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(54) Title: SOLID COMPOSITIONS FOR FUEL CELLS, SENSORS AND CATALYSTS

(57) **Abstract**

Solid materials for use as electrolyte (62) for a fuel cell, or for a sensor, or as a catalyst. Representative structures include lanthanum fluoride, lead potassium fluoride, lead bismuth fluoride, lanthanum strontium fluoride, lanthan strontium lithium fluoride, calcium uranium cesium fluoride, $PbSnF_4$, KSn_2F_5, $SrCl_2 \cdot KCl$, $La_{1-p}OF_{1+2p}$ $0.1 < p < 0.3$, $PbSnF_q \cdot PbSnO_r$ $0.0001 < q, r < 1$, lanthanumoxyfluoride, $Sm_aNd_bF_cO_d$ $2.18 < a, b < 9.82$, $12 < c < 29.45$, $3.25 < d < 12$, $a+b \sim 12$, $c+2d \sim 36$ and the like. In another aspect, the present invention relates to a composite and a process to obtain it of the formula: $A_{1-y}B_yQO_3$ having a perovskite or a perovskite-type structure as an electrode catalyst in combination with: $A_yB_{1-y}F_{2+y}$ as a discontinuous surface coating solid electrolyte, wherein A is independently selected from lanthanum, cerium, neodymium, praseodymium, and scandium, B is independently selected from strontium, calcium, barium or magnesium, Q is independently selected from nickel, cobalt, iron or manganese, and y is between about 0.0001 and 1, which process comprises: (a) obtaining a particulate of: $A_{1-y}B_yQO_3$, wherein A, B and y are defined hereinabove having an average size distribution of between about 50 and 200 Angstroms in diameter; (b) reacting the particle of step (a) with a vapor comprising: $A_yB_{1-y}F_{2+y}$, wherein A, B and y are defined hereinabove, at about ambient pressure at between about 0 and 1000°C; for between about 10 and 30 hr. obtain a composite of between about 25 to 1000 microns in thickness; (c) recovering the composite of step (b) having multiple interfaces between the electrode and electrolyte. In another aspect the invention relates to the heating of these solid materials with oxygen and water to obtain higher ionic conductivity. In another aspect the invention relates to the electrochemical doping of oxide ions present by treatment of the electrode-lanthanum fluoride interface at between about 0 and 400°C in an oxygen environment at between about 10^{-3} and 10^{-6} amperes per square centimeter for between about 1 and 60 minutes. The invention also includes the use of the fuel cells disclosed to generate electricity.

SOLID ELECTROLYTE: e.g. $La_{1-y}Sr_y F_{2-y}$

PEROVSKITE: e.g. $La_y Sr_{1-y}CoO_3$

SOLID COMPOSITIONS FOR

FUEL CELLS, SENSORS AND CATALYSTS

BACKGROUND OF THE INVENTION

Field of the Invention

5   The present invention relates to materials and processes to

prepare polycrystal and monocrystal forms for use in fuel cells in

sensors and as catalysts. In specific embodiments, a fuel cell having

oxygen/solid lanthanum fluoride (as a single crystal)/hydrogen

configuration produces about 1 volt of open circuit potential at

10 essentially ambient temperature. In other specific embodiments,

specific mixed lanthanide or alkaline earth fluorides also produce

electricity at moderate temperatures. Embodiments also include a

porous perovskite-type metallic transition metal oxide electrode and a

lanthanum metal/alkaline earth/fluoride electrolyte which are useful as

15 a solid electrode/electrolyte in a fuel cell, as a sensor, or as a

catalyst.

DESCRIPTION OF THE RELEVANT ART

Fuel cells convert chemical energy to electrical energy directly,

without having a Carnot-cycle efficiency limitation, through

20 electrochemical oxidation-reduction reactions of fuels. Several types

of fuel cells have been or are being investigated at the present time.

These may generally be classified as shown in Figure 1, as Table 1,

depending upon the kinds of electrolyte used and the operation

temperature.

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The solid electrolyte fuel cell which can be considered as the third generation fuel cell technology, is essentially an oxygen-hydrogen (or H_2-CO mixture) fuel cell operated at high temperature (ca. 1000°C) with a solid ceramic oxide material used as 5 the electrolyte. At present, yttrium- or calcium-stabilized zirconium oxides have been used as the electrolyte. The mechanism of ionic conduction is oxygen ion transport via O^{2-} anion in the solid oxide crystal lattice.

Additional references of interest include the following.

10   B.C. LaRoy et al., in the <u>Journal of the Electrochemical Society:</u> <u>Electrochemical Science and Technology</u>, Vol. 120, No. 12 pp. 1668-1673, published in December 1973, disclose some electrical properties of solid-state electrochemical oxygen sensors using vapor deposited thin films. Polycrystalline lanthanum fluoride solid 15 electrolytes were investigated at ambient temperature.

T. Horiba in U.S. Patent No. 4,550,067 discloses secondary cell batteries in which the positive electrode is made of materials such as phthalocyanine complexes, metal porphyrin complexes and the like.

Lyall in U.S. Patent No. 3,625,769 and Fouletier in U.S. Patent 20 No. 4,526,674 each disclose lithium/oxygen fuel cells.

Raleigh in U.S. Patent No. 4,118,194 and Weininger in U.S. Patent No. 3,565,692, each disclose halogen electrochemical cells or the like.

Ledorenko in U.S. Patent No. 4,172,022 and Eliot in U.S. Patent 25 No. 3,645,795, each disclose the use of phthalocyanine compounds in gas sensor electrodes.

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Zeitner in U.S. Patent NO. 3,909,297 discloses a lithium-chloride battery.

In U.S. Patent No. 3,698,955 and 3,719,564, Lilly discloses the use of rare earth fluorides such as lanthanum fluoride as solid
5   electrolytes which are deposited as their films in a battery and a gas sensor respectively.

G.W. Mellors in European Patent Application No. 055,135 discloses a composition which can be used as a solid state electrolyte comprising at least 70 mole percent of cerium trifluoride and/or
10 lanthanum trifluoride an alkaline earth metal compound e.g. fluoride, and an alalki metal compound e.g. lithium fluoride.

Additional references cited also include the following.

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J. Meuldijk, J. and H.W. den Hartog (1983), "Charge Transport in $Sr_{1-x}La_xF_{2+x}$ solid solutions. An Ionic Thermocurrent Study", Physical Review B, 28(2), pp. 1036-1047.

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A.F. Aalders, A. Polman, A.F.M. Arts and H.W. de Wijn (1983), "Fluorine Mobility in $La_{1-x}Ba_xF_{3-x}$ $(0 < x < 0.1)$ Studied by Nuclear Magnetic Resonance", Solid State Ionics, Vol. 9 & 10, pp. 539-542.

A.K. Ivanovshits, N.I. Sorokin, P.P. Fedorov, and B.P. Sobolev (1983), "Conductivity of $Sr_{1-x}Ba_xF_{3-x}$ Solid Solutions with Compositions in the Range $0.03 \leq x \leq 0.40$, "Sov. Phys. Solid State, 25(6), pp. 1007-1010.

J. O'M. Bockris, and T. Otawaga (1984), "The Electrocatalysis of Oxygen Evolution on Perovskites", J. Electrochemical. Soc., 131(2), pp. 290-302.

Additional general information is found in "Fuel Cells" by E.J. Cairns et al. in Kirk-Othmer: Encyclopedia of Chemical Technology, (3rd Ed.), Vol. 3, pp. 545-568; and in "Fuel Cells" by O.J. Adlhart in Van Nostrand's Scientific Encyclopedia, 6th ed., D.M. Considine (ed), Van Nostrand Reinhold Co., New York, pp. 1296-1299, 1986, which are both incorporated herein by reference.

Solid electrolyte fuel cells have several advantages over the other types of fuel cells:

1.   There are no liquids involved and, hence, the problems associated with pore flooding, maintenance of a stable three-phase interface, and corrosion are totally avoided.

2.   Being a pure solid-state device, it poses virtually no maintenance problems. For example, the electrolyte composition is invariant and independent of the composition of the fuel and oxidant streams.

3.   Inexpensive metallic oxides (ceramics) rather than expensive platinum can be used as the electrode catalysts.

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4.   The solid electrolyte fuel cells demand less feed gas prepa-
ration than the phosphoric acid cell (see Figure 1), which requires a
conversion of CO to H_2 via the water-gas shift reaction, or the
molten carbonate cell (see Figure 1), which requires a carbon dioxide
5 loop due to the use of carbonate ions for ionic transport.

The attraction of developing a solid electrolyte fuel cell is its
simplicity. However, a high operation temperature (ca. 1000°C) is by
far the most critical aspect of this type of fuel cell. Although high
operation temperature produces high-quality exhaust heat that can
10 generate additional electrical power, leading to a high overall system
efficiency, maintaining the integrity of the cell components such as
the interconnector is the most difficult challenge.

It is therefore desirable to develop alternative low temperature
solid materials and composites for use as solid electrolytes in fuel
15 cells, as solid sensors and as solid catalysts that can be operated in
a range of 400-600°C or lower (preferably about 200°C, especially at
ambient temperature). Some of the structures described herein have
been examined for usefulness as battery electrolytes. However, none
of the references cited hereinabove, individually or collectively,
20 disclose or suggest the present invention as described herein. The
present invention relates to the design of such low temperature solid
electrolyte fuel cells, sensors, or catalysts based on non-oxide solid
electrolytes, such as solid solutions of lanthanide fluorides (e.g.
$La_xSr_{1-x}F_{2+x}$).

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SUMMARY OF THE INVENTION

The present invention relates to solid materials which have application as an electrolyte for a fuel cell, a sensor or a catalyst. More specifically, the present invention relates to a solid material 5 [AA] for use as an electrolyte for a fuel cell or for a sensor or as a catalyst, each having a polycrystal or single crystal structure, comprising:
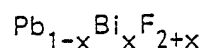
(a)   a structure of the formula:

$$AF_3$$

10 wherein A is independently selected from lanthanum, cerium, neodynium, praseodynium, scandium or mixtures thereof, wherein AF_3 is a single crystal or a portion thereof;
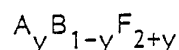
(b)   a structure of the formula:

$$Pb_{1-x}M_xF_{2-x}$$
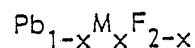
15 wherein M is independently selected from potassium, or silver, and x is between about 0.0001 and 0.25;

(c)   a structure of the formula:

$$Pb_{1-x}Bi_xF_{2+x}$$

wherein x is defined herein above;

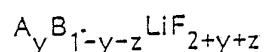20   (d)   a structure of the formula:

$$A_yB_{1-y}F_{2+y}$$

wherein:

A as defined hereinabove,

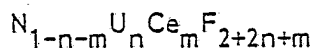B is independently selected from strontium, calcium, barium or 25 magnesium, and y is between about 0.0001 and 1;

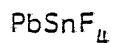(e)   a structure of the formula:

$$A_yB_{1-y-z}LiF_{2+y+z}$$

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wherein A, B and y are as defined hereinabove, z is between about

0.0001 and 0.10 wherein y+z is less than or equal to 1;
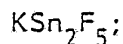
(f)   a structure of the formula:

$$N_{1-n-m}U_nCe_mF_{2+2n+m}$$

5 wherein N is independently selected from calcium, strontium or bar-

ium, n is between about 0.0001 and 0.05, and m is between about

0.0001 and 0.35;

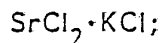(g)   a structure of the formula:

$$PbSnF_4$$

10 with the proviso that $PbSnF_4$ is only useful as a fuel cell electrolyte;

(h)   a structure of the formula:

$$KSn_2F_5;$$

(i)   a structure of the formula:

$$SrCl_2 \cdot KCl;$$

15   (j)   a structure of the formula:

$$LaO_{1-p}F_{1+2p}$$
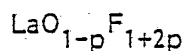
wherein p is between about 0.0001 and 0.9999;

(k)   a structure of the formula:

$$PbSnF_q \cdot PbSnO_r$$
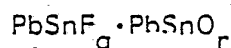
20 wherein q and r are each independently from between about 0.0001

and 1;

(l)   a structure of the formula:

$$(AO_{1.5})_y(GF_2)_{1-y}$$
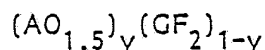
wherein A is as defined hereinabove, y is between about 0.0001 and

25 1, and G is independently selected from calcium and magnesium; and

(m)   a structure of the formula:

$$Sm_aNd_bF_cO_d$$
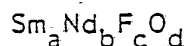
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wherein a and b are each independently between about 2.18 and 9.82 and c is between about 12 and 29.45, and d is between about 3.25 and 12, with the proviso that a+b is about 12 and c+2d is about 36.

In another aspect, the present invention relates to a process for

5   the preparation of an electrolyte for a fuel cell or for a sensor, which process comprises:

(a) reacting a structure of material [AA] above in an atmosphere comprising a mixture of oxygen and water wherein the water is present in between about 1 and 99% by weight at between 100

10 and 1000°C for between about 10 and 50 hrs.

In another aspect, the present invention relates to a process for the preparation of an electrolyte for a fuel cell or for a sensor, which process comprises:

(a) subjecting, for instance, about one gram of a structure of

15 material [AA] above to a current of about 10^{-3} amperes per square centimeter at a temperature of between 0 and 400°C for a time sufficient to transmit a certain amount of coulombs equivalent to a product of one Faraday (coulombs/mole) times X where X is between about 0.001 and 1, depending upon the specific material structure.

20   In another aspect, the present invention relates to a process [BB] for preparing a composite consisting essentially of:
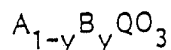
$$A_{1-y}B_yQO_3$$

having a perovskite or a perovskite-type structure as an electrode catalyst in combination with:

25

$$A_yB_{1-y}F_{2+y}$$

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as a discontinuous surface coating solid electrolyte wherein A is independently selected from lanthanum, cerium, neodymium, praseodymium, or scandium, B is independently selected from strontium, calcium, barium or magnesium, Q is independently selected from

5 nickel, cobalt, iron or manganese, and y is between about 0.0001 and 1, which process comprises:

(a) obtaining a particulate of:

$$A_{1-y}B_yQO_3$$
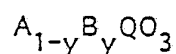
wherein A, B and y are defined hereinabove having an average

10 crystal size distribution of between about 50 and 200 Angstroms in diameter and a surface area of between about 10 and 100 meters ^{2}/grams and formed into a film-like or pellet-like shape having a general thickness of between about 1 and 5mm, a pore size of between about 25 and 200 Anstroms; and

15 (b) reacting the particulate of step (a) with a vapor comprising:
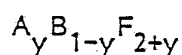
$$A_yB_{1-y}F_{2+y}$$

wherein A, B and y are defined hereinabove, at about ambient pressure at between about 0 and 1000°C: for between about 10 and 30 hr.

20 obtain the composite of between about 25 to 1000 microns in thickness; and

(c) recovering the composite of step (b) having multiple interfaces between:
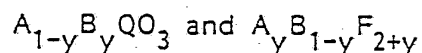
$$A_{1-y}B_yQO_3 \text{ and } A_yB_{1-y}F_{2+y}$$

25 said composite having a pore size of between about 25 and 200 Angstroms and a surface area of between about 10 and 100 meters ^{2}/gram.

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A preferred embodiment in this process [BB] is wherein A is lanthanum, B strontium, Q is cobalt, and especially where y is about 0.3. Another preferred embodiment of process [BB] is wherein A is selected from cerium or scandium, B is selected from strontium or

5   magnesium, Q is selected from nickel, cobalt or manganese and y is between about 0.2 and 0.4.

In another aspect the present invention relates to the use of the composite of Claim 16 selected from electrode/electrolyte for a fuel cell, a sensor, or a contact catalyst for synthesis or degradation.

10   The use of the composite material of Claim 28 as an electrode/electrolyte for a fuel cell or a sensor.

The use of the composite material of Claim 30 as an oxygen sensor or a fuel cell.

In another aspect the present invention relates to the process

15 for the generation of electricity, which process comprises:

(a) contacting a solid electrolyte of [AA] above or prepared by process [BB] above with a fuel at between about 0 and 1000°C.

In another aspect the present invention relates to the process described herein wherein the fuel for the fuel cell is selected from

20 hydrogen, hydrazine, ammonia, fossil fuels, separate components of fossil fuels, or mixtures thereof, wherein all fuels have a boiling point at ambient temperature of 250°C or less. It is especially useful to obtain a fuel cell having an operating temperature between about 10 and 30°C.

25   In another aspect, the composite material may be prepared by replacing the perovskite-type structure of the process [BB] with a

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metal-phthalocyanine structure, wherein the metal is selected from iron, cobalt, nickel and the like.

In still another aspect, the perovskite-type electrode (or the metal-phthalocyanine electrode) and the discontinuous fluoride

5 electrolyte of process [BB] are each thin films of between about 1 and 25 microns on a conventional inorganic catalyst support.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows Table 1 as a comparison of various types of fuel cells.

10   Figure 2 shows the open circuit voltage (V_{oc}) versus time using a single crystal of lanthanum fluoride (LaF_3).

Figure 3 shows a configuration of a fuel cell using, for instance, a single crystal of thinly-machined and polished lanthanium fluoride.

Figure 4 shows a curve of the open circuit voltage versus time

15 using a single crystal of lanthanum fluoride (LaF_3). Figure 4 is at 0.575 volts using Pd/Pt electrodes.

Figure 5 is a table showing the open circuit voltage (V_{oc}) for air, nitrogen, oxygen and hydrogen.

Figure 6 is a cross section of a solid material composite for solid

20 electrode/electrolyte having a Pt contact, a solid coating of an electrode (e.g. $La_{0.7}Sr_{0.3}F_{2.7}$ with a perovskite-type electrode (e.g. $La_{0.7}Sr_{0.3}CoO_3$).

Figure 6A is an enlarged cross section showing the discontinuous nature of the electrolyte on a pore opening of the porous electrode.

25   Figure 7 is a cross section of a solid material composite useful as a solid electrode having a catalyst support, a platinum contact, a solid coating of an electrolyte (e.g., $La_{.7}Sr_{0.3}F_{2.7}$) with a solid

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discontinuous coating of a perovskite-type (e.g., $La_{0.7}Sr_{0.3}CoO_3$) or a metal phthalocyanine (Co,Ni, or Fe phthalocyanine) electrode.

Figure 7A is an enlarged cross section showing the discontinuous nature of the electrolyte in contact with the electrode on the solid

5   support.

DETAILED DESCRIPTION OF THE
INVENTION AND PREFERRED EMBODIMENTS

In the present invention, lanthanum fluoride is the solid electrolyte of choice for a fuel cell, or a sensor. Its properties are

10 shown below in Table 2.

Table 2

PROPERTIES OF LaF_3

-Crystal structure: hexagonal space group is $P6_3/mcm$ $-D^3_{6h}$

-with twelve formula units per cell,,

15   -Melting Point: 1493°C,

-Density: 5.936,

-Dielectric constant: 14 (at 10MHz),

-Thermal conductivity: 0.025 (W $cm^{-1}deg^{-1}$),

-Electrical conductivity ~ 10^{-7} $\Omega^{-1}cm$-1 (at 25°C)

20   -Transmits light from the vacuum ultraviolet into the infrared,

-The effective Debye temperature is: ~360°K,

-The activation energy for fluorine ion diffusion is ~0.45 eV,

-Activation energy for the formation of defects: ~0.07eV,

-Birefringence: $\Delta n = 0.006$,

25   -Thermal expansion coefficient: 11×10^{-6} cm/cm/°C (c-axis,

25°C), a good match is Cu,

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LaF$_3$ has unique physicochemical properties such as high electrical conductivity and high polarizability at room temperature. The Debye temperature of LaF$_3$ is only 360°K, while its melting point is as high as 1766°K. The observed phenomena appear to be associated

5   with the formation of Schottky defects and with the diffusion of defects has the unusually low value of ~0.07 eV, and the room temperature Schottky defect density is about $10^{19}/cm^3$.

Fluorine in LaF$_3$ usually exists in three magnetically nomequivalent sites. Covalent bonding predominates in two of the sites.

10 In the third site, the fluorines make up a layered array with approximately 60% ionic bonding and about 40% π-bonding. The high polarizability and high conductivity of LaF$_3$ at room temperature is primarily due to the motion of F$^-$ ions through the latter sites. The relatively small radius of F$^-$ is almost identical with that of the oxide

15 O^{2-} ion (1.25 A); therefore oxide ions (O^{2-} ions) can substitute for the F$^-$ ions in LaF$_3$. It has been confirmed the oxygen ion transport through the bulk of a single crystal LaF$_3$ by Auger electron spectroscopy. In other words, the solid electrolyte LaF$_3$ serves as a supporting electrolyte analogous to liquid phase in which oxygen ions

20 can move freely.

Lanthanum Fluoride as a Solid Electrolyte for Fuel Cell

Traditionally LaF$_3$ has been extensively used as a F$^-$ ion selective electrode in electroanalytical chemistry. Recently LaF$_3$ has been applied to a room temperature potentiometric oxygen sensor and to a

25 multifunctional sensor for humidity, temperature, oxygen gas, and dissolved oxygen. However, no disclosure exists concerning the use of LaF$_3$ material as a single crystal as a solid electrolyte in a fuel

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cell. In earlier investigations, it was determined that polycrystalline

lanthanum fluoride as a thin film solid electrode was unreliable and

unpredictable. About one of ten electrodes prepared shorted out

under laboratory conditions. As is described below, the single

5   crystal lanthanum fluoride solid electrolyte was reliable and

predictable.

Figure 2 illustrates a result on a LaF_3 fuel cell. In this case, a

single crystal of between about 10 and 100 mils is used. As shown in

Figure 3 , one cm diameter single crystal LaF_3 with a thickness of 25

10   mils was used. A comb-shape noble metal (Pt, Au, or Pd) electrode

(21 + 21A) was sputtered on both sides of the LaF_3 sample 22. One

electrode was exposed to pure hydrogen and the other was exposed to

room air. A Pt/Pt system exhibited an open circuit potential (V_{oc}) of

about 0.6 volts at room temperature. The result was repeatable upon

15   on an on/off cycle of hydrogen. When the Pt/oxygen cathode 21 was

replaced by a Pd electrode with a different configuration, V_{oc} was

increased to 0.88 volts. However, in either case, the observed short

circuit currents were in the order of 10^{-8} Amperes. This small

amount of current is due to the fact that, in the electrode

20   configuration used in our experiments, the total area of the

triple-interface (i.e. gas, electrode catalyst, and solid electrolyte)

available for electrochemical reactions was extremely small. Current

density is greatly increased when a large surface area platinum black

is used as an electrode.

The following electrochemical reactions may take place at each electrode:

Cathode: $O_2 + 4e^- = 2O^{2-}$,

Anode: $2H_2 + 2O^{2-} = 2H_2O + 4e^-$
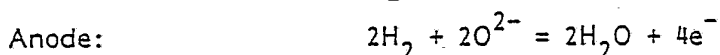
Effect on V_{oc} of Oxygen Partial Pressure Differences Between Working and Counter Electrodes

A study was made to determine how a difference in oxygen partial pressures on either side of the solid electrolyte contributed to the measured V_{oc} values. The relation used was

$V_{oc} = RT/4F$ ln P_{O_2} (At electrode #1)/ P_{O_2} (At electrode #2) where P_{O_2} stands for partial pressure of oxygen at the electrode specified, R is the universal gas constant, T is the temperature in Kelvin, and F is Faraday's constant.

However, from the results seen in Figure 4 and in Figure 5 (Table 3) the oxygen partial pressure differences do not determine the measured V_{oc} with air at working electrode and oxygen at the counter electrode. This will confirm the result that the observed V_{oc} is indeed due to a fuel cell function.

Those solid materials containing both lanthanum and fluorine (especially structure of formula (a)), are very attractive as solid electrolytes in low temperatures (10 to 30°C) solid electrolyte of fuel cells.

In preferred embodiments of material [AA] above, each of the structures (a) through (m) are each independently preferred as a solid electrolyte for a fuel cell, a solid electrolyte for a sensor or as a catalyst, espeacially as fuel cell or a sensor.

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In a preferred embodiment, the solid material material [AA] of the SUMMARY is selected from structures of formula (a), (b), (d), (e) or (j). In another embodiment the solid material of [AA] of the SUMMARY is selected from structures of formula (a), (b), (f), (h), 5 (j) or (k).

Other preferred embodiments of the solid material include the following:

[1] fuel cell of material [AA] above has a useful operational temperature range of between about 0 and 1000°C especially wherein 10 the structure in subpart (a) is AF_3 wherein A is lanthanum, and also where the operational temperature is between about 15 and 30°C;

[2]. the electrolyte of material [AA] is used in a device as a sensor to detect gases selected from oxygen in the gaseous phase ·or dissolved in a liquid;

15   [3] the electrolyte of material [AA] is used for a sensor wherein the sensor has a useful operating range of between about -40°C to + 1000°C; or

[4] the solid material [AA] above as an electrolyte for a sensor of [AA] above is wherein the oxygen sensor has an operating range 20 of between about 0°C and 600°C.

In the present invention the solid materials of [AA] are unless otherwise stipulated, individually preferred as a component of a fuel cell, of a sensor or as a catalyst useful in the interconversion formation and degradation of organic compounds, nitrogen-containing 25 compounds and the like.

It is intended that the solid materials described herein for use as solid electrolytes for fuel and for sensors optionally include

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pretreatment of the surface of the solid, preferably structures of formula (a), especially where A is lanthanum as described herein below.

Pretreatment Using Oxygen Atmosphere

5   An instrinsic single crystal of LaF_3 has a conductivity of 10^{-7} $ohm^{-1} cm^{-1}$ (which is mainly due to F^- ions) at room temperature. It is suggested that the oxygen ion conductivity in LaF_3 may be increased simply by sintering the crystal in an oxygen gas atmosphere because some of F^- ions may be replaced by O^{2-} ions. Recently,

10 Yamazoe et al., (supra) reported that the response time of LaF_3 oxygen sensor was dramatically improved by the treatment of LaF_3 in a stream of air containing 15 torr of water vapor at 150°C for 12 hr. This improvement is presumably due to the formation of a lanthanum oxy-fluoride at the surface (the chemical composition may be written

15 as lanthanum oxyfluoride of the structure (j) in material [AA] above.

        In the present invention, the materials described in the Summary of the Invention (and in Claim 1) are sintered in an oxygen environment at elevated temperature. The material is placed in an oxygen atmosphere containing from 1 to 99 percent by weight of water.

20 Usually the water present is between about 10 and 30 percent by weight especially about 15 percent by weight. The temperature is usually between about 100 and 1000°C, preferably between about 150 and 600°C, especially between about 200 and 400°C.

Pretreatment using Electrical Polarization

25   It is also possible to pretreat a solid material [AA] to enhance its ionic conductivity by contacting the material with a polarizing electrical current. Thus, the electrochemical doping (pumping) of

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oxide ions is achieved by subjecting about 1 gram the material [AA]

to 10^{-3} amperes per square centimeter for between about 1 to 25 hr

at ambient temperature. Stated in another way about 1 gram of the

structure of the material [AA] above is subjected to a certain amount

5   of coulombs equivalent to a product of one Faraday (coulombs/mole)

times X where X is between about 0.001 and 1 a depending on the

specific material [AA] structure (a) to (m). This electrochemical

pumping may be performed between about 0 and 400°C.

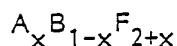An Electrode/Electrolyte Composite

10   Perovskite-type

In general, the electrocatalysts for the above cited low tempera-

ture solid electrolyte fuel cell can be noble metals (e.g. platinum),

their alloys or blacks, metal-phthalocyanines, transition metal cata-

lysts (e.g. Ni/NiO), and metallic transition metal oxides (e.g.

15   $La_{0.9}Sr_{0.1}MnO_3$).

Particularly, it is of interest to use electronically conductive

perovskite-type oxide: e.g.:

$$A_{1-x}B_xQO_3$$
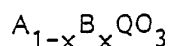
where A, B, Q and x are as defined hereinabove as catalytic

20   electrode materials, especially for the oxygen reaction in conjunction

with the lanthanide fluoride solid electrolyte:

$$A_xB_{1-x}F_{2+x}$$

wherein A is: (La, Ce, Nd, Pr or Sc);

and B is: (Sr, Ca, Ba or Mg);

25   and x is between about 0.001 and 1.

An example of such a composite electrode/electrolyte system

would be: $La_{0.7}Sr_{0.3}CoO_3/La_{0.7}Sr_{0.3}F_{2.7}$.

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On this interface the electronically conductive phase

(electrode: $La_{0.7}Sr_{0.3}F_{2.7}$)

exist adjacently to each other and even may be mixed on an

atomic-level by sharing La and Sr atoms.

5   In designing systems of $A_{1-x}B_xQO_3/A_xB_{1-x}F_{2+x}$,

one can choose atoms for A and B in such a way that there is a

maximum degree of matching in the lattice parameters and thermal

coefficients of the two phases. Therefore, the composite system

$A_{1-x}B_xQO_3/A_xB_{1-x}F_{2+x}$
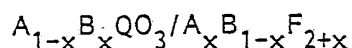
10 can be an ideal site to facilitate the following reaction:

$O_2 + 4e^- = 2O^{2-}$,
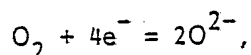
because a well defined, stable atomic-scale three-phase interface (gas,

electrode, electrolyte) can be established in the

$A_{1-x}B_xQO_3/A_xB_{1-x}F_{2+x}$.
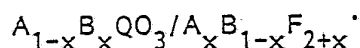
15   The perovskites useful in this invention may be purchased or

may fe formed according to the procedures described in the literature

e.g., T. Kudo et al., U.S. Patent No. 3,804,674, which is

incorporated herein by reference.

A typical perovskite preparation is described below in Example

20 2.

Figure 6 shows the configuration of a composite for use in a fuel

cell. The perovskite-substrate (porous oxide) electrode 61 is treated

with a vapor to deposit the fluoride electrolyte 62 on the surface. As

shown in Figure 6A fluoride 62 or 65 will enter the pores of the

25 perovskite and also be on the surface 64 of the perovskite in a

discontinuous manner. In this way, millions of two material catalytic

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surfaces sites 66 are created to facilitate the electrochemical reaction
at the intersection of the perovskite 61 and fluoride (62 or 65).

Figure 7 shows the configuration of a supported composite for
use in a fuel cell. The perovskite substrate 71 is spray dried onto
5   an inorganic support 70 such as silica, thoria, zirconia, magnesia, or
the like having mechanical stability. The fluoride electrolyte 72 is
then vapor deposited on the surface of the perovskite 71. As shown
in Figure 7A the fluoride electrolyte 72 as a vapor enters the pores
of the perovskite 71 and the substrate 70 in a discontinuous manner.
10 In this way, millions of two-material catalytic surfaces 74 are created
to facilitate the electrochemical reaction at the intersection of the
perovskite 71 and fluoride 72.

Metal Phthalocyanines

The present invention also contemplates the use of
15 metal-phthalocyanines in electrode/electrolyte composites. In this
embodiment of the invention, the metal-phthalocyanine
(Z-phthalocyanine) is used to replace the perovskite-type oxide
described above on a weight to weight basis and is then combined
with the solid electrolyte as is described above. The metal ions (Z-)
20 preferred include iron, cobalt, nickel and the like.

Typical metal-phthalocyanines in these composites include those
described above and, for example, those and similar ones described
by K.V. Kordesch in U.S. Patent No. 3,783,026, which is
incorporated herein by reference.

25   The composites described below in Claims 28, 29, 30 or 31 are
preferred.

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Sensors

The use of the structures disclosed herein are described sensors in analiytical devices to determine components in the vapor phase and also in the liquid phase.

5   These sensors are preferably useful to analyze oxygen, carbon dioxide, methane, ethane, ethylene, ammonia, hydrogen sulfide or the like. Lanthanum fluoride is preferred to analyze oxygen in a gaseous phase or in a liquid, preferably an aqueous solution.

The range of the analysis may be from between about a part per 10 billion to 10,000 parts per million in the gas phase (usually performed in the potentiometric mode). Even high concentrations of a component, for instance, in the liquid phase determined in the current mode because the proportionality is linear rather than logrithmic.

15   For the structures defined above in the summary in a preferred embodiment the solid material for use as an electrolyte in a fuel cell or in a sensor or for use as catalyst is selected from structures of (b), (c), (d), (e), (f), (h), (i), (j), (k), (l), or (m). A more preferred embodiment of the solid material is selected from the 20 structures of (b), (c), (d), or (e). Another preferred embodiment of the solid material is selected from the structures of (k), (l) or (m).

The following Examples are intended to be illustrative only and are not to be construed as limiting in any way.

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EXAMPLE 1

Formation of Solid Thin Films and Fuel Cell Measurements

(aa) As is described in B.C. LaRoy et al., (above, and incorporated herein by reference), lead $_{.75}$ potassium $_{.25}$ fluoride

5   $_{1.75}$ ($Pb_{0.75}K_{0.25}F_{1.75}$) is evaporated onto in a thin polycrystalline film onto a substrate to a thickness of 25 mils. Pt black is coated onto the polycrystalline film. One electrode is exposed to pure hydrogen and the other is exposed to room air. This Pt/solid electrode/Pt system is expected to exhibit a useful open circuit,

10 potential (V_{oc}) of between about 0.5 and 1.0 volts.

(bb) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $Pb_{.75}Bi_{.25}F_{1.75}$.

(cc) The procedure of subpart (aa) above is repeated, except

15 that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $La_{.3}Sr_{.7}F_{2.3}$.

(dd) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $La_{0.4}Sr_{.5}LiF_{2.5}$.

20 (ee) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $Ca_{.88}U_{.02}Ce_{.1}F_{2.14}$.

(ff) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of

25 $PbSnF_4$.

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(gg) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $KSnF_5$.

(hh) The procedure of subpart (aa) above is repeated, except
5   that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $SrCl_2 \cdot KCl$.

(ii) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $LaO_{.7}YF_{1.6}$.

10   (jj) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $PbSnF_{0.3} \cdot PbSnO_{0.4}$.

(kk) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of
15 $(LaO_{1.5})_{0.5}(CaF_2)_{0.5}$.

(ll) The procedure of subpart (aa) above is repeated, except that the $Pb_{0.75}K_{0.25}F_{1.75}$ is replaced by an equivalent weight of $Sm_6Nd_6F_{18}O_9$.

In subparts (bb) to (ll) the fuel cell obtained is expected to
20 generate a useful open circuit potential (V_{oc}) of between about 0.5 and 1.0 volts.

EXAMPLE 2

FORMATION OF A PEROVSKITE FOR AN ELECTRODE

A pure lanthanum nickelate crystal is synthesized by a
25 co-precipitation technique. The starting materials are $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (alternatively acetates and chlorides can be used as the starting materials). The proper amounts of each nitrate

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required to give the desired stoichiometry are weighed and dissolved in doubly distilled water to remove Na^+ and separated quickly by a centrifuge technique at 2000 rpm for 15 min., since $Ni(OH)_2$ tends to dissolve at pH~7. This process is repeated several times. The

5 obtained precipitates are dried in an oven at 100°C overnight. The dried powder is then put in the furnace at 800°C for 16 hours in an O_2 atmosphere. The electrode is made by pressing the powders into 13mm diameter pellet (Beckman model K-13 die) at a pressure of 300kg cm^{-2}. The pellet is sintered at 750°C in an O_2 atmosphere for 48

10 hours and the perovskite pellet is recovered.

A thin film (about 100 micrometers) of $La_{0.5}Sr_{0.5}F_{2.5}$ is prepared on the perovskite layer by conventional vacuum evaporation (LeRoy et al.) using pure materials of lanthanum fluoride and strontium fluoride in a tungsten boat applying a current of about 40

15 amperes in a high vacuum of about 10^{-7} torr. The composite obtained is expected to have a useful open circuit potential of between about 0.5 and 1.0 volts.

EXAMPLE 3

A Porous Substrate-$La_{0.5}Sr_{0.5}CoO_3$ (film)-$La_{0.5}Sr_{0.5}F_{2.5}$ (film)

20 by Spray Pyrolysis/Vacuum Evaporation or Reactive Sputtering

(aa) A thin layer of a perovskite oxide is prepared on a porous substrate (e.g. alumina, zirconia oxide with pore size of abut 100 A with a thickness 1-2 mm) by a spray pyrolysis. As an example, the 50% Sr doped $LaCoO_3$ is prepared as follows: 8.5g $Sr(NO_3)_2$, 23.3g

25 $Co(NO_3)_2 \cdot 6H_2O$ and 17.81g $La(NO_3)_3 \cdot 6H_2O$ (alternatively acetates and chlorides can be used as the starting materials) are dissolved in disltilled water and sprayed onto the hot porous substrate (about 10

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cm by 10 cm) at a flow rate of about 10 mL/min. The homogeneous
constituent is then decomposed at 250°C, followed by quenching
oxygen and heating 500°C, in air for 3hr. The perovskite catalyst
loading should be about 10mg/cm^2. Then, a thin film (about 100μm)

5   of $La_{0.5}Sr_{0.5}F_{2.5}$ is prepared on the perovskite layer by a vacuum
evaporation using pure materials of LaF_3 and SrF_2 in a tungsten boat
and applying a current of about 40 Amperes in high vacuum of about
10^{-7} torr. Alternatively pure metal targets can be used in a
sputtering process in a low pressure fluorine atmosphere (e.g. 10 m

10   torr). The obtained fuel cell is expected to generate an open circuit
potential (V_{oc}) of between about 0.5 and 1.0 volts. (See Figure 6,
6A, 7, 7A).

In the above (aa) subpart the reaction is repeated using an
equivalent weight of nickel phthalocyanine for the perovskite. The

15   composite formed is expected to have a useful open circuit potential of
between about 0.5 and 1.0 volts.

EXAMPLE 4

FORMATION OF A SINGLE CRYSTAL BASED FUEL CELL

A single crystal of lanthanum fluoride is pretreated in an oxygen

20   atmosphere of 50% oxygen. The single crystal is cut into slabs and
one slab is polished down to a thickness of 100-200 micrometers. A
layer of porous platinum black of between 100 and 200 micrometers
thickness is coated on opposite faces of the slab. One electrode is
exposed to pure hydrogen and the other electrode is exposed to room

25   air. This platinum/solid lanthanum fluoride electrolyte/platinum is
expected to exhibit a useful open circuit potential (V_{oc}) of between
about 0.5 and 1.0 volts.

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EXAMPLE 5

LaF$_3$ as a Sensor for Oxygen

(a) Lanthanium fluoride, as a portion of a single crystal, is machined and polished to the dimensions of 2 cm in diameter and 100 micrometers in thickness. This disk is placed in an appropriate electrical circuit in an analytical sensing device.

(b) When the sensor is contacted with a mixture of gases containing oxygen, it is expected that it is possible to detect the presence of oxygen between about 0.1 and 10,000 ppm.

(c) When the sensor is contacted with aqueous solution containing oxygen, it is expected that the sensor will detect oxygen between about 0.1 and 10,000 ppm.

(d) The other solid materials of [AA] above (a) through (m) are also expected to be useful sensors for oxygen in the gas phase or the liquid phase.

(e) The composite materials described herein as the single crystal or polycrystal when machined as described in subpart (a) above, are expected to be able to detect oxygen in a gas phase or in an aqueous solution.

While some embodiments of the invention have been shown and described herein, it will become apparent to those skilled in the art that various modifications and changes can be made in the present invention regarding solid materials for use as electrodes (electrolytes in fuel cell applications, in sensor applications and in catalyst applications) without departing from its spirit and scope. All such modifications and changes coming within the scope of the appended claims are intended to be covered thereby.

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WE CLAIM:

1. A solid material for use as an electrolyte for a fuel cell or for a sensor or as a catalyst each having a polycrystal or single crystal structure, comprising:
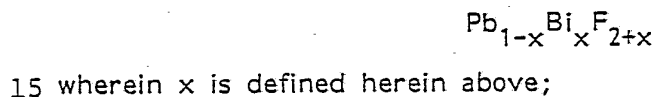
(a) a structure of the formula:

5
$$AF_3$$

wherein A is independently selected from lanthanum, cerium, neodynium, praseodynium, scandium or mixtures thereof; wherein AF_3 is a single crystal or a portion thereof;
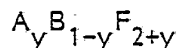
(b) a structure of the formula:

10
$$Pb_{1-x}M_xF_{2-x}$$

wherein M is independently selected from potassium, or silver, and x is between about 0.0001 and 0.25;

(c) a structure of the formula:

$$Pb_{1-x}Bi_xF_{2+x}$$

15 wherein x is defined herein above;

(d) a structure of the formula:

$$A_yB_{1-y}F_{2+y}$$

wherein:

A as defined hereinabove,

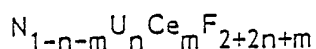20 B is independently selected from strontium, calcium, barium or magnesium, and y is between about 0.0001 and 1;

(e) a structure of the formula:

$$A_yB_{1-y-z}LiF_{2+y+z}$$
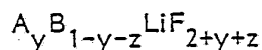
wherein A, B and y are as defined hereinabove, z is between about

25 0.0001 and 0.10;

(f) a structure of the formula:

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$$N_{1-n-m}U_nCe_mF_{2+2n+m}$$
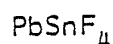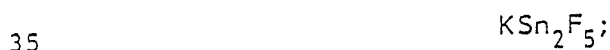
wherein N is independently selected from calcium, strontium or barium, n is between about 0.0001 and 0.05, and m is between about 0.0001 and 0.35;
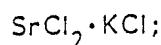
(g) a structure of the formula:

$$PbSnF_4$$

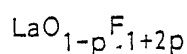with the proviso that $PbSnF_4$ is only useful as a fuel cell electrolyte;

(h) a structure of the formula:

$$KSn_2F_5;$$
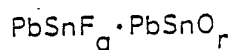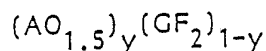
(i) a structure of the formula:

$$SrCl_2 \cdot KCl;$$

(j) a structure of the formula:

$$LaO_{1-p}F_{1+2p}$$

wherein p is between about 0.1 and 0.3;

(k) a structure of the formula:

$$PbSnF_q \cdot PbSnO_r$$

wherein q and r are each independently from between about 0.0001 and 1;

(l) a structure of the formula:

$$(AO_{1.5})_y(GF_2)_{1-y}$$

wherein A is defined hereinabove, y is between about 0.0001 and 1, and G is independently selected from calcium and magnesium; and

(m) a structure of the formula:

$$Sm_aNd_bF_cO_d$$

wherein a and b are each independently between about 2.18 and 9.82 and c is between about 12 and 29.45, and d is between about 3.25 and 12, with the proviso that a+b is about 12 and c+2d is about 36.

2.   A solid material of Claim 1 selected from structures of formula (a), (b), (d), (e) or (j).

3.   A solid material as an electrolyte for a fuel cell of Claim 1 selected from structures of formula (a), (b), (f), (h), (j) or (k).

4.   The solid material as an electrolyte for a fuel cell of Claim 1 wherein the fuel cell has a useful operational temperature range of between about 0 and 1000°C.

5.   The solid material of Claim 4 is useful as an electrolyte wherein the structure in subpart (a) is AF_3 wherein A is lanthanum.

6.   The solid material as an electrolyte of Claim 5 wherein the operational temperature is between about 15 and 30°C.

7.   The solid material as an electrolyte of Claim 1 wherein the electrolyte is used in a device as a sensor to detect oxygen in the gaseous phase or oxygen dissolved in a liquid.

8.   The solid material as an electrolyte for a sensor of Claim 1 wherein the sensor has a useful operating range of between about -40°C to + 1000°C.

9.   The solid material as an electrolyte for a sensor of Claim 3 wherein the sensor has an operating range of between abut 0°C and 600°C.

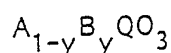10. A process for the preparation of an electrolyte for a fuel cell or for a sensor, which process comprises:

(a) reacting structure of Claim 1 in atmosphere comprising a mixture of oxygen and water wherein the water is present in between
5   about 1 and 99% by weight at between 100 and 1000°C for between about 10 and 50 hrs.

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11. A process for the preparation of an electrolyte for a fuel cell or for a sensor, which process comprises:

(a) subjecting the equivalent of about one gram of a solid material of the structure of [AA] to a current of about 10^{-3} amperes per square centimeter for a time sufficient to transmit a certain amount of coulombs equivalent to a product of one Faraday (coulombs/mole) times X where X is between about 0.001 and 1 at a temperature of between about 0 and 400°C.
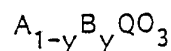
12. A process for preparing a composite comprising:

$$A_{1-y}B_yQO_3$$

having a perovskite or a perovskite-type structure as an electrode catalyst in combination with:
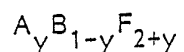
$$A_yB_{1-y}F_{2+y}$$

as a discontinuous surface coating solid electrolyte wherein A is independently selected from lanthanum, cerium, neodymium, praseodymium, and scandium, B is independently selected from strontium, calcium, barium or magnesium, Q is independently select-ed from nickel, cobalt, iron or manganese, and y is between about 0.0001 and 1, which process comprises:
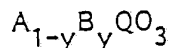
(a) obtaining a particulate of:

$$A_{1-y}B_yQO_3$$

wherein A, B and y are defined hereinabove having an average size distribution of between about 50 and 200 Angstroms in diameter;

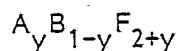(b) contacting the particle of step (a) with a vapor comprising:

$$A_yB_{1-y}F_{2+y}$$

wherein A, B and y are defined hereinabove, at about ambient pres-

20 sure at between about 0 and 1000°C: for between about 10 and 30 hr.

obtain a composite of between about 25 to 1000 microns in thickness;

(c) recovering the composite of step (b) having multiple inter-

faces between:

$$A_{1-y}B_yQO_3$$

25 and

$$A_yB_{1-y}F_{2+y}$$

said composite having a pore size of between about 25 and 200

Angstroms and a surface area of between about 10 and 100 meters

^{2}/gram.

13. The process of Claim 12 wherein A is lanthanum, B

strontium, Q is cobalt.

14. The process of Claim 13 wherein y is about 0.3.

15. The process of Claim 12 wherein A is selected from cerium

or scandium, B is selected from strontium or magnesium, Q is selected

from nickel, cobalt or manganese and y is between about 0.2 and 0.4.

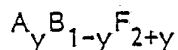16. The composite obtained by the process of Claim 12.

17. The composite obtained by the process of Claim 13.

18. The composite obtained by the process of Claim 14.

19. The composite obtained by the process of Claim 15.

20. A process for preparing a composite comprising:

Z-phthalocyanine as an electrode catalyst in combination with:

$$A_yB_{1-y}F_{2+y}$$

as a discontinuous surface coating solid electrolyte wherein A is

5 independently selected from lanthanum, cerium, neodymium,

praseodymium, and scandium, B is independently selected from

-33-

strontium, calcium, barium or magnesium, Z is independently selected

from nickel, cobalt or iron, and y is between about 0.0001 and 1,

which process comprises:

10   (a) obtaining a particulate of:

Z-Phthalocyanine

wherein Z is defined hereinabove having an average size distribution

of between about 50 and 200 Angstroms in diameter;

        (b) contacting the particlulate of step (a) with a vapor
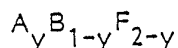
15 comprising:

$$A_y B_{1-y} F_{2-y}$$
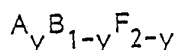
wherein A, B and y are defined hereinabove, at about ambient pres-

sure at between about 0 and 1000°C: for between about 10 and 30 hr.

obtain a composite of between about 25 to 1000 microns in thickness;

20   (c) recovering the composite of step (b) having multiple inter-

faces between:

Z-Phthalocyanine

and

$$A_y B_{1-y} F_{2-y}$$

25 said composite having a pore size of between about 25 and 200

Angstroms and a surface area of between about 10 and 100 meters

^{2}/gram.

        21. The process of Claim 20 wherein A is lanthanum, B is

strontium, and Z is iron.

        22. The process of Claim 21 wherein y is about 0.3.

        23. The process of Claim 21 wherein A is selected from cerium

or scandium, B is selected from strontium or magnesium, Q is selected

from nickel, cobalt or manganese and y is between about 0.2 and 0.4.

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24. The composite obtained by the process 20.

25. The composite obtained by the process 21.

26. The composite obtained by the process 22.

27. The composite obtained by the process 23.

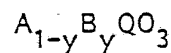28. A composite consisting essentially of:

$$A_{1-y}B_yQO_3$$
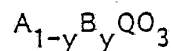
having a perovskite or a perovskite-type structure as a solid

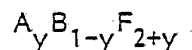electrode catalyst in combination with:

$$A_yB_{1-y}F_{2+y}$$

as a discontinuous surface coating solid electrolyte on the perovskite

wherein A is independently selected from lanthanum, cerium,

neodymium, praseodymium, or scandium, B is independently selected

from strontium, calcium, barium or magnesium, Q is independently

selected from nickel, cobalt, iron or manganese, and y is between

about 0.0001 and 1 wherein the perovskite has an average size

distribution of between about 50 and 200 Angstroms in diameter;

and the composite layer of between about 25 to 1000 microns in

thickness;

said composite having multiple interfaces between:

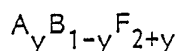$$A_{1-y}B_yQO_3$$

and

$$A_yB_{1-y}F_{2+y}$$

and a pore size of between about 25 and 200 Angstroms and a surface

area of between about 10 and 100 meters ^{2}/gram.

29. The composite of Claim 28 which further includes a suitable

inorganic support.

-35-

30. A composite consisting essentially of a Z-phthalocyanine wherein Z is a metal selected from iron, cobalt or nickel as a solid electrolyte in combination with:

$$A_y B_{1-y} F_{2+y}$$

5 as a discontinuous surface coating solid electrolyte on the surface fo the Z-phthalocyanine wherein A is independently selected from lanthanum, cerium, neodynium, praseodymium or scandium, B is independently selected from strontium, calcium, barium or magnesium, and y is between about 0.0001 and 1 wherein the Z-phthalocyanine 10 has an average size distribution of between about 50 and 200 Angstroms in diameter and the composite is between aobut 25 and 1000 microns in thickness, said composite having multiple interfaces between the Z-phthalocyanine and $A_y B_{1-y} F_{2+y}$ and a pore size of between about 25 and 200 Angstroms and a surface area of between 15 about 10 and 100 meters ^{2}/gram.

31. The composite of Claim 30 wherein the composite further includes a suitable inorganic support.

32. The use of the composite of Claim 28 selected from electrode/electrolyte for a fuel cell, a sensor, or a contact catalyst for synthesis or degradation.

33. The use of the composite of Claim 30 as an electrode/electrolyte for a fuel cell a sensor or contact catalyst.

34. The use of the composite of Claim 28 as an oxygen sensor.

35. A process for the generation of electricity, which process comprises:

(a) contacting a solid material of Claim 1 with a fuel at between about 0 and 1000°C.

-36-

36. The process of Claim 35 wherein the fuel for the fuel cell is selected from hydrogen, hydrazine, ammonia, fossil fuels, separate components of fossil fuels, or mixtures thereof, wherein all fuels have a boiling point at ambient temperature of 250°C or less.

37. The process of Claim 36 wherein in step (a) the operating temperature is between about 10 and 30°C.

38. The solid material of Claim 1 wherein the crystal structure is selected from (b), (c), (d), (e), (f), (h), (i), (j), (k), (l) or (m).

39. The solid material of Claim 1 wherein the crystal structure is selected from structures of (b), (c), (d), or (e).

40. The solid material of Claim 1 wherein the crystal structure is selected from structures of (k), (l) or (m).
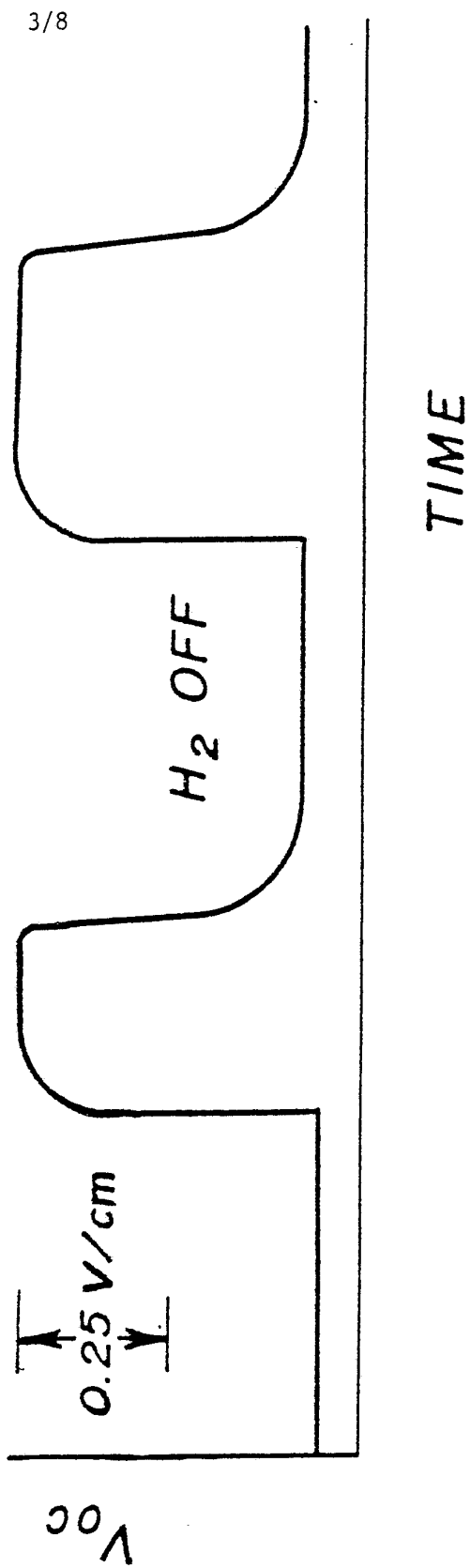
FIGURE 1

Table I. Fuel cell types

	Phosphoric Acid	Molten Carbonate	Alkaline	High-Temperature Solid Oxide	Solid Polymer
Electrolyte	Conc. H_3PO_4	K_2CO_3–Li_2CO_3	KOH solution	ZrO_2–Y_2O_3 or ZrO_2–CaO	Sulfonated fluoro-carbon acidic ion exchange membrane
Electrolyte support	Phenolic fiber(SiC)	$LiAlO_2$	Asbestos	Electrolyte itself	Electrolyte itself
Electrode (catalyst)	Pt	Ni, NiO	Pt, Pt–Au alloy	NiO–ZrO_3 – $La_{0.9}Sr_{0.1}MnO_3$	Pt
Anode fuel	H_2(reformer product)	H_2–CO	H_2(high purity)	H_2–CO	H_2
Cathode oxidant	Air	Air + CO_2	O_2(high purity)	Air	O_2
Temperature (°C)	160–190	600–700	82–104	900–1100	82
Pressure (atm)	<120 psia	<120 psia	60 psia	Atm	60 psia

Cell voltage (V)	<0.8	<0.85	<0.97	<0.90	<0.95
Impurity tolerance	<2000 ppm CO" <1ppm H₂S"	No H₂S	High-purity feeds, no CO and CO₂	Not yet defined	Strict moisture control
Development status	Nearest to commercialization	Next nearest to commercialization	Apollo and Columbia space flights	Third-generation technology	Gemini space flights
Anodic reaction	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{-2} \rightarrow H_2O(g) + CO_2 + 2e^-$	$H_2 + 2OH^- \rightarrow 2H_2O(g) + 2e^-$	$H_2 + O^{-2} \rightarrow H_2O(g) + 2e^-$ or $CO + O^{-2} \rightarrow CO_2 + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$
Cathodic reaction	$2e^- + \frac{1}{2}O_2 + 2H^+ \rightarrow H_2O(g)$	$CO_2 + \frac{1}{2}O_2 + 2e^- \rightarrow CO_3^{-2}$	$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$	$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$
Overall reaction	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l)$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$ $H_2 + \frac{1}{2}C_2 \rightarrow CO_2$ or $CO + \frac{1}{2}O_2 \rightarrow CO_2$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l)$

FIGURE 1 (con't)

SUBSTITUTE SHEET
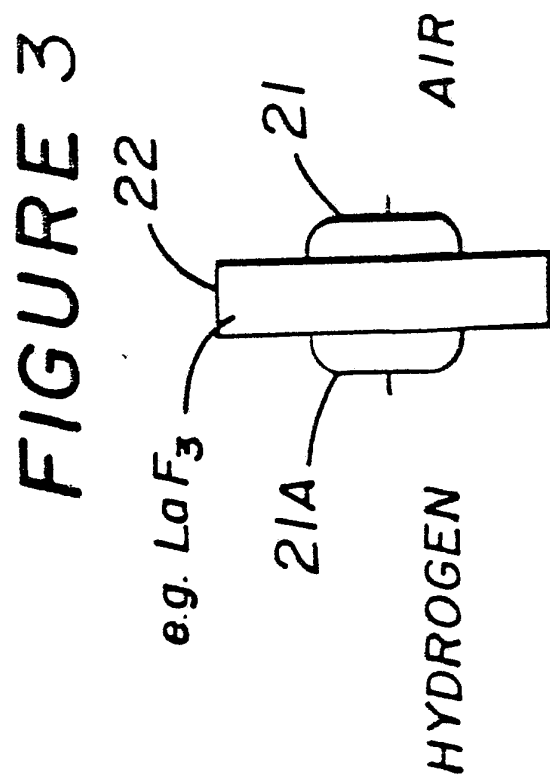
FIGURE 2
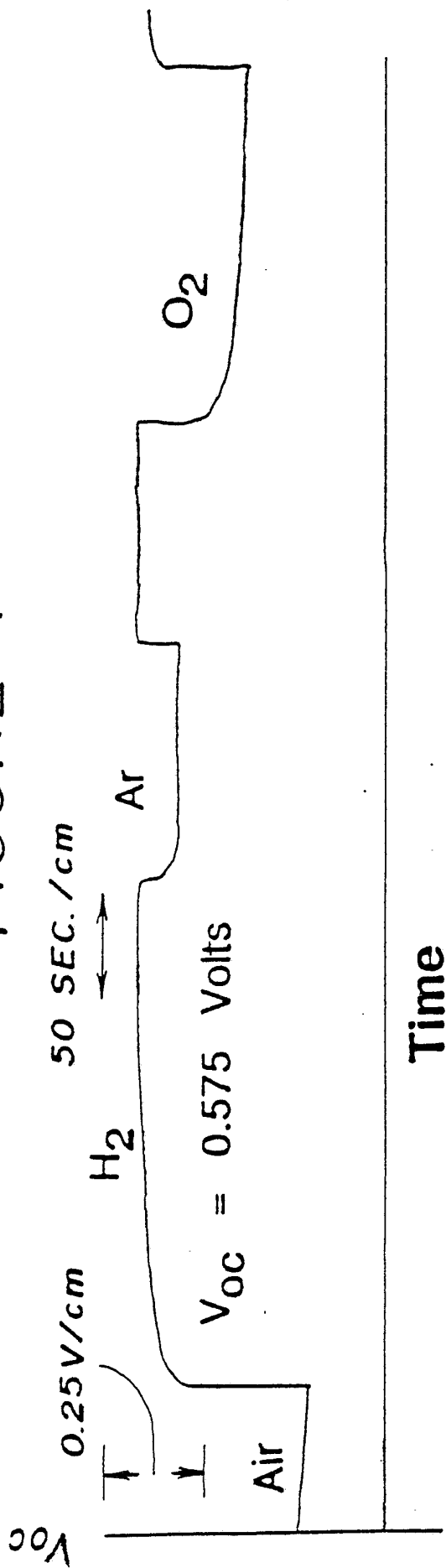
FIGURE 3

FIGURE 4

FIGURE 5

Table 3.

Reading	V_{oc}				V_{oc}(experimental) $=V_{oc}$(air)$-V_{oc}$(oxy.)	V_{oc} from theory
	Air	N_2	O_2	H_2		
1.	100	134	72	---	28	9.8
2.	112	---	80	800	32	9.8
3.	151	223	140	800	11	9.8

FIGURE 6

SOLID ELECTROLYTE: e.g. $La_{1-y} Sr_y F_{2-y}$

PEROVSKITE: e.g. $La_y Sr_{1-y} CoO_3$

62

61

6A

Pt

FIGURE 6A