(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 August 2013 (22.08.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/122693 A1

(51) International Patent Classification:
C25B 11/04 (2006.01) *C25B 1/04* (2006.01)

(21) International Application Number:
PCT/US2013/020603

(22) International Filing Date:
8 January 2013 (08.01.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/598,377 14 February 2012 (14.02.2012) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

[Continued on next page]

(54) Title: ELECTROCATALYSTS HAVING MIXED METAL OXIDES

(57) 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.

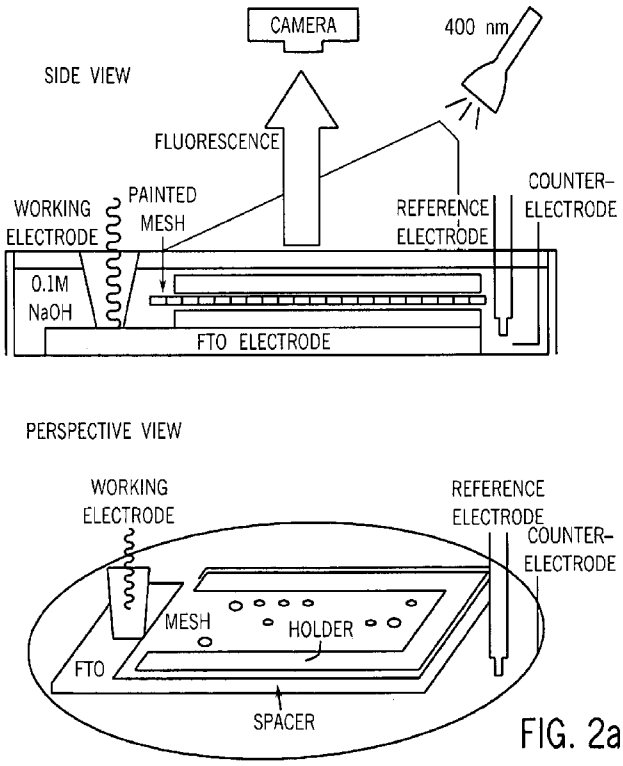

FIG. 2a

WO 2013/122693 A1

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

ELECTROCATALYSTS 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 February 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 2 stores an aqueous solution. An anode 4 and a cathode 6 are positioned in a water based electrolyte solution 3 and then linked to a current source (not shown). A diaphragm 8 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.

[0008] Some mixed metal oxide catalytic anodes have been tried in well-defined stoichiometry (e.g. $NiCo_2O_4$). Also, some nonstoichiometric mixed oxides have been studied. See E. Potvin, et al., Electrocatalytic Activity Of Ni-Fe Anodes For Alkaline Water Electrolysis, 31 Mat. Chem. & Phys. 311-318 (1992); K. Fatih, et al., $Cu_xCo_{3-x}O_4/LaPO_4$-bonded Ni Electrodes For Oxygen Evolution In Alkaline Solution: Preparation, Physicochemical Properties, And Electrochemical Behavior, 75 Can. J. Chem. 1597-1607 (1997); M. I. Godinho, et al., Effect Of The Partial Replacement Of Fe By Ni And/or Mn On The Electrocatalytic Activity For Oxygen Evolution Of The $CoFe_2O_4$ Spinel Oxide Electrode, 47 Electrochim. Acta 4307-4314 (2002); R. N. Singh, et al., Electrocatalytic Properties Of New Active Ternary Ferrite Film Anodes For O_2 Evolution In Alkaline Medium, 47 Electrochim. Acta 3873-3879 (2002); A. Kahoul et al., Electrocatalytic Activity And Stability Of $La_{1-x}Ca_xCoO_3$ Perovskite-type

Oxides In Alkaline Medium, 89 Catal. Today 287-291 (2004); R. Singh, et al., Effect Of Partial Substitution Of Cr On Electrocatalytic Properties Of $MnFe_2O_4$ Towards O_2-Evolution In Alkaline Medium, 31 Int. J. Hydrogen Energy 1372-1378 (2006); F. Méndez-Martínez et al., $Zn_{x-1}Cu_xMn_2O_4$ Spinels; Synthesis, Structural Characterization And Electrical Evaluation, 54 J. Mex. Chem. Soc. 2-6 (2010); M. Kumar et al., New Ternary Fe, Co, And Mo Mixed Oxide Electrocatalysts For Oxygen Evolution, 36 International Journal Of Hydrogen Energy 8831-8838 (2011); R. Singh et al., New $NiFe_{2-x}Cr_xO_4$ Spinel Films For O_2 Evolution In Alkaline Solutions, 51 Electrochimica Acta 5515-5523 (2006); M. Kumar et al., New Ternary Mixed Oxides Of Fe, Ni And Mo For Enhanced Oxygen Evolution, 36 International Journal Of Hydrogen Energy 12968-12705 (2011). However, these mixed metal oxide catalysts, when applied to oxygen formation or consumption reactions, suffered from one or more deficiencies.

[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. patent 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.

[0015] 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:

[0016] (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;

[0017] (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;

[0018] (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;

[0019] (d) nickel oxide, chromium oxide, and a third oxide selected from the group consisting of aluminum oxide, titanium oxide and zinc oxide;

[0020] (e) nickel oxide, calcium oxide, and a third oxide selected from the group consisting of aluminum oxide, strontium oxide and barium oxide; and

[0021] (f) cobalt oxide, aluminum oxide, and a third oxide selected from the group consisting of barium oxide and bismuth oxide.

[0022] 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.

[0023] 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).

[0024] 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.

[0025] 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/cm^2, 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.

[0026] 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 MΩ cm^{-1}) 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 $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$, $Ti(OEt)_4$, $(NH_4)_{10}W_{12}O_{41}\bullet 5H_2O$, and NH_4VO_3. Nitric acid can also be added to the solutions of Fe, Bi, and Ti to prevent precipitation upon mixing with other metal salt solutions.

[0027] For each catalyst composition, the relevant metal solutions were mixed in the desired ratios, and 1μL of the resulting solution was deposited on an FTO-coated glass electrode. The electrode, decorated with numerous catalyst compositions, is then heated to 500 °C for 6 h to calcine the deposits into the corresponding metal

oxides. The O_2-sensitive fluorescence-quenching assay was performed on these electrodes containing the catalyst arrays.

[0028] Particularly preferred metal oxides have metal content ratios as follows: $Ni_{60}Al_{20}Fe_{20}$, $Ni_{40}Al_{40}Fe_{20}$ and $Co_{60}Al_{20}Fe_{20}$. One selected Al-Fe-Ni oxide catalyst was found to operate at $\Delta\eta$ = -135 mV @ 10mA/cm^2 relative to a competitive cobalt oxide anode.

[0029] 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.

[0030] 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.

[0031] Our testing to date indicates that our anodes are likely to reduce overpotentials significantly for a variety of applications.

[0032] 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 our invention. The claims should therefore be looked to in order to understand the full claimed scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] FIG. 1 schematically depicts a system for conducting electrolysis of water;

[0034] FIG. 2a depicts equipment for conducting our preferred screening assays;

[0035] FIG. 2b is a table of representative sets of metal oxide combinations that we tested;

[0036] FIG. 2c depicts how our assay system's results can be displayed (with corners of the triangle representing pure single metal oxide); and

[0037] FIG. 2d represents how representative compounds can be positioned on an FTO plate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0038] 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.

[0039] 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 $A_{(100\ \% - p)}\ B_{(p-q)}\ C_q\ O_m$, 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 mixes of these oxides,

in a single array. We interposed $Co_{40}Fe_{40}Ni_{20}$ oxide spots for calibration and reference.

[0041] As shown in FIG. 2d arrays were formed on fluorine-tin oxide-coated glass by pipette deposition of mixtures of solutions of the corresponding metal salts (e.g. 5mM 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 (11,302 unique compositions). Following calcination, the arrays were electrolyzed at 670 mV vs. Ag/AgCl (overpotential = 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_2 evolution measurements were performed by electrolysis of the array at 670 mV v. Ag/AgCl in argon purged 0.1 M NaOH. As one example, for a Co-Al-Ni triad, an optimum around $Co_{20}Al_{20}Ni_{60}O_x$ was found. However, it displayed only moderately greater 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 $Ni_{60}Al_{20}Fe_{20}$, $Ni_{40}Al_{40}Fe_{20}$ and $Co_{60}Al_{20}Fe_{20}$ 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 ($Ni_{40}Al_{40}Fe_{20}$) 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_2-Sensitive Fluorescence-Quenching Assay For The Combinatorial Discovery Of Electrocatalysts 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_2-sensitive paint to detect electrocatalytic oxygen evolution in a way that allowed us to screen candidates from an extremely large number of possible ternary compositions. Through spatially resolved photographic O_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.

Claims

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, 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, 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;

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% 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.

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, 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, 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.

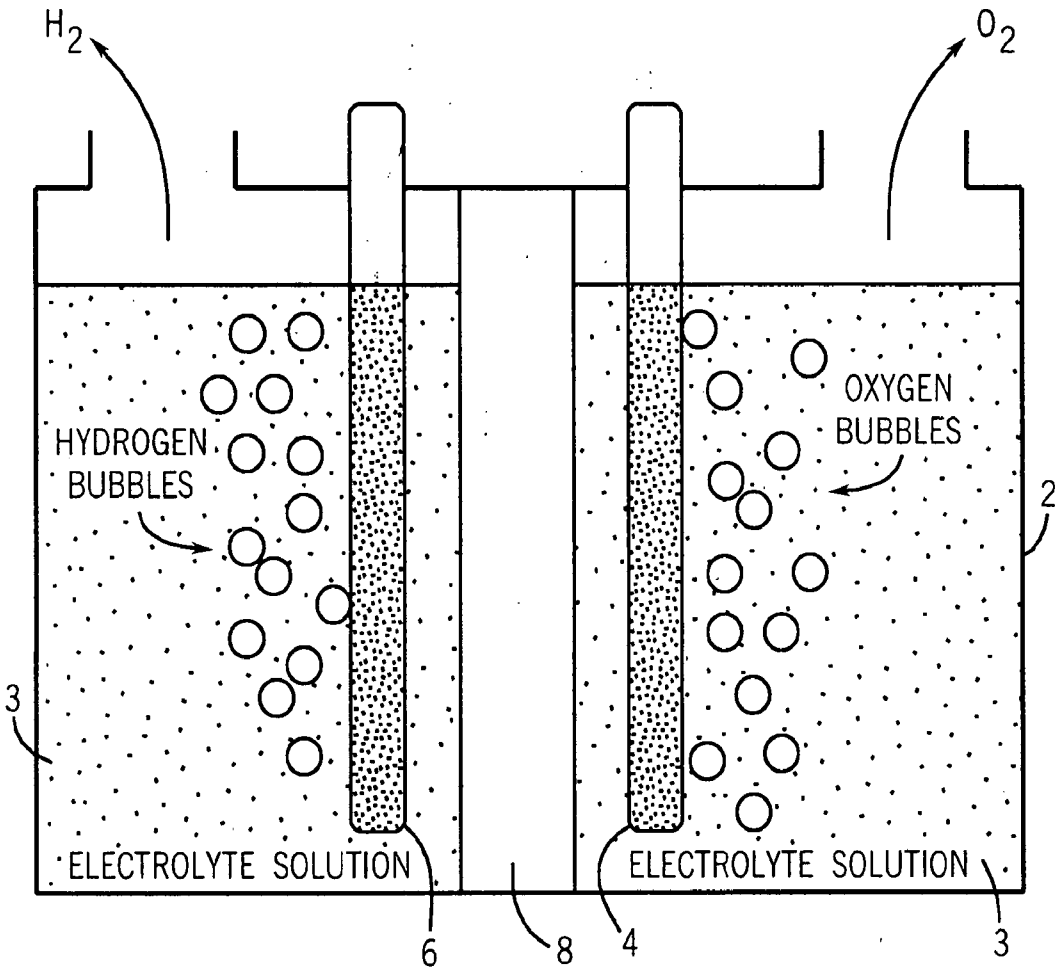
H_2
O_2
HYDROGEN BUBBLES
OXYGEN BUBBLES
ELECTROLYTE SOLUTION
ELECTROLYTE SOLUTION
2
3
3
4
6
8

FIG. 1

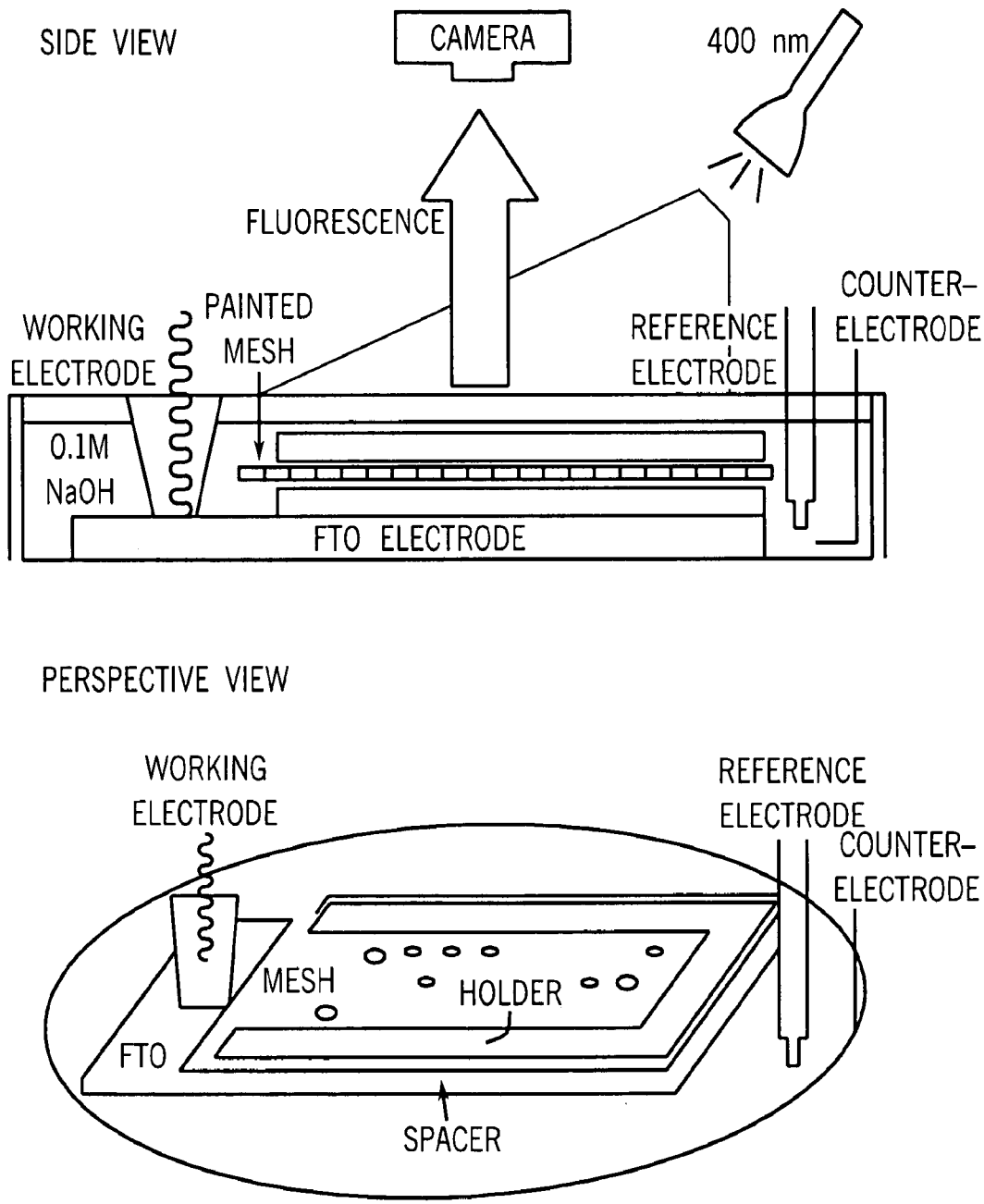
SIDE VIEW
CAMERA
400 nm
FLUORESCENCE
WORKING ELECTRODE
PAINTED MESH
REFERENCE ELECTRODE
COUNTER-ELECTRODE
0.1M NaOH
FTO ELECTRODE
PERSPECTIVE VIEW
WORKING ELECTRODE
REFERENCE ELECTRODE
COUNTER-ELECTRODE
MESH
HOLDER
FTO
SPACER

FIG. 2a

METAL-ION TRIADS TESTED (M1-M2-M3)		
Co-Al-Fe	Co-La-Ca	Ni-Al-Cr
Co-Al-Ni	Co-Ce-Al	Ni-Ca-Fe
Co-Fe-Ni	Co-La-Al	Ni-Mg-Fe
Co-Fe-Mn	Ni-Al-Fe	Ni-Zn-Fe
Co-Fe-Cr	Ni-Fe-Mn	Ni-Ce-Al
Co-La-Fe	Ni-Fe-Cr	Ni-La-Al
Co-Ce-Fe	Ni-Ce-Fe	Ni-La-Fe

FIG. 2b

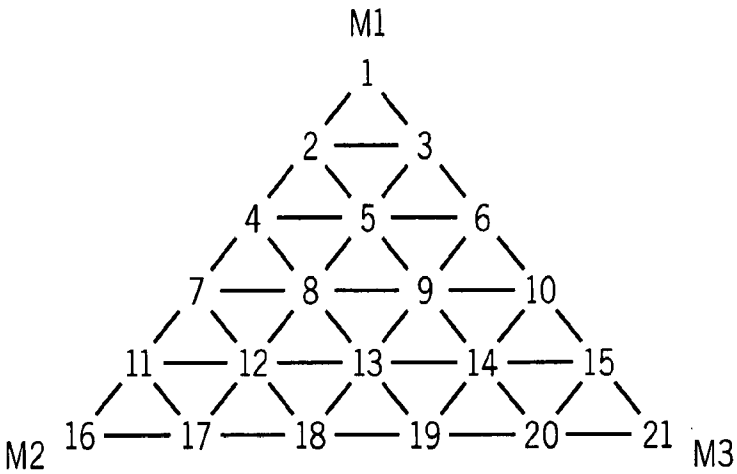

FIG. 2c

	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

FIG. 2d

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/020603

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B11/04 C25B1/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25B C25C C25D H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/205431 A1 (NGUYEN THINH T [CH] ET AL) 22 September 2005 (2005-09-22) claims 1,7-10,15,16,22	1-9
X	US 6 423 204 B1 (RAY SIBA P [US] ET AL) 23 July 2002 (2002-07-23) claims 1,4	6-9
X	US 2002/056650 A1 (RAY SIBA P [US] ET AL) 16 May 2002 (2002-05-16) claims 1-6,16	6-9
X	US 4 552 630 A (WHEELER DOUGLAS J [US] ET AL) 12 November 1985 (1985-11-12) claims 1,12	1-9

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 June 2013	28/06/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hammerstein, G

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/020603

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 147 033 A (YUASA BATTERY CO LTD; SHOJI MAKISHIMA; HIRAI HIDEFUMI) 2 April 1969 (1969-04-02) page 3, lines 21-72	1-9
X	M. Hamadani ET AL: "Co3O4 and Co-Based Spinel Oxides Bifunctional Oxygen Electrodes", Int. J. Electrochem. Sci., 30 April 2010 (2010-04-30), pages 556-577, XP055066692, Retrieved from the Internet: URL:http://www.electrochemsci.org/papers/vol5/5040556.pdf [retrieved on 2013-06-13] the whole document	1-9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/020603

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1, 4-6, 9(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continuation of Box II.2

Claims Nos.: 1, 4-6, 9(all partially)

Present claims 1 and 6 relate to an extremely large number of anodes and a method comprising said anodes, the anodes comprising possible combinations of three metal oxides. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of these combinations, namely the oxides explicitly mentioned at pages 9 and 10 of the description. These oxides comprise nickel oxide or cobalt oxide, aluminium oxide and iron oxide. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1, 4-6 and 9 (PCT Guidelines 9.19 and 9.23). The search of claims 1, 4-6 and 9 was restricted to those claimed anodes and the respective methods comprising combinations of three metal oxides which appear to be supported as set out above, and a generalisation extending to the subject-matter of claims 2, 3 and 7, 8, i.e. metal oxides which comprise nickel oxide or cobalt oxide, and aluminium oxide or gallium oxide, and iron oxide or chromium oxide.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/020603

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