

An improved electrocatalyst and a method of preparing the same

Technical Field

The present invention relates to an improved electrocatalyst and a method of preparing
5 the same.

Background

Green hydrogen derived from electrochemical water splitting is poised as a suitable
candidate to replace emission-intensive fuels. However, current methods of producing
green hydrogen are very expensive due to the use of costly electrocatalysts which use
10 precious metals such as platinum, ruthenium and iridium.

While double and triple layered hydroxides of metals have been considered as
electrocatalysts which do not use precious metals, conventional synthesis methods for
these layered hydroxides typically involve either hydrothermal synthesis methods or co-
precipitation methods which require strict regulation of solution pH. The high temperature
15 and pressure of hydrothermal synthesis and strict pH regulation requirements of co-
precipitation methods prevent industrial upscaling of these synthesis techniques.

There is therefore a need for an improved electrocatalyst a method of preparing the
same.

Summary of the invention

20 The present invention seeks to address these problems, and/or to provide an improved
electrocatalyst and a method of preparing the same.

According to a first aspect, the present invention provides an electrocatalyst comprising
multi-metal hydroxide, the multi-metal hydroxide comprising hydroxides of at least five
metals. In particular, the electrocatalyst does not comprise noble metals or platinum
25 group metals.

Each of the at least five metals comprised in the multi-metal hydroxide may be any
suitable metal. For example, the each of the at least five metals may be transition metals.

According to a particular aspect, the multi-metal hydroxide may comprise five metals. In
particular, the at least five metals comprised in the multi-metal hydroxide may be, at
30 least: cobalt (Co), nickel (Ni), iron (Fe), tungsten (W) and molybdenum (Mo).

The electrocatalyst may comprise a suitable amount of the at least five metals. For example, the electrocatalyst may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on the total weight of a metal precursor solution from which the electrocatalyst is prepared.

- 5 According to a particular aspect, the electrocatalyst may have a total overpotential of ≤ 0.75 V.

According to another particular aspect, the electrocatalyst may be prepared by a method utilising temperatures $\leq 100^{\circ}\text{C}$.

- 10 According to another particular aspect, the electrocatalyst may be prepared by a method utilising atmospheric pressure.

According to a second aspect, there is provided an electrode comprising a substrate and the electrocatalyst according to the first aspect, wherein the electrocatalyst may be loaded on a surface of the substrate.

- 15 According to a third aspect, there is provided a method of preparing the electrocatalyst according to the first aspect, the method comprising:

- mixing salts of the at least five metals to form a metal precursor solution;
- mixing the metal precursor solution with a weak base;
- adding a coordinating compound to form a mixture;
- shaking the mixture for a pre-determined period of time at a pre-determined
- 20 temperature, wherein the pre-determined temperature is $\leq 100^{\circ}\text{C}$; and
- collecting a precipitate comprising the electrocatalyst.

- 25 According to a particular aspect, the at least five metals may be as described above. In particular, the at least five metals may comprise at least: cobalt (Co), nickel (Ni), iron (Fe), tungsten (W), molybdenum (Mo).

The mixing to form the precursor solution may comprise mixing a suitable amount of the salts of the at least five metals. For example, the precursor solution may comprise the at least five metals Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on the total weight of the metal precursor solution.

The weak base may be any suitable weak base. For example, the weak base may be, but not limited to, urea, pyridine, methylamine, ammonia-based compounds, or a mixture thereof.

The coordinating compound may be any suitable coordinating compound. For example,
5 the coordinating compound may be, but not limited to, triethanolamine (TEA), monoethanolamine, diethanolamine, sodium citrate, or a mixture thereof.

According to a particular aspect, the method may further comprise repeating the adding a coordinating compound, with shaking of the mixture between each repetition of the adding a coordinating compound.

10 According to another particular aspect, the method may further comprise drying the precipitate comprising the electrocatalyst. The drying may be by any suitable means.

The method may further comprise forming a dispersion of electrocatalyst in solvent to form catalyst ink. The catalyst may be deposited on a surface of a substrate. Accordingly, the method may further comprise depositing the catalyst ink on a surface of a substrate.

15 Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

20 Figure 1 shows a schematic representation of the preparation of the electrocatalyst according to one embodiment;

Figure 2 shows a bar graph showing the composition of precursor solutions prepared according to one embodiment;

Figure 3 shows total overpotential of electrocatalysts prepared from the precursor
25 solutions shown in Figure 2; and

Figure 4 shows a comparison of the total overpotential of different electrocatalysts.

Detailed Description

As explained above, there is a need for an improved electrocatalyst and a method of preparing the same.

In general terms, the present invention provides an improved electrocatalyst which may be suitable for use as an electrocatalyst for water-splitting applications. In particular, the improved electrocatalyst excludes the use of precious metals such as platinum, ruthenium and iridium. Further, the improved electrocatalyst may serve as both the
5 cathode and anode of an electrolyser, to catalyse the hydrogen evolution and oxygen evolution reactions respectively. This enables the electrocatalyst to be utilised more efficiently and provides an avenue for scaling up a water-splitting method. The method of preparing the electrocatalyst may also be more economical as it avoids the use of precious metals, which are expensive, and also utilises low temperature and pressure
10 and overall, milder synthesis conditions.

According to a first aspect, the present invention provides an electrocatalyst comprising multi-metal hydroxide, the multi-metal hydroxide comprising hydroxides of at least five metals. In particular, the electrocatalyst does not comprise noble metals or platinum group metals.

15 Each of the at least five metals comprised in the multi-metal hydroxide may be any suitable metal. For example, the each of the at least five metals may be transition metals. In particular, the at least five metals may comprise, but is not limited to, cobalt (Co), nickel (Ni), iron (Fe), tungsten (W), molybdenum (Mo), copper (Cu), zinc (Zn), zirconium (Zr), vanadium (V), chromium (Cr), tungsten (W), titanium (Ti), manganese (Mn).

20 According to a particular aspect, the at least five metals comprised in the multi-metal hydroxide may be, at least: cobalt (Co), nickel (Ni), iron (Fe), tungsten (W) and molybdenum (Mo).

According to a particular aspect, the multi-metal hydroxide may comprise hydroxides of five metals. The multi-metal hydroxide may comprise hydroxides of five transition metals.

25 In particular, the transition metals may comprise cobalt (Co), nickel (Ni), iron (Fe), tungsten (W) and molybdenum (Mo).

The electrocatalyst may comprise a suitable amount of the at least five metals. For example, the electrocatalyst may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on the total weight of a
30 metal precursor solution from which the electrocatalyst is prepared. In particular, electrocatalyst may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.27-0.35:0.01-0.06:0.05-0.39:0.12-0.23:0.15-0.36 based on the total weight of a metal

precursor solution from which the electrocatalyst is prepared. Even more in particular, the metal precursor solution from which the electrocatalyst is prepared may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.35:0.01:0.20:0.13:0.31, 0.28:0.05:0.31:0.21:0.15, 0.30:0.06:0.05:0.23:0.36, or 0.27:0.02:0.39:0.12:0.20.

5 According to a particular aspect, the electrocatalyst may have a total overpotential of ≤ 0.75 V. Overpotential may be used to calculate the overpotential of a given current density. The lower the total overpotential, the higher is the performance of the electrocatalyst. For the purposes of the present application, total overpotential, η , may refer to the extra potential required to overcome the intrinsic thermodynamic limit in
10 electrochemical water splitting (in both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)).

The electrocatalyst may have a suitable total overpotential. For example, the electrocatalyst may have a total overpotential of ≤ 0.75 V, 0.60-0.76 V, 0.67-0.75 V, 0.70-0.71 V. In particular, the electrocatalyst may have a suitable HER and OER, thereby
15 providing a suitable total overpotential. According to a particular aspect, when the electrocatalyst has a suitable total overpotential, in which each of the HER and OER has a suitable overpotential, the electrocatalyst may be used as a single catalyst for both the HER and OER.

The electrocatalyst may be prepared by a suitable method. In particular, the method may
20 be one which utilises mild process conditions. For example, the electrocatalyst may be prepared by a method utilising temperatures $\leq 100^\circ\text{C}$ and/or atmospheric pressure. In particular, the method may utilise temperatures $\leq 95^\circ\text{C}$.

According to a second aspect, there is provided an electrode comprising a substrate and the electrocatalyst according to the first aspect, wherein the electrocatalyst may be
25 loaded on a surface of the substrate. The electrode may be suitable for use in water-splitting reactions.

The substrate may be any suitable substrate. For example, the substrate may be, but not limited to, carbon-based substrates, nickel-based substrates, titanium-based substrates. In particular, the substrate may be, but not limited to, a glassy carbon
30 substrate, nickel foam, nickel mesh, titanium mesh, or a combination thereof.

The electrocatalyst may be loaded on a surface of the substrate by any suitable means. For example, the electrocatalyst may be loaded on a surface of the substrate by depositing the electrocatalyst on a surface of the substrate.

5 The electrode may comprise a suitable amount of electrocatalyst loaded on a surface of the substrate. For example, the amount of electrocatalyst loaded on a surface of the substrate may be 0.01-20 mg/cm². In particular, the electrocatalyst loading on the substrate may be 0.05-15 mg/cm², 0.1-10 mg/cm², 0.5-8 mg/cm², 1-6 mg/cm², 2-5 mg/cm², 3-4 mg/cm². Even more in particular, the amount may be 0.1-5 mg/cm², preferably about 0.5 mg/cm².

10 The electrode may be used as both the anode and cathode. This advantageously reduces manufacturing complexity of electrodes and choice of electrodes for various applications, such as water splitting. In particular, the electrode may be used for both oxygen evolution and hydrogen evolution.

15 According to a third aspect, there is provided a method of preparing the electrocatalyst according to the first aspect, the method comprising:

- mixing salts of the at least five metals to form a metal precursor solution;
- mixing the metal precursor solution with a weak base;
- adding a coordinating compound to form a mixture;
- shaking the mixture for a pre-determined period of time at a pre-determined
- 20 temperature, wherein the pre-determined temperature is $\leq 100^{\circ}\text{C}$; and
- collecting a precipitate comprising the electrocatalyst.

According to a particular aspect, the at least five metals may be as described above in relation to the first aspect. In particular, the at least five metals may comprise at least:

25 cobalt (Co), nickel (Ni), iron (Fe), tungsten (W), molybdenum (Mo).

Any suitable salt of the at least five metals may be used for forming the metal precursor solution. For example, each of the salt of the at least five metals may be hydrated salts. The hydrated salt of the at least five metals may be the same or different and may each be, but not limited to, hydrated nitrates, chlorides, or oxide salts. In particular, the salt

30 may be, but not limited to, cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ammonium tungsten oxide hydrate ($(\text{NH}_4)_8\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$, $x \approx 4.8$), ammonium molybdate

(para) tetrahydrate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$. It will be appreciated that many different combinations of salts may be possible in preparing the electrocatalyst.

The mixing to form the metal precursor solution may comprise mixing a suitable amount of the salts of the at least five metals. For example, the metal precursor solution may
5 comprise the at least five metals Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on the total weight of the metal precursor solution. In particular, metal precursor solution formed may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.27-0.35:0.01-0.06:0.05-0.39:0.12-0.23:0.15-0.36 based on the total weight of a metal precursor solution. Even more in particular, the metal
10 precursor solution may comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.35:0.01:0.20:0.13:0.31, 0.28:0.05:0.31:0.21:0.15, 0.30:0.06:0.05:0.23:0.36, or 0.27:0.02:0.39:0.12:0.20.

The weak base may be any suitable weak base. In particular, the weak base may be any suitable base which enables hydrolysis of the metal salts in the metal precursor solution.
15 For example, the weak base may be, but not limited to, urea, pyridine, methylamine, ammonia-based compounds, or a mixture thereof. The ammonia-based compounds may be any suitable compound such as, but not limited to, ammonia solution, ammonium hydroxide, or a mixture thereof. According to a particular aspect, the weak base may be urea.

20 The method may further comprise shaking the mixture of the metal precursor solution and the weak base for a suitable period of time. The shaking may be under suitable conditions. For example, the shaking may comprise shaking the mixture at room temperature.

The suitable period of time for the shaking may be 3-10 minutes. In particular, the shaking
25 may be for 4-9 minutes, 5-8 minutes, 6-7 minutes. Even more in particular, the shaking may be for about 5 minutes.

The adding a coordinating compound may comprise adding any suitable coordinating compound. For the purposes of the present application, a coordinating compound may be defined as a complex in which metal atoms are bound to a number of anions or neutral
30 molecules by sharing electrons. The adding of the coordinating compound may enable the formation of metal hydroxides from the metal precursor solution and may also stabilise the hydrolysis reaction.

The coordinating compound may be any suitable coordinating compound. For example, the coordinating compound may be, but not limited to, triethanolamine (TEA), monoethanolamine, diethanolamine, sodium citrate, or a mixture thereof. In particular, the coordinating compound may be TEA.

- 5 According to a particular aspect, the method may comprise adding the coordinating compound in batches of smaller volume. In particular, the method may comprise repeating the adding a coordinating compound, with shaking of the mixture between each repetition of the adding a coordinating compound. The shaking between each repetition of the adding a coordinating compound may be under suitable conditions. For
10 example, the shaking may be at room temperature. The shaking between each repetition of the adding a coordinating compound may be for a period of 1-5 minutes.

The shaking the mixture formed following the adding of the coordinating compound may be for any suitable period of time. For example, the shaking may be for a period of 12-72 hours. In particular, the period of time may be 18-66 hours, 24-60 hours, 30-54 hours,
15 36-48 hours, 42-45 hours. Even more in particular, the period of time may be about 24-72 hours, preferably about 24 hours.

According to a particular aspect, the shaking may comprise shaking for a first pre-determined period of time at a first pre-determined temperature followed by shaking for a second pre-determined period of time at a second pre-determined temperature. The
20 pre-determined temperature may be any suitable temperature below the boiling point of solvent used for mixing the salts of the at least five metals to form the metal precursor solution.

For example, the first pre-determined period of time may be 12-36 hours. In particular, the first pre-determined period of time may be 18-24 hours. Even more in particular, the
25 first pre-determined period of time may be about 24 hours. The second pre-determined period of time may be 30-54 hours. In particular, the second pre-determined period of time may be 36-48 hours. Even more in particular, the second pre-determined period of time may be about 48 hours.

The first pre-determined temperature may be any suitable temperature. For example, the
30 first pre-determined temperature may be room temperature. The second pre-determined temperature may be any suitable temperature. For example, the second pre-determined

temperature may be $\leq 100^{\circ}\text{C}$, preferably $\leq 95^{\circ}\text{C}$. In particular, the second pre-determined period of time may be $25-100^{\circ}\text{C}$, $30-95^{\circ}\text{C}$, $35-90^{\circ}\text{C}$, $40-80^{\circ}\text{C}$, $50-75^{\circ}\text{C}$, $60-70^{\circ}\text{C}$.

The shaking at the pre-determined temperature of $\leq 100^{\circ}\text{C}$ enables precipitation of the precipitate comprising the electrocatalyst. The precipitate may comprise a multi-metal hydroxide comprising at least five metals. Once the precipitate is formed, the collecting may be by any suitable means. For example, the collecting may be by centrifugation, filtration, drying, sedimentation, or a combination thereof.

According to a particular aspect, any of the shaking steps of the method may comprise shaking the respective mixtures with inert beads to facilitate mixing during the shaking step. For example, the inert beads may be ceramic beads, zirconia beads, or a combination thereof. The shaking steps may be performed at a suitable shaking speed. For example, the shaking speed may be a speed of 1000-1500 rpm. In particular, the shaking speed may be 1100-1400 rpm, 1200-1300 rpm. Even more in particular, the shaking speed may be about 1200 rpm.

The method may further comprise washing the collected precipitate. The washing may be using a suitable solvent.

The method may further comprise drying the precipitate comprising the electrocatalyst. In particular, the drying may be following the washing of the collected precipitate. The drying may be by any suitable means. In particular, the drying may be in an oven at a pre-determined temperature.

The method may further comprise forming a dispersion of electrocatalyst in solvent to form catalyst ink. The catalyst may be deposited on a surface of a substrate. Accordingly, the method may further comprise depositing the catalyst ink on a surface of a substrate. The substrate with the catalyst ink may be used for forming an electrode.

The method according to the present invention may be automated using a suitable controller unit. The controller unit may be automated. For example, the method may be automated workstation, such as a Zinsser workstation.

As can be seen, the method is a low-cost method since mild process conditions are used, and low-cost and easily available materials, including aqueous solvents, are used for preparing the electrocatalyst. Accordingly, the method may be easily scaled up to

prepare the electrocatalysts on a larger scale. The method enables the incorporation of at least five metals into a hydroxide/double hydroxide structure, thereby creating a new phase or phase mixtures with unique compositions or electrocatalysts. The method of the present invention also does not involve strict monitoring of pH of mixtures to enable the precipitation of the electrocatalyst. In contrast, prior art methods involve synthesis of hydroxide/double hydroxide at temperatures about the boiling point of the solvent used and under high pressure.

Having now generally described the invention, the same will be more readily understood through reference to the following example which is provided by way of illustration, and is not intended to be limiting.

Example

Preparation of electrocatalyst

A high-throughput automated workstation (Zinsser Analytics) was used to synthesize the mixed-metal hydroxides. The workstation allowed for the auto-pipetting of predetermined volumes of liquids as well as the shaking and heating of solution vials. For the workstation's setup, glass vials containing 7 precursor solutions and de-ionized water were loaded into the workstation blocks. The 7 precursor solutions included 0.4 M aqueous urea, 0.2 M triethanolamine (TEA) and five solutions of metal salts. The five aqueous metal salt solutions were prepared with the concentration of the metal species in the solution fixed at 0.2 M. The five salts used to introduce cobalt (Co), nickel (Ni), iron (Fe), tungsten (W) and molybdenum (Mo) into the hydroxide structure were cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ammonium tungsten oxide hydrate ($(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$, $x \approx 4.8$) and ammonium molybdate (para) tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) respectively.

For the synthesis, 8 mL glass vials, each with two zirconia balls were used as the reaction vessels. The zirconia balls facilitate mixing within the vials during the shaking step of the synthesis, and all shaking steps were conducted with shaking speed of 1200 rpm.

A schematic representation of the synthesis route is as shown in Figure 1. Into these glass vials, 2.25 mL of deionized water was first pipetted, followed by the addition of the metal salt solutions. Varying volumes of each of the five metal solutions were added,

totalling to 1.25 mL. A case study example consisting of 23 randomly selected proportions of the five metal salt solutions were synthesised. The compositions of the metal salt solutions are pictorially depicted in Figure 2 and tabularised in Table 1.

Sample ID	Co	Ni	Fe	W	Mo
0	0.02	0.29	0.34	0.32	0.03
1	0.35	0.01	0.20	0.13	0.31
2	0.28	0.05	0.31	0.21	0.15
3	0.18	0.19	0.08	0.23	0.32
4	0.26	0.15	0.26	0.10	0.23
5	0.07	0.18	0.35	0.07	0.33
6	0.35	0.08	0.18	0.33	0.06
7	0.14	0.21	0.17	0.01	0.47
8	0.39	0.16	0.02	0.32	0.11
9	0.21	0.20	0.23	0.19	0.17
10	0.48	0.30	0.12	0.06	0.04
11	0.15	0.26	0.06	0.34	0.19
12	0.30	0.06	0.05	0.23	0.36
13	0.12	0.15	0.35	0.28	0.10
14	0.21	0.31	0.02	0.09	0.37
15	0.29	0.47	0.15	0.09	0.00
16	0.11	0.33	0.24	0.18	0.14
17	0.18	0.25	0.25	0.03	0.29
18	0.00	0.31	0.19	0.33	0.17
19	0.23	0.19	0.22	0.23	0.13
20	0.05	0.11	0.19	0.49	0.16
21	0.27	0.02	0.39	0.12	0.20
22	0.05	0.34	0.14	0.24	0.23

Table 1: Compositions of metal precursor solutions prepared based on weight fraction

5

After the addition of the metal salt solutions, 1.25 mL of the urea solution was also added before the vials were shaken for 5 min at room temperature. Subsequently, 5 additions of 250 μ L aqueous TEA was introduced to the vials, interspaced by 1 min shaking at room temperature. After 5 additions of TEA, the vials were first shaken for 24 h at room temperature, following by shaking for an additional 48 h at 95°C. The precipitates were then collected via centrifuging, washed twice with a mixture of water and ethanol and dried in an oven at 60 °C.

10

Eletrochemical testing

0.196 cm² glassy carbon discs polished to mirror finish with 0.3 µm alumina slurry was used as the substrate. 5 mg mL⁻² dispersions of the as-prepared catalysts were prepared with 80:20:2 ethanol:H₂O:Nafion solution via ultrasonication in an ice bath for 30 mins. 19.6 µL of the catalyst ink was deposited onto the polished glassy carbon and dried under
5 an infrared lamp to achieve a 0.5 mg cm⁻² catalyst loading.

The catalyst-loaded glassy carbon substrates were attached to a rotating disc electrode set-up and all electrochemical measurements were conducted at a rotation speed to 1600 rpm. All electrochemical testing was conducted in 1 M aqueous potassium hydroxide with a graphite counter electrode and Hg/HgO reference electrode. To
10 stabilize the catalysts, 5 cyclic voltammetry scans at 10 mV s⁻¹ were conducted at the voltage range of electrochemical testing, followed by a linear sweep voltammetry (LSV) at the same range to measure the electrochemical performance of the catalysts. LSV data were collected with a step size of 1 mV, while iR compensation was conducted using the current interrupt feature.

15 *Results*

The electrochemical performance of the synthesized multi-metal hydroxides in the form of their linear sweep voltammograms and overpotentials for both oxygen evolution and hydrogen evolution reactions is now described.

The electrochemical performance of the catalysts were evaluated by linear sweep
20 voltammetry, with the current density used for comparison normalised against the electrode geometric area. The overpotential for oxygen evolution is defined as the potential above the thermodynamic potential of oxygen evolution at 1.23 V vs. reversible hydrogen electrode. From the LSV curves, the overpotential at 10 mA cm⁻² (η^{OER}_{10}) are extracted.

25 On the other hand, the thermodynamic potential of hydrogen evolution is 0V vs. RHE. The overpotential, η^{HER}_{10} , is defined as |V| at -10 mA cm⁻².

The lowest η^{OER}_{10} achieved was 0.268 V with sample 12, while the lowest η^{HER}_{10} achieved was 0.371V for sample 1. Sample 1 also achieved the lowest combined η^{OER}_{10} and η^{HER}_{10} at 0.674 V. Overall, the synthesized mixed-metal hydroxides achieved generally good
30 OER and HER performances, as can be seen from Figure 3 which provides the total

overpotential of the synthesised samples. In Figure 3, the samples are ranked in order of increasing total overpotential.

Additionally, X-ray fluorescence (XRF) spectra were collected for one of the synthesized samples, i.e. sample 21. The XRF results confirm the presence of all five of the metal elements in the multi-metal hydroxide synthesised, as can be seen in Table 2.

Element	at. (%)
Ni	2.02
Co	30.82
W	12.69
Mo	9.51
Fe	44.92

Table 2: Tabulated atomic percentage of the five metals in sample 21

To further reflect the performance improvement with additional metals incorporated, additional samples with three or less than three metals were also synthesized with a similar procedure and their electrochemical performance were tested. Significantly higher overpotentials were demonstrated for these samples, as well as for sample ID 15, which does not contain Mo. The composition of the samples, as well as the oxygen and hydrogen evolution capabilities of the samples, are shown in Table 3.

Sample	Material	$\eta_{\text{OER}_{10}}^{\text{OER}}$ (V)	$\eta_{\text{HER}_{10}}^{\text{HER}}$ (V)
This work (sample 12)	$\text{Co}_{0.3}\text{Ni}_{0.06}\text{Fe}_{0.0498}\text{W}_{0.2304}\text{Mo}_{0.36}$	0.268	0.445
This work (sample 1)	$\text{Co}_{0.3496}\text{Ni}_{0.0096}\text{Fe}_{0.3104}\text{W}_{0.1296}\text{Mo}_{0.3112}$	0.303	0.371
This work (sample 15)	$\text{Co}_{0.2896}\text{Ni}_{0.4696}\text{Fe}_{0.1504}\text{W}_{0.0904}$	0.335	0.562
Additional Sample 1	$\text{Co}_{0.52}\text{Ni}_{0.04}\text{Fe}_{0.34}$	0.399	0.537
Additional Sample 2	$\text{Co}_{0.4904}\text{Fe}_{0.4896}\text{Mo}_{0.02}$	0.384	0.442
Additional Sample 3	$\text{Fe}_{0.4496}\text{Mo}_{0.5504}$	0.404	0.398

Table 3: Comparison between multi-metal hydroxides with samples 5 metals and with 3 or less than 3 metals

Figure 4 shows the comparison of the total overpotential of samples 1, 12 and 15, as well as the additional samples prepared as shown in Table 3 with three or less metals incorporated.

In conclusion, it can be seen that the mixed-metal hydroxide electrocatalyst containing at least 5 metals may be suitable for bifunctional water splitting applications.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. An electrocatalyst comprising multi-metal hydroxide, the multi-metal hydroxide comprising hydroxides of at least five metals.
- 5 2. The electrocatalyst according to claim 1, wherein each of the at least five metals are transition metals.
3. The electrocatalyst according to claim 1 or 2, wherein the multi-metal hydroxide comprises five metals.
- 10 4. The electrocatalyst according to any preceding claim, wherein the at least five metals comprise at least: cobalt (Co), nickel (Ni), iron (Fe), tungsten (W), molybdenum (Mo).
- 15 5. The electrocatalyst according to claim 4, wherein the at least five metals comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on total weight of a metal precursor solution from which the electrocatalyst is prepared.
- 20 6. The electrocatalyst according to any preceding claim, wherein the electrocatalyst does not comprise noble metals or platinum group metals.
7. The electrocatalyst according to any preceding claim, wherein the electrocatalyst is prepared by a method utilising temperatures $\leq 100^{\circ}\text{C}$.
- 25 8. The electrocatalyst according to any preceding claim, wherein the electrocatalyst is prepared by a method utilising atmospheric pressure.
9. The electrocatalyst according to any preceding claim, wherein the electrocatalyst has a total overpotential of $\leq 0.75\text{ V}$.
- 30 10. An electrode comprising a substrate and the electrocatalyst according to any preceding claim loaded on a surface of the substrate.

11. A method of preparing the electrocatalyst according to any of claims 1 to 9, the method comprising:

- mixing salts of the at least five metals to form a metal precursor solution;
- mixing the metal precursor solution with a weak base;
- adding a coordinating compound to form a mixture;
- shaking the mixture for a pre-determined period of time at a pre-determined temperature, wherein the pre-determined temperature is $\leq 100^{\circ}\text{C}$;

and

- collecting a precipitate comprising the electrocatalyst.

12. The method according to claim 11, wherein the at least five metals comprise at least: cobalt (Co), nickel (Ni), iron (Fe), tungsten (W), molybdenum (Mo).

13. The method according to claim 12, wherein the at least five metals comprise at least Co, Ni, Fe, W and Mo in a weight ratio of 0.07-0.35:0.01-0.18:0.05-0.39:0.07-0.33:0.06-0.36 based on total weight of the metal precursor solution.

14. The method according to any of claims 11 to 13, wherein the weak base comprises at least one of: urea, pyridine, methylamine, an ammonia-based compound, or a mixture thereof.

15. The method according to any of claims 11 to 14, wherein the coordinating compound comprises: triethanolamine (TEA), monoethanolamine, diethanolamine, sodium citrate, or a mixture thereof.

16. The method according to any of claims 11 to 15, further comprising repeating the adding a coordinating compound, with shaking of the mixture between each repetition of the adding a coordinating compound.

17. The method according to any of claims 11 to 16, wherein the method further comprises drying the precipitate comprising the electrocatalyst.

18. The method according to any of claims 11 to 17, further comprising forming a dispersion of electrocatalyst in solvent to form catalyst ink.

19. The method according to claim 18, further comprising depositing the catalyst ink on a surface of a substrate.