$ based on the corresponding BET surface area.

5 Referring to Fig. 2, minor SrCO_3 impurities in the catalyst precursor (Sr_4IrO_6) can be detected. The reliability factors are $R_{\text{wp}}=6.24\ \%$, $R_p=4.68\ \%$, $\chi^2=3.481$. The refined lattice parameters for Sr_4IrO_6 are $a=b=9.6467(2)$, $c=11.8668(4)$.

10 Referring to Fig. 5, possible phases related to Sr-Ir-O in the catalyst precursor (Sr_4IrO_6) cannot be identified, and a phase pure rutile IrO_2 is confirmed. The reliability factors are $R_{\text{wp}}=6.24\ \%$, $R_p=4.68\ \%$, $\chi^2=3.481$.

Referring to Fig. 7, Fig.7(a) is an image showing a selected area of the diffraction pattern of the catalyst precursor (Sr_4IrO_6) after chemical leaching. The inset picture is the selected-area-electron-diffraction from an acid-treated Sr_4IrO_6 particle. Fig. 7(b) are spectra showing the Ir L_{III} -edge extended X-ray absorption fine structure from a catalyst of the present invention ($\text{HP-IrO}_x\text{H}_y$) and a comparative embodiment (rutile IrO_2). Fig. 7(c) are graphs showing the cyclic voltammetry (CV) curves of the catalyst and a comparative embodiment (activated Iridium oxide film (AIROF)). Fig. 7(d) is a graph showing the thermogravimetry profile of the catalyst. Fig. 7(e) is a graph showing the kinetic barriers for the first and second dehydration processes of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units with two $-\text{OH}_2$ groups in a "head-to-head" arrangement. Fig. 7(f) is a graph showing the kinetic barriers for the first dehydration process of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units with an $-\text{OH}$ group and an $-\text{OH}_2$ group in a "head to head" arrangement. Fig. 7(g) is a graph showing the energy of two optimized $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra systems with different initial Ir-Ir distances. Fig. 7(h) is a diagram showing the IrO_6 octahedra arrangements in Sr_4IrO_6 -type H_8IrO_6 and rutile-type H_8IrO_6 . The H atoms are omitted for simplification. Fig. 7(i) is a schematic showing the formation of μm -sized catalyst from the catalyst precursor.

Referring to Fig. 18, at potentials $<\sim 1.50\text{V}$, the specific activity of $\text{HP-IrO}_x\text{H}_y\text{-BM}$ is close to the specific activity of $\text{HP-IrO}_x\text{H}_y$. This corresponds to findings in Figs. 16 and 18 that the ball-milling process merely induces a surface area increment. At potentials $>\sim 1.50\text{V}$, the specific activity of $\text{HP-IrO}_x\text{H}_y\text{-BM}$ outperforms the specific activity of $\text{HP-IrO}_x\text{H}_y$, which is depicted by the improvement factor gradually increasing as the potential increases. This is likely due to facilitated mass transfer within the catalyst layer.

35 Referring to Fig. 20, the comparative embodiments in Fig. 20(a) are (Ir/C-FC ($0.375\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), $\text{IrO}_x\text{H}_y\text{-AA}$ ($0.375\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), $\text{IrO}_2\text{-SA}$ ($0.375\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), $\text{IrO}_x\text{@TiO}_2$ (Heraeus, $0.3\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), $\text{IrO}_2\text{@TiO}_2$ (Umicore, $2.5\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), NSTF (3M, $0.375\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), $\text{Sr}_2\text{CaIrO}_6$ ($0.4\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$), and Hybrid IrO_x ($0.2\ \text{mg}_{\text{Ir}}\ \text{cm}^{-2}$)). For a fair comparison, a membrane thickness of $\sim 50\ \mu\text{m}$, $80\ ^\circ\text{C}$, $1\ \text{atm}$ was used. Department of Energy's (DOE) 2026 target: $3.0\ \text{A}\ \text{cm}^{-2}$ @ $1.8\ \text{V}$, noble metal loading of $0.5\ \text{mg}\ \text{cm}^{-2}$. DOE 2031 target: $3.0\ \text{A}\ \text{cm}^{-2}$ @ $1.6\ \text{V}$, noble metal loading of $0.125\ \text{mg}\ \text{cm}^{-2}$.

Referring to Fig. 23, the S-number from chronopotentiometric measurements in an H-cell with said $\text{HP-IrO}_x\text{H}_y\text{-BM}$ anode is also included (as shown in Fig. 24).

45 Referring to Fig. 24, the potential vibration can be related to bubble release induced transient change of ohmic resistance.

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Detailed Disclosure of Embodiments

Herein, the present invention provides an Ir catalyst as a solution for the production of hydrogen, as an anode involved in the oxygen evolution reaction in proton exchange membrane water electrolyzers (PEMWEs). The Ir catalyst described herein has surprisingly high activity and stability, which helps to reduce the costs of producing, using, and replacing the catalyst in PEMWEs.

The Ir catalyst described herein may be formed by acid-leaching of a Sr_3IrO_6 precursor. The acid-leaching may surprisingly lead to a formation of an amorphous, hierarchically porous, and support-free Ir catalyst through the self-assembly of densely isolated single IrO_6 octahedra. The Ir catalyst consequently possesses a surprisingly high surface area, and exhibits a superior electrochemical performance as compared to other state-of-the-art Ir-based catalysts.

The present invention provides a catalyst comprising IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. In particular, the present invention provides a catalyst consisting essentially of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. The present invention also provides a catalyst consisting of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. The present invention also provides a catalyst which is IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$.

In some embodiments, the catalyst consists essentially of IrO_xH_y where IrO_xH_y is present in the catalyst in a range of about 95 wt% to about 100 wt%, from about 95 wt% to about 99 wt%, from about 95 wt% to about 98 wt%, from about 95 wt% to about 97 wt%, from about 95 wt% to about 96 wt%, from about 96 wt% to about 100 wt%, or from about 96 wt% to about 100 wt%, from about 97 wt% to about 100 wt%, from about 98 wt% to about 100 wt%, from about 99 wt% to about 100 wt% or about 95 wt%, about 96 wt%, about 97 wt%, about 98 wt%, about 99 wt%, about 100 wt%, or any value or range therein. The catalyst may be 100 wt% IrO_xH_y . It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, the catalyst consists essentially of IrO_xH_y where IrO_xH_y is present in the catalyst in a range of about 95 at% to about 100 at%, from about 95 at% to about 99 at%, from about 95 at% to about 98 at%, from about 95 at% to about 97 at%, from about 95 at% to about 96 at%, from about 96 at% to about 100 at%, or from about 96 at% to about 100 at%, from about 97 at% to about 100 at%, from about 98 at% to about 100 at%, from about 99 at% to about 100 at% or about 95 at%, about 96 at%, about 97 at%, about 98 at%, about 99 at%, about 100 at%, or any value or range therein. The catalyst may be 100 at% IrO_xH_y . It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, X may be in a range of about 3.60 to about 4.00, from about 3.60 to about 3.99, from about 3.60 to about 3.98, from about 3.60 to about 3.97, from about 3.60 to about 3.96, from about 3.60 to about 3.95, from about 3.60 to about 3.94, from about 3.60 to about 3.93, from about 3.60 to about 3.92, from about 3.60 to about 3.91, from about 3.60 to about 3.90, from about 3.60 to about 3.89, from about 3.60 to about 3.88, from about 3.60 to about 3.87, from about 3.60 to about 3.86, from about 3.60 to about 3.85, from about 3.60 to about 3.84, from about 3.60 to about 3.83, from about 3.60 to about 3.82, from about 3.60 to about 3.81, from about 3.60 to about 3.80, from about 3.60 to about 3.79, from about 3.60 to about 3.78, from about 3.60 to about 3.77, from about 3.60 to about 3.76, from about 3.60 to about 3.75, from about 3.60 to about 3.74, from about 3.60 to about 3.73, from about 3.60 to about 3.72, from about 3.60 to about 3.71, from about 3.60 to about 3.70, from about 3.60 to about 3.69, from about 3.60 to about 3.68, from about 3.60 to

about 3.67, from about 3.60 to about 3.66, from about 3.60 to about 3.65, from about 3.60 to about 3.64, from about 3.60 to about 3.63, from about 3.60 to about 3.62, from about 3.60 to about 3.61, or from about 3.61 to about 4.00, from about 3.62 to about 4.00, from about 3.63 to about 4.00, from about 3.64 to about 4.00, from about 3.65 to about 4.00, from about 3.66 to about 4.00, from about 3.67 to about 4.00, from about 3.68 to about 4.00, from about 3.69 to about 4.00, from about 3.70 to about 4.00, from about 3.71 to about 4.00, from about 3.72 to about 4.00, from about 3.73 to about 4.00, from about 3.74 to about 4.00, from about 3.75 to about 4.00, from about 3.76 to about 4.00, from about 3.77 to about 4.00, from about 3.78 to about 4.00, from about 3.79 to about 4.00, from about 3.80 to about 4.00, from about 3.81 to about 4.00, from about 3.82 to about 4.00, from about 3.83 to about 4.00, from about 3.84 to about 4.00, from about 3.85 to about 4.00, from about 3.86 to about 4.00, from about 3.87 to about 4.00, from about 3.88 to about 4.00, from about 3.89 to about 4.00, from about 3.90 to about 4.00, from about 3.91 to about 4.00, from about 3.92 to about 4.00, from about 3.93 to about 4.00, from about 3.94 to about 4.00, from about 3.95 to about 4.00, from about 3.96 to about 4.00, from about 3.97 to about 4.00, from about 3.98 to about 4.00, from about 3.99 to about 4.00, or about 3.60, about 3.61, about 3.62, about 3.63, about 3.64, about 3.65, about 3.66, about 3.67, about 3.68, about 3.69, about 3.70, about 3.71, about 3.72, about 3.73, about 3.74, about 3.75, about 3.76, about 3.77, about 3.78, about 3.79, about 3.80, about 3.81, about 3.82, about 3.83, about 3.84, about 3.85, about 3.86, about 3.87, about 3.88, about 3.89, about 3.90, about 3.91, about 3.92, about 3.93, about 3.94, about 3.95, about 3.96, about 3.97, about 3.98, about 3.99, about 4.00, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, Y may be in a range of about 3.20 to about 4.00, from about 3.20 to about 3.98, from about 3.20 to about 3.96, from about 3.20 to about 3.94, from about 3.20 to about 3.92, from about 3.20 to about 3.90, from about 3.20 to about 3.88, from about 3.20 to about 3.86, from about 3.20 to about 3.84, from about 3.20 to about 3.82, from about 3.20 to about 3.80, from about 3.20 to about 3.78, from about 3.20 to about 3.76, from about 3.20 to about 3.74, from about 3.20 to about 3.72, from about 3.20 to about 3.70, from about 3.20 to about 3.68, from about 3.20 to about 3.66, from about 3.20 to about 3.64, from about 3.20 to about 3.62, from about 3.20 to about 3.60, from about 3.20 to about 3.58, from about 3.20 to about 3.56, from about 3.20 to about 3.54, from about 3.20 to about 3.52, from about 3.20 to about 3.50, from about 3.20 to about 3.48, from about 3.20 to about 3.46, from about 3.20 to about 3.44, from about 3.20 to about 3.42, from about 3.20 to about 3.40, from about 3.20 to about 3.38, from about 3.20 to about 3.36, from about 3.20 to about 3.34, from about 3.20 to about 3.32, from about 3.20 to about 3.30, from about 3.20 to about 3.28, from about 3.20 to about 3.26, from about 3.20 to about 3.24, from about 3.20 to about 3.22, or from about 3.22 to about 4.00, from about 3.24 to about 4.00, from about 3.26 to about 4.00, from about 3.28 to about 4.00, from about 3.30 to about 4.00, from about 3.32 to about 4.00, from about 3.34 to about 4.00, from about 3.36 to about 4.00, from about 3.38 to about 4.00, from about 3.40 to about 4.00, from about 3.42 to about 4.00, from about 3.44 to about 4.00, from about 3.46 to about 4.00, from about 3.48 to about 4.00, from about 3.50 to about 4.00, from about 3.52 to about 4.00, from about 3.54 to about 4.00, from about 3.56 to about 4.00, from about 3.58 to about 4.00, from about 3.60 to about 4.00, from about 3.62 to about 4.00, from about 3.64 to about 4.00, from about 3.66 to about 4.00, from about 3.68 to about 4.00, from about 3.70 to about 4.00, from about 3.72 to about 4.00, from about 3.74 to about 4.00, from about 3.76 to about 4.00, from about 3.78 to about 4.00, from about 3.80 to about 4.00, from about 3.82 to about 4.00, from about 3.84 to about 4.00, from about 3.86 to about 4.00, from about 3.88 to about 4.00, from about 3.90 to about 4.00, from about 3.92 to about 4.00, from about 3.94 to about 4.00, from about 3.96 to about 4.00, from about 3.98 to about 4.00, or about 3.20, about 3.22, about 3.24, about 3.26, about 3.28, about 3.30, about 3.32, about 3.34, about 3.36, about 3.38, about 3.40, about 3.42, about 3.44, about 3.46, about 3.48,

about 3.50, about 3.52, about 3.54, about 3.56, about 3.58, about 3.60, about 3.62, about 3.64, about 3.66, about 3.68, about 3.70, about 3.72, about 3.74, about 3.76, about 3.78, about 3.80, about 3.82, about 3.84, about 3.86, about 3.88, about 3.90, about 3.92, about 3.94, about 3.96, about 3.98, about 4.00, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, the catalyst may be amorphous. Advantageously, an amorphous catalyst may exhibit higher intrinsic activity as compared to crystalline catalysts. Amorphous IrO_xH_y catalysts are known to be more prone to dissolution or loss of Ir in harsh OER conditions. They are hence considered to be less stable as compared to rutile IrO_2 catalysts. However, the inventors have surprisingly found that the catalyst of the present invention may be amorphous and yet exhibit high stability and durability in PEMWEs. This allows the catalysts to be used over a longer period, thus reducing the overall cost of the catalyst, and subsequently the hydrogen production cost.

In some embodiments, the catalyst may be hierarchically porous. Advantageously, a hierarchically porous catalyst may exhibit an increased surface area. In some embodiments, the surface area of the present catalyst may be increased by about 400 times as compared to its precursor. A hierarchically porous structure in a catalyst also advantageously enhances the mass transport in an electrode, particularly an anode. This allows the catalyst of the present invention to advantageously exhibit superior electrochemical performance, which may be higher than state-of-the-art Ir-based catalysts. The inventors have surprisingly found that a hierarchically porous catalyst may be formed through acid leaching of Sr^{2+} cations in a Sr_2IrO_6 precursor to generate free and isolated IrO_xH_y octahedra. The inventors have also surprisingly found that a hierarchically porous catalyst may be formed due to an initial IMD of about 6 Å, which forms a framework comprising corner- and edge-shared IrO_6 octahedra through dehydration within μm -sized particles. The inventors have further surprisingly found that the catalyst of the present invention may be highly porous due to the densification of the lattice. The catalyst may comprise micropores, mesopores and/or macropores. The catalyst may comprise at least two of mesopores, micropores or macropores. The catalyst may comprise micropores and mesopores. The catalyst may comprise mesopores and macropores. The catalyst may comprise micropores and macropores.

In some embodiments, the catalyst may be support-free. Advantageously, a support-free catalyst may be used in MEAs without a support material. Generally, use of a support material is mandatory to ensure fine dispersion of nano- IrO_xH_y particles. However, support materials that are both highly conductive and stable in harsh OER conditions have not been disclosed in the state of the art. Hence, the use of support materials that are less conductive or less stable in harsh OER conditions would negatively impact the activity and/or stability of an IrO_xH_y catalyst. Advantageously, a support-free catalyst may exhibit a higher activity and/or stability in OER conditions as compared to supported catalysts. While support-free IrO_xH_y catalysts may have been previously disclosed, it is difficult to produce such catalysts in large-scale production as they may be accompanied by massive dissolution and/or loss of Ir. However, the inventors have surprisingly found that the catalyst of the present invention may be produced without significant loss in Ir, therefore making it more cost-effective, and more suitable for large scale production.

In some embodiments, the catalyst may have a BET surface area in a range of about 30 m^2/g to about 50 m^2/g , from about 30 m^2/g to about 49 m^2/g , from about 30 m^2/g to about 48 m^2/g , from about 30 m^2/g to about 47 m^2/g , from about 30 m^2/g to about 46 m^2/g , from about 30 m^2/g to about 45 m^2/g , from about 30 m^2/g to about 44 m^2/g , from about 30 m^2/g to about 43 m^2/g , from about 30 m^2/g to about 42 m^2/g , from about 30 m^2/g to about 41 m^2/g , from about 30 m^2/g to about 40 m^2/g , from

about 30 m²/g to about 39 m²/g, from about 30 m²/g to about 38 m²/g, from about 30 m²/g to about 37 m²/g, from about 30 m²/g to about 36 m²/g, from about 30 m²/g to about 35 m²/g, from about 30 m²/g to about 34 m²/g, from about 30 m²/g to about 33 m²/g, from about 30 m²/g to about 32 m²/g, from about 30 m²/g to about 31 m²/g, or from about 31 m²/g to about 50 m²/g, from about 32 m²/g to about 50 m²/g, from about 33 m²/g to about 50 m²/g, from about 34 m²/g to about 50 m²/g, from about 35 m²/g to about 50 m²/g, from about 36 m²/g to about 50 m²/g, from about 37 m²/g to about 50 m²/g, from about 38 m²/g to about 50 m²/g, from about 39 m²/g to about 50 m²/g, from about 40 m²/g to about 50 m²/g, from about 41 m²/g to about 50 m²/g, from about 42 m²/g to about 50 m²/g, from about 43 m²/g to about 50 m²/g, from about 44 m²/g to about 50 m²/g, from about 45 m²/g to about 50 m²/g, from about 46 m²/g to about 50 m²/g, from about 47 m²/g to about 50 m²/g, from about 48 m²/g to about 50 m²/g, from about 49 m²/g to about 50 m²/g, or about 30 m²/g, about 31 m²/g, about 32 m²/g, about 33 m²/g, about 34 m²/g, about 35 m²/g, about 36 m²/g, about 37 m²/g, about 38 m²/g, about 39 m²/g, about 40 m²/g, about 41 m²/g, about 42 m²/g, about 43 m²/g, about 44 m²/g, about 45 m²/g, about 46 m²/g, about 47 m²/g, about 48 m²/g, about 49 m²/g, about 50 m²/g, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

The pore sizes of the catalyst may be in a range of about 1 nm to about 200 nm, from about 1 nm to about 195 nm, from about 1 nm to about 190 nm, from about 1 nm to about 185 nm, from about 1 nm to about 180 nm, from about 1 nm to about 175 nm, from about 1 nm to about 170 nm, from about 1 nm to about 165 nm, from about 1 nm to about 160 nm, from about 1 nm to about 155 nm, from about 1 nm to about 150 nm, from about 1 nm to about 145 nm, from about 1 nm to about 140 nm, from about 1 nm to about 135 nm, from about 1 nm to about 130 nm, from about 1 nm to about 125 nm, from about 1 nm to about 120 nm, from about 1 nm to about 115 nm, from about 1 nm to about 110 nm, from about 1 nm to about 105 nm, from about 1 nm to about 100 nm, from about 1 nm to about 95 nm, from about 1 nm to about 90 nm, from about 1 nm to about 85 nm, from about 1 nm to about 80 nm, from about 1 nm to about 75 nm, from about 1 nm to about 72 nm, from about 1 nm to about 70 nm, from about 1 nm to about 65 nm, from about 1 nm to about 60 nm, from about 1 nm to about 59 nm, from about 1 nm to about 55 nm, from about 1 nm to about 50 nm, from about 1 nm to about 45 nm, from about 1 nm to about 40 nm, from about 1 nm to about 35 nm, from about 1 nm to about 34 nm, from about 1 nm to about 30 nm, from about 1 nm to about 25 nm, from about 1 nm to about 24 nm, from about 1 nm to about 23 nm, from about 1 nm to about 20 nm, from about 1 nm to about 15 nm, from about 1 nm to about 11 nm, from about 1 nm to about 10 nm, from about 1 nm to about 5 nm, or from about 5 nm to about 200 nm, from about 10 nm to about 200 nm, from about 11 nm to about 200 nm, from about 15 nm to about 200 nm, from about 20 nm to about 200 nm, from about 23 nm to about 200 nm, from about 24 nm to about 200 nm, from about 25 nm to about 200 nm, from about 30 nm to about 200 nm, from about 34 nm to about 200 nm, from about 35 nm to about 200 nm, from about 40 nm to about 200 nm, from about 45 nm to about 200 nm, from about 50 nm to about 200 nm, from about 55 nm to about 200 nm, from about 59 nm to about 200 nm, from about 60 nm to about 200 nm, from about 65 nm to about 200 nm, from about 70 nm to about 200 nm, from about 72 nm to about 200 nm, from about 75 nm to about 200 nm, from about 80 nm to about 200 nm, from about 85 nm to about 200 nm, from about 90 nm to about 200 nm, from about 95 nm to about 200 nm, from about 100 nm to about 200 nm, from about 105 nm to about 200 nm, from about 110 nm to about 200 nm, from about 115 nm to about 200 nm, from about 120 nm to about 200 nm, from about 125 nm to about 200 nm, from about 130 nm to about 200 nm, from about 135 nm to about 200 nm, from about 140 nm to about 200 nm, from about 145 nm to about 200 nm, from about 150 nm to about 200 nm, from about 155 nm to about 200 nm, from about 160 nm to about 200 nm, from about 165 nm to about 200 nm, from about 170 nm to about 200 nm, from about 175 nm to about 200 nm, from about 180 nm to about 200 nm, from about 185 nm to about 200 nm,

from about 190 nm to about 200 nm, from about 195 nm to about 200 nm, or about 1 nm, about 5 nm, about 10 nm, about 11 nm, about 15 nm, about 20 nm, about 23 nm, about 24 nm, about 25 nm, about 30 nm, about 34 nm, about 35 nm, about 40 nm, about 45 nm, about 50 nm, about 55 nm, about 59 nm, about 60 nm, about 65 nm, about 70 nm, about 72 nm, about 75 nm, about 80 nm, about 85 nm, about 90 nm, about 95 nm, about 100 nm, about 105 nm, about 110 nm, about 115 nm, about 120 nm, about 125 nm, about 130 nm, about 135 nm, about 140 nm, about 145 nm, about 150 nm, about 155 nm, about 160 nm, about 165 nm, about 170 nm, about 175 nm, about 180 nm, about 185 nm, about 190 nm, about 195 nm, about 200 nm, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

The catalyst may be hierarchically porous. The catalyst may comprise at least two of mesopores, micropores or macropores.

The catalyst may comprise micropores with pore sizes in a range of about 0.1 nm to about 2.0 nm, from about 0.1 nm to about 1.9 nm, from about 0.1 nm to about 1.8 nm, from about 0.1 nm to about 1.7 nm, from about 0.1 nm to about 1.6 nm, from about 0.1 nm to about 1.5 nm, from about 0.1 nm to about 1.4 nm, from about 0.1 nm to about 1.3 nm, from about 0.1 nm to about 1.2 nm, from about 0.1 nm to about 1.1 nm, from about 0.1 nm to about 1.0 nm, from about 0.1 nm to about 0.9 nm, from about 0.1 nm to about 0.8 nm, from about 0.1 nm to about 0.7 nm, from about 0.1 nm to about 0.6 nm, from about 0.1 nm to about 0.5 nm, from about 0.1 nm to about 0.4 nm, from about 0.1 nm to about 0.3 nm, from about 0.1 nm to about 0.2 nm, or from about 0.1 nm to about 2.0 nm, from about 0.2 nm to about 2.0 nm, from about 0.3 nm to about 2.0 nm, from about 0.4 nm to about 2.0 nm, from about 0.5 nm to about 2.0 nm, from about 0.6 nm to about 2.0 nm, from about 0.7 nm to about 2.0 nm, from about 0.8 nm to about 2.0 nm, from about 0.9 nm to about 2.0 nm, from about 1.0 nm to about 2.0 nm, from about 1.1 nm to about 2.0 nm, from about 1.2 nm to about 2.0 nm, from about 1.3 nm to about 2.0 nm, from about 1.4 nm to about 2.0 nm, from about 1.5 nm to about 2.0 nm, from about 1.6 nm to about 2.0 nm, from about 1.7 nm to about 2.0 nm, from about 1.8 nm to about 2.0 nm, from about 1.9 nm to about 2.0 nm, or about 0.1 nm, about 0.2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 2.0 nm, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

The catalyst may comprise mesopores with pore sizes in a range of about 2 nm to about 20 nm, from about 2 nm to about 19 nm, from about 2 nm to about 18 nm, from about 2 nm to about 17 nm, from about 2 nm to about 16 nm, from about 2 nm to about 15 nm, from about 2 nm to about 14 nm, from about 2 nm to about 13 nm, from about 2 nm to about 12 nm, from about 2 nm to about 11 nm, from about 2 nm to about 10 nm, from about 2 nm to about 9 nm, from about 2 nm to about 8 nm, from about 2 nm to about 7 nm, from about 2 nm to about 6 nm, from about 2 nm to about 5 nm, from about 2 nm to about 4 nm, from about 2 nm to about 3 nm, or from about 3 nm to about 20 nm, from about 4 nm to about 20 nm, from about 5 nm to about 20 nm, from about 6 nm to about 20 nm, from about 7 nm to about 20 nm, from about 8 nm to about 20 nm, from about 9 nm to about 20 nm, from about 10 nm to about 20 nm, from about 11 nm to about 20 nm, from about 12 nm to about 20 nm, from about 13 nm to about 20 nm, from about 14 nm to about 20 nm, from about 15 nm to about 20 nm, from about 16 nm to about 20 nm, from about 17 nm to about 20 nm, from about 18 nm to about 20 nm, from about 19 nm to about 20 nm, or about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm,

or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

- 5 The catalyst may comprise macropores with pore sizes in a range of about 20 nm to about 200 nm, from about 20 nm to about 190 nm, from about 20 nm to about 180 nm, from about 20 nm to about 170 nm, from about 20 nm to about 160 nm, from about 20 nm to about 150 nm, from about 20 nm to about 140 nm, from about 20 nm to about 130 nm, from about 20 nm to about 120 nm, from about 20 nm to about 110 nm, from about 20 nm to about 105 nm, from about 20 nm to about 100 nm, from about 20 nm to about 90 nm, from about 20 nm to about 80 nm, from about 20 nm to about 72 nm, from about 20 nm to about 70 nm, from about 20 nm to about 60 nm, from about 20 nm to about 59 nm, from about 20 nm to about 50 nm, from about 20 nm to about 40 nm, from about 20 nm to about 34 nm, from about 20 nm to about 30 nm, from about 20 nm to about 24 nm, from about 20 nm to about 23 nm, or from about 23 nm to about 200 nm, from about 24 nm to about 200 nm, from about 30 nm to about 200 nm, from about 34 nm to about 200 nm, from about 40 nm to about 200 nm, from about 50 nm to about 200 nm, from about 59 nm to about 200 nm, from about 60 nm to about 200 nm, from about 70 nm to about 200 nm, from about 72 nm to about 200 nm, from about 80 nm to about 200 nm, from about 90 nm to about 200 nm, from about 100 nm to about 200 nm, from about 105 nm to about 200 nm, from about 110 nm to about 200 nm, from about 120 nm to about 200 nm, from about 130 nm to about 200 nm, from about 140 nm to about 200 nm, from about 150 nm to about 200 nm, from about 160 nm to about 200 nm, from about 170 nm to about 200 nm, from about 180 nm to about 200 nm, from about 190 nm to about 200 nm, or about 20 nm, about 23 nm, about 24 nm, about 30 nm, about 34 nm, about 40 nm, about 50 nm, about 59 nm, about 60 nm, about 70 nm, about 72 nm, about 80 nm, about 90 nm, about 100 nm, about 105 nm, about 110 nm, about 120 nm, about 130 nm, about 140 nm, about 150 nm, about 160 nm, about 170 nm, about 180 nm, about 190 nm, about 200 nm, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).
- 30 In some embodiments, the oxidation state of Ir in the catalyst may be 4+. Advantageously, an Ir catalyst with an oxidation state of 4+ may be thermodynamically more stable as compared to other Ir catalysts with a different oxidation state,

- In some embodiments, the mass of Ir based on the total weight of the catalyst may be in a range of about 60 wt% to about 90 wt%, from about 60 wt% to about 89 wt%, from about 60 wt% to about 88 wt%, from about 60 wt% to about 87 wt%, from about 60 wt% to about 86 wt%, from about 60 wt% to about 85 wt%, from about 60 wt% to about 84 wt%, from about 60 wt% to about 83 wt%, from about 60 wt% to about 82 wt%, from about 60 wt% to about 81 wt%, from about 60 wt% to about 80 wt%, from about 60 wt% to about 79 wt%, from about 60 wt% to about 78 wt%, from about 60 wt% to about 77 wt%, from about 60 wt% to about 76 wt%, from about 60 wt% to about 75 wt%, from about 60 wt% to about 73 wt%, from about 60 wt% to about 72 wt%, from about 60 wt% to about 71 wt%, from about 60 wt% to about 70 wt%, from about 60 wt% to about 69 wt%, from about 60 wt% to about 68 wt%, from about 60 wt% to about 67 wt%, from about 60 wt% to about 66 wt%, from about 60 wt% to about 65 wt%, from about 60 wt% to about 64 wt%, from about 60 wt% to about 63 wt%, from about 60 wt% to about 62 wt%, from about 60 wt% to about 61 wt%, or from about 61 wt% to about 90 wt%, from about 62 wt% to about 90 wt%, from about 63 wt% to about 90 wt%, from about 64 wt% to about 90 wt%, from about 65 wt% to about 90 wt%, from about 66 wt% to about 90 wt%, from about 67 wt% to about 90 wt%, from about 68 wt% to about 90 wt%, from about 69 wt% to about 90 wt%, from about 70 wt% to about 90 wt%, from about 71 wt% to about 90 wt%, from about 72 wt% to about 90 wt%, from about 73 wt% to about 90 wt%, from about 75 wt%

to about 90 wt%, from about 76 wt% to about 90 wt%, from about 77 wt% to about 90 wt%, from about 78 wt% to about 90 wt%, from about 79 wt% to about 90 wt%, from about 80 wt% to about 90 wt%, from about 81 wt% to about 90 wt%, from about 82 wt% to about 90 wt%, from about 83 wt% to about 90 wt%, from about 84 wt% to about 90 wt%, from about 85 wt% to about 90 wt%, from about 86 wt% to about 90 wt%, from about 87 wt% to about 90 wt%, from about 88 wt% to about 90 wt%, from about 89 wt% to about 90 wt%, or about 60 wt%, about 61 wt%, about 62 wt%, about 63 wt%, about 64 wt%, about 65 wt%, about 66 wt%, about 67 wt%, about 68 wt%, about 69 wt%, about 70 wt%, about 71 wt%, about 72 wt%, about 73 wt%, about 75 wt%, about 76 wt%, about 77 wt%, about 78 wt%, about 79 wt%, about 80 wt%, about 81 wt%, about 82 wt%, about 83 wt%, about 84 wt%, about 85 wt%, about 86 wt%, about 87 wt%, about 88 wt%, about 89 wt%, about 90 wt%, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, X may be 3.76 and Y may be 3.52. In some other embodiments, X may be 6 and Y may be 8.

In some embodiments, the catalyst may be $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$. In some other embodiments, the catalyst may be $\text{IrO}_2 \cdot 4\text{H}_2\text{O}$.

The present invention further provides a method of preparing a catalyst comprising IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. In particular, the present invention also provides a method of preparing a catalyst consisting essentially of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. The present invention further provides a method of preparing a catalyst consisting of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$. The present invention also provides a method of preparing a catalyst which is IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$.

In some embodiments, the method may comprise:

- (i) immersing Sr_4IrO_6 in acid to form a mixture; and
- (ii) subjecting the mixture of step (i) to agitation for more than 12 hours.

Sr_4IrO_6 advantageously comprises a high Sr^{2+} ion content. The inventors have surprisingly found that acid leaching of Sr_4IrO_6 precursor may unexpectedly lead to the formation of an amorphous, hierarchically porous, and/or support-free catalyst. The inventors have also surprisingly found that acid leaching of Sr_4IrO_6 precursor may lead to a 400-times increase in surface area of the catalyst, which advantageously allows the catalyst to exhibit high activity. The inventors have also surprisingly found that the method of the present invention allows for the complete removal of all the Sr^{2+} ions found in the Sr_4IrO_6 precursor despite the high Sr^{2+} ion content.

In some embodiments, step (ii) may be repeated at least once. Step (ii) may be repeated once, twice, three times, four times, five times, six times, seven times, eight times, nine times, or ten times.

In some embodiments, the method may further comprise:

- (iii) subjecting the mixture of step (ii) to centrifugation to obtain a powder; and
- (iv) ball milling the powder of step (iii).

The inventors have surprisingly found that ball-milling process does not affect the characteristics and activity of the catalyst of the present invention. The inventors have also surprisingly found that the ball-milled catalyst of the present invention advantageously exhibits a further increase to its BET surface area. The ball-milled catalyst of the present invention further advantageously exhibits a higher mass

activity as compared to non-ball-milled catalysts. The ball-milled catalyst of the present invention also advantageously achieves a lower cell voltage than a non-ball-milled catalyst when used in MEAs.

5 Also, the inventors have surprisingly found that the disclosed methods of producing the disclosed catalysts may be suitable for large scale production. Further, the inventors have surprisingly found that the disclosed methods may also provide a way for easy recycling of dissolved Ir during chemical leaching, specifically the loss/dissolution of Ir, which reduces the overall material cost of production of the catalyst, and addresses the high scarcity of Ir and its high cost.

10 In some embodiments, the mixture of step (i) may be subjected to agitation in a range of about 6 hours to about 42 hours, from about 6 hours to about 41 hours, from about 6 hours to about 40 hours, from about 6 hours to about 39 hours, from about 6 hours to about 38 hours, from about 6 hours to about 37 hours, from about 6 hours to about 36 hours, from about 6 hours to about 35 hours, from about 6 hours to about 34 hours, from about 6 hours to about 33 hours, from about 6 hours to about 32 hours, from about 6 hours to about 31 hours, from about 6 hours to about 30 hours, from about 6 hours to about 29 hours, from about 6 hours to about 28 hours, from about 6 hours to about 27 hours, from about 6 hours to about 26 hours, from about 6 hours to about 25 hours, from about 6 hours to about 24 hours, from about 6 hours to about 23 hours, from about 6 hours to about 22 hours, from about 6 hours to about 21 hours, from about 6 hours to about 20 hours, from about 6 hours to about 19 hours, from about 6 hours to about 18 hours, from about 6 hours to about 17 hours, from about 6 hours to about 16 hours, from about 6 hours to about 15 hours, from about 6 hours to about 14 hours, from about 6 hours to about 13 hours, from about 6 hours to about 12 hours, from about 6 hours to about 11 hours, from about 6 hours to about 10 hours, from about 6 hours to about 9 hours, from about 6 hours to about 8 hours, from about 6 hours to about 7 hours, or from about 7 hours to about 42 hours, from about 8 hours to about 42 hours, from about 9 hours to about 42 hours, from about 10 hours to about 42 hours, from about 11 hours to about 42 hours, from about 12 hours to about 42 hours, from about 13 hours to about 42 hours, from about 14 hours to about 42 hours, from about 15 hours to about 42 hours, from about 16 hours to about 42 hours, from about 17 hours to about 42 hours, from about 18 hours to about 42 hours, from about 19 hours to about 42 hours, from about 20 hours to about 42 hours, from about 21 hours to about 42 hours, from about 22 hours to about 42 hours, from about 23 hours to about 42 hours, from about 24 hours to about 42 hours, from about 25 hours to about 42 hours, from about 26 hours to about 42 hours, from about 27 hours to about 42 hours, from about 28 hours to about 42 hours, from about 29 hours to about 42 hours, from about 30 hours to about 42 hours, from about 31 hours to about 42 hours, from about 32 hours to about 42 hours, from about 33 hours to about 42 hours, from about 34 hours to about 42 hours, from about 35 hours to about 42 hours, from about 36 hours to about 42 hours, from about 37 hours to about 42 hours, from about 38 hours to about 42 hours, from about 39 hours to about 42 hours, from about 40 hours to about 42 hours, from about 41 hours to about 42 hours, or about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, about 12 hours, about 13 hours, about 14 hours, about 15 hours, about 16 hours, about 17 hours, about 18 hours, about 19 hours, about 20 hours, about 21 hours, about 22 hours, about 23 hours, about 24 hours, about 25 hours, about 26 hours, about 27 hours, about 28 hours, about 29 hours, about 30 hours, about 31 hours, about 32 hours, about 33 hours, about 34 hours, about 35 hours, about 36 hours, about 37 hours, about 38 hours, about 39 hours, about 40 hours, about 41 hours, about 42 hours, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

In some embodiments, the mixture of step (i) may be subjected to agitation for about 24 hours.

In some embodiments, the acid may be selected from the group consisting of perchloric acid, and nitric acid.

5 In some embodiments, the Sr_4IrO_6 may be obtained by mixing SrCO_3 and IrO_2 , and calcining the mixed SrCO_3 and IrO_2 at a temperature at or above 1000 °C. In some embodiments, the calcination temperature may be in a range of about 900 °C to about 1500 °C, from about 900 °C to about 1450 °C, from about 900 °C to about 1400 °C, from about 900 °C to about 1350 °C, from about 900 °C to about 1300 °C, from about 900 °C to about 1250 °C, from about 900 °C to about 1200 °C, from about 900 °C to about 1150 °C, from about 900 °C to about 1100 °C, from about 900 °C to about 1050 °C, 10 from about 900 °C to about 1000 °C, from about 900 °C to about 950 °C, or from about 950 °C to about 1500 °C, from about 1000 °C to about 1500 °C, from about 1050 °C to about 1500 °C, from about 1100 °C to about 1500 °C, from about 1150 °C to about 1500 °C, from about 1200 °C to about 1500 °C, from about 1250 °C to about 1500 °C, from about 1300 °C to about 1500 °C, from about 1350 °C to about 1500 °C, from about 1400 °C to about 1500 °C, from about 1450 °C to about 1500 °C, or about 900 °C, about 950 °C, about 1000 °C, about 1050 °C, about 1100 °C, about 1150 °C, 15 about 1200 °C, about 1250 °C, about 1300 °C, about 1350 °C, about 1400 °C, about 1450 °C, about 1500 °C, or any value or range therein. It is to be appreciated that the above ranges should be interpreted as including and supporting any sub-ranges or discrete values (which may or may not be a whole number) that are within the stated range(s).

20

The present invention also provides a catalyst obtained by the method as disclosed herein.

25 The present invention further provides a use of the catalyst as disclosed herein to produce hydrogen.

25

In some embodiments, the catalyst may be used in a water electrolyzer. In some embodiments, the catalyst may be used in a regenerative fuel cell, or a rechargeable metal-air battery.

30 The inventors have also surprisingly found that the disclosed catalysts may be used in oxygen evolution reactions as the anodes of PEM water electrolyzers to provide an accelerated oxygen evolution reaction as compared to the commercially available catalysts.

Exemplary, non-limiting embodiments of the disclosed catalysts, methods of producing them, and uses thereof will now be disclosed.

35

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 40 limiting the scope of the invention.

Example 1A: Procedure for preparing hierarchically porous $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ catalyst (HP- $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$)

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Example 1A-a: Preparation of Sr_4IrO_6 catalyst precursor

A solid-state method was used to obtain the Sr_4IrO_6 catalyst precursor (Fig. 1(a)). Firstly, stoichiometric amounts of SrCO_3 and IrO_2 were mixed and hand-milled in a mortar for approximately 1 hour. The mixture was then calcined at 1200 °C for 0.5 hours, at a heating rate of 5 °C min⁻¹ in

ambient air, to obtain the Sr_4IrO_6 catalyst precursor. A small amount of SrCO_3 may be present in the final product (Fig. 2).

Example 1A-b: Preparation of $\text{HP-IrO}_2 \cdot 1.76\text{H}_2\text{O}$ catalyst

About 200 mg of Sr_4IrO_6 was immersed in 40 mL of 0.1 M HClO_4 and shaken for 24 hours at room temperature. The process was repeated once, before centrifugation of the mixture to collect a powder. 2 to 3 rounds of water washing were then applied to the powder. The powder was then dried in ambient air at room temperature for 24 hours to provide $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$.

Example 1B: Procedure for preparing a hierarchically porous and ball milled $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ catalyst (HP- $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ -BM)

Example 1B-a: Preparation of Sr_4IrO_6 catalyst precursor

A solid-state method was used to obtain the Sr_4IrO_6 catalyst precursor (Fig. 1(a)). Firstly, stoichiometric amounts of SrCO_3 and IrO_2 were mixed and hand-milled in a mortar for approximately 1 hour. The mixture was then calcined at 1200 °C for 0.5 hours, at a heating rate of 5 °C min⁻¹ in ambient air, to obtain the Sr_4IrO_6 catalyst precursor. A small amount of SrCO_3 may be present in the final product (Fig. 2).

Example 1B-b: Preparation of $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ catalyst

About 200 mg of Sr_4IrO_6 was immersed in 40 mL of 0.1 M HClO_4 and shaken for 24 hours at room temperature. The process was repeated once, before centrifugation of the mixture to collect a powder. 2 to 3 rounds of water washing were then applied to the powder. The powder was then dried in ambient air at room temperature for 24 hours to provide $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$.

Example 1B-c: Ball-milling - Preparation of HP- $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ -BM catalyst

About 200 mg of as-prepared $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ was added into an 80 mL ZrO_2 grinding bowl, together with about 50 g of 3 mm ZrO_2 grinding balls. The catalyst was then placed in a planetary ball mill (FRITSCH PULVERISETTE 7 premium line) and subjected to a rotational speed of about 200 rpm to 1000 rpm for 2 hours to provide the HP- $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$ -BM.

Example 2: Characterization

Example 2a: General characterization procedures

X-ray powder diffraction (XRD) measurements were performed with a BRUKER D8 Advance diffractometer in Bragg-Brentano geometry with Cu-K α radiation. A GSAS program and EXPGUI interface were used for the Rietveld refinement. Scanning electron microscopy was performed with a JEOL JSM-7600F scanning electron microscope. Transmission electron microscopy (TEM) and focused ion beam scanning electron microscopy (FIB-SEM) were performed on a JEOL 2100F and HITACHI HT 7820 transmission electron microscopes. The surface composite was analyzed with X-ray photoelectron spectroscopy (Kratos AXIS Supra). The BET surface areas were measured with nitrogen adsorption-desorption tests (ASAP Tri-Star II 3020). X-ray adsorption spectroscopy experiments were performed at Singapore Synchrotron Light Source, XAFCA beamline. Small angle X-ray scattering was performed with Xenocs Nanoinxider. The Athena software packages were used for the data analysis. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on PerkinElmer ELAN DRC-e.

Spin-polarized density functional theory (DFT) was completed within the Vienna ab initio simulation package (VASP). The ion-electron interaction was described using the projector-augmented plane-wave and the exchange-correlation interaction is described using the Perdew–Burke–Ernzerhof functional of the generalized gradient approximation. A cut-off energy of 500 eV with $3 \times 3 \times 3$ Monkhorst–Pack k-point grids was used for the calculation of two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units. All the systems were optimized until energy and force were less than 10^{-5} eV and 0.01 eV/Å respectively. The vacuum layer larger than 15 Å was used to prevent the interaction between periodical slabs. Grimme's D3 method was adopted to consider the van der Waals (vdW) interactions. The climbing-image nudged elastic band (CINEB) method was used to identify locate transition states and kinetic barriers. Phonon bands were obtained employing density functional perturbation theory as implemented in Phonopy code.

Example 2b: Characterization of catalyst precursor Sr_4IrO_6 and catalysts $\text{HP-IrO}_2\cdot 1.76\text{H}_2\text{O}$ and $\text{HP-IrO}_2\cdot 1.76\text{H}_2\text{O-BM}$

In the Sr_4IrO_6 precursor (**Fig. 1a**), Ir and Sr atoms were found to be alternately arranged along the c-axis, forming IrO_6 octahedrons that are separated by chains composed solely of Sr atoms. All Ir atoms in Sr_4IrO_6 are fully coordinated to six oxygen atoms, and each IrO_6 octahedron is strictly isolated by Sr atoms. The tetravalent state of Ir and the structural characteristics of isolated IrO_6 octahedra were confirmed by X-ray adsorption analysis (**Fig. 3**). As depicted in the scanning electron microscope (SEM) images (**Fig. 1b** and **Fig. 4**), the as-synthesized Sr_4IrO_6 precursor was found to exhibit large solid particle sizes mostly exceeding 10 μm.

After acid-leaching of Sr^{2+} ions from the Sr_4IrO_6 precursor, the particles remain μm-sized (**Fig. 4**), but additional slits with a typical width of 100 nm were observed on the surface (**Fig. 1c**). The disappearance of the X-ray photoelectron spectroscopy (XPS) signal from Sr_3d (**Fig. 1d**), indicating that the Sr^{2+} ions were successfully leached. Furthermore, when the acid-treated Sr_4IrO_6 was subjected to additional calcination at 1000 °C, a pure rutile IrO_2 phase was obtained (**Fig. 5**), confirming the complete removal of Sr^{2+} ions.

The microstructure and surface area changes induced by Sr^{2+} leaching, were further analysed with focused ion beam (FIB-SEM) and transmission electron microscopy (TEM). **Fig. 1e** and **1f** shows the cross-section of a catalyst prepared by focused ion beam (FIB) milling. A highly porous bulk structure, with apparent macropores (diameter > 100 nm), was observed. The specimen was further thinned (**Fig. 1g**) and the local structure was analysed with TEM (**Fig. 1h**). A hierarchically porous structure was observed, with pore/channel widths varying from approximately 10 to over 100 nm.

The acid-treated Sr_4IrO_6 was found to exhibit a high BET surface area of 40.3 m²/g (**Fig. 1g**, **Fig. 6**). This surface area was calculated to be equivalent to the formation of nano- IrO_2 particles with a diameter of approximately 12.8 nm. Due to the large particle size of the as-prepared Sr_4IrO_6 precursor, analysing the corresponding surface area and pore size distribution was unsuccessful. Instead, an estimated surface area of <0.092 m²/g was calculated, assuming the Sr_4IrO_6 precursor took the shape of a spherical particle with a diameter of >10 μm. The presence of surface slits and bulk pores/channels (**Fig. 1c**, **1e-h**) could indicate that a simple Sr^{2+} leaching process can stimulate the development of a hierarchically porous structure within the μm-sized particles (i.e., a support-free structure). Intriguingly, such a change in morphology resulted in a remarkable ~400 times increase in surface area, highlighting the promoting effect of the Sr^{2+} leaching process.

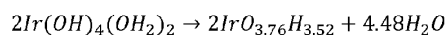
To better understand the origin of the surface area increment induced by Sr^{2+} leaching, the properties of the acid-treated Sr_4IrO_6 were analyzed. The powder X-ray diffraction pattern in **Fig. 7a** showed no diffraction peaks, and the selected-area electron diffraction from an acid-treated Sr_4IrO_6 particle

(inset of **Fig. 7a**) was not found to exhibit any diffraction patterns. These observations confirm that the acid-treated Sr_4IrO_6 is amorphous and lacks a long-range-ordered structure. Additionally, the position of the Ir-L_{III} absorption edge from the acid-treated Sr_4IrO_6 is similar to that of rutile IrO_2 (**Fig. 8**), confirming that the acid treatment does not induce the redox of the initial Ir^{4+} state. This is reasonable as protons from the electrolyte are expected to enter the lattice, and hence maintaining charge neutrality. Consequently, the acid-treated Sr_4IrO_6 can be described as $\text{HP-IrO}_x\text{H}_y$, representing an amorphous Ir hydroxide with a hierarchically porous structure.

The analysis of the Ir L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra from $\text{HP-IrO}_x\text{H}_y$ and rutile IrO_2 (**Fig. 7b**) revealed the presence of local structures corresponding to edge- and corner-sharing IrO_6 octahedra in $\text{HP-IrO}_x\text{H}_y$. This suggests that Sr^{2+} leaching triggers the self-assembly of initially isolated IrO_6 octahedra, leading to the formation of Ir-O(H)-Ir bonds. Furthermore, the formed local active motif in $\text{HP-IrO}_x\text{H}_y$ was found to exhibit similarities to rutile IrO_2 , as indicated by the positions of scattering peaks, which are close to those of rutile IrO_2 . Specifically, two marked scattering peaks (~ 1.63 Å and ~ 2.85 Å) correspond to the Ir-O path in the first Ir-O shell and the Ir-Ir1 path in the edge-sharing IrO_6 octahedra. The broad scattering peak above 3 Å is mainly attributed to the Ir-Ir2 path. In the acid-treated Sr_4IrO_6 , three scattering peaks are observed at positions of ~ 1.60 Å, ~ 2.85 Å, and ~ 3.32 Å. By comparing these spectra with those of rutile IrO_2 as a reference, the three scattering peaks in $\text{HP-IrO}_x\text{H}_y$ can be attributed to the first Ir-O shell, the edge-sharing IrO_6 octahedra, and the corner-sharing IrO_6 octahedra, respectively.

Due to its amorphous nature, determining the structure of $\text{HP-IrO}_x\text{H}_y$ is highly challenging. Nevertheless, the formation of a rutile IrO_2 -like structure has been proposed and identified in several amorphous IrO_xH_y phases, such as activated iridium oxide film (AIROF) and electrodeposited iridium oxide film (EIROF). The cyclic voltametric (CV) curves profiles reflect the electrochemical redox behavior of various IrO_xH_y materials, and can be considered as a “fingerprint” for material identification. Hence, a thorough comparison of the CV curves obtained from $\text{HP-IrO}_x\text{H}_y$ and previously reported IrO_xH_y catalysts was conducted (**Fig. 9**). The comparison revealed that the formed $\text{HP-IrO}_x\text{H}_y$, derived from Sr_4IrO_6 , exhibits similarities to AIROF. Representative CV curves from $\text{HP-IrO}_x\text{H}_y$ and AIROF (prepared by electrochemical oxidation of Ir nano particles on the surface of the Ir metal, **Fig. 10**) are shown in **Fig. 7c**. In both CV curves, a couple of redox peaks between ~ 0.60 V and ~ 1.05 V can be attributed to the redox process of $\text{Ir}^{3+}/\text{Ir}^{4+}$. Another pair of redox peaks, including a less pronounced oxidation peak (appeared at ~ 1.3 V but masked by the OER current) and a distinctive reduction peak (~ 1.4 V), can be associated with the redox process of $\text{Ir}^{4+}/\text{Ir}^{5.5+}$ ($x \geq 0$).

Considering the ion exchange between H^+ and Sr^{2+} ions during the chemical leaching process, the stoichiometry of $\text{HP-IrO}_x\text{H}_y$ should be IrO_6H_8 (disregarding the possible presence of adsorbed or crystal water). In this stoichiometry, the IrO_6 octahedron can be represented as $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$. However, based on the thermogravimetry profile of $\text{HP-IrO}_x\text{H}_y$ (**Fig. 7d**), the calculated values for x and y are 3.76 and 3.52, respectively. It is important to note that these values include the contribution from adsorbed or crystal water. Consequently, the content of OH/H₂O in $\text{HP-IrO}_x\text{H}_y$ is significantly lower than the theoretical values, suggesting that the self-assembly of $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra occurs through a dehydration process, which can be expressed by the following equation:



The occurrence of dehydration is further supported by the instability of H_8IrO_6 , which possesses a structure similar to Sr_4IrO_6 and can be the most likely intermediate after the Sr^{2+} leaching from Sr_4IrO_6 . From the calculated phonon spectra from the optimized H_8IrO_6 (**Fig. 11**), a large imaginary phonon mode around Γ point can be observed, indicating that such an H_8IrO_6 structure is dynamically unstable. A model

system was then employed, consisting of two isolated $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra, to investigate the dehydration process with DFT simulation. Initially, three possibilities were considered: dehydration between two -OH groups (case 1), between -OH₂ and -OH (case 2), and between two -OH₂ groups (case 3). The Ir-Ir distance is fixed at 6 Å to be consistent with the practical Ir-Ir distance of 5.932 Å in Sr_4IrO_6 (based on the XRD refinement in **Fig. 2**). It was found that case 3 is unlikely, as the two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra, with two -OH₂ groups in a "head-to-head" arrangement, prefer to rotate to the arrangement of "head-to-head" -OH₂ and -OH, i.e., case 2 (**Fig. 12**). Thus, the dehydration processes in case 1 (**Fig. 7e**) and case 2 (**Fig. 7f and Fig. 13**) were explored. In both cases, the first dehydration processes (loss of the first H₂O molecule) led to the formation of corner-sharing IrO_6 octahedra and were kinetically favorable (**Fig. 7e-f**). Specifically, the corresponding kinetic barriers are 0.257 and 0.187 eV for case 1 and case 2 (**Fig. 7e-f**), respectively, both of which are easily conquered at room temperature. Additional calculations showed that further dehydration (loss of the second H₂O molecule) was favorable in case 1 with a kinetic barrier of 0.270 eV (**Fig. 7e**) but unlikely to occur in case 2 with a high kinetic barrier of 0.412 eV (**Fig. 13**). As a result, the formation of edge-sharing IrO_6 octahedra was expected to be the final state in case 1 (**Fig. 7e**). This theoretical prediction aligns with the experimental findings of the formation of both corner- and edge-sharing IrO_6 octahedra in HP- IrO_xH_y .

It is worth noting that the hydrolysis method, which also involves the dehydration process of free monomeric $[\text{IrO}_x\text{H}_y]^z$ complexes, has long been used for the preparation of IrO_xH_y nanoparticles or colloids. Considering this, it can be recalled that after the leaching of Sr^{2+} from Sr_4IrO_6 , the resulting IrO_xH_y octahedra are initially isolated. If follow the previous findings, the self-assembly of these IrO_xH_y octahedra should lead to the formation of IrO_xH_y nanoparticles or clusters, while the formation of μm -sized porous particles, which were observed, should not occur.

Apart from the dehydration reaction, another crucial requirement for the self-assembly of $\text{Ir}^{4+}\text{O}_x\text{H}_y$ octahedra is that the two octahedra should be in close proximity, with an intermolecular distance (IMD) below a critical value (the IMD is defined as Ir-Ir distance between the two $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra units). In comparison to the random distribution of free monomeric $[\text{IrO}_x\text{H}_y]^z$ complexes in solution, the isolated IrO_xH_y octahedra derived from Sr_4IrO_6 exhibit a distinctive feature, namely, a confined IMD of approximately 6 Å. This confined IMD is inherited from the IMD of IrO_6 octahedra in the initial Sr_4IrO_6 precursor lattice.

Next, two isolated $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra were employed as a model system to investigate the critical intermolecular distance (IMD). The initial IMDs between the two octahedra were varied from 6.0 Å to 9.5 Å, with increments of 0.5 Å. Subsequently, the two octahedra were allowed to move freely, and the optimized structures were examined. It was found that a critical IMD of 8.5 Å exists. Specifically, when the IMD is ≤ 8.0 Å (**Fig. 14**), the two isolated octahedra spontaneously approach each other. The corresponding reduced system energies (**Fig. 7g**) indicate the thermodynamic feasibility of this approach. In contrast, when the IMD is ≥ 8.5 Å, such approaching behavior does not occur (**Fig. 14**), and the system energies remain high (**Fig. 7g**), suggesting that the driving force, such as intermolecular forces, between the two octahedra is relatively weak. Interestingly, the confined IMD (~ 6 Å) of IrO_6 octahedra in Sr_4IrO_6 is lower than the critical IMD. This implies that when Sr^{2+} leaches out from the lattice of Sr_4IrO_6 , the IrO_6H_8 octahedra prefer to approach each other (leading to the dehydration and formation of -Ir-O(H)-Ir-framework) rather than dispersing into the solution.

Simultaneously, the initial loose arrangement of IrO_6 octahedra in Sr_4IrO_6 likely plays a crucial role in the formation of a highly porous structure. **Fig. 7h** illustrates the arrangement of IrO_6 octahedra in Sr_4IrO_6 -type and rutile-type H_8IrO_6 , with the latter being the most likely motif in HP- IrO_xH_y . In a single unit of Sr_4IrO_6 -type H_8IrO_6 , there are six isolated $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra occupying a space of approximately 976 Å³. On the other hand, in a single unit of rutile-type H_8IrO_6 , the occupied space is

around $192 \text{ \AA}^3$ when there are six equivalent $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra. By considering the conservation of Ir atoms/octahedra, it can be found that the Sr^{2+} leaching and $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ self-assembly in a single H_8IrO_6 unit result in a significant volume change of approximately $784 \text{ \AA}^3$ (an 80 % reduction), leading to densification. Evidently, such densification accompanied by a distinctive volume change, if it does not cause particle shrinkage, will induce the formation of a porous structure within the particle.

Based on the aforementioned findings, the process of the formation of $\text{HP-IrO}_x\text{H}_y$ from Sr_4IrO_6 can be summarized as follows (as depicted in **Fig. 7i**): Firstly, the leaching of Sr^{2+} enables the generation of free and isolated IrO_xH_y octahedra, such as $\text{Ir}(\text{OH})_4(\text{OH}_2)_2$ octahedra. Secondly, with an initial IMD of approximately $6 \text{ \AA}$ (which is below the critical value of $8.5 \text{ \AA}$), the formation of a framework comprising corner- and edge-sharing IrO_6 octahedra through dehydration within μm -sized particles is facilitated. Thirdly, the densification of the lattice ensures the high porosity of the resulting framework, which is observed to be hierarchically porous in this study.

Building on the results of $\text{HP-IrO}_x\text{H}_y$, ball milling (BM) was employed to further reduce the particle size of the catalyst. The BET surface area of the ball-milled $\text{HP-IrO}_x\text{H}_y$ ($\text{HP-IrO}_x\text{H}_y\text{-BM}$) increased to $80.4 \text{ m}^2/\text{g}$ (Fig. 15). Furthermore, comprehensive analysis was conducted to assess the impact of the BM process on the formation of the AIROF-like phase. XPS analysis (Fig. 16), CV profile comparison (Fig. 17), and intrinsic activity evaluation (Fig. 18) all confirm that the BM process does not affect the formation of the AIROF-like phase.

Example 3: Evaluation of OER activity of catalysts

Example 3a: Preparation of electrodes

The electrodes were prepared by drop-casting as-prepared catalyst ink ($10 \mu\text{L}$) on a glassy carbon rotating disk electrode (RDE) with a surface area of 0.196 cm^2 . The ink was prepared by mixing 2 mg catalyst powder with 1 mg acetylene black carbon, which was ultrasonically dispersed in the solution contains $750 \mu\text{L H}_2\text{O}$, $245 \mu\text{L}$ isopropanol, and $5 \mu\text{L}$ Nafion solution (5 wt.%, Sigma Aldrich). The electrochemical tests were conducted in 0.1 M HClO_4 , and the temperature was set to be 25°C (controlled with a circulating water bath). OER measurements were performed with a biologic SP-150 potentiostat coupled with a modulated speed rotator (Pine Research Instrumentation). A Pt plate was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. A high rotation speed of 2500 rpm was applied to ensure a fast O_2 bubble removal. At least three measurements were performed when evaluating the OER activities of different catalysts.

Example 3b: Evaluation of OER activity of catalysts

A rotating disk electrode (RDE)-based three electrode system was applied to study the catalytic activity of selected electrocatalysts, including IrO_xH_y nanoparticle from Alfa-Aldrich ($\text{IrO}_x\text{H}_y\text{-AA}$), 20 wt. % Ir nanoparticle/C from Fuel Cell store (Ir/C-FC), and the $\text{HP-IrO}_x\text{H}_y\text{-BM}$. In **Fig. 19**, the mass activities of state-of-the-art nano IrO_2 , nano Ir, and AIROF-like nano IrO_xH_y are summarized to assess the advancement of the $\text{HP-IrO}_x\text{H}_y\text{-BM}$. As expected, the mass activities of nano IrO_2 catalysts are significantly lower compared to the AIROF-like catalysts, emphasizing the superior intrinsic activity of AIROF. The Tafel plot obtained from $\text{HP-IrO}_x\text{H}_y\text{-BM}$ exhibits a nearly parallel trend to those from AIROF-like catalysts, such as $\text{IrO}_x\text{H}_y\text{-AA}$, Ir nanoparticle ($2.1 \pm 0.4 \text{ nm}$), and Ir/C-FC. This correspondence suggests the presence of the AIROF-like active motif in $\text{HP-IrO}_x\text{H}_y\text{-BM}$. Most importantly, $\text{HP-IrO}_x\text{H}_y\text{-BM}$ demonstrated the highest mass activity among these Ir-based catalysts, further supporting its cost competitiveness as a water oxidation catalyst in practical MEAs.

Example 4: Use of catalyst in a water electrolyzer*Example 4a: Preparation of water electrolyzer*

The MEA was prepared by a catalyst-coated membrane (CCM) method. The Nafion 212 membrane was air sprayed with $0.375 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ IrO_xH_y (IrO_2 -SA, Ir/C-FC, IrO_xH_y -AA, and HP- IrO_xH_y -BM) and $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ 40 wt. % Pt/C on each side as anode and cathode catalysts, respectively. The catalyst ink was prepared by mixing 50 mg of IrO_xH_y or 40 wt. % Pt/C catalyst with 7.41 mL isopropanol, 2.47 mL deionized water and 0.12 mL 5 wt. % Nafion D-520 solution, then ultrasonicated it for at least one hour. The CCM was then sandwiched between the Pt-coated Ti felt (anode porous transport layer) and Toray 090 carbon paper (cathode gas diffusion layer). Two Pt-coated Ti blocks with a single serpentine channel were used as bipolar plates and current collectors. Viton gaskets with suitable thickness were also placed to prevent liquid/gas leakage. The torque applied to assemble the cell was 8.5 Nm and the active area of the MEA was 5 cm^2 .

Example 4b: General electrochemical characterization procedures

The electrochemical tests were performed with an Autolab potentiostat or a biologic SP-150 with a 20 A booster. The cell temperature was maintained at 80°C by two electric heating plates and measured by a thermocouple placed beside the two bipolar plates. Deionized water was preheated in a heating coil before being pumped into the cell at 2 ml min^{-1} by a peristaltic pump. The PEMWE was first pretreated/activated with chronoamperometry at 1.8 V for 30 min. The polarization curve was obtained by chronopotentiometry of current densities from 10 mA cm^{-2} to 4 A cm^{-2} at each current density for 60 seconds. EIS measurements, in a range of 10 Hz–20 kHz with current perturbations of $\pm 200 \text{ mA}$, were carried out at each current step to determine the high frequency resistance, which was obtained from the high frequency intercept of the Nyquist plot with the real axis. The fixed current stability tests were conducted by applying the current density of 1 A cm^{-2} for 400 hours. The outlet anolytes were collected at different time points and the dissolved Ir in the collected electrolyte was measured by ICP-MS. A model solar profile, extracted from a practical solar profile was also used to mimic the durability of PEMWE with solar power supply. The applied power input was controlled under 35 W. The same profile pattern was applied for 7 cycles and the outlet anolyte (after each cycle) was collected and the dissolved Ir was measured by ICP-MS.

Example 4c: Evaluation of catalyst activity in MEA

Fig. 20a illustrates the polarization curves of MEAs with the HP- IrO_xH_y -BM anode and the state-of-the-art Ir-based MEAs in PEMWEs. The MEA with the Ir/C-FC anode catalyst exhibits significantly inferior performance, despite its high mass activity over RDE measurements (**Fig. 19**). This difference can be attributed to the oxidation-induced degradation of the carbon support. Due to the high intrinsic activity of AIROF-like catalysts, the two MEAs with IrO_xH_y -AA and HP- IrO_xH_y -BM outperform the MEA with the rutile IrO_2 from Sigma-Aldrich (IrO_2 -SA). For example, at a current density of 1 A cm^{-2} , the corresponding cell voltage decreases from 1.81 V (IrO_2 -SA) to 1.57 V (IrO_xH_y -AA) and 1.54 V (HP- IrO_xH_y -BM). Notably, even lower cell voltages are achieved with the MEA utilizing HP- IrO_xH_y -BM, especially at high current densities. For example, additional drop in cell overpotential ($\Delta\eta_{\text{overall}}$) of approximately 190 mV was observed at a working current density of 4 A cm^{-2} . As a result, the record high performance of the MEA with HP- IrO_xH_y -BM anode catalyst surpasses the U.S. Department of Energy's (DOE) 2026 technical targets for PEMWEs and approaches the DOE 2031 final target.

In PEMWEs, the overall cell overpotential can be primarily attributed to three factors: cell Ohmic loss, electrode kinetic loss, and mass-transport related loss. Therefore, the $\Delta\eta_{overall}$ can be expressed as follows:

$$\Delta\eta_{overall} = \Delta\eta_o + \Delta\eta_k + \Delta\eta_m$$

- 5 , where $\Delta\eta_o$, $\Delta\eta_k$, and $\Delta\eta_m$ are anode-difference-induced change of Ohmic loss, electrode kinetic loss, and mass-transport related loss, respectively.

$$\Delta\eta_o = i \times \Delta R$$

- 10 , where i is the current density and ΔR is the anode-difference-induced change of cell ohmic resistance (which can be estimated from the measured high-frequency resistances (HFRs)). It was found that, for both anodes, the HFRs (**Fig. 21**) were almost unchanged as the current density increased, and a reduction (ΔR) of $\approx 20 \text{ m}\Omega \text{ cm}^2$ was observed when the anode was changed from $\text{IrO}_x\text{H}_y\text{-AA}$ to $\text{HP-IrO}_x\text{H}_y\text{-BM}$. Thus, the lower cell voltages can be partially related to a reduced HFRs.

- 15 The analysis of electrode kinetic and mass-transport related losses was conducted by subtracting the total Ohmic loss, referred to as the HFR-free cell voltage (or overpotential) from the measured cell voltage, which includes the contributions from Ohmic losses, electrode kinetic losses, and mass-transport related losses. **Fig. 20b** illustrates the Tafel plots of the iR-corrected cell voltages. The Tafel slopes were determined by fitting the data from 0.01 A cm^{-2} to 0.1 A cm^{-2} (inset of **Fig. 20b**), where the mass-transport related loss is considered negligible. At low current densities ($\leq 0.1 \text{ A cm}^{-2}$), the HFR-free cell voltages with the two anodes exhibit close proximity to each other. Tafel slopes of $41.5 \pm 1.4 \text{ mV dec}^{-1}$ and 39.6 ± 0.8
20 mV dec^{-1} are obtained from $\text{HP-IrO}_x\text{H}_y\text{-BM}$ and $\text{IrO}_x\text{H}_y\text{-AA}$, respectively. Based on Tafel kinetics, it is reasonable to conclude that the kinetic losses for the two anodes are nearly identical, i.e., $\Delta\eta_k \approx 0$. Consequently, other than the Ohmic loss, observed $\Delta\eta_{overall}$ can be predominantly attributed to the mass-transport related loss ($\Delta\eta_m$) within the anode catalyst layer. As a result, the enhanced performance (especially at high current densities) of the MEA with $\text{HP-IrO}_x\text{H}_y\text{-BM}$ is primarily associated with
25 facilitated mass-transport. Similar to the venation pathway in a tree, a hierarchical transport structure is deemed as an optimal solution for mass transport. Thus, compared to the catalyst layer with non-structured nano IrO_xH_y particles (**Fig. 22 a-b**), we assert that the key role is played by the layer composed of hierarchically porous $\text{HP-IrO}_x\text{H}_y\text{-BM}$ particles (**Fig. 22 c-d**).

Example 5: Evaluation of catalyst stability

- 30 A common concern regarding the practical application of amorphous IrO_xH_y materials, such as AIROF, is the dissolution or loss of Ir in harsh OER conditions. Generally, amorphous IrO_xH_y materials are often considered more prone to dissolution compared to rutile IrO_2 . However, the dissolution of an OER catalyst may be largely exaggerated in model three-electrode electrochemical cells, and the catalyst may actually be quite stable under device operation. Therefore, initially, such deviations induced by the
35 measurement protocol were taken into consideration.

- The dissolution of $\text{HP-IrO}_x\text{H}_y\text{-BM}$ was evaluated using both a PEMWE and a three-electrode H-cell, and chronopotentiometric measurements were employed. Both the PEMWE (**Fig. 23**) and the H-cell (**Fig. 24**) with $\text{HP-IrO}_x\text{H}_y\text{-BM}$ anodes exhibited stable performance. This is reasonable considering the short working hours and the intrinsic high stability of Ir. The activity versus stability of $\text{HP-IrO}_x\text{H}_y\text{-BM}$
40 during operation is then assessed using the S-number metric, which considers Ir dissolution. In the PEMWE measurement (**Fig. 23a**), the S-number increases from 1.5×10^8 ($\sim 41 \text{ h}$) to 0.94×10^9 ($\sim 354 \text{ h}$) to 1.1×10^9 ($\sim 380 \text{ h}$). Consistent with previous reports, this monotonic increment can be related to the

effect of operation time. Intriguingly, the S-number of HP-IrO_xH_y-BM in the MEA-based electrolyzer is approximately three orders of magnitude higher than that (1.6×10^6) in the H-cell, highlighting the significantly improved stability of HP-IrO_xH_y-BM in practical PEMWEs.

One of the major advantages of PEMWEs is their rapid response to load changes. Therefore, a qualified catalyst for PEMWEs should exhibit high durability under significantly fluctuating input power, particularly from renewable energy sources. In **Fig. 23b** (solid line), a typical power output profile obtained from solar panels during the daytime is presented. Apparently, electrochemical measurements based on such renewable energy power profiles can differ from the commonly used potentiostatic/galvanostatic measurements, which involve more stable input power profiles. The durability of the PMEWE with the HP-IrO_xH_y-BM anode was then assessed using a simulated power input profile (open dots in **Fig. 23b**), which was cycled 7 times. The recorded voltage and current profiles are shown in **Fig. 23c**. In 7 cycles, the voltage/current profiles exhibited a high degree of overlap, indicating excellent durability of the PEMWE. Furthermore, the stable HFR-free cell voltages (**Fig. 25**) also suggest the robustness of the anode during the cycling process.

To evaluate the activity versus durability of HP-IrO_xH_y-BM and predict the corresponding lifetime, the total Ir dissolution was measured in each cycle. To differentiate it from the commonly used S-number, the concept of D-number was introduced to emphasize the applied power input profile from renewable energy sources. As shown in **Fig. 23d**, over the course of 7 cycles, the estimated D-numbers can range from 2.3×10^8 to $\sim 1.0 \times 10^9$. It is important to note that the evolution of the D-number differs significantly from that of the S-number (**Fig. 23a**). On one hand, the D-number reached a relatively stable value of $\sim 1.0 \times 10^9$ in ~ 30 hours (initial 3 cycles), which is much shorter than the time required for the S-number (~ 150 hours). On the other hand, the increase in the D-number was not consistently monotonic. From cycle 3 to 7, the D-numbers exhibited slight variations in the vicinity of 1.0×10^9 .

Based on the Ir-loading of 0.375 mg cm^{-2} employed in this study, the estimated lifetime for HP-IrO_xH_y-BM is approximately $38,000 \pm 11,000$ hours, considering the average amount of dissolved Ir from cycle 3 to 7. Finally, considering the scalable synthetic methods illustrated in **Fig. 1b&c**, the impressive performance demonstrated in **Fig. 20a&c**, and the projected long lifetime depicted in **Fig. 23d**, the newly developed HP-IrO_xH_y-BM holds significant potential for implementation in next-generation PEM-based devices that are integrated with renewable energy sources.

As evidenced in the examples above, the inventors of the present invention have surprisingly found that the disclosed catalysts exhibit high activity. This disclosed catalysts are advantageously amorphous, hierarchically porous, and support-free. The disclosed catalysts consequently possess a surprisingly high surface area, and exhibits a superior electrochemical performance as compared to other state-of-the-art Ir-based catalysts. Additionally, the inventors have also surprisingly found that the disclosed catalysts may be highly stable in acidic media. This allows the catalysts to be used over a longer period, thus reducing the overall cost of producing, using, and replacing the catalyst, and subsequently the hydrogen production cost.

Also, the inventors have surprisingly found that the disclosed methods of producing the disclosed catalysts may be suitable for large scale production. Further, the inventors have surprisingly found that the disclosed methods may also provide a way for easy recycling of dissolved Ir during chemical leaching, specifically the loss/dissolution of Ir, which reduces the overall material cost of production of the catalyst, and addresses the high scarcity of Ir and its high cost.

The inventors have also surprisingly found that the disclosed catalysts may be used in oxygen evolution reactions as the anodes of PEM water electrolyzers to provide an accelerated oxygen evolution reaction as compared to the commercially available catalysts.

5

Comparative Examples

Comparative Example 1

10 Stoichiometric amounts of SrCO₃, IrO₂, Co₃O₄ were thoroughly ground and calcined at 1150 °C for 12 hours under ambient air to afford an SrCo_{0.5}Ir_{0.5}O₃ precursor.

15 Cation leaching of the SrCo_{0.5}Ir_{0.5}O₃ precursor then took place by electrochemically cycling the precursor in HClO₄ to produce a catalyst with a core portion of SrCoIrO₃ and an amorphous IrO₃H₂ surface portion (Comparative Example 1).

[Table A]

Parameters	HP-IrO ₂ ·1.76H ₂ O (Present Invention)	Core portion of SrCoIrO ₃ and an amorphous IrO ₃ H ₂ surface phase (Comparative Example 1)
Mass activity (Tafel Plot)	130 A/g _{Ir} (1.5 V VS. RHE)	80 A/g _{Ir} (1.5 V VS. RHE)

20 As seen in Table A, the catalyst of the present invention exhibits a higher mass activity as compared to the catalyst in Comparative Example 1. The catalyst of Comparative Example 1 differs from the present invention by its chemical composition and structure, where the core portion of the catalyst comprises the precursor, while the surface phase comprises an amorphous IrO₃H₂. The catalyst of the present invention consists or consists essentially of HP-IrO_xH_y (HP-IrO₂·1.76H₂O). It can hence be seen that a catalyst that consists or consists essentially of IrO_xH_y is important for increased activity and electrochemical performance.

25

Industrial Applicability

30 The present invention generally relates to iridium catalysts, methods of producing them, and their uses in oxygen evolution reactions (OERs). The catalysts of the present invention can be used and applied as electrocatalysts for the OER in various energy conversion and storage applications, such as electrolyzers, rechargeable metal-air batteries, and regenerative fuel cells.

35 Advantageously, the disclosed catalysts may have high activity and stability in acidic media. The disclosed catalysts may possess higher OER catalytic activities, outperforming most benchmark Ir catalysts, including commercially available ones.

Further advantageously, the disclosed methods of producing the disclosed catalysts may be suitable for large scale production. The disclosed methods may also provide a way for easy recycling of dissolved Ir during chemical leaching, specifically the loss/dissolution of Ir.

40 Also advantageously, the disclosed catalysts may be used in oxygen evolution reactions as the anodes of PEM water electrolyzers. Due to the above properties of the disclosed catalysts, the material costs of producing them may be lower, which helps to address the high scarcity of Ir and its high cost.

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

We claim:

1. A catalyst consisting essentially of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$.
- 5 2. The catalyst of claim 1, wherein the catalyst consists of IrO_xH_y .
3. The catalyst of claim 1 or 2, wherein $3.70 < X < 3.90$, and $3.40 < Y < 3.80$.
4. The catalyst of any one of claims 1 to 3, wherein the catalyst is amorphous.
- 10 5. The catalyst of any one of claims 1 to 4, wherein the catalyst comprises mesopores, micropores and/or macropores.
6. The catalyst of any one of claims 1 to 5, wherein the catalyst is support-free.
- 15 7. The catalyst of any one of claims 1 to 6, wherein the catalyst has a BET surface area of about 35 m^2/g to about 45 m^2/g .
8. The catalyst of any one of claims 1 to 7, wherein the oxidation state of Ir is 4+.
- 20 9. The catalyst of any one of claims 1 to 8, wherein the mass of Ir is about 70 wt% to about 80 wt% based on the total weight of the catalyst.
10. The catalyst of any one of claims 1 to 9, wherein X is 3.76 and Y is 3.52.
- 25 11. The catalyst of any one of claims 1 to 10, wherein the catalyst is $\text{IrO}_2 \cdot 1.76\text{H}_2\text{O}$.
12. A method of preparing a catalyst consisting essentially of IrO_xH_y , wherein X and Y fulfill an equation $4 + Y = 2X$, the method comprising:
 - 30 (i) immersing Sr_4IrO_6 in acid to form a mixture; and
 - (ii) subjecting the mixture of step (i) to agitation for more than 12 hours.
13. The method of claim 12, wherein step (ii) is repeated at least once.
- 35 14. The method of claim 12 or 13, further comprising:
 - (iii) subjecting the mixture of step (ii) to centrifugation to obtain a powder; and
 - (iv) ball milling the powder of step (iii).
- 40 15. The method of any one of claims 12 to 14, wherein the mixture of step (i) is subjected to agitation for about 12 hours to about 36 hours.
16. The method of any one of claims 12 to 15, wherein the mixture of step (i) is subjected to agitation for about 24 hours.
- 45 17. The method of any one of claims 12 to 16, wherein the acid is selected from the group consisting of perchloric acid and nitric acid.
18. The method of any one of claims 12 to 17, wherein the Sr_4IrO_6 is obtained by mixing SrCO_3 and IrO_2 , and calcining the mixed mixing SrCO_3 and IrO_2 at a temperature at or above 1000 °C.

19. A catalyst obtained by the method of any one of claims 12 to 18.

20. Use of the catalyst of any one of claims 1 to 11 or 19 to produce hydrogen.