CATALYSTS HAVING MIXED METAL OXIDES

Applicant: Wisconsin Alumni Research Foundation, (US)
Inventors: Shannon S. Stahl, Madison, WI (US);
           James B. Gerken, Madison, WI (US);
           Jamie Y. Chen, Madison, WI (US);
           Robert C. Massé, Sheboygan, WI (US);
           Sarah E. Shaner, Madison, WI (US);
           Nicholas J. Porubsky, Madison, WI (US)
Assignee: Wisconsin Alumni Research Foundation, Madison, WI (US)

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ABSTRACT

Disclosed are methods for generating oxygen via an electrolysis reaction. One places an anode and a cathode in aqueous solution, and uses an external source of electricity to drive the electrolysis reaction from the anode and cathode. The anode has at least three metal oxides, preferably with nickel oxide or cobalt oxide as at least one of the oxides. Also disclosed are electrodes designed for catalyzing oxygen consumption or formation reactions, where the electrodes have a mix of such three metal oxides.
FIG. 1
<table>
<thead>
<tr>
<th>METAL-ION TRIOADS TESTED (M1-M2-M3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Al-Fe</td>
</tr>
<tr>
<td>Co-Al-Ni</td>
</tr>
<tr>
<td>Co-Fe-Ni</td>
</tr>
<tr>
<td>Co-Fe-Mn</td>
</tr>
<tr>
<td>Co-Fe-Cr</td>
</tr>
<tr>
<td>Co-La-Fe</td>
</tr>
<tr>
<td>Co-Ce-Fe</td>
</tr>
</tbody>
</table>

**FIG. 2b**

```
M1
1
2 —— 3
4 —— 5 —— 6
7 —— 8 —— 9 —— 10
11 —— 12 —— 13 —— 14 —— 15
16 —— 17 —— 18 —— 19 —— 20 —— 21
M2
M3
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**FIG. 2c**

```
R 1 2 3 4 5 6 7
8 9 10 11 12 13 14 R
R 15 16 17 18 19 20 21

R=REFERENCE OXIDE
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**FIG. 2d**
CATALYSTS HAVING MIXED METAL OXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority based on U.S. provisional No. 61/598,377, which was filed Feb. 14, 2012.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH/DEVELOPMENT

[0002] This invention was made with government support under 0802907 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to electrocatalysts. More particularly, it relates to electrodes comprising a mix of at least three metal oxides, and their use for catalyzing oxygen gas related reactions (especially their use as anodes in water electrolysis to generate oxygen or their use as cathodes to facilitate consuming oxygen in a fuel cell).

[0004] Developing effective catalysts is important in rendering the storage of renewable energy practical. If (for example) solar or wind generated energy can be efficiently stored as hydrogen gas generated by water oxidation, this has the potential for reducing dependence upon fossil fuels.

[0005] FIG. 1 schematically depicts a prior art water electrolysis system. A container stores an aqueous solution. An anode and a cathode are positioned in a water-based electrolyte solution and then linked to a current source (not shown). A diaphragm isolates gases that are developed by splitting water into its constituent elements.

[0006] This reaction involves transfer of four protons and four electrons with the formation of each oxygen-oxygen bond. In the past, a substantial amount of energy to drive that reaction had been required over the theoretical minimums required (the “overpotential”). Efforts were therefore made to try to reduce the amount of overpotential needed to drive the reaction by using specialized catalytic anodes.

[0007] Such anodes need to be able to withstand strongly oxidizing aqueous conditions to be practical over prolonged periods. Also, it is desirable that they be composed of relatively inexpensive earth-abundant elements (to reduce costs and minimize environmental concerns) and that they be able to operate under a range of pH conditions (especially strongly basic conditions). However, it has proved challenging to develop such catalysts which are not susceptible to oxidative or hydrolytic degradation, don’t require expensive precious metals, and also don’t require high overpotentials.


[0009] The search for further improved mixed metal oxide anodes for oxygen formation or consumption reactions was made difficult by the fact that the number of possible combinations of cations in more complex oxide mixtures far exceeds the number that are practical to sequentially individually synthesize and test. Adding further complexity is the fact that performance may vary over various pH conditions of interest.

[0010] There have been attempts to use a test system where a single mixed-oxide material would act simultaneously in photovoltaic light-harvesting and electrocatalytic water-splitting. So far, few high performing anodic catalysts have been identified with this method. An approach tried to study a number of candidate catalysts simultaneously together in an array. However, this approach typically assumed that the tested material would be a photovoltaic electrocatalyst. It therefore suffered because it did not investigate catalysis independent of light harvesting.

[0011] Yet another approach involved using scanning electrochemical microscopy as a means of evaluating potential catalysts. However, this required expensive oxygen-selective microelectrodes that were slowly scanned across the anode surface, and also suffered from inaccuracies.

[0012] Apart from uses of these mixed metal materials as anodes there is also some interest in developing cathodes capable of more efficiently catalyzing oxygen consumption in fuel cells.

[0013] Further, the art has developed a variety of mixed metal oxide catalysts for a variety of unrelated applications (e.g. production of aluminum as described in U.S. Pat. No. 7,033,469). However, there is still a need for improved electrodes configured to be suitable for use in catalyzing oxygen gas formation or consumption reactions.

SUMMARY OF THE INVENTION

[0014] We developed a combinatorial fluorescence based photoassay to more efficiently screen catalyst candidates based on direct detection of evolved oxygen in a water-oxygen reaction. We used the assay to screen ternary mixed metal oxide combinations. We then discovered the value of certain ternary mixed oxides for oxygen production and/or consumption reactions, particularly where at least one oxide is nickel oxide or cobalt oxide.
Our catalysts are well suited to generate oxygen via an electrolysis reaction. One can place an anode of the present invention, and a conventional cathode, in aqueous solution, and using an external source of electricity drives the electrolysis reaction from the anode and cathode. The anode has at least three metal oxides selected from the group consisting of:

(a) nickel oxide or cobalt oxide as one oxide, aluminum oxide or gallium oxide as a second oxide, and iron oxide or chromium oxide as a third oxide;
(b) nickel oxide, iron oxide, and a third oxide selected from the group consisting of barium oxide, cerium oxide, calcium oxide, strontium oxide, gallium oxide, magnesia oxide and strontium oxide;
(c) nickel oxide, cobalt oxide, and a third oxide selected from the group consisting of barium oxide, calcium oxide, chromium oxide, chromium oxide and zinc oxide;
(d) nickel oxide, chromium oxide, and a third oxide selected from the group consisting of aluminum oxide, titanium oxide and zinc oxide;
(e) nickel oxide, calcium oxide, and a third oxide selected from the group consisting of aluminum oxide, strontium oxide and barium oxide; and
(f) cobalt oxide, aluminum oxide, and a third oxide selected from the group consisting of barium oxide and bismuth oxide.

A particularly preferred form is where a metal oxide portion of the electrode has at least 5% aluminum oxide or gallium oxide by weight, at least 5% of cobalt oxide and/or nickel oxide by weight, and at least 5% of iron oxide and/or chromium oxide by weight.

In our most preferred electrolysis reactions hydrogen is generated at the cathode, and oxygen is generated at an anode of the present invention. Resulting collected hydrogen can be stored and used for future energy needs (e.g. in an automobile that consumes hydrogen), and resulting collected oxygen can be used for one of many varied purposes (e.g. steelmaking).

These electrodes are believed to also have utility for other electrocatalytic purposes besides just water electrolysis. For example, they could form part of the cathode structure in an oxygen fuel cell system.

Our mixed oxide catalysts can preferably be prepared by taking water soluble salts of the metals, typically presented as the nitrate, and dissolving them separately in a solvent of 9% aqueous glycerol. The resulting solutions, preferably at a metal ion concentration of about 5 mM, are blended to produce the desired ratio of metals in the final catalyst. The blended solution is placed on an electrode, such as indium-tin oxide, and allowed to evaporate to dryness, leaving a solid deposit. This deposit, having a metal concentration of 0.05-0.1 μMol/cm², is then calcined. Note that we prefer to use the nitrate salt in this process as it tends to quickly decompose to the desired oxide in air.

In one approach mixed-metal catalyst arrays can be prepared from 5 mM aqueous solutions of metal salt precursors. These solutions were prepared using purified water (18.2 MQ cm⁻³) containing 9 vol% glycerol. The nitrate salts can then be added, except that where Mo, Ti, W, and/or V are additional additives we prefer to use (NH₄)₂MoO₄, (NH₄)₂WO₄, NH₄H2TiO3, NH₄H₂W₂O₇, NH₂H₂O, and NH₂VO₃. Nitric acid can also be added to the solutions of Fe, Bi, and Ti to prevent precipitation upon mixing with other metal salt solutions.

For each catalyst composition, the relevant metal solutions were mixed in the desired ratios, and 1 μL of the resulting solution was deposited on an FTO-coated glass electrode. The electrode, coated with numerous catalyst compositions, is then heated to 500° C. for 3 h to calcine the deposits into the corresponding metal oxides. The O₂-sensing fluoresceine-quenching assay was performed on these electrodes containing the catalyst arrays.

Particularly preferred metal oxides have metal content ratios as follows: NiₓAlₓFeₓO₃-x, NiₓAlₓFeₓO₃-x, and CoₓAlₓFeₓO₃-x. One selected Al—Fe—Ni oxide catalyst was found to operate at Δη = -135 mV @ 10 mAV/cm² relative to a competitive cobalt oxide anode.

Water electrolysis reactions can be conducted in a large scale production facility, or can be conducted in a residential size generation system. Using the latter approach homeowners could, for example, use energy generated by their own solar cells or wind turbine to create a way of refueling their automobiles.

It will be appreciated that the metal salts we most prefer to use in our ternary mixes are available in relatively high quantities, at relatively low cost. This is an important factor in making such fuel generation systems more commercially practical.

Our testing to date indicates that our anodes are likely to reduce overpotentials significantly for a variety of applications.

The above and still other advantages of the present invention will be apparent from the description that follows. It should be appreciated that the following description is merely of preferred embodiments of the invention. The claims should therefore be looked to in order to understand the full claimed scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically depicts a system for conducting electrolysis of water;
FIG. 2a depicts equipment for conducting our preferred screening assays;
FIG. 2b is a table of representative sets of metal oxide combinations that we tested;
FIG. 2c depicts how our assay system’s results can be displayed (with corners of the triangle representing pure single metal oxide); and
FIG. 2d represents how representative compounds can be positioned on an FTO plate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

We developed the FIG. 2 apparatus having an anode with an array of varied mixes of metal oxide compositions, an electrolyte bath, and an optical system for detecting oxygen evolution. As the anode was brought to overpotential, different points in the array had varied oxygen production rates.

To measure which oxide mixtures had which oxygen production, we use a mesh coated with an oxygen-sensitive paint (Binary Unicoat Pressure Sensitive Paint available from Innovative Science Solution), held parallel to the anode at a small distance from it. The mesh fluoresced green in the presence of, or both red and green in the absence of, oxygen. The emitted light was detected by a camera. Sequential images of the mesh were processed to determine the magnitude of the shift in fluorescence over a given spot in the array.
These images were calibrated by co-observation of reference regions of known electrocatalytic activity in the array. [0040] As represented by the depictions in FIGS. 2b and 2c, we elected to study representative ternary mixtures A{sub 1}(100%+p) B{sub q}(r) C{sub o}, where p and q are varied in steps of 20% from 0 to 100% and m freely varies to fit the oxidation states of the cations in the catalyst resting state. This allowed us to screen a triad representative of a wide range of mixtures of these oxides, in a single array. We interposed Co{sub o}Fe{sub p}Ni{sub r} oxide spots for calibration and reference.

[0041] As shown in FIG. 2d, arrays were formed on fluoro-tin oxide-coated glass by pipette deposition of mixtures of solutions of the corresponding metal salts (e.g. 5 mM in 9% aqueous glycerol nitrate) with subsequent calcination in air at 500°C for 6 hours to form the mixed oxide.

[0042] With respect to the FIG. 2b experiments, screens were performed on 589 triads for a total of 2624 three-metal combinations (11302 unique compositions). Following calcination, the arrays were electrolyzed at 670 mV vs. Ag/AgCl (openpotential=416 mV), or subjected to a constant current of 5 mA, for 60 minutes to bring the oxides to steady-state catalytic conditions.

[0043] Subsequent catalytic O{sub 2} evolution measurement were performed by electrolysis of the array at 670 mV vs. Ag/AgCl in argon purged 0.1 M NaOH. As one example, for a Co—Al—Ni triad, an optimum around Co{sub 0.25}Al{sub 0.25}Ni{sub 0.5}O{sub 2} was found. However, it displayed only moderately greener activity than the reference spots or the well known catalysts of pure cobalt or nickel oxide.

[0044] Additional assays were performed on other triads. While most triads did not yield results of significant interest, certain anodes were an exception, particularly where cobalt oxide and/or nickel oxide was included with at least two other metal oxides. For example, particularly advantageous results were achieved when aluminum oxide and/or gallium oxide was also included, and a third oxide such as iron oxide and/or chromium oxide was included. In this regard, we identified Ni{sub 0.25}Al{sub 0.25}Fe{sub 0.25}, Ni{sub 0.4}Al{sub 0.6}Fe{sub 2.0} and Co{sub 0.6}Al{sub 0.4}Fe{sub 2.0} as having excellent levels of performance in oxygen formation reactions. Mixtures identified as particularly promising from the screening were reproduced individually and subjected to steady-state Tafel plot analysis (evaluating the effect of current versus overpotential).

[0045] Prolonged electrolysis of one highly active composition (Ni{sub 0.4}Al{sub 0.6}Fe{sub 2.0}) was performed, and stable current densities higher than a similarly prepared nickel oxide catalyst were observed once steady-state was achieved.

[0046] Our screening assay can also be used to optimize anodes for various pH conditions. Operation at above pH 12 (e.g. at about pH 13) is the likely most desired general operational pH, albeit we also expect that a variety of other alkaline pH conditions will be of interest for various applications and mixes.

[0047] It will be appreciated from our laboratory’s recent article (J. Gerken et al., Development Of An O{sub 2}-Sensitive Fluorescence-Quenching Assay For The Combinatorial Discovery Of Electrocatals For Water Oxidation, 51 Angew. Chem. Int. Ed. 6676-6680 (May 24, 2012), that we propose use of reversible fluorescence-quenching of a commercially available dual-chromophore O{sub 2}-sensitive paint to detect electrocatalytic oxygen evolution in a way that allows us to screen candidates from an extremely large number of possible ternary compositions. Through spatially resolved photographic O{sub 2}-sensing, the relative activities of a large array of potential catalysts were determined simultaneously and normalized to an internal standard.

[0048] While a number of preferred embodiments of the present invention have been described above, the present invention is not limited to just these disclosed examples. For example, use of still other proportions of oxides is intended to be within the claims, as is the possibility of also including additional types of metal oxides (e.g. molybdenum or chromium in minor amounts). There are other modifications that are meant to be within the scope of the invention and claims. Thus, the claims should be looked to in order to judge the full scope of the invention.

INDUSTRIAL APPLICABILITY

[0049] The present invention provides improved electrodes, such as anodes useful in water hydrolysis reactions to generate oxygen or as cathodes to consume oxygen in a fuel cell.

We claim:
1. A method for generating oxygen via an electrolysis reaction, comprising:
   placing an anode and a cathode in aqueous solution; and
   using an external source of electricity to drive the electrolysis reaction from the anode and cathode;
   wherein the anode comprises at least three metal oxides selected from the group consisting of:
   (a) nickel oxide or cobalt oxide as a first oxide, and/or oxide or chromium oxide as a second oxide, and iron oxide as a third oxide;
   (b) nickel oxide, iron oxide, and a third oxide selected from the group consisting of barium oxide, cerium oxide, calcium oxide, gallium oxide, magnesium oxide and strontium oxide;
   (c) nickel oxide, cobalt oxide, and a third oxide selected from the group consisting of barium oxide, calcium oxide, chromium oxide, strontium oxide and zinc oxide;
   (d) nickel oxide, chromium oxide, and a third oxide selected from the group consisting of aluminum oxide, titanium oxide and zinc oxide;
   (e) nickel oxide, calcium oxide, and a third oxide selected from the group consisting of aluminum oxide, chromium oxide and calcium oxide;
   (f) cobalt oxide, aluminum oxide, and a third oxide selected from the group consisting of barium oxide and bismuth oxide;
   whereby oxygen is generated.

2. The method of claim 1, wherein the anode comprises aluminum oxide and iron oxide.

3. The method of claim 1, wherein a metal oxide portion of the anode comprises at least 5% or weight of aluminum oxide and/or gallium oxide, at least 5% by weight of iron oxide and/or chromiun oxide, and at least 5% by weight of cobalt oxide and/or nickel oxide.

4. The method of claim 1, wherein hydrogen is generated at the cathode, and oxygen is generated at the anode.

5. The method of claim 1, wherein the aqueous solution is alkaline.

6. An electrode configured for catalyzing oxygen gas formation or consumption, the electrode comprising at least three metal oxides selected from the group consisting of:
   (a) nickel oxide or cobalt oxide as a first oxide, and/or oxide or chromiun oxide as a second oxide, and iron oxide or chromium oxide as a third oxide;
(b) nickel oxide, iron oxide, and a third oxide selected from the group consisting of barium oxide, cerium oxide, calcium oxide, gallium oxide, magnesium oxide and strontium oxide;
(c) nickel oxide, cobalt oxide, and a third oxide selected from the group consisting of barium oxide, calcium oxide, chromium oxide, strontium oxide and zinc oxide;
(d) nickel oxide, chromium oxide, and a third oxide selected from the group consisting of aluminum oxide, titanium oxide and zinc oxide;
(e) nickel oxide, calcium oxide, and a third oxide selected from the group consisting of aluminum oxide, strontium oxide and barium oxide; and
(f) cobalt oxide, aluminum oxide, and a third oxide selected from the group consisting of barium oxide and bismuth oxide.
7. The electrode of claim 6, wherein the electrode comprises aluminum oxide and iron oxide.
8. The electrode of claim 6, wherein a metal oxide portion of the electrode comprises at least 5% by weight of aluminum oxide and/or gallium oxide, at least 5% by weight of iron oxide and/or chromium oxide, and at least 5% by weight of cobalt oxide and/or nickel oxide.
9. The electrode of claim 6, wherein at least one of the oxides was formed from a nitrate salt subjected to calcination.