There is also a need to develop highly active, stable, and inexpensive electrochemical catalysts, capable of maximizing the hydrogen production. In this regard, there is a need for catalyst systems that utilise relatively inexpensive, earth abundant materials. As used herein, “earth abundant” means present in the Earth’s crust at concentrations of greater than 1 ppm.

It is to be understood that, if any prior art is referred to herein, such reference does not constitute an admission that the prior art forms a part of the common general knowledge in the art, in Australia or any other country.

SUMMARY

According to one example, there is provided a method of fabricating a catalyst on a substrate comprising:

providing a substrate having a layer of metal thereon; and

contacting the layer of metal with a corrosive solution to form the catalyst.

In an aspect, there is provided a method of fabricating a catalyst on a substrate comprising:

providing the substrate;

applying a seed layer to the substrate;

forming a layer of metal on the seed layer, the layer of metal comprising one or more metals selected from Ni, Mo, Co, Fe, Cu, Mn and Zn; and

contacting the layer of metal with a corrosive metal halide solution to form the catalyst.

As used herein, the term “catalyst” has its ordinary technical meaning of a material that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.

The method may further comprise a step of forming the layer of metal on the substrate to form a metalized substrate.

In some examples, the layer of metal comprises an earth-abundant metal. The layer of metal may include one or more transition metals. The layer of metal may comprise one or more metals selected, for example, from nickel, molybdenum, iron, cobalt, copper, manganese, zinc and/or a combination thereof. Nickel (Ni) and Ni-based materials exhibit good catalytic activity in electrolytic processes, such as hydrogen generation via water splitting. Ni is also inexpensive and readily available and has shown a relatively good catalytic performance in both oxygen evolution reactions (OER) and hydrogen evolution (HER) reactions.

The thickness of the layer of metal can be tailored as desired. However, the thickness should preferably be sufficient to possess adequate structural flexibility to adhere to most support materials. Further preferably, the metal layer thickness is sufficiently thick to prevent complete film etch/removal during the solution corrosion process. Accordingly, the metal layer should comprise the required quantity of metal necessary for the corrosion process to be performed, and thereby the catalyst to be formed, while maintaining the desired conductive properties of the metal layer, required for its intended application, for example to perform as an electrode in electrochemical applications, such as hydrogen generation via water splitting.

The substrate may be completely covered by the layer of metal, such that none of the substrate is exposed during the subsequent corrosion step.

In some examples, the layer of metal has a minimum thickness of 0.5 μm. In some examples, the layer of metal has a minimum thickness of 1.0 μm. In some examples, the layer of metal has a minimum thickness of 1.5 μm. In some examples, the layer of metal has a minimum thickness of 2 micron. In some examples, the layer of metal has a minimum thickness of 2.5 μm.

In one example, the thickness of the layer of metal is a maximum of 10 microns. In one example, the thickness of the layer of metal is a maximum of 8 microns. In one example, the thickness of the layer of metal is a maximum of 7 microns. In one example, the thickness of the layer of metal is a maximum of 5 microns. In one example, the thickness of the layer of metal is a maximum of 3 microns.

Aside from acting as sacrificial metal layer for the catalyst generation, the layer of metal serves also as a chemical protection layer for the underlying substrate which can be otherwise damaged in harsh chemical environments, such as may exist during, for example, electrolysis operations and water splitting reactions. This further eliminates the need for a chemically robust material to serve, for example, as an electrode substrate.

In some examples, forming the layer of metal on the substrate comprises electroplating the metal on the substrate. The layer of metal, can be, for example applied by electroplating the substrate using a metal halide electrolyte. In one example the layer of metal is applied by electroplating the substrate using an electrolyte comprising a chloride solution of an earth abundant metal. The earth abundant metal may be a transition metal. In one example the layer of metal is applied by electroplating the substrate with a Ni(II) chloride solution as the electrolyte, to thereby form a layer of Ni on the substrate. In another example, a Ni(II) sulphate solution is used as the electrolyte to apply a layer of Ni on the substrate. In yet another example, a Ni(II) acetate solution is used as the electrolyte to apply a layer of Ni on the substrate.

In some examples, an alternative suitable metal deposition technique may be used to apply the layer of metal on the substrate. For example, in some examples the layer of metal is applied by one or more of electroless plating, chemical vapour deposition or wet chemistry.

While the deposited layer of metal may comprise only a single metal, for example Ni, in other examples the deposited layer of metal may comprise two or more metals. The combination of metals may include nickel. The combination of metals may further include one or more of Mo, Co, Fe, Cu, Mn and Zn. Examples of metal combinations that may be in the metal layer include: Ni-Mo, Ni-Co, Ni-Fe, Ni-Fe-Cu, Ni-Mo-Zn, Ni-Fe-Mo and Ni-Mn-Fe-Mo.

In some other examples forming the layer of metal on the substrate comprises applying a metal plate or foil on the substrate. In some examples, the metal plate or foil is attached to the substrate using an adhesive layer such as Ag paint. In other examples the metal plate or foil is attached to the back side of the substrate by soldering.

The substrate can be selected from a broad range of materials including, but not limited to, semiconductors (such as Si and/or GaAs), metals (such as Cu mesh, Cu

plate or stainless steel), non-metals and polymers (such as polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE).

In some examples, the substrate is an electrode.

In one example, the substrate is photovoltaic cell. In one example, the substrate is a GaAs PV cell.

Where the present method is applied to the fabrication of a catalyst on a semiconductor, the method advantageously enables the avoidance of solution-induced semiconductor corrosion which can compromise the performance and lifetime of the photoelectrodes. Additionally, where the semiconductor forms part of a semiconductor-based photoelectrode device, the layer of metal formed on the semiconductor substrate during the present method protects the semiconductor during the water splitting operation, thereby stabilizing the performance of the photoelectrode device.

The present method includes contacting the layer of metal on the substrate with a corrosive solution to form the catalyst. As used herein, the term “corrosive solution” means an aqueous solution that chemically reacts with and oxidises the metal layer.

In some examples, contacting the layer of metal with a corrosive solution comprises dipping the substrate with the layer of metal provided thereon into the corrosive solution.

In other examples, contacting the layer of metal with a corrosive solution comprises spraying or otherwise applying the corrosive solution to the layer of metal.

In some examples, the corrosive solution is a halide solution. The corrosive solution may be, for example, a metal halide solution. In an example, the corrosive solution is a transition metal halide solution.

The metal halide may be present in solution at a minimum concentration of 1 mM. In another example, the metal halide may be present in solution at a minimum

concentration of 1.5 mM. In another example, the metal halide may be present in solution at a minimum concentration of 5 mM. In another example, the metal halide may be present in solution at a minimum concentration of 10 mM.

The metal halide may be present in solution at a maximum concentration of 1 M. In an example, the metal halide may be present in solution at a maximum concentration of 0.5 M. In another example, the metal halide may be present in solution at a maximum concentration of 0.1 M. In another example, the metal halide may be present in solution at a maximum concentration of 0.05 M. In another example, the metal halide may be present in solution at a maximum concentration of 0.01 M.

The pH of the corrosive solution may be acidic. The pH may be less than 7. The pH may be at least 2. In an example, the pH is at least 2.5. In another example, the pH is at least 3.

The corrosive solution may include one or more metal salts. The metal salts may comprise one or more transition metal salts.

The corrosive solution may be, for example, a metal chloride solution.

The corrosive solution may comprise one or more transition metal chlorides. The transition metal chloride may comprise nickel chloride and/or iron chloride.

The corrosive solution may comprise one or more transition metal nitrates. The transition metal nitrates may comprise nickel nitrate and/or iron nitrate.

In some examples, the corrosive solution is a mixture of Ni(II) and Fe(III) chlorides. In other examples, the corrosive solution is a mixture of Ni(II) and Fe(III) nitrates.

The molar ratio of Ni:Fe may be at least 1:2. In an example, the molar ratio is a maximum of 2:1. In one example, the molar ratio of the mixture of Ni(II) and Fe(III) chloride or the mixture of Ni(II) and Fe(III) nitrates is 1:1. In another example, the molar ratio of the mixture of Ni(II) and Fe(III) chloride or the mixture of Ni(II) and Fe(III) nitrates is 1:2. In yet another example, the molar

ratio of the mixture of Ni(II) and Fe(III) chloride or the mixture of Ni(II) and Fe(III) nitrates is 2:1.

The temperature of the corrosion step may be ambient or elevated. By “elevated temperature” is meant a temperature that is higher than ambient. In some examples, the step of contacting the layer of metal to a corrosive solution is performed at room temperature. In other examples, the step of contacting the layer of metal to a corrosive solution is performed at a minimum of 40°C. In other examples, the step of contacting the layer of metal to a corrosive solution is performed at a minimum of 60°C. In yet other examples, the step of contacting the layer of metal to a corrosive solution is performed at a maximum of the 90 °C. In yet other examples, the step of contacting the layer of metal to a corrosive solution is performed at a maximum of 80°C.

The metal layer may be exposed to the corrosion solution for a sufficient amount of time to initiate the corrosion of the metal and form a corrosion product. The exposure time of the layer of metal to the corrosive solution can be adjusted as desired, with a longer time providing a larger conversion of metal to catalyst. The optimum amount of time will be dependent on a number of factors including concentration and temperature of the corrosion solution. The metal layer may be exposed to the corrosion solution for a period of time up to 60 minutes. In an example, the metal layer is exposed to the corrosion solution for a period of time up to 30 minutes. In another example, the metal layer is exposed to the corrosion solution for a period of time up to 15 minutes. In another example, the metal layer is exposed to the corrosion solution for a period of time up to 10 minutes. In another example, the metal layer is exposed to the corrosion solution for a period of time up to 5 minutes.

During the corrosion step, the corrosive solution reacts with at least some of the metal in the metal layer to form a corrosion product. The corrosion product may form in situ at the outer surface of the metal layer, such that a layer of corrosion product forms on the unreacted metal of the metal layer. The corrosion product may comprise the catalyst.

In some examples, the catalyst is an electrocatalyst.

In some examples, the catalyst comprises one or more metal hydroxides.

In some examples, the catalyst comprises a monometallic hydroxide.

In some examples, the catalyst is a multimetallic hydroxide.

In some examples, the catalyst is a multimetallic layered double hydroxide (LDH).

In some examples, the catalyst includes one or more transition metals. The one or more transition metals may be selected from Ni, Fe, Co, Mo and Cu. The catalyst may include at least nickel. In some examples, the catalyst is selected from NiFe hydroxide, NiCoFe hydroxide, NiMo hydroxide, NiCuFe hydroxide and/or a combination thereof.

In an example, when the layer of metal is contacted with the corrosive solution, a redox process occurs at the metal surface, wherein the metal is oxidised and thereby forming monometallic or multimetallic layered double hydroxides (LDH) catalysts.

In one example, the catalyst is a NiFe LDH catalyst.

In some examples, the method further includes applying a seed layer to the substrate prior to forming or applying the layer of metal. The seed layer may facilitate the adhesion of the layer of metal to the substrate.

In some examples, the seed layer has a minimum thickness of 50 nm

In some examples, the thickness of the seed layer is approximately 100 nm.

In some examples, the composition of the seed layer includes Ti and/or Ni.

In some examples, the seed layer includes at least one of a layer of Ti and a layer of Ni.

In some examples, the layer of Ti has a minimum thickness of 50 nm.

In some examples, the layer of Ni has a minimum thickness of 50 nm.

In some examples, applying a seed layer to the substrate comprises depositing the seed layer by electron beam evaporation. In some other examples, applying a seed layer to the substrate comprises depositing the seed layer by thermal evaporation. In yet some examples, applying a seed layer to the substrate comprises depositing the seed layer by sputter deposition.

According to another example, there is provided a method of regenerating a catalyst on a metal surface, the method including:

removing any spent or residual catalyst from the metal surface to produce a cleaned metal surface; and

contacting the cleaned metal surface with a corrosive solution to regenerate fresh catalyst thereon.

The method provides an effective way of regenerating a catalyst on a used metal or metal plated substrate, further reducing the cost involved in replacing a metal substrate or redepositing fresh substrates before generating fresh catalyst thereon.

In some examples, the metal surface comprises a surface of a metal foil.

In other examples, the metal surface comprises a metallised surface of a substrate.

In some examples, removing any spent or residual catalyst from the metal surface comprises treating the metal surface with an etchant.

In some examples, the etchant comprises a mineral acid. In one example, the etchant includes hydrochloric acid (HCl). In some other examples, the etchant includes sulphuric acid (H_2SO_4). In some other examples, the etchant includes a combination of hydrochloric acid (HCl) and sulphuric acid (H_2SO_4).

According to another example, there is provided a catalyst fabricated by the method according to any of the examples discussed above.

According to another example, there is provided a substrate comprising thereon a catalyst fabricated according to any of the examples discussed above.

According to another example, there is provided an electrode comprising a catalyst fabricated by the method according to any of the examples discussed above.

Advantages of the present method include:

- The method can be inexpensive,
- It can be applied to a variety of metallic surfaces
- The method does not require elevated temperatures. It can be conducted at ambient temperature.
- Given that the method can largely occur on the metal surface and may not require high temperature activity, the substrate may comprise a wide variety of compositions having a suitable thin conductive metal layer thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments will now be described by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram showing embodiments of the fabrication process disclosed herein.

Figure 2 shows photographs of electroplated Ni on various substrates before and after the formation of NiFe LDH.

Figure 3 (a) is an EDS mapping image of a cross-section region of NiFe LDH formed on a Ni surface. Reference EDS mapping images of Ni, Fe and O are shown on the right.

Figure 3 (b) - (c) are SEM images of (b) Ni electroplated on a Si surface and (c) NiFe LDH formed on a Ni surface.

Figures 4 (a) - (c) are graphs showing performance comparisons between Ni electroplated Si with and without NiFe LDH catalyst: (a) Forward LSV scans at