cathode can mitigate the depletion of the metal fuel by allowing the regeneration of the metal on the anode. Cathodes that can be used for both the ORR and OER are known as bifunctional cathodes. In order to operate electrochemical cells at high efficiency, electrocatalysts may be used in the cathode to improve the kinetics for the ORR and OER. However, the catalysts required for these reactions typically contain expensive previous metals such as platinum to achieve high performance, which limits their widespread application and large scale implementation.

In addition, many of the non-noble metal catalysts show poor activity. Slow kinetics for the ORR and OER create a large overpotential, a drop in voltage before current can be drawn from the cell for discharge cycles, or an increase in the voltage required to generate oxygen for charging cycles. This overpotential reduces cell efficiency, and/or requires the use of higher catalyst loadings.

Furthermore, many of the catalysts show poor durability. The harsh chemical environment of cells (strong acid or strong base electrolytes) can cause catalyst corrosion through oxidation and/or dissolution of metals. In addition, voltage cycling experienced during charging and discharging induces migration of metal particles into the electrolyte.

As such, there is a need to provide catalysts that overcome, or at least ameliorate, one or more of the disadvantages described above.

Summary

There is provided a catalyst for a metal air battery or fuel cell comprising a mixed metal oxide consisting of at least one lanthanide element and at least two different transition metal elements.

In an aspect, there is provided a composite catalyst for a metal air battery or fuel cell comprising a mixed metal

oxide and a conducting additive, wherein the mixed metal oxide is an oxide consisting of lanthanum, cobalt and manganese and has a perovskite structure, wherein:

the conducting additive is a carbon material, and

the composite catalyst is made by a co-hydrothermal method comprising the precipitation of the mixed metal oxide in the presence of a carbon material.

The catalyst may be bifunctional such that it may be used in a cathode to improve the kinetics for the ORR and OER.

Due to the bifunctional nature of the catalyst, the depletion of the metal after prolonged usage may be circumvented by the regeneration of the metal. In addition, the use of expensive precious metals such as platinum to achieve high performance may be avoided. Due to the use of elements that are more commonly available than platinum, the cost of the catalyst may be at least ten times lower than a catalyst that contains platinum. This may lead to the widespread application of the catalyst in industries that produce electric vehicles and large-scale energy storage systems.

The catalyst may have a significantly greater OER performance and comparable ORR performance to a platinum-based catalyst. Furthermore, the catalyst may show little degradation after prolonged periods of time compared to a platinum-based catalyst, thus demonstrating good stability and durability.

Due to the low conductivity of the catalyst, the catalyst performance may be improved by incorporating additives. The catalyst may additionally comprise a conducting additive that may increase the electrical conductivity of the catalyst in a synergistic manner due to strong coupling between the mixed metal oxide and conducting additive. While the mixed metal oxide catalyzes the ORR or OER, the conducting additive may provide an electronic percolation network for the electrons that are consumed or generated during ORR and OER respectively. In addition, the conducting additive may serve as the matrix where the catalyst may be anchored. Consequently, the resultant catalyst may perform even better than a catalyst without a conducting additive.

In another aspect, there is provided an air electrode comprising the catalyst as described above.

In another aspect, there is provided a metal air battery or fuel cell comprising a catalyst as described above. Advantageously, the metal air battery or fuel cell may be

electrically rechargeable and have high capacity. In addition, the metal air battery disclosed herein may be able to perform continuously for long periods of time.

There is provided a method for forming a catalyst for a metal air battery or fuel cell comprising a mixed metal oxide consisting of at least one lanthanide element and at least two different transition metal elements, comprising:

(i) mixing a solution containing a lanthanide element with a solution containing at least two different transition metal elements;

(ii) adjusting the pH of the solution from step (i) by adding an alkaline solution;

(iii) hydrothermally treating the mixture from step (ii) to form a precipitate from the solution;

(iv) separating the precipitate from the solution;

(v) drying the precipitate until complete dryness to form a precursor; and

(vi) calcinating the precursor to form the catalyst.

In another aspect, there is provided a method for forming a composite catalyst for a metal air battery or fuel cell comprising a mixed metal oxide and a conducting additive, wherein the mixed metal oxide is an oxide consisting of lanthanum, cobalt and manganese and has a perovskite structure, wherein the conducting additive is a carbon material, the method comprising the steps of:

(i) mixing a solution containing a lanthanide element with a solution containing manganese and cobalt elements;

(ii) adjusting the pH of the solution from step (i) by adding an alkaline solution;

(iii) hydrothermally treating the mixture from step (ii) to form a precipitate from the solution in the presence of the carbon material;

(iv) separating the precipitate from the solution;

(v) drying the precipitate until complete dryness to form a precursor; and

(vi) calcinating the precursor to form the composite catalyst.

The step of calcination may lead to the formation of a single phase perovskite structure. An improved bifunctional catalytic activity with good stability and activity may be obtained due to the catalyst having a perovskite structure. Advantageously, the concentration of the metals in the solution may be varied to control the shape and morphology of the catalyst. The shape and morphology may be more uniform at lower concentrations of metals in the solution. Likewise, the pH of the solution from step (i), heating conditions in step (iii) and the calcination step may be used to control the shape and morphology of the catalyst.

In addition, the method may additionally comprise the step of adding a conducting additive after adjusting the pH of the solution. Advantageously, the method may produce catalysts with delicate morphology and structure control and intimate

contact between the mixed metal oxide and the conducting additive.

There is provided a method for forming a catalyst for a metal air battery or fuel cell comprising a mixed metal oxide consisting of at least one lanthanide element and at least two different transition metal elements, comprising:

(i) mixing a solution containing a lanthanide element with a solution containing at least two different transition metal elements;

(ii) heating the mixture from step (i) to obtain a gel;

(iii) heating the gel stepwise to form a baked gel;

(iv) grinding the baked gel to form a powder;

(v) calcinating the powder until complete dryness to form the catalyst.

There is provided a method for forming a catalyst for a metal air battery or fuel cell comprising a mixed metal oxide catalyst and a conducting additive, comprising:

(i) mixing the catalyst as mentioned above with a conducting additive in an alcoholic medium to form a slurry;

(ii) drying the slurry to form a powder; and

(iii) grinding the powder.

In another aspect, there is provided the use of a composite catalyst as defined above in an air electrode, metal air battery or fuel cell.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term "catalyst" as used herein refers to a catalyst capable of catalyzing ORR and OER. In the context of this disclosure, the catalyst comprises a mixed metal oxide consisting of at least one lanthanide element and at least two different transition metal elements. In the context of this disclosure, the catalyst is free of an alkaline earth metal.

Claims

1. A composite catalyst for a metal air battery or fuel cell comprising a mixed metal oxide and a conducting additive, wherein the mixed metal oxide is an oxide consisting of lanthanum, cobalt and manganese and has a perovskite structure, wherein:
the conducting additive is a carbon material, and
the composite catalyst is made by a co-hydrothermal method comprising the precipitation of the mixed metal oxide in the presence of a carbon material.

2. The composite catalyst according to claim 1, wherein the mixed metal oxide has the chemical formula $La(M', M'')O_{3-\delta}$.

3. The composite catalyst according to claim 2, wherein M' is cobalt and M'' is manganese.

4. The composite catalyst according to claim 2, wherein the ratio of $M':M''$ is selected from the group consisting of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9.

5. The composite catalyst according to claim 2, wherein the ratio of $La:(M'+M'')$ is 1:1.

6. The composite catalyst according to claim 1, wherein the composite catalyst has the ability to catalyze oxygen reduction and evolution reactions.

7. The composite catalyst according to claim 1, wherein the carbon material is selected from the group consisting of carbon nanotube, carbon black and graphene oxide.

8. The composite catalyst according to claim 1, wherein the co-hydrothermal method comprises the step of:

(i) mixing a solution containing a lanthanide element with a solution containing manganese and cobalt elements;

(ii) adjusting the pH of the solution from step (i) by adding an alkaline solution;

(iii) hydrothermally treating the mixture from step (ii) to form a precipitate from the solution in the presence of the carbon material;

(iv) separating the precipitate from the solution;

(v) drying the precipitate until complete dryness to form a precursor; and

(vi) calcinating the precursor to form the composite catalyst.

9. The composite catalyst according to claim 1, wherein the carbon material is selected from the group consisting of carbon nanotube and N-doped reduced graphene oxide (NrGO).

10. An air electrode comprising a composite catalyst according to claim 1.

11. A metal air battery or fuel cell comprising a composite catalyst according to claim 1.

12. A method for forming a composite catalyst for a metal air battery or fuel cell comprising a mixed metal oxide and a conducting additive, wherein the mixed metal oxide is an oxide consisting of lanthanum, cobalt and manganese and has a perovskite structure, wherein the conducting additive is a carbon material, the method comprising the steps of:

(i) mixing a solution containing a lanthanide element with a solution containing manganese and cobalt elements;

(ii) adjusting the pH of the solution from step (i) by adding an alkaline solution;

(iii) hydrothermally treating the mixture from step (ii) to form a precipitate from the solution in the presence of the carbon material;

(iv) separating the precipitate from the solution;

(v) drying the precipitate until complete dryness to form a precursor; and

(vi) calcinating the precursor to form the composite catalyst.

13. The method according to claim 12, wherein the hydrothermal treating is carried out at a temperature of 100°C to 200°C.

14. The method according to claim 12, wherein the drying of the precipitate is carried out at a temperature of 50°C to 100°C or freeze dried for 3 days.

15. The method according to claim 12, wherein the calcination is performed in the temperature range of 700°C to 1000°C.

16. The method according to claim 12, wherein calcination leads to formation of the composite catalyst having the perovskite structure.

17. The method according to claim 12, additionally comprising the step of adding a conducting additive after adjusting the pH of the solution.

18. The method according to claim 12, further comprising the steps of:

(i) mixing the composite catalyst with an alcoholic medium to form a slurry;

(ii) drying the slurry to form a powder; and

(iii) grinding the powder.

19. The use of a composite catalyst of claim 1 in an air electrode, metal air battery or fuel cell.