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(57) Abstract: The invention relates to a method for producing a battery electrode which comprises : - A first step during which a substrate (1), either made of an electrode material or comprising at least partly on its surface, a layer of an electrode material, is introduced in a reaction vessel; - A vapor deposition step during which a metal precursor, that is a metal raw material, is fed with a carrier gas in said reaction vessel, either simultaneously or separately, with an oxidizing agent that includes ozone and/or oxygen, to obtain said substrate (1) coated with a thin film (2a) of at least one oxide of said metal precursor; - A pore forming step during which at least part of said thin film (2a) is vaporized to make it porous, to obtain said substrate (1) coated with a porous thin film (2), forming like this, said battery electrode; and the battery electrode obtained according to said process and the battery comprising said battery electrodes.



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Battery electrode and method for producing the same

The present invention relates to a battery electrode that is suitable as an electrode used for a battery such as a metal-air battery or a fuel cell, a method for producing the same and a battery comprising it.

5 An electrochemical catalyst for an oxygen reduction reaction (ORR) and an oxygen evolution reaction (OER) is important for an electrode used for a battery such as a metal-air battery or a fuel cell.

Oxides of transition metals such as manganese, cobalt, and nickel have been extensively studied in connection with such a catalyst. These oxides of transition metals
10 can be produced in a liquid phase or a gas phase. A chemical vapor deposition (CVD) method and an atomic layer deposition (ALD) method have been studied to produce such oxides in a gas phase. Japanese patent application JP-A-2011-071210, discloses a method for producing a metal oxide film that utilizes the ALD method.

It has been considered that high-temperature annealing is necessary when
15 producing oxides of transition metals in order to improve catalytic activity. Therefore, oxides of transition metals have been normally produced using an annealing step. Electrochemical catalytic activity can be obtained by heating a film of manganese oxide formed on glassy carbon using the ALD method at 480°C in the air for a long time (K. L. Pickrahn, et al.; Adv. Ener. Mater. 201200230, (2012). This work suggests that combustion
20 of glassy carbon (base) and production of carbon dioxide occur due to annealing in the air, and the oxide film becomes porous, and exhibits improved catalytic activity. However, the mechanism by which the film becomes porous has not been fully clarified, and a mere fact that electrochemical catalytic activity is improved by annealing is insufficient as an index for improving the performance of the film. Specifically, the film described in the prior art
25 document exhibits electrochemical catalytic activity, but does not necessarily exhibit the desired catalytic activity.

The subject-matter of the present patent application is based on the idea that the improvement of the electrochemical catalytic activity of said metal oxide would not only be dependent on the annealing conditions, but also on the film-forming conditions, the composition of the film, and the like. The inventors developed a battery electrode that
5 includes a thin film of a metal oxide that exhibits excellent electrochemical catalytic activity, and a method for producing the same.

According to a first embodiment, the invention relates to a method for producing a battery electrode which comprises the following steps:

- A first step during which a substrate 1, either made of an electrode material or
10 comprising at least partly on its surface a layer of an electrode material, is introduced in a reaction vessel;
- A vapor deposition step during which a metal precursor, that is a metal raw material, is fed with a carrier gas in said reaction vessel, either simultaneously or separately, with an oxidizing agent that includes ozone and/or oxygen, to obtain said
15 substrate 1 coated with a thin film 2a of at least one oxide of said metal precursor;
- A pore forming step during which at least part of said thin film 2a is vaporized to make it porous, to obtain said substrate 1 coated with a porous thin film 2, forming like this, said battery electrode.

The method as hereinabove defined, makes it possible to easily produce a battery
20 electrode that exhibits excellent electrochemical catalytic activity.

Examples of the vapor deposition method used during said vapor deposition step, include a chemical vapor deposition (CVD) method, an atomic layer deposition (ALD) method, a physical vapor deposition (PVD) method, a resistance heating deposition method, an electronic beam deposition method, a molecular beam epitaxy method, an
25 ion-plating method, an ion beam deposition method, a sputtering method, a thermal CVD

method, a catalytic CVD method, a photo-CVD method, a plasma CVD method, and a metal organic chemical vapor deposition (MOCVD) method.

According to a preferred embodiment, said vapor deposition step is chosen from an atomic layer deposition (ALD) method or a chemical vapor deposition (CVD) method.

5 Both methods are indeed preferable from the viewpoint of the uniformity of the material, and a capability to easily form a thin film 2a that exhibits excellent undercoat (electrode material) coverage.

When using an ALD method or a CVD method as the vapor deposition method, the thin film 2a is formed by introducing the electrode material into a reaction vessel of a vapor
10 deposition device, and feeding a metal oxide raw material and an oxidizing agent to the reaction vessel either simultaneously or separately.

Since the ALD method and the CVD method vaporize the raw material, and deposit the raw material on the electrode material using the resulting gas (vapor), the vapor pressure of said metal raw material at 80°C is preferably 1.33Pa (0.01Torr) or more, and
15 more preferably 13,33Pa (0.1Torr) or more. Such a metal precursor makes it possible to form a thin film 2a that includes a specific metal oxide while setting the pressure inside the reaction vessel at 1.33Pa to 1.01×10^5 Pa (0.01 to 760Torr), for example. A compound that includes a metal species that forms a specific metal oxide may be used as the raw material. A commercially available reagent or the like may be appropriately used as the metal
20 precursor corresponding to each metal.

In the method as hereinabove defined, said electrode material is a material which exhibits electrical conductivity. Examples of such materials are conductive carbon such as glassy carbon or carbon nanofibers, a metal such as platinum, gold, copper, nickel, iron, an alloy such as stainless steel, a metal oxide such indium tin oxide (ITO) or zinc oxide (ZnO)
25 or mixtures thereof.

According to a particular embodiment, said vapor deposition step of the method as hereinbefore defined, is repeated several times, in order to reach a predetermined thickness of said film 2a.

In the method as hereinabove defined, said substrate 1 may be made of the electrode material only. If said substrate 1 comprises a material other than said electrode material, said electrode material is preferably located on the external surface of said substrate in order to allow the thin film 2 may be formed on said electrode material.

A titanium layer or the like (not illustrated in Figure 1) may be provided between the substrate 1 (electrode material) and the thin film 2 in order to improve adhesion, for example. According to this particular embodiment the titanium is brought before the use of the herein above defined method.

In the method as hereinabove defined, said substrate may have a flat shape, a curved shape, or a combination thereof. The substrate surface on which the thin film is formed may have irregularities.

In the method as hereinabove defined, said metal raw material (hereinafter may be referred to as "metal precursor") is an organometallic compound that includes a specific metal element, an organometallic complex that includes a specific metal element, an inorganic metal compound that includes a specific metal element, an inorganic metal complex that includes a specific metal element, and the like. Said specific metal element is namely selected among the elements that belong to Groups 3 to 11 in the periodic table and is preferably a transition metal oxide. Specific examples of said metal element includes manganese (Mn), cobalt (Co), (Ni), iron (Fe), copper (Cu), tantalum (Ta), titanium (Ti), niobium (Nb), zirconium (Zr), hafnium (Hf), zinc (Zn), lanthanum (La), cerium (Ce), vanadium (V), molybdenum (Mo), tin (Sn), tungsten (W), or mixtures thereof.

According to a particular embodiment of the invention said metal element of said metal raw material is manganese (Mn) and said metal raw material used in said vapor

deposition step, is a compound selected from a compound of the formula (1):



and/or from a compound of the formula (2):



5 said formulas (1) and/or (2) wherein L^1 , L^2 , and L^3 are bonded to the Manganese atom via a covalent bond, a coordination bond, or an ionic bond, and are independently selected from a hydrogen atom, a carbonyl group a group or a ligand having a skeleton selected from the group consisting of a substituted or unsubstituted alkyl, preferably having from one to six carbon atoms, a substituted or unsubstituted allyl, a substituted or
10 unsubstituted allylalkyl preferably having from three to nine carbon atoms, a substituted or unsubstituted diketone, a substituted or unsubstituted cycloalkyl preferably having from five to eight carbon atoms, a substituted or unsubstituted cycloalkenyl preferably having from five to eight carbon atoms, a substituted or unsubstituted silyl, a substituted or unsubstituted amino, a substituted or unsubstituted silylamino, a substituted or
15 unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl, or a mixture thereof.

According to a more particular embodiment of the invention said metal element of said metal raw material is manganese (Mn) and said metal raw material used in said vapor deposition step, is a compound selected from a compound of the formula (3):



wherein Cp is a cyclopentadienyl group, and R^1 to R^{10} are a substituent that substitutes Cp, and are independently an hydrogen atom, or a group or a ligand having a structure selected from the group consisting of a substituted or unsubstituted alkyl preferably having from one to six carbon atoms, a substituted or unsubstituted allyl, a

substituted or unsubstituted allylalkyl preferably having from three to nine carbon atoms, , a substituted or unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl or a mixture thereof.

As examples of compounds of the formulas (1), (2) or (3), mention may be done of
5 bis(ethyl cyclopentadienyl) manganese (EtCp_2Mn)、 bis(cyclopentadienyl) manganese (Cp_2Mn) 、 bis(methyl cyclopentadienyl) manganese (MeCp_2Mn), bis(isopropyl cyclopentadienyl) manganese (iPrCp_2Mn), [bis(methyl cyclopentadienyl) manganese tri carbonyl] [$\text{MeCpMn}(\text{CO})_3$], bis(tert-butyl cyclopentadienyl) manganese, [$(\text{t-BuCp})_2\text{Mn}$], bis(ethyl cyclopentadienyl) manganese 2,4-dimethylpentanedione] [(DMPD)(EtCp)Mn],
10 bis(pentamethyl cyclopentadienyl) manganese [$(\text{CH}_3)_5\text{Cp}_2\text{Mn}$] or tris(2,2,6,6-tetramethyl heptane-3,5-dione) manganese [$(\text{thd})_3\text{Mn}$] or a mixture thereof.

The choice of a manganese precursor allows the thin film 2 to be easily produced, and said film 2 exhibits high electrochemical catalytic activity.

According to another particular embodiment of the method hereinabove defined,
15 said vapor deposition step is achieved using a metal precursor of the formula (3). According to this embodiment, a high vapor pressure and high reactivity are achieved.

In the vapor deposition step (film forming step), of the hereinabove defined process, said oxidizing agent used when forming the thin film 2a by the CVD method or the ALD method includes water, oxygen, ozone, oxygen plasma, nitrogen dioxide, and the like.
20 These oxidizing agents may be used in combination, or may be used in combination with another gas (e.g., nitrogen, air, or inert gas). The oxidizing agent may be fed to the reaction vessel together with the metal precursor when using the CVD method, and may be fed to the reaction vessel separately from the metal precursor when using the ALD method, for example. It is expected that a high deposition rate can be achieved when using the CVD
25 method. It is expected that a thin film 2a having a uniform thickness can be formed when using the ALD method (e.g., when the substrate 1 has a complex structure).

According to a particular embodiment, of the hereinabove defined method, said oxidizing agent comprises ozone.

In the vapor deposition step of the hereinabove defined process, nitrogen is generally first introduced into the reaction vessel to set the pressure inside the reaction vessel
5 20 to about 1.33Pa to 1.01×10^5 Pa (0.01 to 760Torr), preferably about 13,33Pa to 1.33×10^4 Pa (0.1 to 100Torr), and more preferably about 1.33×10^2 Pa to 1.33×10^3 Pa (1 to 10Torr). The reaction vessel is then is heated in order that the temperature of said electrode material during said vapor deposition step is about 20°C to 300°C, preferably 25°C to 200°C, and more preferably about 50°C to 150°C.

10 Said metal precursor raw is optionally heated, and fed to the reaction vessel 20 together with the carrier gas, such as nitrogen or other inert gases.

Said oxidizing agent is also fed to the reaction vessel, optionally together with the carrier gas.

At the end of said film forming step, said thin film 2a is formed on said substrate 1.
15 The thickness of said thin film 2a can be increased by increasing the duration time of the deposition and/or by achieving several times and successively, said vapor deposition step.

Said thin film 2a generally includes organic substance and/or volatile substance derived from said metal precursor, oxygen derived from said oxidizing agent and the like, since the deposition temperature is relatively low. Said organic and/or volatile substances,
20 oxygen and the like can be removed from the film through the pore-forming step to obtain the porous thin film 2. Said thin film 2a can also be formed so that no organic substance and/or volatile substance are present in the thin film 2a by choosing the appropriate raw material, oxidizing agent, and deposition conditions.

In the pore forming step of the hereinabove defined process, said thin film 2a is
25 made porous to form the porous thin film 2, by vaporizing at least part of said electrode

material and/or part of said thin film 2a. The heating temperature is generally maintained between 400°C and 700°C, more particularly between 420°C and 650°C, such as between 450°C to 600°C, and more preferably between 450°C and 550°C.

The atmosphere during heating may be air, inert gas (e.g., nitrogen), gas including
5 ozone, or the like. The pressure during heating is not particularly limited, but may be 1.33Pa to 1.01×10^6 Pa (0.01 to 7600Torr) and more particularly may be a pressure almost equal to 1 atmosphere (10^5 Pa). The temperature increase/decrease sequence during the pore-forming step is not particularly limited.

According to a particular embodiment, of the hereinabove defined process, said
10 pore forming step includes heating said substrate 1 coated with said thin film 2a, obtained at said vapor deposition step, at a temperature of from 450°C to 600°C in the presence of oxygen or water.

According to another particular embodiment, of the hereinabove defined process,

said pore forming step includes heating said substrate 1 coated with said thin film
15 2a, obtained at said vapor deposition step also comprising oxygen, at a temperature of from 450°C to 600°C, using the oxygen included in the thin film as an oxidizing agent.

According to another particular embodiment, of the hereinabove defined process,

said pore forming step includes heating said substrate 1 coated with said thin film
2a, obtained at said vapor deposition step, at a temperature of from 450°C to 600°C in the
20 presence of ozone.

According to a particular embodiment, of the hereinabove defined process, in said vapor deposition step, it is preferable to hold the substrate 1 in a state in which a specific temperature is reached in a specific atmosphere. The holding time differs depending on the composition and the thickness of the thin film 2a, and the like. For example, the holding

time is 1 minutes to 5 hours, preferably 10 minutes to 3 hours, more preferably 20 minutes to 2 hours, and still more preferably 30 minutes to 2 hours.

If said thin film 2a includes organic substance and volatile substance derived from said metal precursor, oxygen derived from said oxidizing agent and the like, the thin film 2a
5 can be made porous by the pore-forming step irrespective of the type of the electrode material that forms or that comprises on the substrate 1 on its surface to form the porous thin film 2, mainly because the organic substance and the volatile substance included in the thin film 2a are vaporized and removed during said pore-forming step.

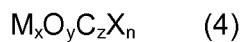
If said thin film 2a includes an organic substance and a volatile substance derived
10 from the metal precursor, and the like, the thin film 2a can be made porous by the pore-forming step irrespective of the type of the electrode material that forms the substrate 1 to form the porous thin film 2 when oxygen (e.g., air) or ozone (e.g., mixed gas of ozone and nitrogen) are present in the atmosphere, mainly because the organic substance and the volatile substance included in the thin film 2a are vaporized and removed during said
15 pore-forming step, or oxidized to produce carbon dioxide, and the like, vaporized, and removed.

If said thin film 2a includes oxygen derived from the oxidizing agent (including oxygen included in the metal oxide), the thin film 2a can also be made porous by the pore-forming step irrespective of the type of the electrode material that forms the substrate
20 1 to form the porous thin film 2, mainly because the metal oxide and excess oxidizing agent included in the thin film 2a are vaporized and removed due to heat applied during the pore-forming step, or vaporized and removed due to a change in the oxidation number of the metal oxide.

If said thin film 2a neither includes an organic substance, or a volatile substance, or
25 an oxidizing agent (e.g., oxygen), the thin film 2a can be made porous to form the porous thin film 2 using a conductive carbon material such as glassy carbon or carbon nanofibers

as the electrode material that forms the substrate 1, and allowing an oxidizing agent such as ozone to be present in the atmosphere during the pore-forming step, mainly because the thin film 2a is made porous when carbon included in the substrate 1 (electrode material) is oxidized by the oxidizing agent to produce carbon dioxide or carbon monoxide, vaporized, and removed, for example.

The material for forming the thin film 2 may have a composition represented by the formula (4):



wherein

M is a metal atom such as manganese, cobalt, nickel, iron, copper, tantalum, titanium, niobium, zirconium, hafnium, zinc, lanthanum, cerium, vanadium, molybdenum, tin, tungsten,

O is an oxygen atom,

C is a carbon atom, and

X is at least one atom selected from the group consisting of nitrogen (N), silicon (Si), (P) and (S).

According to a preferred embodiment of the method as hereinbefore defined, the metal oxide included in said thin film 2 of said battery electrode obtained by the hereinabove defined method, is manganese oxide, cobalt oxide, or nickel oxide and more preferably manganese oxide, or a mixture of a plurality of manganese oxides, selected from the group consisting of dimanganese trioxide (Mn_2O_3), trimanganese tetraoxide (Mn_3O_4) (manganese(II,III) oxide), dimanganese trioxide (Mn_2O_3) (manganese(III) oxide), manganese dioxide (MnO_2) (manganese(IV) oxide), and manganese monoxide (manganese(II) oxide) (MnO) ; and particularly preferably trimanganese tetraoxide (Mn_3O_4)

(manganese(II,III) oxide).

By implementing said pore forming step, said thin film 2 formed on the electrode material has a shape following the shape of the surface of the electrode material. Said thin film 2 may be a uniform sheet-like film that does not have a through-hole and the like, or
5 may have a through-hole and the like.

By implementing said pore forming step, said resulting thin film 2 is porous. The pores (voids) are formed in the inner part or the surface of the thin film 2. The pores may or may not be formed through the thin film 2. The pores may be exposed on the surface of said thin film 2, or may be present inside said thin film 2. The size of the pores (voids) is not
10 particularly limited. When the pores are approximated to a sphere having the same volume, the diameter of the sphere is 0.001 to 10nm, preferably 0.01 to 5nm, and more preferably 0.1 to 3nm. The evaluation of the porous character of said film 2 is made by observation, measurement, and the like using a scanning electron microscope (SEM), for example. The porous structure can also be characterized by the specific surface area.

15 Said thin film 2 need not necessarily have a uniform thickness over the entirety thereof. It may have a thickness distribution. Its average thickness of the thin film 2 can be estimated by microscopic observation, ellipsometry. The thickness of the thin film 2 is generally between 0.01nm and 500nm, preferably between 0.1nm and 300nm, and more preferably between 0.1nm to 200nm.

20 According to another particular embodiment of the present invention, the method as hereinbefore defined, further comprises an annealing step during which said substrate 1 coated with said porous thin film 2, obtained at said pore forming step, is heated in air, nitrogen or nitrogen comprising less than 1% of ozone.

The hereinbefore defined method can also optionally comprise some auxiliary
25 steps such as a preliminary cleaning of the reaction vessel, optionally some cooling steps or replacing the gas inside the reaction vessel with another gas, and the like.

According to another aspect, the invention relates to a battery electrode which is produced by the method for producing a battery electrode, as hereinbefore defined.

According to a last embodiment, the invention relates to a battery comprising as electrodes, at least one battery electrode, as hereinbefore defined.

5 The advantages of the methods are the following:

- Said battery electrode that exhibits excellent electrochemical catalytic activity. It can efficiently catalyze an oxygen reduction reaction (ORR) and an oxygen evolution reaction (OER). Therefore, said battery electrode is suitable as an electrode used for a battery such as a metal-air battery or a fuel cell. Moreover, the discharge voltage can be
10 increased while decreasing the charge voltage, and energy can be efficiently utilized.

- Since the method for producing a battery electrode includes the thin film-forming step that feeds the metal precursor and the specific oxidizing agent to the reaction vessel to form the thin film of the metal oxide on the electrode material using the vapor deposition method, and the pore-forming step that vaporizes at least part of the electrode material or
15 the thin film, the method can form a excellent porous thin film.

Figure 1 is a schematic cross-sectional view illustrating a battery electrode 10 produced by the method for producing a battery electrode according to one embodiment of the invention. The battery electrode 10 illustrated in Figure 1 has a configuration in which a thin film 2 is formed on a substrate 1. The substrate 1 and the thin film 2 form the battery
20 electrode 10. The thin film 2 is formed on the substrate 1.

Figure 2 is a non limitative schematic illustration of the method according the invention. The vapor deposition device 100 includes a quartz tube (reaction vessel 20) into which the substrate 1 (electrode material) can be introduced, an exhaust means 30 that can evacuate (decompress) the quartz tube (decompress the quartz tube), a furnace
25 (heating means 40) that can externally heat the quartz tube, a precursor feeding section 50

that feeds a metal precursor to the quartz tube, an oxidizing agent feeding section 60 that feeds an oxidizing agent, and a carrier gas feeding means 70 that circulates a carrier gas for introducing the metal precursor and the oxidizing agent into the quartz tube, each section being connected via an appropriate tube. The vapor deposition device 100 also includes a plurality of valves that can open and close each tube (pipe) (not illustrated on Figure 2). The exhaust means 30 and the heating means 40 may be implemented by an appropriate pump, heater, or the like. The vapor deposition device 100 may further include a pressure measurement means, a flow rate measurement means, a temperature measurement means, a control means, and the like (not illustrated on Figure 2). The substrate 1 is introduced into the reaction vessel 20 (quartz tube) of the vapor deposition device 100. Note that at least the surface of the substrate 1 is formed of the electrode material. The quartz tube is decompressed to about 1.33Pa to 1.33×10^3 Pa (0.01 to 10Torr) by operating the exhaust means 30 to remove residual gas such as air from the quartz tube. Nitrogen is introduced into the reaction vessel 20 from the carrier gas feeding means 70 to set the pressure inside the reaction vessel 20 to about 1.33Pa to 1.01×10^5 Pa (0.01 to 760Torr), preferably about 13.33Pa to 1.33×10^4 Pa (0.1 to 100Torr), and more preferably about 1.33×10^2 Pa to 1.33×10^3 Pa (1 to 10Torr). The quartz tube is heated using the heating means 40 to heat the substrate 1 (electrode material). The quartz tube is heated so that the temperature of the substrate 1 is about 23°C to 300°C, preferably about 23°C to 200°C, and more preferably about 50°C to 150°C. The metal precursor contained in the precursor feeding section 50 is optionally heated, and fed to the reaction vessel 20 together with the carrier gas fed from the carrier gas feeding means 70. In the example illustrated in Figure 2, the metal precursor is fed from the precursor feeding section 50 merges with the flow of the carrier gas. Optionally, the carrier gas may be bubbled into the precursor feeding section 50 to feed the metal compound to the reaction vessel 20.

After optionally removing excess metal precursor from the quartz tube, the oxidizing agent contained in the oxidizing agent feeding section 60 is fed to the reaction vessel 20 together with the carrier gas fed from the carrier gas feeding means 70. The oxidizing

agent feeding section 60 may be optionally configured to pass oxygen gas through an ozonizer.

The thin film 2a can thus be formed on the substrate 1. Note that the thickness of the thin film 2a can be increased by performing the raw material feeding step that feeds the metal oxide raw material (metal precursor) to the reaction vessel 20, and/or the oxidizing agent feeding step that feeds the oxidizing agent to the reaction vessel 20 for a longer time, or repeating the raw material feeding step and the oxidizing agent feeding step a plurality of times. The deposition time and/or the repetition count are adjusted so that the thin film 2a has a predetermined thickness. The thin film 2a thus formed normally includes an organic substance and a volatile substance derived from the metal precursor, oxygen derived from the oxidizing agent, and the like, since the deposition temperature is relatively low. The organic substance, the volatile substance, oxygen, and the like can be removed from the film through the pore-forming step to obtain the porous thin film 2. The thin film 2a can also be formed so that an organic substance and a volatile substance are not present in the thin film 2a by changing the raw material, the oxidizing agent, and deposition conditions. In such a case, the porous thin film 2 is similarly formed by performing the pore-forming step. The details thereof are described below.

The invention is described in more detail below by way of experimental examples. (2Torr). The electrode material was heated to 100°C by heating the reaction vessel. (EtCp)₂Mn at 80°C was fed to the reaction vessel by bubbling with nitrogen (carrier gas) (0.08Pa.m³/s = 50sccm). Oxygen (0.08Pa.m³/s = 50sccm) was passed through an ozonizer to produce ozone, which was used as the oxidizing agent. The metal precursor and the oxidizing agent were successively fed by operating the corresponding valve. The feeding operation was performed using a computer-controlled pneumatic valve.

Example 1

A thin film of manganese oxide was by the ALD method using (EtCp)₂Mn as a metal

precursor, and using gas including ozone as an oxidizing agent.

As an electrode material, a glassy carbon (diameter: 5 mm, thickness: 4 mm) or a platinum plate (diameters: 5 mm, thickness: 4 mm) was introduced into a quartz reaction vessel (diameter: 48 mm, length: 100 cm). After decompressing the reaction vessel using a vacuum pump, nitrogen was introduced into the reaction vessel at a flow rate of 0.34Pa.m³/s (200sccm) to adjust the pressure inside the reaction vessel to 2.66x10²Pa

Figure 3 illustrates the metal precursor/oxidizing agent feeding scheme:

(1) - (EtCp)₂Mn is introduced into the reaction vessel for 5 seconds at a flow rate of 1.69x10⁻³Pa.m³/s (1sccm).

(2) - Nitrogen gas is introduced into the reaction vessel for 30 seconds at a flow rate of 0.42Pa.m³/s (250sccm) to remove excess (EtCp)₂Mn.

(3) The oxidizing agent (including ozone) is introduced into the reaction vessel for to measure the thickness of the thin film, and the deposition rate of the thin film was calculated, and found to be about 0.36nm/cycle. Note that the invention is not limited to the above deposition rate. 10 seconds at a flow rate of 1.69x10⁻³Pa.m³/s (1sccm).

(4) Nitrogen gas is introduced into the reaction vessel for 30 seconds at a flow rate of 0.42Pa.m³/s (250sccm) to remove excess oxidizing agent. The above steps were repeated a given number of times to deposit a thin film of manganese oxide having a given thickness on the electrode material. After completion of deposition, the atmosphere inside the reaction vessel was replaced with nitrogen, and cooled to room temperature, and the substrate (electrode material) and the thin film (battery electrode) were removed.

A plurality of samples including a thin film having a thickness of about 36nm was produced by the above operation. The flow rate and the introduction time of each raw material were fixed. Note that the flow rate and the introduction time of each raw material

may be appropriately changed.

Some of the samples were observed using a scanning electron microscope (SEM)

Example 2

A thin film of manganese oxide was formed using the ALD method. A plurality of
5 samples including a thin film having a thickness of about 30nm were produced in the same
manner as in Example 1, except that oxygen gas was used as the oxidizing agent, and the
temperature of the electrode material during the reaction was set to 120°C. Some of the
samples were observed using a scanning electron microscope (SEM) to measure the
thickness of the thin film, and the deposition rate of the thin film was calculated, and found
10 to be about 0.30nm/cycle. Note that the invention is not limited to the above deposition
rate.

Example 3

Samples produced in the same manner as in Experimental Example 2, and
samples produced in the same manner as in Experimental Example 2, except that ozone
15 was used as the oxidizing agent and were subjected to an annealing treatment. The
annealing treatment was performed under the following four conditions.

- (1) The sample was heated to 320°C in the air, and held at 320°C for 2 hours.
- (2) The sample was heated to 480°C in the air, and held at 480°C for 2 hours.
- (3) The sample was heated to 480°C in nitrogen, and held at 480°C for 2 hours.
- 20 (4) The sample was heated to 120°C in nitrogen gas including ozone, and held
at 120°C for 30 minutes. The ozone concentration in the atmosphere was about 0.4%.

Each sample was assigned a sample number. Table 1 shows the annealing
conditions. The samples that were not subjected to the annealing treatment are also listed

in Table 1.

Table 1

Sample	Oxidizing agent	Substrate temperature	Substrate ^(*1)
1	O ₃	120°C	GC
2	O ₃	120°C	GC
3	O ₃	120°C	GC
4	O ₃	120°C	GC
5	O ₂	120°C	Pt
6	O ₂	120°C	GC
7	O ₂	120°C	GC
8	O ₂	120°C	GC
9	O ₂	120°C	GC
10	O ₂	120°C	Pt
11	O ₂	120°C	GC

(*1) GC: glassy carbon, Pt: platinum plate

Table 1 (to follow)

Sample	Annealing treatment		ORR voltage ^(*2)	OER voltage ^(*3)	SEM (Figure 5)
	At m.	T°C			
1	Not performed		-	2.3	(a)
2	Air	320°C	-	1.96	-
3	Air	480°C	0.63	1.8	(b)
4	N ₂	480°C	-	1.86	-
5	Air	480°C	-	1.81	(b)
6	Not performed		-	2.57	(c)
7	Air	320°C	-	1.8	-
8	Air	480°C	0.62	1.85	(e)
9	N ₂	480°C	0.47	1.89	(f)
10	Air	480°C	0.49	2.11	-
11	O ₃ /air	120°C	0.58	2.35	(d)

(*2) Voltage (vs RHE) at which current is -0.3 mA/cm²

(*3) Voltage (vs RHE) at which current is +10 mA/cm²

Example 4

5 The electrochemical catalytic activity of some of the samples obtained by the above experimental examples was determined. The battery electrode in which the thin film of manganese oxide was formed was used as a work electrode, and connected to a rotating electrode-type electrochemical analyzer ("WaveDriver 20, AFMSRCE" manufactured by Pine Research Instrumentation).

10 The work electrode, the counter electrode (platinum), and the reference electrode

(mercury/mercury oxide) were immersed in an electrolyte solution (0.1 mol/l potassium hydroxide aqueous solution). Oxygen gas was bubbled through the electrolyte solution for about 10 minutes to effect saturation. A voltage scan operation was performed while rotating the work electrode at 1600 rpm to measure the ORR/OER activity.

5 The ORR activity was measured while performing the voltage scan operation from 0V to -0.9V (vs. Hg/HgO). The voltage when the current value was $-3\text{mA}/\text{cm}^2$, was recorded as a value with respect to the reversible hydrogen electrode (RHE) (see Table 1).

 The OER activity was measured while performing the voltage scan operation from 0 V to 2V (vs. Hg/HgO). The voltage when the current value was $+10\text{mA}/\text{cm}^2$, was recorded as a value with respect to the reversible hydrogen electrode (RHE) (see Table 1).

10

Example 5

A thin film having a thickness of about 72nm was formed on a silicon substrate in the same manner as described above. The XRD (X-ray diffraction pattern) was measured using the samples immediately after ALD deposition, and the samples subjected to an annealing treatment under different conditions. The results are illustrated by Figures 4A and 4B. The thin film (thickness: about 72nm) illustrated in Figure 4A was formed on the silicon substrate by the ALD method using $(\text{EtCp})_2\text{Mn}$ as a metal precursor, and using gas including ozone (O_3) as an oxidizing agent. Figure 4A illustrates the results for the sample immediately after deposition ("As grown"), and the samples subjected to the annealing treatment at 200°C, 400°C, 450°C, or 500°C for 2 hours in the air.

15

20

The thin film (thickness: about 60nm) illustrated in Figure 4B was formed on the silicon substrate by the ALD method using $(\text{EtCp})_2\text{Mn}$ as a metal precursor, and using gas including oxygen (O_2) as an oxidizing agent. Figure 4B illustrates the results for the sample immediately after deposition ("As grown"), and the samples subjected to the annealing treatment at 200°C, 400°C, 450°C, or 500°C for 2 hours in the air. Note that the theoretical diffraction patterns of Mn_2O_3 and Mn_3O_4 are also illustrated in Figures 4A and 4B.

25

As illustrated in Figure 4A, it was found that Mn_3O_4 was included in the thin film of manganese oxide immediately after deposition. As illustrated in Figure 4A, a significant peak attributed to Mn_2O_3 was observed when the annealing temperature was 450°C or 500°C. This suggests that Mn_3O_4 was converted into Mn_2O_3 when the annealing temperature was higher than about 400°C. A peak attributed to Mn_3O_4 was not observed when the annealing temperature was 500°C. This suggests that Mn_3O_4 was converted into Mn_2O_3 when the annealing temperature was higher than about 450°C.

As illustrated in Figure 4B, it was found that a clear peak attributed to Mn_2O_3 and a clear peak attributed to Mn_3O_4 were not observed in the thin film of manganese oxide immediately after deposition (i.e., the thin film had an amorphous structure). As illustrated in Figure 4B, a significant peak attributed to Mn_2O_3 was observed when the annealing temperature was 450°C or 500°C. This suggests that crystals of Mn_2O_3 were produced when the annealing temperature was higher than about 400°C. A broad peak attributed to Mn_3O_4 was observed when the annealing temperature was 200°C or 400°C. This suggests that crystals of Mn_3O_4 were produced when the annealing temperature was low.

Example 6

Figure 5 are scanning electron microscope (SEM) images of the cross section of a thin film formed on a silicon substrate under the same conditions as those for each sample shown in Table 1.

Figure 5(a) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 1 (before the annealing treatment).

Figure 5(b) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 3 or 5 (before the annealing treatment).

Figure 5(c) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 6 (after the annealing treatment).

Figure 5(d) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 11 (after the annealing treatment).

Figure 5(e) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 8 (after the annealing treatment).

5 Figure 5(f) illustrates the SEM image of the sample corresponding to the deposition conditions for Sample No. 9 (after the annealing treatment).

Experimental results

As illustrated in Table 1, when using ozone for ALD deposition (Samples No. 1 to 5), the OER activity was observed in the samples (Samples No. 2 to 4) subjected to the annealing treatment at a voltage lower than that of the sample (Sample No. 1) that was not
10 subjected to the annealing treatment. Specifically, it was confirmed that the catalytic performance was improved by the annealing treatment. It is considered that the catalytic performance was improved since the main component of the material forming the thin film was changed from Mn_3O_4 to Mn_2O_3 due to the annealing treatment.

15 The ORR activity was observed only when the glassy carbon electrode was used, and the annealing treatment was performed at 480°C in the air (Sample No 3).

It is considered that the ORR activity was observed since the utilization rate of the component involved in the catalytic reaction was increased along with formation of pores in the thin film, and an increase in surface area.

20 As shown on Figures 5(a) and 5(b), the configuration of the thin film changed to only a small extent due to the annealing treatment when using the silicon substrate. Therefore, it is considered that the thin film of Sample No. 3 was made porous when carbon included in the glassy carbon substrate was oxidized due to oxygen in the air to produce carbon dioxide or carbon monoxide, vaporized, and removed.

As shown in Table 1, when using oxygen for ALD deposition (Samples No. 6 to 11), the OER activity was improved by heating at about 480°C irrespective of the gas species used for the annealing treatment. The OER activity was also improved by heating when using the platinum substrate (Sample No. 10). It is considered that carbon remaining in the thin film was oxidized and removed during the annealing treatment performed in the air, and the thin film became porous. It is considered that the thin film became porous during the annealing treatment performed in nitrogen due to the reaction between carbon in the thin film and oxygen, and vaporization.

It was confirmed that the ORR activity was improved by heating when using an atmosphere including ozone for the annealing treatment (Sample No. 11). It is considered that the strong oxidative effect of ozone made it possible to remove carbon at a low temperature, and the thin film became porous to exhibit the ORR activity. Since the treatment temperature was low, an improvement in OER activity due to an improvement in crystallinity and a change in crystal structure was not observed.

As shown by Figures 5(d), 5(e), and 5(f), when using oxygen for ALD deposition as the oxidizing agent, the samples showing improved ORR activity became porous due to the annealing treatment even when the thin film was formed on the silicon substrate.

The invention includes configurations that are substantially the same as the configurations described in the above embodiments (e.g., in function, method and effect, or objective and effect). The invention also includes a configuration in which an unsubstantial element of the above embodiments is replaced by another element. The invention also includes a configuration having the same effects as those of the configurations described relating to the above embodiments, or a configuration capable of achieving the same object as those of the above-described configurations. The invention further includes a configuration obtained by adding known technology to the configurations described in the above embodiments.

Claims

1. Method for producing a battery electrode which comprises the following steps:

- A first step during which a substrate 1, either made of an electrode material or comprising at least partly on its surface a layer of an electrode material, is introduced in a
5 reaction vessel;

- A vapor deposition step during which a metal precursor, that is a metal raw material, is fed with a carrier gas in said reaction vessel, either simultaneously or separately, with an oxidizing agent that includes ozone and/or oxygen, to obtain said substrate 1 coated with a thin film 2a of at least one oxide of said metal precursor;

10 - A pore forming step during which at least part of said thin film 2a is vaporized to make it porous, to obtain said substrate 1 coated with a porous thin film 2, forming like this, said battery electrode.

2. Method according to Claim 1, wherein said vapor deposition step is chosen from an atomic layer deposition (ALD) method or a chemical vapor deposition (CVD) method.

15 3. Method according to anyone of Claim 1 or 2, wherein, said electrode material is selected from glassy carbon or carbon nanofibers, platinum, gold, copper, nickel, iron, stainless steel, indium tin oxide (ITO) or zinc oxide (ZnO).

4. Method according to anyone of Claims 1 to 3, wherein said vapor deposition step is repeated several times, in order to reach a predetermined thickness of said film 2a.

20 5. Method according to anyone of Claims 1 to 4, wherein said metal raw material used in said vapor deposition step, is a compound selected from a compound of the formula (1):



and/or from a compound of the formula (2):



said formulas (1) and/or (2) wherein L^1 , L^2 , and L^3 are bonded to the Manganese atom via a covalent bond, a coordination bond, or an ionic bond, and are independently
5 selected from a hydrogen atom, a group or a ligand having a skeleton selected from the group consisting of a substituted or unsubstituted alkyl, a substituted or unsubstituted allyl, a substituted or unsubstituted allylalkyl, a substituted or unsubstituted diketone, a substituted or unsubstituted cycloalkyl, a substituted or unsubstituted cycloalkenyl, a substituted or unsubstituted silyl, a substituted or unsubstituted amino, a substituted or unsubstituted
10 silylamino, a substituted or unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl or a mixture thereof.

6. Method according to Claim 5, wherein said metal raw material used in said vapor deposition step, is a compound selected from a compound of the formula (1):



15 and/or from a compound of the formula (2):



said formulas (1) and/or (2) wherein L^1 , L^2 , and L^3 are bonded to the Manganese atom via a covalent bond, a coordination bond, or an ionic bond, and are independently
selected from a hydrogen atom, a carbonyl group a group or a ligand having a skeleton
20 selected from the group consisting of a substituted or unsubstituted alkyl, having from one to six carbon atoms, a substituted or unsubstituted allyl, a substituted or unsubstituted allylalkyl having from three to nine carbon atoms, a substituted or unsubstituted diketone, a substituted or unsubstituted cycloalkyl having from five to eight carbon atoms, a substituted or unsubstituted cycloalkenyl having from five to eight carbon atoms, a substituted or

unsubstituted silyl, a substituted or unsubstituted amino, a substituted or unsubstituted silylamino, a substituted or unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl or a mixture thereof.

7. Method according to anyone of Claims 5 or 6, wherein said metal raw material
5 used in said vapor deposition step, is a compound selected from a compound of the formula (3):



wherein Cp is a cyclopentadienyl group, and R^1 to R^{10} are a substituent that substitutes Cp, and are independently an hydrogen atom, or a group or a ligand having a
10 structure selected from the group consisting of a substituted or unsubstituted alkyl, a substituted or unsubstituted allyl, a substituted or unsubstituted allylalkyl, a substituted or unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl or a mixture thereof.

8. Method according to Claim 7, wherein said metal raw material used in said vapor
15 deposition step, is a compound selected from a compound of the formula (3):



wherein Cp is a cyclopentadienyl group, and R^1 to R^{10} are a substituent that substitutes Cp, and are independently an hydrogen atom, or a group or a ligand having a structure selected from the group consisting of a substituted or unsubstituted alkyl having
20 from one to six carbon atoms, a substituted or unsubstituted allyl, a substituted or unsubstituted allylalkyl having from three to nine carbon atoms, a substituted or unsubstituted cyclopentadienyl, and a substituted or unsubstituted phenyl or a mixture thereof.

9. Method according to anyone of Claims 5 to 8, wherein said compounds of the

formulas (1), (2) or (3), are selected from bis(ethyl cyclopentadienyl) manganese, bis(cyclopentadienyl) manganese, bis(methyl cyclopentadienyl) manganese, bis(isopropyl cyclopentadienyl) manganese, [bis(methyl cyclopentadienyl) manganese tricarbonyl], bis(tert-butyl cyclopentadienyl) manganese, [bis(ethyl cyclopentadienyl) manganese
5 2,4-dimethylpentanedione], bis(pentamethyl cyclopentadienyl) manganese, and $[(\text{CH}_3)_5\text{Cp}]_2\text{Mn}$, tris(2,2,6,6-tetramethylheptane-3,5-dione) or a mixture thereof.

10. Method according to anyone of Claims 1 to 9, wherein said oxidizing agent comprises ozone.

11. Method according to anyone of Claims 1 to 10, wherein said pore forming step
10 includes heating said substrate 1 coated with said thin film 2a, obtained at said vapor deposition step, at a temperature of from 450°C to 600°C in the presence of oxygen or water.

12. Method according to anyone of Claims 1 to 11, wherein said pore forming step
includes heating said substrate 1 coated with said thin film 2a, obtained at said vapor
15 deposition step also comprising oxygen, at a temperature of from 450°C to 600°C, using the oxygen included in the thin film as an oxidizing agent.

13. Method according to Claim 10, wherein said pore forming step includes heating said substrate 1 coated with said thin film 2a, obtained at said vapor deposition step, at a temperature of from 450°C to 600°C in the presence of ozone.

20 14. Method according to anyone of Claims 1 to 13, further comprising an annealing step during which said substrate 1 coated with said porous thin film 2, obtained at said pore forming step, is heated in air, nitrogen or nitrogen comprising less than 1% of ozone.

15. Battery electrode which is produced by the method for producing a battery electrode, according to anyone of Claims 1 to 14.

16. Battery comprising as electrodes at least one battery electrode obtained by the method according to anyone of Claims 1 to 14.

FIG.1

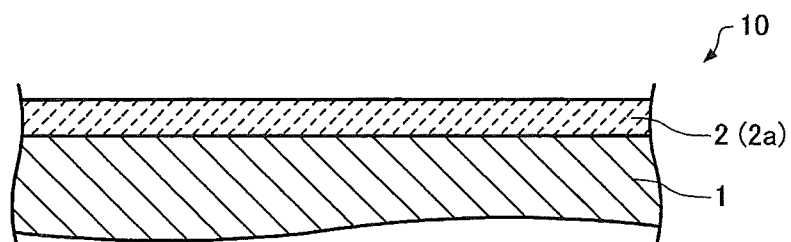


FIG.2

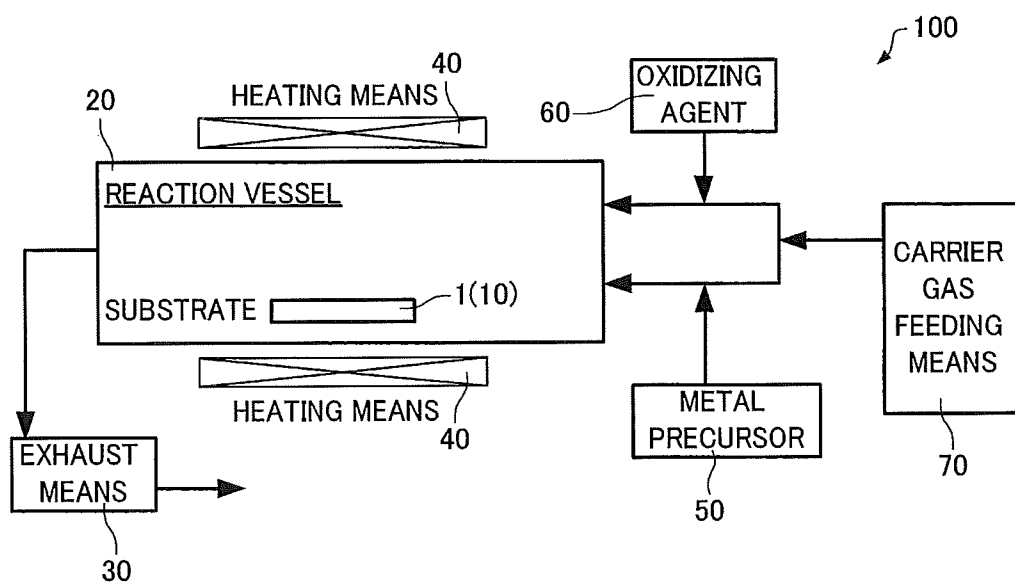


FIG.3

FEEDING SEQUENCE

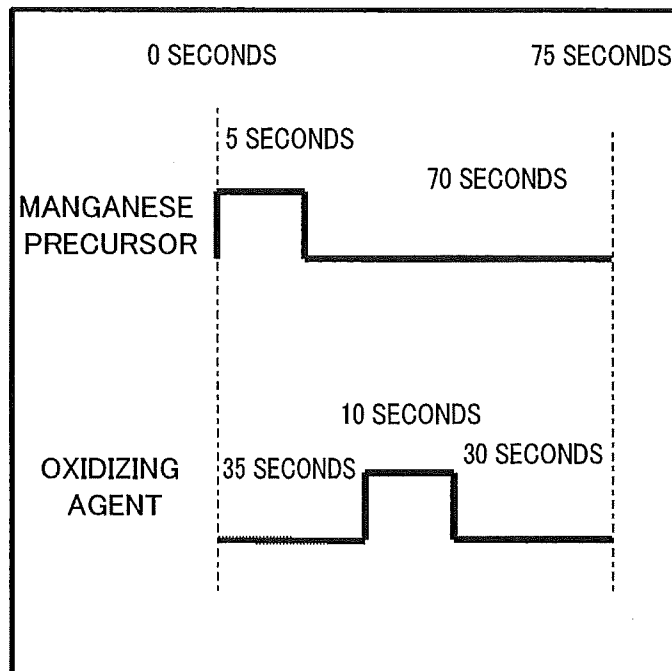


FIG.4A

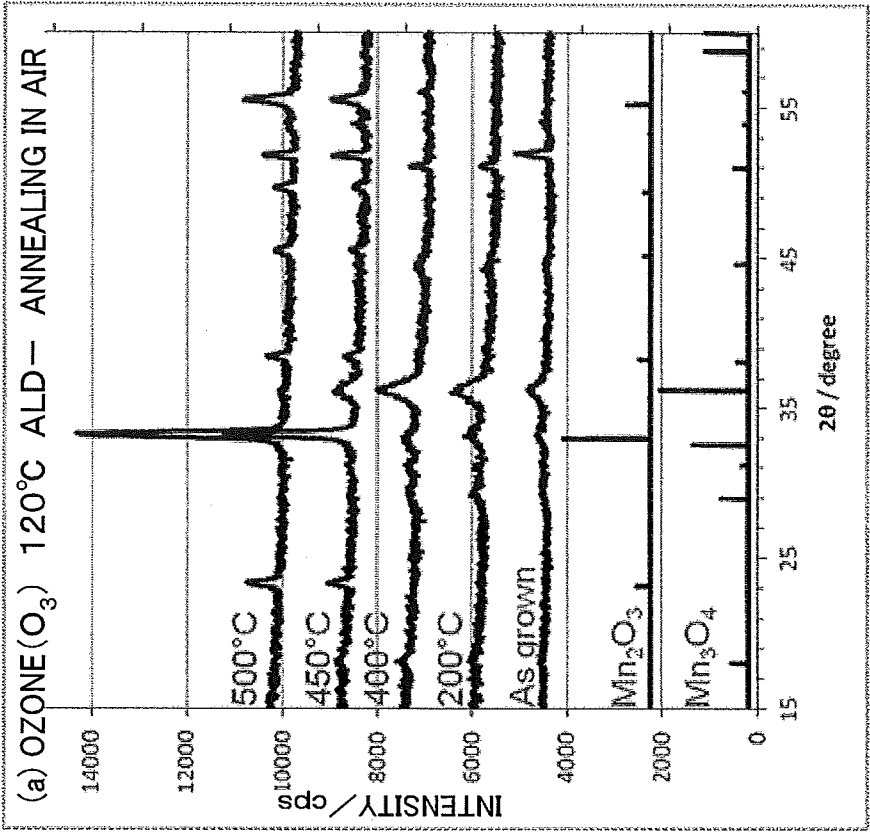


FIG.4B

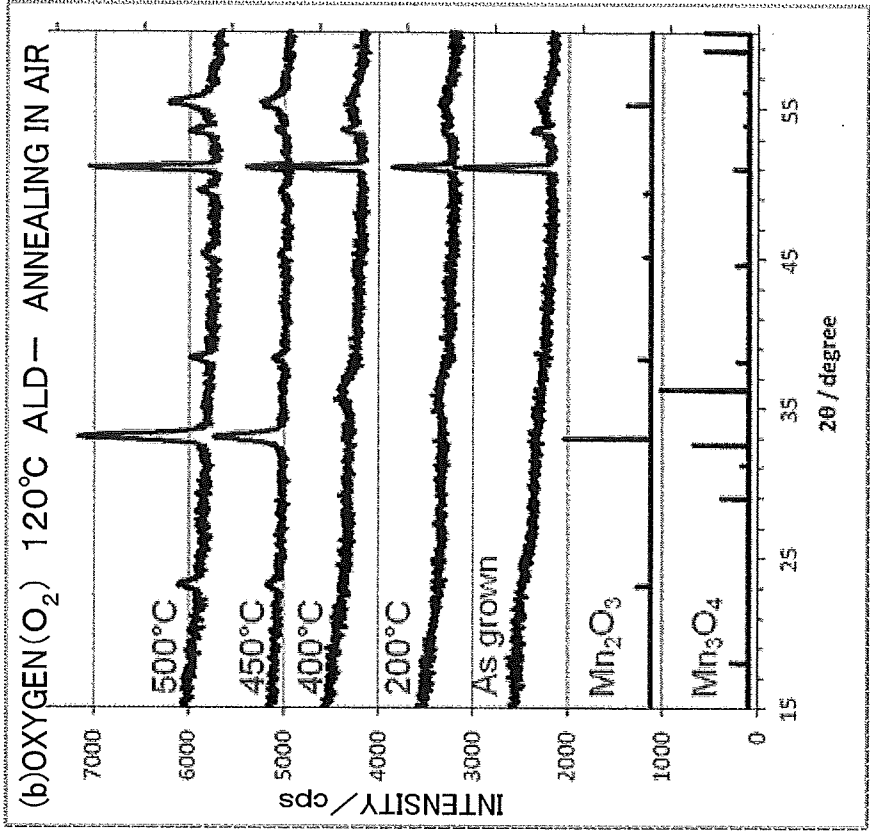
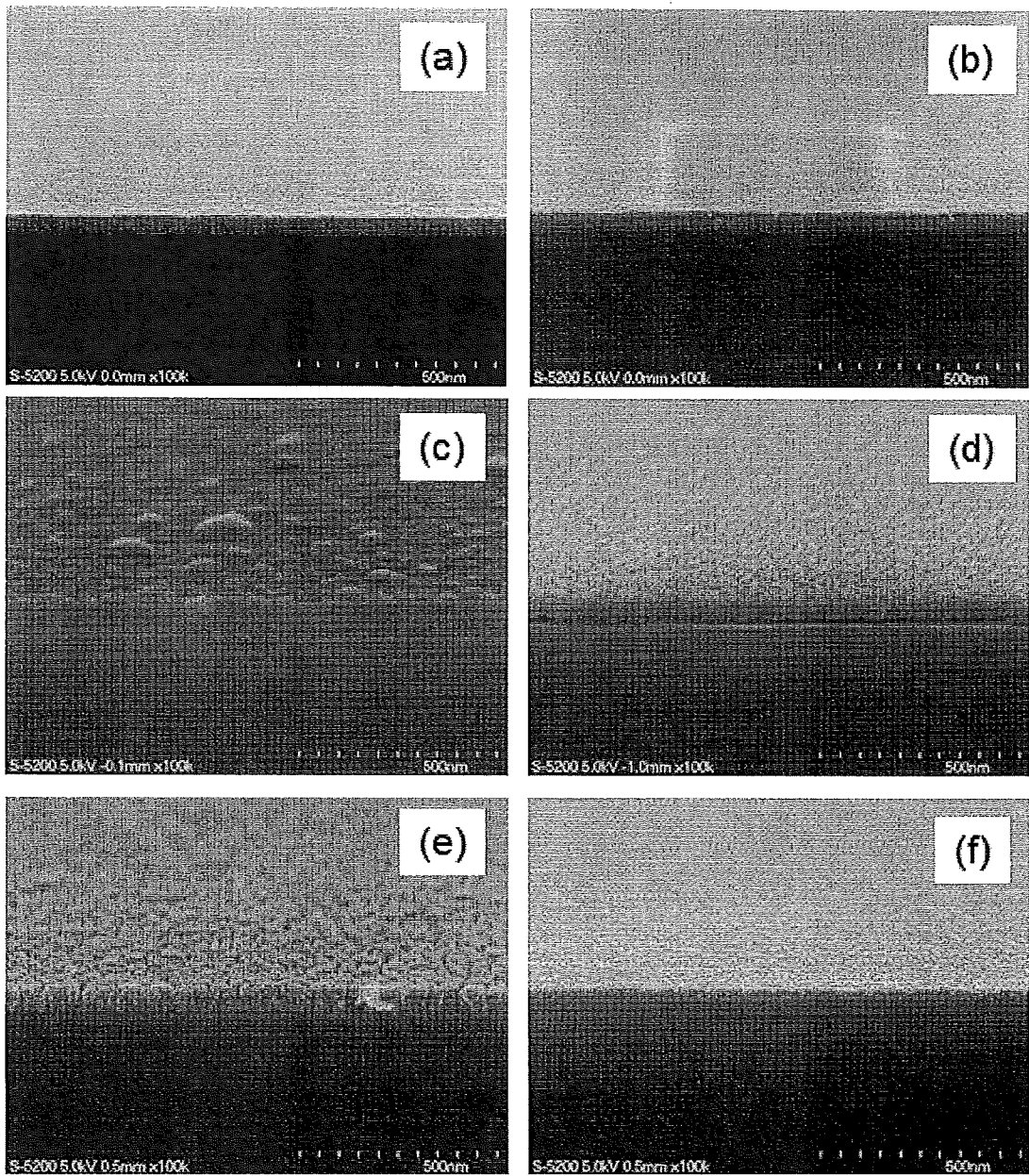


FIG.5



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/062963

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/88 H01M4/90 C23C16/40 C23C16/455 C23C16/56 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) H01M C23C		
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, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KATIE L. PICKRAHN ET AL: "Active MnO x Electrocatalysts Prepared by Atomic Layer Deposition for Oxygen Evolution and Oxygen Reduction Reactions", ADVANCED ENERGY MATERIALS, vol. 2, no. 10, 1 October 2012 (2012-10-01), pages 1269-1277, XP055208485, ISSN: 1614-6832, DOI: 10.1002/aenm.201200230 cited in the application the whole document	1-15
A	US 6 806 183 B2 (KANG CHANG-SEOK [KR] ET AL) 19 October 2004 (2004-10-19) column 17, line 60 ----- -/-	13,14
☒ Further documents are listed in the continuation of Box C. ☒ 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 20 August 2015		Date of mailing of the international search report 28/08/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Schuhmacher, Jörg

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/062963

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J. Ng ET AL: "Nanostructured Manganese Oxide Supported onto Particulate Glassy Carbon as an Active and Stable Oxygen Reduction Catalyst in Alkaline-Based Fuel Cells", Journal of the Electrochemical Society, 16 May 2014 (2014-05-16), pages D3105-D3112, XP055208482, DOI: 10.1149/2.014407jes Retrieved from the Internet: URL: http://jes.ecsdl.org/content/161/7/D3105.full.pdf [retrieved on 2015-08-19] abstract; page D3105 page D3107; figure 2	15,16
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Information on patent family members

International application No

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