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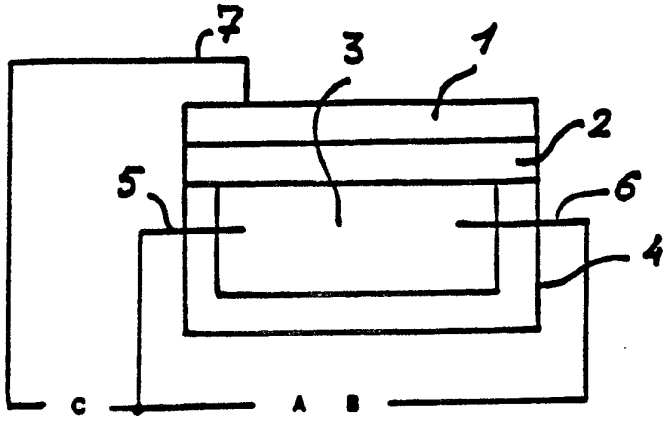
(54) Title: HALF-CELL WITH A SOLID-STATE REFERENCE ELECTRODE FOR A CERAMIC SENSOR



(57) Abstract

The sensor includes a measuring electrode (1) for contact with a medium in which a measuring is to be undertaken, e.g. measuring the gas concentration, an electrolyte layer (2), e.g. of nasicon, and a body (3) that is in contact with the electrolyte layer and which constitutes a combination of a heating unit, and a temperature sensor and a reference electrode, and which is encapsulated in a capsule (4), e.g. of glass. Two contacts (5, 6) to the body (3) make it possible to heat the reference electrode and/or measure its temperature-dependent impedance. The measured value of the measuring electrode (1) is obtained between a contact (7) to this electrode and one of the contacts (5, 6) to the body (3).

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Half-cell with a solid-state reference electrode for a ceramic sensor.

The invention relates to a half-cell for a ceramic sensor with an ion-conductive solid-state electrolyte material, said half-cell receiving later on a measuring electrode, and consisting of a layer of solid-electrolyte material and a body that is in contact with said layer and is made from a material presenting electronic as well as ionic conductivity.

The disclosure of US patent No. 4 908 118 deals with a sensor for monitoring hydrogen concentrations in gases. A reference electrode exhibiting sodium ion activity and consisting for instance of Na_xWO_3 is used in said sensor. The reference electrode is produced by mixing nasicon-electrolyte powder with an appropriate carrier followed by sintering.

Owing to its design and due to the fact that a detector electrode of platinum, palladium or palladium oxide is used in said known sensor, i.e. a material having a great hydrogen permeability, this prior art sensor is specifically determined to measure the hydrogen concentration in gases.

DE-OS 38 11 864 deals with a measuring device specifically determined to measure the partial pressure of oxygen in molten glass at high temperatures. This measuring device makes use of a reference electrode of platinum which through an oxygen-ion-conductive, heat-resistant material is in electro-chemically conductive contact with the fluid in which measuring is to be effected. Said measuring device also includes a hotwire coiled around the reference electrode for comparing the reference temperature of the melt and for adjusting the ambient temperature of reference to the temperature of the melt.

EP-A2-189 038 deals with a sensor which is likewise specifically determined for oxygen measuring

by means of a solid electrolyte body exhibiting oxygen-ion-conductivity.

The invention is based on the recognition that the above mentioned prior art is limited by the fact that said known sensors only allow a specific measuring, viz. hydrogen and oxygen, respectively, that there is a need for a type of sensor which may easily be designed so as to measure many other substances and in many other fluids and that the prior art sensors due to their specific design cannot easily be conformed to various measuring purposes.

The invention differs from the above referenced prior art in that the solid-state electrolyte layer closes an encapsulated electron and ion-conductive body.

The advantage of such a design is that the body embedded in its encapsulation and provided with its solid-state electrolyte layer may be produced as a half-cell on to which a task-specific measuring electrode is applied in dependence on the specific measuring task.

The electron- and ion-conductive body may appropriately be in connection with contacts to apply an electric current for heating the body and/or measuring the temperature of the body.

The invention also relates to a ceramic sensor with a half-cell of the above stated type and with a measuring electrode determined to be brought into contact with the medium in which measuring is to be effected, said sensor according to the invention being characterized in that the measuring electrode is formed as a covering applied to the electrolytic layer.

A contact for the measured value may appropriately be provided in relation to one of the contacts of the body. The advantage of a sensor so designed - besides the possibility of easy conforming to a spe-

cific purpose by a suitable choice of the nature of the measuring electrode - is to be found in that by applying a suitable current signal to the body between its contacts, the body may be rapidly heated to the temperature that is the most appropriate for the actual measuring, and by measuring its temperature-dependent impedance between said contacts, information is immediately supplied about the actual temperature in the sensor and thus about the suitability of said temperature for the actual measuring.

The invention will now be explained in detail in the following with reference to the schematical drawings, in which

Fig. 1 illustrates a preferred embodiment of the sensor according to the invention, and

Fig. 2 is a function chart illustrating the mode of operation of this sensor.

Fig. 1 shows a preferred embodiment of the sensor according to the invention. Reference numeral 1 shows a measuring electrode intended to be placed in the medium in which a measuring shall be undertaken. This electrode is formed as a layer of a material of an appropriate type adjusting itself into thermo-dynamic balance with the substance the concentration of which is to be measured. The measuring electrode may for instance consist of platinum if oxygen measuring is desired, and of palladium or palladium oxides if hydrogen measuring is desired, or Na_2CO_3 for CO_x-measuring, Na_2SO_4 for SO_x-measuring, and so on.

Reference numeral 3 shows a body constituting a combination of a heating unit, a temperature sensor and a reference electrode, and consisting e.g. of a sodium-cobaltite compound. Said unit may be provided by the thick-film technology as well as by the thin-film technology.

Body 3 is accommodated within a capsule 4, e.g. of glass, and is kept encapsulated therein by an

electrolyte layer 2 that may consist of stabilized ZrO_2 or nasicon.

The sensor is provided so that the body 3 is in connection with contacts 5, 6, while the measuring electrode 1 is in connection with a contact 7.

The flow chart in Fig. 2 illustrates the mode of operation of the sensor according to the invention. Within a measuring period, as shown along the time axis in the chart, a preferably pulse-width modulated current signal is at first applied, as shown by partial period A - between the contacts 5 and 6 - with the purpose of heating the body 3 to the temperature wanted for the actual measuring. The dot-and-dash line in partial period A in the chart reflects the pulse width modulation.

After completion of partial period A, the temperature in body 3 is measured in partial period B, e.g. by measuring the temperature-dependent impedance of the electrode between contacts 5 and 6.

In partial period C, between the contact 7 of the measuring electrode 1 and one or the other contact of the body 3, e.g. contact 5, sensor measuring is effected with the view of obtaining the desired value of measurement.

Said sensor measuring may be potentiometric (measurement of electromotive force) or potentiostatic (measurement of current).

A sensor so designed may be produced in quite small dimensions e.g. of 2 x 3 x 8 mm, with threads of a diameter e.g. of 0.1 mm.

The sensor may be used for measurement in pure gases, combustion gases or atmosphere, at temperarures exceeding 200°C. It may also be used for measurement in drinking water, sea water or domestic or industrial effluent, normally at temperatures not exceeding e.g. 80°C. It may further - normally at temperatures below

40°C - be used for measuring in fermenters or flavouring agents, or in medical experiments and examinations.

A particular advantage of the sensor according to the invention consists in that a possible heating in partial period A rapidly makes the temperature in body 3 to rise to the value of temperature that is most convenient for the actual measuring and in that the following temperature measurement in partial period B promptly gives an indication as to whether the actual temperature in body 3 has attained the correct value of the desired measuring.

It should, moreover, be observed that the activation of the sensor in partial period A is not absolutely necessary, provided measuring at ambient temperature be effected, meaning that only temperature measuring (partial period B) and sensor measuring (partial period C) are effected.

It has been mentioned in the preceding that the electrolyte layer 2 may consist of stabilized ZrO_2 or nasicon but other materials may as well be used, such as Na-β"-Al_2O_3 or various polymers.

The choice of convenient combinations of materials for the measuring electrode 1, the electrolyte layer 2 and the body 3 offers the possibility of designing sensors for specific measuring purposes.

PATENT CLAIMS

1. A half-cell for a ceramic sensor with a ion-conductive solid-state electrolyte material, said half-cell receiving later on a measuring electrode, and consisting of a layer (2) of solid-electrolyte material and a body (3) that is in contact with said layer and is made from a material presenting electronic as well as ionic conductivity, characterized in that the solid-state electrolyte layer (2) closes an encapsulated electron and ion-conductive body (3).

2. A half-cell for a ceramic sensor according to claim 1, characterized in that the electron- and ion-conductive body (3) is in connection with contacts (5, 6) to apply an electric current for heating the body (3) and/or measuring the temperature of the body (3).

3. A ceramic sensor with a half-cell according to claim 1 or 2, and with a measuring electrode determined to come into contact with the medium in which measuring is to be effected, characterized in that the measuring electrode (1) is formed as a covering applied to the electrolyte layer (2).

4. A ceramic sensor according to claim 3, characterized in that a contact (7) for the measured value is provided on the measuring electrode (1) in relation to one of the contacts of the body (3).

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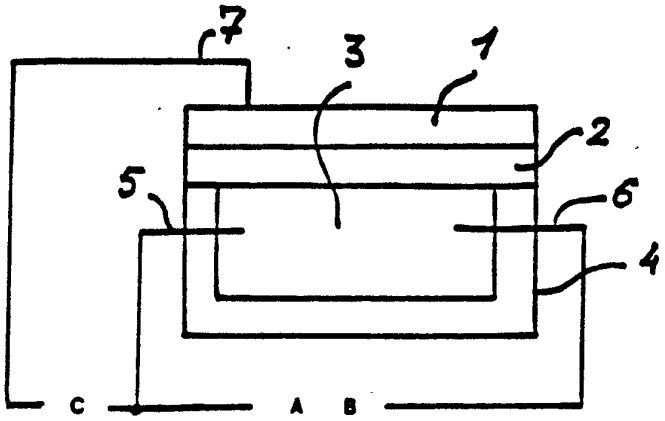

FIG. 1

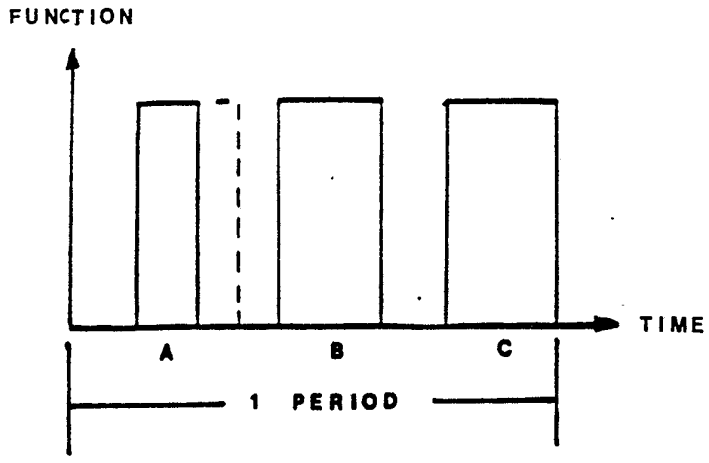

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 92/00135

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: G 01 N 27/30, 27/406

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	G 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4272350 (MICHEL CROSET ET AL) 9 June 1981, see column 3, line 3 - line 19; figures 10,11; claim 1	1
Y		1-4
	--	
X	US, A, 4908118 (SONYA AMMENDE ET AL) 13 March 1990, see column 2, line 28 - line 45; figure 1	1
Y		1-4
	--	
Y	DE, A1, 3811864 (SCHOTT GLASWERKE) 19 October 1989, see figure 1; claim 1	1-4
	--	

* Special categories of cited documents: [10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13th August 1992	1992 -08- 17
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Inger Löfgren

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4264425 (SHINJI KIMURA ET AL) 28 April 1981, see the whole document --	1-4
A	US, A, 3915830 (ARNOLD O. ISENBERG) 28 October 1975, see the whole document --	1-4

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/DK 92/00135

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 01/07/92
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		FR-A-B-	2444272	80-07-11
		JP-C-	1461872	88-10-14
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		JP-B-	63009179	88-02-26
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		EP-A-B-	0268768	88-06-01
		JP-A-	63140954	88-06-13
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