A method for preparing a metal-doped ruthenium oxide material by heating a mixture of a doping metal and a source of ruthenium under an inert atmosphere. In some embodiments, the doping metal is in the form of iridium black or lead powder, and the source of ruthenium is a powdered ruthenium oxide. An iridium-doped or lead-doped ruthenium oxide material can perform as an oxygen evolution catalyst and can be fabricated into electrodes for electrolysis cells.

20 Claims, 3 Drawing Sheets
Electrolyzer Performance Comparison, Nafion 115, 70°C

FIG. 2
FIG. 3

$E$ vs. NHE (Volts)

$I$ (Amps/cm$^2$)

- Comm IrO$_2$-2H$_2$O
- Pb(25%)-d-RuO$_2$
- Pb(7.5%)-d-RuO$_2$
prising a doping metal and a source of ruthenium, and heating rapidly with use resulting in loss of performance of the PEM material. It has previously been reported that a catalyst based on a non-stoichiometric ruthenium oxide enhances the electrolysis of water (5). Also iridium ruthenium oxide catalysts can enhance the production of oxygen gas at the anode. A desirable oxygen evolution catalyst is also provided, as is a membrane electrode assembly or an electrolysis cell comprising the electrode. Included in various embodiments is an electrolysis cell comprising the membrane electrode assembly.

In a further aspect, another method of making a metal-doped material is provided. The method includes preparing a mixture comprising ruthenium oxide and a doping metal selected from the group consisting of Ir and Pb, and heating the mixture in an inert atmosphere such that an iridium-doped or lead-doped ruthenium oxide oxygen evolution catalyst is produced. In some embodiments of the method, both the doping metal and the ruthenium oxide are in powder form, and the heating is performed at a temperature below the sintering temperatures of both powders. In such embodiments, the iridium can be in the form of iridium black, and the lead can be in the form of lead powder. In embodiments of the method, including but not limited to embodiments where the doping metal is in powder form and embodiments that include ruthenium oxide, the ruthenium oxide oxygen evolution catalyst is at least partially oxidized by the ruthenium oxide so as to produce the metal-doped ruthenium oxide material. In embodiments of the method, including but not limited to embodiments involving oxygen evolution catalysts, embodiments where the doping metal and the ruthenium source are in powder form, and embodiments where the doping metal is at least partially oxidized, the doping metal can be Ir or Pb. In embodiments of the method, including but not limited to embodiments involving oxygen evolution catalysts, embodiments where the doping metal and the ruthenium source are in powder form, embodiments where the doping metal is at least partially oxidized, and embodiments where the doping metal is Ir or Pb, the metal-doped ruthenium oxide material can be represented as MOₓRuO_{2-0.05} where M is the doping metal and X is about 0.05, and/or can comprise about 5 to about 25 atomic % of the doping metal.

In another aspect, a metal-doped ruthenium oxide material prepared by any of the methods described in the preceding paragraph is provided. An electrode comprising the metal-doped ruthenium oxide material is also provided, as is a membrane electrode assembly or an electrolysis cell comprising the electrode. Included in various embodiments is an electrolysis cell comprising the membrane electrode assembly.

For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying drawing, in which:
performs as an oxygen evolution catalyst, the catalyst can be particularly about 9 to about 12 atomic % of the doping metal. Particularly about 5 to about 18 atomic %, and even more represented as MO \_x RuO \_2, where M is the doping metal and X is about 0.05. Also, the metal-doped ruthenium oxide material, including material performing as oxygen evolution catalysts, can comprise about 5 to about 25 atomic %, more particularly about 5 to about 18 atomic %, and even more particularly about 9 to about 12 atomic % of the doping metal.

In embodiments where the metal-doped ruthenium oxide performs as an oxygen evolution catalyst, the catalyst can be fabricated into an electrode by taking the catalyst and mixing it with binder to form an ink. The catalyst ink is then deposited onto a proton exchange membrane and hot pressed to form the electrode.

The electrode can be electrochemically evaluated in a three-electrode cell or in a PEM-based membrane-electrode assembly (MEA). For example, referring to FIG. 1, an electrolysis cell 2 can contains a MEA 4 comprising a metal-doped ruthenium oxide anode 6, a platinum cathode 8, and a PEM 10. The electrolysis cell 2 is connected to a power supply or potentialstat 12 and can include a reference electrode (not shown) of mercury-mercury sulfate. In this embodiment, the electrolyte can be 1 N H\_2SO\_4.

The catalyst can be subject to various electrochemical performance tests, including current-voltage and constant-current characterization in a PEM electrolysis cell as well as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a three-electrode cell. For example, current-voltage and constant-current characterization of the catalyst can be carried out by fabricating an electrolysis MEA with the given catalyst as described above, and then testing the MEA in an electrolysis test system. In this case, a power supply is used to power the cell. In one case, the power supply steps through increasing current settings. As the current is increased, the cell voltage increases. The test is terminated when a maximum set voltage is reached. In the case of potentiodynamic and EIS studies, an electrode with the given catalyst is fabricated similar to that described above. The electrode (referred to as the working electrode) is then inserted into the three-electrode cell. Potentiodynamic studies are used to characterize the electrode performance in a similar way to the current-voltage characterization of the electrolysis cell. EIS can be used to characterize electrode performance and to determine catalyst stability.

The methods of the present invention provide a stabilized ruthenium oxide oxygen evolution catalyst. Although not wishing to be bound by any hypothesis, the inventors’ general approach to the stabilization of ruthenium was guided by the hypothesis that ruthenium in the oxidation state III would be stabilized (prevented from being re-oxidized to state IV) when combined with materials that are both stable and have a strong propensity to stay oxidized, particularly in an acidic environment at oxygen evolution potentials.

The present invention may be better understood by referring to the accompanying examples, which are intended for illustration purposes only and should not in any sense be construed as limiting the scope of the invention as defined in the claims appended hereto.

**EXAMPLE 1**

Iridium-Doped Ruthenium Oxide

Iridium black and anhydrous ruthenium oxide were chosen as the starting materials. The objective was to dope ruthenium oxide with minimal amounts of iridium; ratios in the range of 5-18 atomic % iridium-doped ruthenium oxides were fabricated. The starting materials were weighed out and mixed by hand using a mortar and pestle. The ground up materials were then heat treated in a furnace at 300°C. for a minimum of 14 hours under flowing argon. The 300°C. temperature was chosen as it is approximately the creep temperature of ruthenium oxide and below the sintering temperature of both materials. The novel oxygen evolution catalyst was fabricated under flowing argon to allow iridium to preferentially react with oxygen from the ruthenium oxide versus oxygen from the environment. The iridium-doped ruthenium oxide catalyst was then fabricated into a PEM-based MEA. The MEA was assembled into a test cell and characterized for electrochemical performance in comparison to a commercially available iridium-ruthenium oxide catalyst.

As shown in FIG. 2, the iridium-doped ruthenium oxide catalyst outperformed the commercially available iridium-ruthenium oxide catalyst. In the region of interest, 200-mA/cm\(^2\), the iridium-doped ruthenium oxide catalyst can operate at an efficiency of 85%, 2% greater than the commercially available catalyst. An electrolyzer system fabricated from MEA with the iridium-doped ruthenium oxide catalyst can
sustain electrolysis at twice the current density and at the same efficiency of commercial catalyst in the range of 100 to 200-mA/cm².

EXAMPLE 2

Lead-Doped Ruthenium Oxide

200 mesh lead powder and anhydrous ruthenium oxide were chosen as the starting materials. The objective was to dope ruthenium oxide with minimal amounts of lead. Two compositions of lead-doped ruthenium oxide were fabricated with 7.5 and 25 atomic percent lead. The starting materials were weighed out and mixed by hand using a mortar and pestle. The ground up materials were then heat treated in a furnace at 300°C for a minimum of 18 hours under flowing argon. The 300°C temperature was chosen as it is approximately the creep temperature of ruthenium oxide and below the sintering temperature of both materials. The novel oxygen evolution catalyst was fabricated under flowing argon to allow the lead powder to preferentially react with oxygen from the ruthenium oxide versus oxygen from the environment. The lead-doped ruthenium oxide catalyst was then fabricated into an electrode and electrochemically evaluated in a three-electrode cell.

To characterize the performance of the lead-doped ruthenium oxide catalyst three different electrodes were prepared. Electrodes were fabricated from the 7.5 and 25 mole % lead-doped ruthenium oxide and a standard of commercially available hydrous iridium oxide. As shown in the FIG. 3, the lead-doped ruthenium oxide catalyst can outperform commercially available hydrous iridium oxide at current densities lower than 18-mA/cm². This performance is comparable to the highest performing oxygen evolution catalyst.

REFERENCES

The following publications are incorporated by reference herein:


Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be utilized without departing from the principles and scope of the invention, as those skilled in the art will readily understand. Accordingly, such modifications may be practiced within the scope of the following claims.

What is claimed is:

1. A method of making a metal-doped material, comprising:
   a) preparing a mixture comprising a doping metal and a source of ruthenium; and
   b) heating the mixture in an inert atmosphere such that a metal-doped ruthenium oxide material is produced;

3. The method of claim 1, wherein both the doping metal and the source of ruthenium are in powder form, and the heating is performed at a temperature below the sintering temperatures of both powders.

4. The method of claim 1, wherein the source of ruthenium is ruthenium oxide.

5. The method of claim 4, wherein the heating is performed such that the doping metal is at least partially oxidized by the ruthenium oxide so as to produce the metal-doped ruthenium oxide material.

6. The method of claim 1, wherein the doping metal is Ir or Pb.

7. The method of claim 1, wherein the metal-doped ruthenium oxide material is represented as MO₉RuOₓ₊₂₋ₓ, wherein M is the doping metal and X is about 0.05.

8. The method of claim 1, wherein the metal-doped ruthenium oxide material comprises about 5 to about 25 atomic % of the doping metal.


10. An electrode comprising the metal-doped ruthenium oxide material of claim 9.

11. A membrane electrode assembly or an electrolysis cell comprising the electrode of claim 10.

12. A method of making a metal-doped material, comprising:
   a) preparing a mixture comprising ruthenium oxide and a doping metal selected from the group consisting of Ir and Pb; and
   b) heating the mixture in an inert atmosphere such that an iridium-doped or lead-doped ruthenium oxide oxygen evolution catalyst is produced;

13. The method of claim 12, wherein both the doping metal and the ruthenium oxide are in powder form, and the heating is performed at a temperature below the sintering temperatures of both powders.

14. The method of claim 13, wherein the iridium is in the form of iridium black, and the lead is in the form of lead powder.

15. The method of claim 12, wherein the heating is performed such that the doping metal is at least partially oxidized by the ruthenium oxide so as to produce the oxygen evolution catalyst.

16. The method of claim 12, wherein the ruthenium oxide oxygen evolution catalyst is represented as MO₉RuOₓ₊₂₋ₓ, wherein M is the doping metal and X is about 0.05.

17. The method of claim 12, wherein the ruthenium oxide oxygen evolution catalyst comprises about 5-25 atomic % of the doping metal.
18. A ruthenium oxide oxygen evolution catalyst prepared by the method of claim 12.

19. An electrode comprising the ruthenium oxide oxygen evolution catalyst of claim 18.

20. A membrane electrode assembly or an electrolysis cell comprising the electrode of claim 19.

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