



(19) **United States**

(12) **Patent Application Publication**
Stevens et al.

(10) **Pub. No.: US 2008/0011604 A1**
(43) **Pub. Date: Jan. 17, 2008**

(54) **PROCESS AND DEVICE FOR WATER
ELECTROLYSIS COMPRISING A SPECIAL
OXIDE ELECTRODE MATERIAL**

(30) **Foreign Application Priority Data**

Jun. 23, 2004 (FR)..... 04 06839

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Publication Classification

(51) **Int. Cl.**
C25B 11/04 (2006.01)
C25B 1/06 (2006.01)
C25B 9/00 (2006.01)
(52) **U.S. Cl.** **204/242; 204/293**

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(57) **ABSTRACT**

The invention relates to a method for water electrolysis consisting in using an electrode containing at least one type of oxide material of general formula $A_{2-x-y}A'_x A''_y M_{1-z} M'_z O_{4+\delta}$, wherein A is a lanthanide and/or alkaline and/or alkaline earth metal cation, A' is at least one lanthanide and/or alkaline and/or alkaline earth metal cation, A'' is a cation gap, M is a transition metal element, M' is at least one type of transition metal element, wherein said metal is such that $0 < y < 0.30$, preferably $0 < y \leq 0.20$; $-0.1 \leq \delta < 0.25$, preferably $0 \leq \delta < 0.10$; $0 \leq x \leq 1$ and $0 \leq z \leq 1$. An associated device is also disclosed.

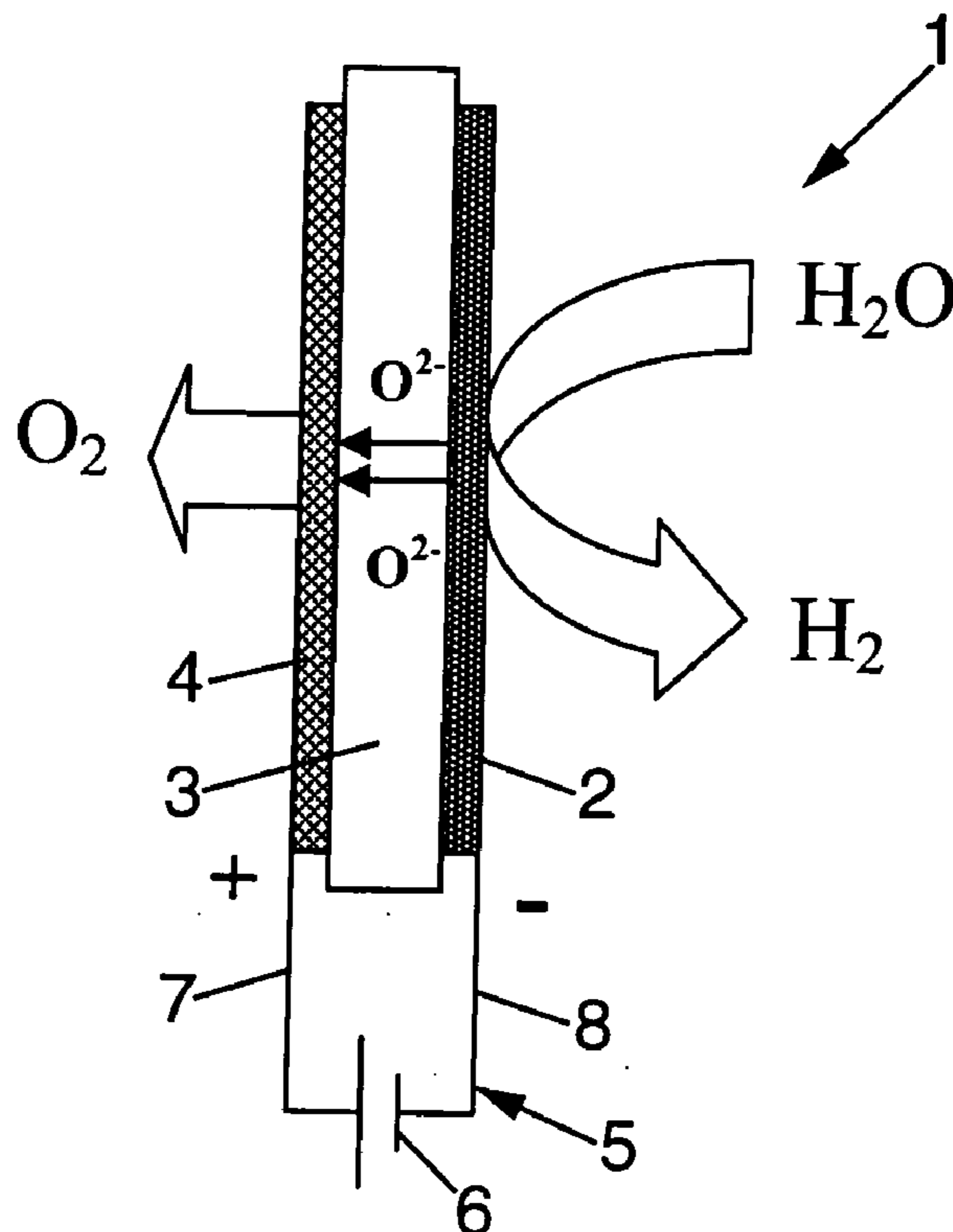
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(21) Appl. No.: **11/570,859**

(22) PCT Filed: **Jun. 21, 2005**

(86) PCT No.: **PCT/FR05/01556**

§ 371(c)(1),
(2), (4) Date: **Dec. 18, 2006**



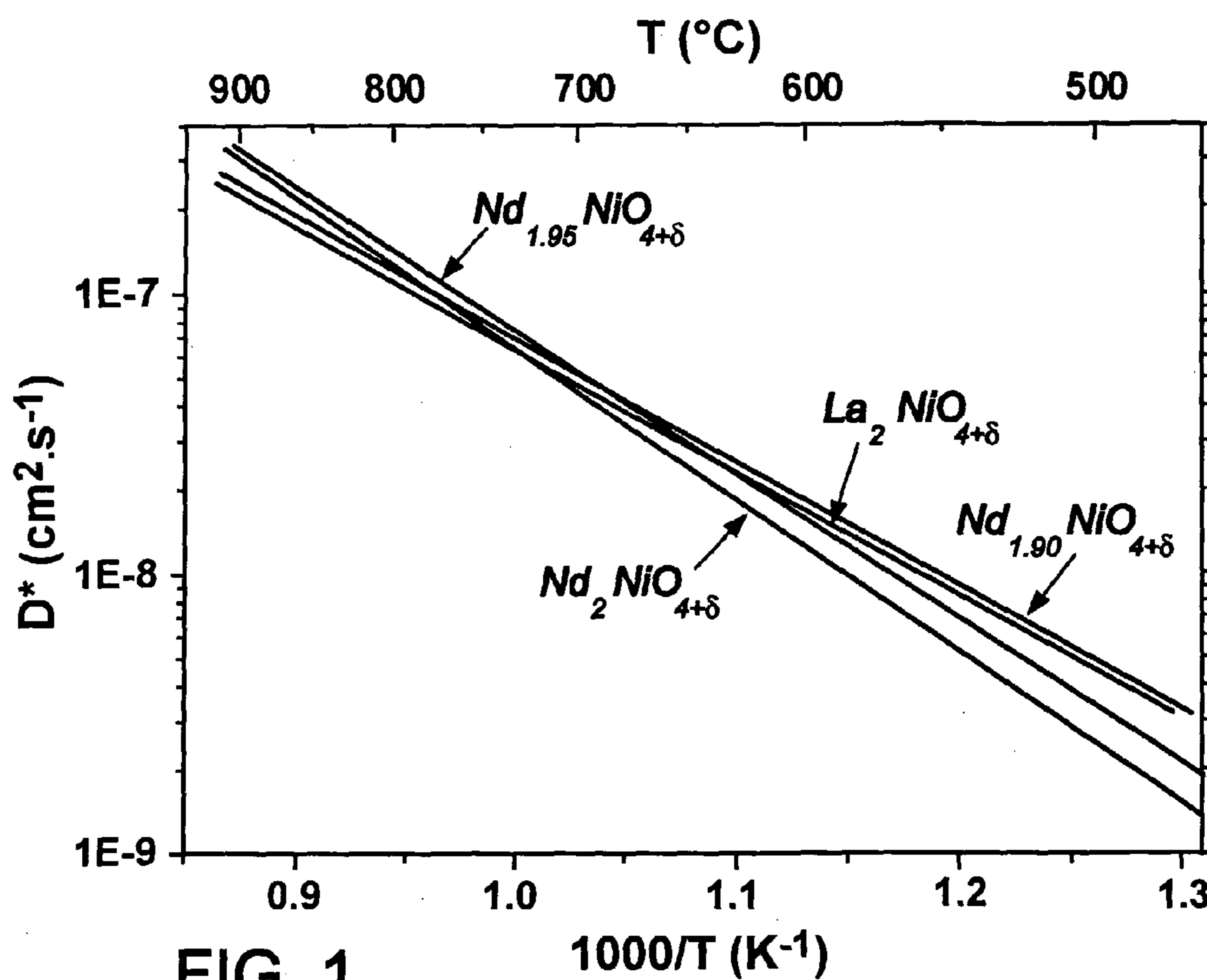


FIG. 1

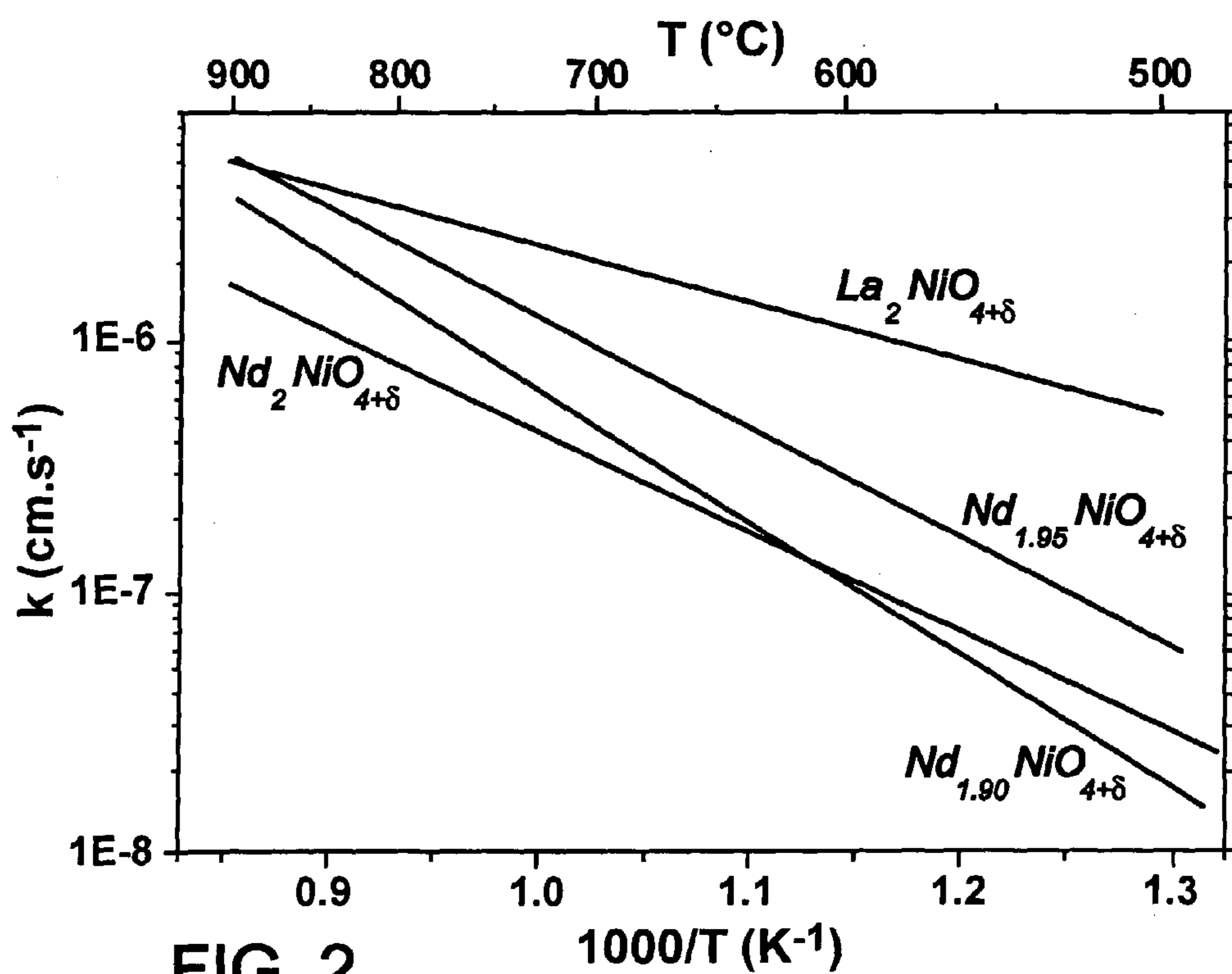


FIG. 2

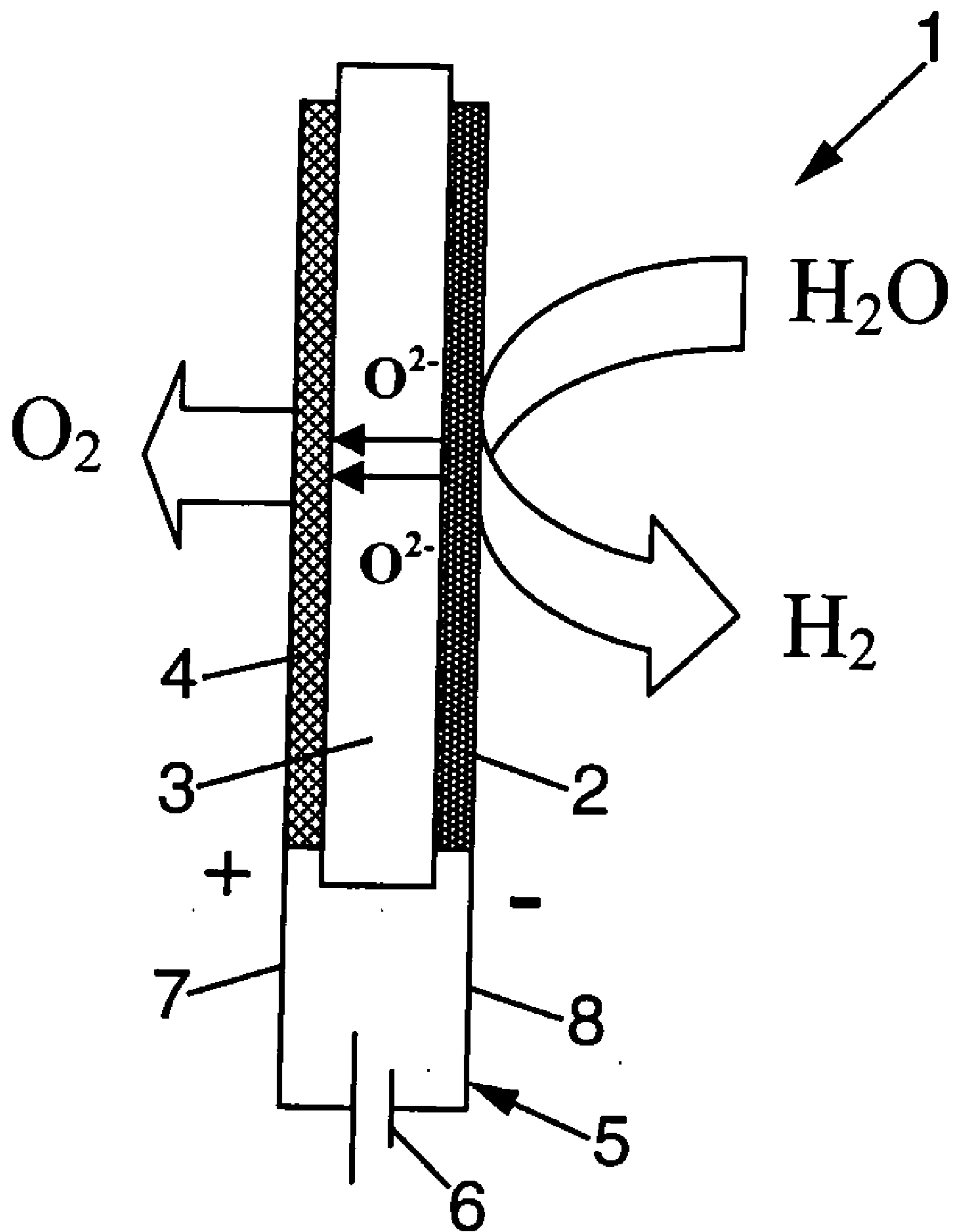


FIG. 3

**PROCESS AND DEVICE FOR WATER
ELECTROLYSIS COMPRISING A SPECIAL OXIDE
ELECTRODE MATERIAL**

[0001] The invention relates to a process for water electrolysis consisting in using an electrode comprising at least one special oxide material, particularly at high temperature. The invention also relates to a device for implementing such a water electrolysis process.

[0002] The future use of hydrogen as an energy carrier requires the development of a process that provides large-scale production at low cost. The electrolysis of water enables hydrogen to be produced from water by using electrical energy to break down the water. The electrochemical reaction used is the reverse of the fuel cell principle. The water electrolysis process used industrially today is several decades old. It operates at a temperature of around 80 to 120° C. and the electrical efficiencies of said process are around 45 to 65%. This energy conversion efficiency is too low for this technique to be able to be used for the production of hydrogen as an energy carrier.

[0003] The low operating temperature is partly responsible for the low energy conversion efficiency. A process operating at a high temperature (i.e. generally at a temperature greater than or equal to 600° C.) has a better electrical efficiency since the reactions at the electrodes are facilitated and because thermal energy may also be used in the electrochemical conversion process. Among the various techniques for producing hydrogen by high-temperature electrolysis of water (described, for example, in the article "High-temperature steam electrolysis", by E. Schouler, E. Fernandez and H. Bernard, RGE, March 1982) none have succeeded on an industrial scale, mainly due to the prohibitive cost, and also for the reasons explained below.

[0004] The core of the electrochemical cell is composed of an anode or positive electrode, a cathode or negative electrode and a solid, ceramic-based electrolyte. The oxygen ions flow through the electrolyte from the cathode toward the anode. The solid electrolyte most commonly used is "yttria stabilized zirconia" or YSZ, also known as yttriated zirconia. The cathode, which is the site of the reduction of water to produce hydrogen and O²⁻ anions that will flow through the electrolyte, is most commonly a cermet (ceramic/metal composite) of the type where nickel is dispersed in the stabilized zirconia (YSZ), optionally doped with ruthenium Ru. The anode, which releases the charges and which is the site of the oxidation of O²⁻ ions to oxygen, is most commonly based on mixed-conducting oxides, such as SnO₂-doped In₂O₃ and lanthanum manganite LaMnO₃ doped with calcium or strontium.

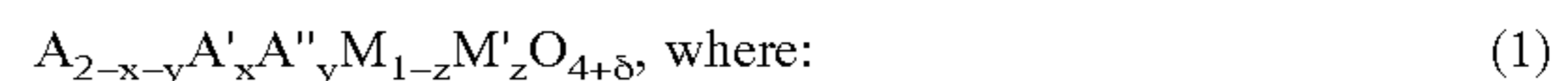
[0005] The production of hydrogen requires the coupling, as a battery, of many elementary cells, the creation of interconnections that allow two contiguous cells to be connected electrically while ensuring a seal between two anode and cathode compartments, is generally achieved with a specific material generally known to a person skilled in the art, for example with a Cr—MgO—Al₂O₃ cermet-type material covered in platinum on the oxygen (anode) side and with nickel on the hydrogen (cathode) side. Lastly the geometry of such batteries is generally of tubular or planar type, preferably tubular.

[0006] The only high-temperature process experimented with today (the process known as "Hot Elly", called the

Dornier System process in the aforementioned article) relates to an electrolyzer that operates at 1000° C. Such an electrolyzer is of tubular geometry and uses small concentric cylindrical tubes, predominantly made of zirconia. The electrodes (nickel-yttriated zirconia cermet for the cathode and lanthanum manganite for the anode) are deposited by spraying. But the materials and the manufacturing process used are too costly for a commercial application to be reasonably envisaged.

[0007] It is in order to solve these problems of the prior art that another type of oxide material must be used as the electrode of at least one electrochemical cell for the electrolysis of water. It is this that the process according to the invention achieves.

[0008] The process according to the invention is a water electrolysis process comprising the use of an electrode containing at least one oxide material of the following general formula:



[0009] A is a metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

[0010] A' is at least one metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

[0011] A'' is a cationic vacancy, that is to say a cation A and/or cation A' vacancy;

[0012] M is a metal belonging to the group formed by metals of transition elements;

[0013] M' is at least one metal belonging to the group formed by metals of transition elements;

[0014] said material being such that

[0015] $0 \leq y < 0.30$, preferably $0 \leq y \leq 0.20$;

[0016] $-0.1 \leq \delta < 0.25$, preferably $0 \leq \delta < 0.25$, more preferably $0 \leq \delta < 0.10$;

[0017] $0 \leq x \leq 1$; and

[0018] $0 \leq z \leq 1$.

[0019] The previous formula therefore includes the case where x is equal to 0 or 2, that is to say the case where a single metal cation is present, and also, independently or not of the previous case, the case where z is equal to 0 or 1, that is to say the case where a single metal is present,

[0020] A' may represent several metal cations and M' may also independently represent several metals; a person skilled in the art knows how to rewrite the formula (I) depending on the number of components.

[0021] The previous formula therefore includes the case where δ is equal to 0, that is to say the case where there is no oxygen superstoichiometry or substoichiometry.

[0022] The previous formula therefore includes the case where y is equal to 0, that is to say the case where there is no cation vacancy.

[0023] In addition, the presence of an oxygen superstoichiometry or substoichiometry coefficient δ , preferably an oxygen superstoichiometry coefficient δ , with a value other

than 0 may contribute advantageously to the ionic conductivity of the material. In such a case, preferably $0 < \delta < 0.25$, more preferably $0 < \delta < 0.10$.

[0024] According to a particularly preferred embodiment of the invention, M and M' are of mixed valency, that is to say that advantageously such metals contribute to the electronic conductivity of the material.

[0025] Advantageously, such materials according to the invention have good thermal stability in terms of composition. This has been shown by TGA (thermogravimetric analysis) measurements in air, and confirmed by X-ray diffraction at temperature, on two materials which are $\text{Nd}_{1-95}\text{NiO}_{4+\delta}$ and $\text{Nd}_{1-90}\text{NiO}_{4+\delta}$. Indeed, measurement of the oxygen superstoichiometry or substoichiometry coefficient δ as a function of the temperature, over a range from room temperature, i.e. about 20°C ., to 1000°C . does not show any changes and confirms that the loss of mass is directly and solely proportional to the variation of the oxygen content of the material.

[0026] Advantageously, when according to an embodiment of the invention y is other than 0, the A" vacancies are randomly distributed. Indeed, the electron diffraction pattern obtained by transmission electron microscopy of the material that is $\text{Nd}_{1-90}\text{NiO}_{4+\delta}$ does not reveal any elongation or smearing of the main (001) spots, which reveals a perfect order along the c axis and the absence of intergrowths of the Ruddlesden-Popper type within the $\text{A}_2\text{MO}_{4+\delta}$ stacks, thus confirming such a random distribution of the neodymium vacancies.

[0027] The term "lanthanide" is understood according to the invention to mean lanthanum La or an element of the lanthanides group such as Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu and Y. The term "alkali metal" is understood according to the invention to mean an element other than hydrogen from group 1 (IUPAC version) of the Periodic Table of the Elements. The term "alkaline-earth metal" is understood according to the invention to mean an element from group 2 (IUPAC version) of the Periodic Table of the Elements. The term "transition metal" is understood according to the invention to mean an element from groups 3 to 12 (IUPAC version) of the Periodic Table of the Elements, including of course the elements from period 4 such as titanium Ti or gallium Ga, the elements from period 5 such as zirconium Zr or tin Sn and the elements from period 6 such as tantalum Ta or mercury Hg. Preferably, according to the invention, the transition metal is an element from period 4.

[0028] When y is other than 0, the material of the process according to the invention is advantageously characterized by very detailed measurements of (A and/or A')/(M and/or M') ratio(s) by Castaing microprobe (or EPMA, the acronym for, "Electron Probe Microanalysis"), which allows the exact composition of the material to be established and optionally the cation vacancy structure of said material to be evaluated.

[0029] In a preferred embodiment of the invention, said process is such that:

[0030] A and A' are chosen independently from the group formed by lanthanum La, praseodymium Pr, strontium Sr, calcium Ca and neodymium Nd, preferably neodymium Nd, strontium Sr and calcium Ca, even more preferably neodymium Nd, and such that:

[0031] M and M' are chosen independently from the group formed by chromium Cr, manganese Mn, iron Fe, cobalt Co, nickel Ni and copper Cu, preferably nickel Ni and copper Cu, even more preferably nickel Ni.

[0032] In the particular cases according to the invention where x is not equal to 0 or 2, and z is not equal to 0 or 1, the number of type A cations is at least 2: A and A', and the number of type M cations is at least 2: M and M'.

[0033] In such a case, and in a more general way, preferably:

[0034] A is chosen from the group formed by lanthanum La, praseodymium Pr, and neodymium Nd, preferably neodymium Nd;

[0035] A' is chosen from the group formed by strontium Sr and calcium Ca, preferably calcium Ca;

[0036] M is chosen from the group formed by chromium Cr, manganese Mn, iron Fe, cobalt Co, nickel Ni and copper Cu, preferably nickel Ni; and

[0037] M' is chosen from the group formed by manganese Mn, iron Fe, copper Cu or cobalt Co, preferably copper Cu or manganese Mn.

[0038] In a particularly preferred embodiment according to the invention, the material has a crystallographic structure of the K_2NiF_4 type, as shown for example in "Inorganic Crystal Structures", p. 30, by B. G. Hyde and S. Anderson, Wiley Interscience Publication (1988). The structure is thus formed of layers of oxygen-containing MO_6 octahedra shifted with respect to one another by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, A atoms ensuring cohesion between the layers. When additional oxygens O_i are present, they may be inserted between these layers in the vacant interstitial sites.

[0039] In a preferred embodiment, the material of the process according to the invention possesses an oxygen surface exchange coefficient k greater than 1×10^{-8} cm/s at 500°C . and greater than 2×10^{-6} cm/s at 900°C . for oxygen. The variation in said coefficient follows an Arrhenius law, which makes it easy to calculate this coefficient for another temperature in the temperature range of interest in the invention.

[0040] In a preferred embodiment, independently or not of the previous embodiment, the material of the process according to the invention possesses an electronic conductivity σ_e at least equal to 70 S/cm, preferably at least equal to 80 S/cm, even more preferably greater than 90 S/cm at 700°C .

[0041] In a preferred embodiment, independently or not of the previous embodiment, the material of the process according to the invention possesses an oxygen diffusion coefficient greater than 1×10^{-9} cm²/s at 500°C . and greater than 1×10^{-7} cm²/s at 900°C . The variation in said coefficient follows an Arrhenius law, which makes it easy to calculate this coefficient for another temperature in the temperature range of interest in the invention.

[0042] In a preferred embodiment, the material of the process according to the invention possesses an oxygen surface exchange coefficient k greater than 1×10^{-8} cm/s at 500°C . and greater than 2×10^{-6} cm/s at 900°C . for oxygen, an electronic conductivity σ_e at least equal to 70 S/cm, preferably at least equal to 80 S/cm, even more preferably

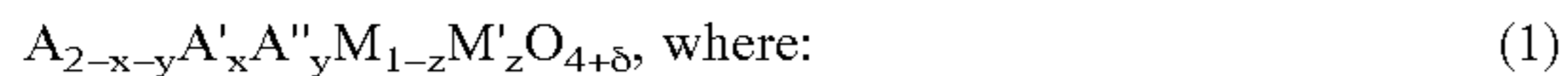
greater than 90 S/cm at 700° C. and an oxygen diffusion coefficient greater than 1×10^{-9} cm²/s at 500° C. and greater than 1×10^{-7} cm²/s at 900° C.

[0043] In an embodiment of the process according to the invention, said material is such that δ is not equal to 0, preferably $0 < \delta < 0.25$, even more preferably $0 < \delta < 0.10$.

[0044] Preferably, the process according to the invention is implemented at a temperature greater than or equal to 600° C.

[0045] The invention also relates to a device for implementation of the process according to the invention.

[0046] The invention thus relates to a water electrolyzer type device comprising at least one electrochemical cell comprising a solid electrolyte, a cathode and an anode, which comprises at least one oxide material of the following general formula:



[0047] A is a metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

[0048] A' is at least one metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

[0049] A'' is a cationic vacancy, that is to say a cation A and/or cation A' vacancy;

[0050] M is a metal belonging to the group formed by metals of transition elements;

[0051] M' is at least one metal belonging to the group formed by metals of transition elements;

[0052] said material being such that

[0053] $0 \leq y < 0.30$, preferably $0 \leq y \leq 0.20$;

[0054] $-0.1 \leq \delta < 0.25$, preferably $0 \leq \delta < 0.25$, more preferably $0 \leq \delta < 0.10$;

[0055] $0 \leq x \leq 1$; and

[0056] $0 \leq z \leq 1$.

[0057] Said device also most often comprises at least one interconnector between two electrolysis cells. Besides the anode, all the other parts of said device are generally components known to a person skilled in the art.

[0058] Advantageously, the device according to the invention allows, with the use of the anode according to the invention having at the same time good electronic conductivity and good ionic conductivity when δ is other than 0, and also good thermal stability and sufficient efficiency from an industrial point of view. In such a case, preferably $0 < \delta < 0.25$ more preferably $0 < \delta < 0.10$.

[0059] The invention will be better understood and other features and advantages will appear on reading the description that follows, given without limitation, with reference to FIGS. 1 to 3.

[0060] FIG. 1 is a graph showing, for the four materials used according to the invention, the oxygen diffusion coefficient D^* (cm²/s) as a function of $1000/T$ (K⁻¹), where T is the temperature.

[0061] FIG. 2 is a graph showing, for the four materials used according to the invention, the oxygen surface exchange coefficient k (cm/s) as a function of $1000/T$ (K⁻¹), where T is the temperature.

[0062] FIG. 3 is a diagram of the principle for the electrolysis of water, as observed by the process and device according to the invention.

[0063] FIGS. 1 and 2 are explained below in the examples,

[0064] FIG. 3 is a diagram of the principle for the electrolysis of water, as observed by the process and device according to the invention. A device 1 can be seen therein, which is an electrochemical cell for the electrolysis of water, consisting of an anode 4, a cathode 2 and an electrolyte 3. An electrical connection is provided by a device 5 made up of a generator 6 and two electrical connecting wires 7 and 8.

EXAMPLES

[0065] The examples that follow illustrate the invention without in any way limiting the scope thereof.

[0066] Two materials were synthesized: Nd_{1.95}NiO_{4+ δ} and Nd_{1.90}NiO_{4+ δ} having y values equal to 0.05 and 0.10 respectively. These materials were synthesized indifferently by solid state reaction of Nd₂O₃ and NiO oxides at 1100° C. or by soft chemistry or sol-gel methods, for example from the decomposition of neodymium and nickel nitrates in solution with final annealing at 1100° C. Their oxygen superstoichiometry values were equal to $\delta=0.15$ and $\delta=0.06$ respectively, determined by chemical analysis of Ni³⁺ (iodometry)

[0067] Their electronic conductivities σ_e were measured at 700° C., equal to 100 S/cm and 80 S/cm respectively. Their oxygen surface exchange coefficients k were equal to 5.5×10^{-8} cm/s and 1.7×10^{-8} cm/s respectively at 500° C. and to 5.5×10^{-6} cm/s and 1.7×10^{-6} cm/s respectively at 900° C. Their oxygen diffusion coefficients were equal to 3.2×10^{-9} cm²/s and 5.2×10^{-9} cm²/s respectively at 500° C. and to 3.5×10^{-7} cm²/s and 2.5×10^{-7} cm²/s respectively at 900° C. The percentages of Ni³⁺ cations at 700° C., determined by TGA (thermogravimetric analysis) in air, were equal to 35% and 28% respectively. The variation in the oxygen stoichiometry within this temperature range, in which the operating temperature of the electrolyzer lies, was small and had no influence over the thermal expansion coefficient, which remained constant and equal to 12.7×10^{-6} K⁻¹.

[0068] A material Nd₂NiO₄ was also used, having respectively x, y and z values equal to 0. This material was synthesized indifferently by solid state reaction of La₂O₃ and NiO oxides at 1100° C. or by soft chemistry or sol-gel methods, for example from the decomposition of lanthanum and nickel nitrates in solution with final annealing at 1100° C. The oxygen superstoichiometry value was equal to $\delta=0.22$, determined by chemical analysis of Ni³⁺ (iodometry). The electronic conductivity σ_e of said material at 700° C. was equal to 38 S/cm, and its oxygen surface exchange coefficient k was equal to 3×10^{-13} cm/s at 500° C. and 1.8×10^{-6} cm/s at 900° C., and its oxygen diffusion coefficient was 2.5×10^{-9} cm²/s and 2×10^{-7} cm²/s respectively at 500° C. and 900° C.

[0069] A material La₂NiO_{4+ δ} was also used, having respectively x, y and z values equal to 0. This material was

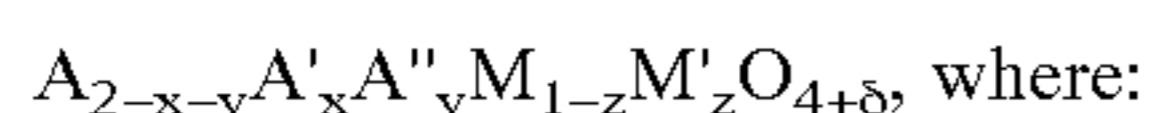
synthesized indifferently by solid state reaction of La_2O_3 and NiO oxides at 1100°C . or by soft chemistry or sol-gel methods, for example from the decomposition of lanthanum and nickel nitrates in solution with final annealing at 1100°C . The oxygen superstoichiometry value was equal to $\delta=0.16$, determined by chemical analysis of Ni^{3+} (iodometry). The electronic conductivity σ_e of said material at 700°C . was equal to 50 S/cm , and its oxygen surface exchange coefficient k was equal to $5\times 10^{-7}\text{ cm/s}$ at 500°C . and $5\times 10^{-6}\text{ cm/s}$ at 900°C ., and its oxygen diffusion coefficient was $4.5\times 10^{-9}\text{ cm}^2/\text{s}$ and $2.2\times 10^{-1}\text{ cm}^2/\text{s}$ respectively at 500°C . and 900°C . The percentage of Ni^{3+} cations at 700°C ., determined by TGA (thermogravimetric analysis) in air, was equal to 26%. Its thermal expansion coefficient remained constant with the temperature and was equal to $13.0\times 10^{-6}\text{ K}^{-1}$.

[0070] The electrochemical properties of these four materials were evaluated in a three-electrode assembly in a half-cell of electrode material/YSZ/electrode material type, where the counterelectrode and the working electrode are symmetrical, and are painted onto the electrolyte and annealed at 1100°C . for 2 hours. The platinum reference electrode was placed far from the other two electrodes. The behavior of this material was analyzed under conditions close to those of high temperature water electrolysis, that is to say under current and in a temperature range from 500 to 800°C .

[0071] FIG. 1 is a graph showing, for the four materials used according to the invention, the oxygen diffusion coefficient $D^*(\text{cm}^2/\text{s})$ as a function of $1000/T(\text{K}^{-1})$, where T is the temperature. Each curve is a straight line. The four materials according to the invention were $\text{Nd}_2\text{NiO}_{4+\delta}$, $\text{La}_2\text{NiO}_{4+\delta}$, $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ and $\text{Nd}_{1.90}\text{NiO}_{4+\delta}$. It can be seen that in the temperature range of interest in the invention, the materials used according to the invention generally had, to within the measurement error, a high, and therefore beneficial, coefficient D^* .

[0072] FIG. 2 is a graph showing, for the four materials used according to the invention, the oxygen surface exchange coefficient $k(\text{cm/s})$ as a function of $1000/T(\text{K}^{-1})$, where T is the temperature. Each curve is a straight line. The four materials according to the invention were $\text{Nd}_2\text{NiO}_{4+\delta}$, $\text{La}_2\text{NiO}_{4+\delta}$, $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ and $\text{Nd}_{1.90}\text{NiO}_{4+\delta}$. It can be seen that in the temperature range of interest in the invention, the materials used according to the invention generally had a high, and therefore beneficial, coefficient k .

1. A process for electrolysis of water comprising the use of an electrode comprising at least one oxide material of the following general formula:



A is a metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

A' is at least one metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

A'' is a cationic vacancy, that is to say a cation A and/or cation A' vacancy;

M is a metal belonging to the group formed by metals of transition elements;

M' is at least one metal belonging to the group formed by metals of transition elements;

said material being such that

$$0 \leq y \leq 0.30, \text{ preferably } 0 \leq y \leq 0.20;$$

$$-0.1 \leq \delta < 0.25, \text{ preferably } 0 \leq \delta < 0.25, \text{ more preferably } 0 \leq \delta < 0.10;$$

$$0 \leq x \leq 1; \text{ and}$$

$$0 \leq z \leq 1.$$

2. The process as claimed in the preceding claim 1, wherein:

A and A' are chosen independently from the group formed by lanthanum La, praseodymium Pr, strontium Sr, calcium Ca and neodymium Nd, preferably neodymium Nd, strontium Sr and calcium Ca, even more preferably neodymium Nd, and wherein:

M and M' are chosen independently from the group formed by chromium Cr, manganese Mn, iron Fe, cobalt Co, nickel Ni and copper Cu, preferably nickel Ni and copper Cu, even more preferably nickel Ni.

3. The process as claimed in claim 1, wherein:

A is chosen from the group formed by lanthanum La, praseodymium Pr, and neodymium Nd, preferably neodymium Nd; and

A is chosen from the group formed by strontium Sr and calcium Ca, preferably calcium Ca;

and wherein:

M is chosen from the group formed by chromium Cr, manganese Mn, iron Fe, cobalt Co, nickel Ni and copper Cu, preferably nickel Ni; and

M' is chosen from the group formed by manganese Mn, iron Fe, copper Cu or cobalt Co, preferably copper Cu or manganese Mn.

4. The process as claimed in claim 1, wherein said material has a crystallographic structure of the K_2NiF_4 type.

5. The process as claimed in claim 1, wherein said material possesses an oxygen surface exchange coefficient k greater than $1\times 10^{-8}\text{ cm/s}$ at 500°C . and greater than $2\times 10^{-6}\text{ cm/s}$ at 900°C . for oxygen.

6. The process as claimed in claim 1, wherein said material possesses an electronic conductivity σ_e at least equal to 70 S/cm , preferably at least equal to 80 S/cm , even more preferably greater than 90 S/cm at 700°C .

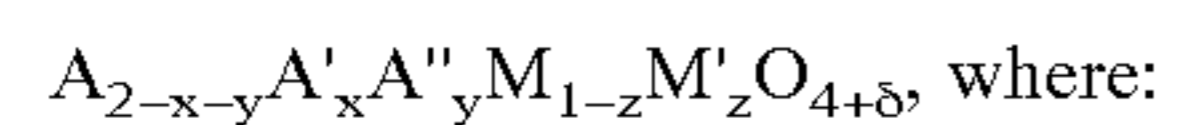
7. The process as claimed in claim 1, wherein said material possesses an oxygen diffusion coefficient greater than $1\times 10^{-9}\text{ cm}^2/\text{s}$ at 500°C . and greater than $1\times 10^{-7}\text{ cm}^2/\text{s}$ at 900°C .

8. The process as claimed in claim 1, wherein said material possesses an oxygen surface exchange coefficient k greater than $1\times 10^{-8}\text{ cm/s}$ at 500°C . and greater than $2\times 10^{-6}\text{ cm/s}$ at 900°C . for oxygen, an electronic conductivity σ_e at least equal to 70 S/cm , preferably at least equal to 80 S/cm , even more preferably greater than 90 S/cm at 700°C . and an oxygen diffusion coefficient greater than $1\times 10^{-9}\text{ cm}^2/\text{s}$ at 500°C . and greater than $1\times 10^{-7}\text{ cm}^2/\text{s}$ at 900°C .

9. The process as claimed in claim 1, wherein said material is such that δ is not equal to 0, preferably $0 < \delta < 0.25$, even more preferably $0 < \delta < 0.10$.

10. The process as claimed in claim 1, wherein said process is implemented at a temperature greater than or equal to 600° C.

11. A water electrolyzer type device comprising at least one electrochemical cell comprising a solid electrolyte, a cathode and an anode, which comprises at least one oxide material of the following general formula:



A is a metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

A' is at least one metal cation belonging to the group formed by lanthanides and/or alkali metals and/or alkaline-earth metals;

A'' is a cationic vacancy, that is to say a cation A and/or cation A' vacancy;

M is a metal belonging to the group formed by metals of transition elements;

M' is at least one metal belonging to the group formed by metals of transition elements;

said material being such that

$$0 < y < 0.30, \text{ preferably } 0 < y \leq 0.20;$$

$$-0.1 \leq \delta < 0.25, \text{ preferably } 0 \leq \delta < 0.25, \text{ more preferably } 0 \leq \delta < 0.10;$$

$$0 \leq x \leq 1; \text{ and}$$

$$0 \leq z \leq 1.$$

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