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10 AN IMPROVED TEMPERATURE COMPENSATED ELECTROCHEMICAL
 GAS SENSOR AND METHOD FOR CLOSELY TRACKING THE
 TEMPERATURE VARIATIONS OF A GAS TO BE SENSED

Field of Invention

15 This invention relates to electrochemical gas sensors for
 electrically signalling the concentration of an electrochemically
 active gas, such as oxygen, in a gas mixture and more part-
 icularly to improved apparatus and methods for closely tracking
 temperature variations of the gases applied to the gas sensor
20 permitting accurate compensation for the temperature var-
 iations.

Background of Invention

 Electrochemical gas sensors are well known in the prior
25 art for accurately detecting the concentration of an electro-
 chemically active gas, such as oxygen, in a gas mixture. The
 concentration of the gas is externally signalled by the elec-
 trical signal generated by the presence of the active gas that
 is oxidized or reduced at the surface of the gas sensing
30 cathode electrode. The gas sensors comprise anode and cathode
 electrodes immersed in a pool of a liquid electrolyte. The
 electrical output signal from these gas sensors are in the
 form of an electrical current that corresponds to the partial
 pressure of the active gas being sensed. The current signal
35 can be converted to a voltage signal by the mounting of a

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1 suitable resistor across the output terminals of the gas sensor
to derive a voltage signal in millivolts. Conventionally,
a printed circuit board is mounted to the gas sensor at the
back side thereof with a suitable resistor thereon for providing
5 the voltage output signal. It is known that the gas sensor
output signals are dependent on the temperature of the gas
mixture applied thereto. The output signals from the sensors
increase with an increase in the temperature of the applied
gases. This change in output signal is due to the change in
10 the diffusion rate of the gas mixture through the input membrane
for the gas sensor. At the higher temperatures, the electrical
output signal increases due to the high diffusion rate of the
gases through the input membrane for the gas sensor. As a
result, the output signal increase results in an erroneous
15 output signal of the concentration of the gas sensed. To
compensate the output signals for the temperature variations
and provide accurate output signals, a suitable thermistor is
conventionally mounted on the printed circuit board on the rear
of the gas sensor. The thermistor provides an electrical output
20 signal for adjusting or compensating the sensor output signal
for the temperature variations in the applied gas. This enables
the gas sensor to provide accurate measurements of the con-
centrations of the sensed active gas at various temperatures
without any additional correction being required. These gas
25 sensors have a sensing membrane at the front side for receiving
the gas mixture to be analyzed. A pool of electrolyte is stored
between the input sensing membrane and an expansion membrane.
The thermistor is spaced from the electrolyte. This prior art
arrangement of the thermistor in gas sensors has been found to
30 take a long time to equilibrate the changes in temperature of the gas
mixture applied to the sensor in order to provide a temperature
compensation signal. The thermistor in these prior art sensor
arrangements is exposed to the gas undergoing analysis im-
mediately upon application of the gas mixture to the sensor,
35 while it takes 30-40 minutes for the sensor body to see a change



1 in the temperature of the applied gas mixture. As a result
of this time delay there is an initial low reading due to the
adjustment performed by the thermistor. This time delay may be
on the order of 30 minutes to one hour. In medical applications
5 wherein it is necessary to monitor the oxygen concentration
given to a patient in a critical care unit, this delay may be
too long and the error associated with the delayed temperature
tracking could be up to 10 per cent of the oxygen required by a
patient and could be detrimental to the patient. Accordingly,
10 there is a present need for an improved apparatus and method
for more closely tracking and compensating a sensor electrical
output signal for errors introduced by varying temperatures of
the gas mixtures applied to the gas sensor to be analyzed.

15 Summary of Invention

The present invention is an improved, more sensitive,
electrochemical gas sensor having improved methods and means for
tracking the temperature changes in the gases applied to the
sensors for permitting the temperature compensation signals
20 to be rapidly developed and utilized without any time delay,
for providing correct, temperature compensated output signals
and thereby accurate electrical output signals representative
of the concentrations of the electrochemical active gases
applied to the gas sensor to be analyzed. The above advantages
25 are produced with small change in the cost of producing the
improved gas sensor.

From a structural standpoint, the improved electro-
chemical gas sensor includes thermistor means mounted adjacent
to an expansion membrane, that is in contact with the gas sensor
electrolyte and contains same, in a substantially thermal
30 isolated relationship with respect to the temperature of the
gases to be sensed conveyed to the gas sensor so that any
change in the temperature of the gas to be sensed is not
directly conveyed to the thermistor means whereby the gas
35 sensor and the thermistor means both experience any change in

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1 temperature of the gas to be sensed at substantially the same
time whereby said thermistor means provides electrical output
signals in response to the sensed temperature changes in the
gases being sensed without any substantial time delays between
5 the temperature changes in the gases to be sensed and the
electrical output signals provided by the thermistor means.

From a broad method standpoint, the present invention
comprehends the provision of an electrochemical gas sensor to
provide an electrical output signal in response to the app-
10 lication of a gas mixture to the gas sensor having an electro-
chemically active gas to be sensed therein due to the production
of a cathodic reaction whereby the electrical output signal is
representative of the concentration of the sensed electro-
chemically active gas that varies with the temperatures of the
15 gas mixtures thereby resulting in erroneous electrical output
signals due to the temperature variations of the gas mixture,
mounting thermistor means in the gas sensor in a preselected
thermal insulative manner for minimizing any direct heat transfer
to the thermistor means so that the gas sensor body and the
20 thermistor means are exposed to the temperature variations of the
gas mixture at essentially the same time for thereby permitting
accurate compensation of the electrical output signals from the
gas sensor, without any time delay, thereby providing accurate
output signals of the concentrations of the sensed gases despite
25 temperature variations in the applied gas mixtures.

The method includes the steps of mounting the thermistor
means in a heat sink adjacent the gas sensor electrolyte and
providing a plurality of thermal insulators stacked in the gas
sensor with the thermistor means lead wires spiraled into coils
30 and electrically accessible outside the gas sensor.



1 Brief Description of the Drawings *embodiments of*

These and other features of the present invention may be more fully appreciated when considered in light of the following specification and drawings, in which:

5 Fig. 1 is cross sectional view of a prior art electrochemical gas sensor having thermistor temperature compensation;

Fig. 2 is a graphical illustration of the gas sensor of Fig. 1 electrical output signal variations due to increased temperatures of the gas mixture applied to the gas sensor;

10 Fig. 3 is a cross sectional view of an electrochemical gas sensor having means for closely tracking temperature variations of the gas mixtures applied to the gas sensor and embodying the present invention;

Fig. 4 is a view from the top of an unpatted, thermistor, looking towards the back side of the gas sensor of Fig. 3 and illustrating the spiral assembly of the thermistor leads, in part illustrated in dotted outline;

Fig. 5 is a side view of the thermistor arrangement as viewed in Fig. 4;

20 Fig. 6 is a detached view of the top of the printed circuit board assembly as utilized in the gas sensor of Fig. 3; and

Fig. 7 is a graphical illustration of the gas sensor of Figs. 3-6 electrical output signal variations due to the increase in the temperature of the gas mixture applied to the gas sensor.

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1 Detailed Description of the Preferred Embodiment of the Invention

2 An understanding of the problem of the present day
3 organization of electrochemical gas sensors and the temperature
4 compensation of the sensor electrical output signals by means
5 of thermistor means leads to a better appreciation of the need for
6 the improvements disclosed herein and the benefits of the novel
7 structures. The electrochemical gas sensor 10 is illustrated in
8 Fig. 1 as a prior art galvanic type of gas sensor for prod-
9 ucing a cathodic reaction at the gas sensing cathode electrode
10 12 for the gas sensor. The cathodic reaction is produced in
11 response to gas mixtures applied to the gas sensor 10 when the
12 cathode electrode 12 and the associated anode electrode 14 are
13 wet by a suitable electrolyte 16 stored in the container 18
14 defining the body for the sensor 10. The electrolyte 16 has a
15 preselected volume defined between the thin sensing membrane 20
16 and the expansion membrane 22 spaced on the opposite side of
17 the anode electrode 14 from the cathode electrode 12. The back
18 side of the container 18 is closed off by the provision of a
19 printed circuit board 24 illustrated spaced from the membrane 22
20 and mounting a thermistor 26 and a plurality of resistors 28.
21 An electrical connector 30 is connected to the printed circuit
22 board 24 for deriving the electrical output signals produced
23 by the aforementioned cathodic reaction and the thermistor
24 signals to be combined for compensating for any temperature
25 changes in the gas mixture applied to the gas sensor 10 in a
26 well known manner. This structure is typical of the prior art
27 galvanic type of electrochemical gas sensors capable of sensing
28 the concentrations of electrochemically active gases, such as
29 oxygen, in the gas mixtures applied to the gas sensor in parts
30 per million. It should be recognized by those skilled in the
31 art that the present invention is also applicable to other types
32 of gas sensors including polarographic type gas sensors.

33 As illustrated in Fig. 1, the open end of the container
34 18 is illustrated with an open ended threaded member 32 for
35 receiving the gas mixtures applied to the gas sensor 10. This

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1 permits the gas sensor 10 to be threaded to a suitable gas
block for receiving the gas mixtures flowing through to
impinge against the sensing membrane 20. Such a gas block may
be constructed of aluminum or plastic. The gas block is
5 diagrammatically illustrated in dotted outline secured to the
member 32 in Fig. 1. Upon the application of the gas mixture
to be analyzed to the gas sensor 10 the concentration of the
electrochemical active gas in the gas mixture produces a cathodic
current that is due to the oxidation or reduction of the active
10 gas providing an electrical current output signal from the
sensor 10 representative of the concentration of the active
gas in the gas mixture. The electrical current can be converted
to a voltage output signal by the provision of a suitable output
resistor coupled across the output terminals of the sensor 10.
15 A ten ohm resistor mounted on the printed circuit board 24,
for example will convert the output currents to a voltage signal
in millivolts. It is also well known that electrical output
signals from the gas sensors 10 are also dependent on the temp-
erature and the temperature variations of the gas mixtures
20 applied to the sensor. The electrical output signals increase
in magnitude with the increases in the temperatures of the gas
mixture being sensed or analyzed. This change in output signal
is due to the change in the diffusion rate of the applied gas
through the thin sensing membrane 20. At the higher gas temp-
25 eratures the output electrical signals increase due to the high
diffusion rate of the applied gas through the sensing membrane
20 and thereby the derived output signals erroneously signal
the concentration of the sensed active gas in the applied gas
mixture. The prior art gas sensors utilized a temperature
30 sensing device in the form of the thermistor 26 mounted on the
printed circuit board 24 for the gas sensor 10 to provide an
electrical output signal representative of the temperature change
in the applied gas to the gas sensor. The thermistor output
signal is utilized as a temperature compensating signal for the
35 erroneously generated sensor output signal to provide the correct

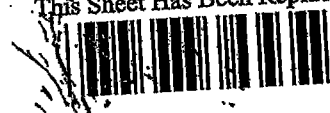
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1 output signal compensated for the temperature variations,
as well known, without the need for additional corrections.
The thermistor signals are utilized to cancel out the temp-
erature components of the sensor generated signals in a
5 known circuit manner. As can be appreciated from viewing
Fig. 1, the gas mixture to be analyzed is immediately exposed
to the thermistor 26 and as a result signals a temperature
change that produces an initial low, erroneous output signal
from the gas sensor 10. It is known that the gas sensor body
10 takes a time period on the order of 30-40 minutes to change in
temperature before it will correctly signal the temperature
change in the applied gas mixture. This time delay in pro-
viding accurate electrical output signals has been found to
be between 30 minutes to one hour. For a patient in a critical
15 care unit wherein the supply of oxygen, for example, is mon-
itored this time delay is excessive and the errors introduced
with the delayed temperature tracking by the thermistor could
be up to 10% of the required oxygen supply and could be
detrimental to a patient.

20 The time delay introduced by the erroneous temperature
tracking by the thermistor 26 for the gas sensor 10 is
graphically illustrated in Fig. 2 for a temperature change from
24 degrees centigrade to 40 degrees centigrade for tests con-
ducted on three different gas sensors of the type of gas sensor
25 10. The space between the vertical lines in Fig. 2 represent
5 minutes in time. All three gas sensors signalled an immediate
drop in the value of the electrical output signal due to the
thermistor 26 being immediately exposed to the temperature
change with a gradual increase in value as the sensor body
30 absorbs the temperature change with time. The electrical output
signal reaches a steady state condition after the time delay
period required by the sensor body and associated elements to
reach the changed temperature, in the above example the 40 de-
grees C. This time delay period for the cells of Fig. 2 can
35 be seen to be substantial, on the order of 30 minutes.

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1 With the above prior art structures and problems in
mind, the improved gas sensor 10' of the present invention will
be examined in conjunction with the structures illustrated in
Figs. 3-6 and the graphical representation of Fig. 7. The
5 basic structure of the galvanic type electrochemical gas
sensor 10 of Fig. 1 is illustrated in Fig. 3 but illustrating
the improved arrangement for sensing the applied gas temperatures
and tracking the temperatures without introducing the time
delays of the prior art structures. The thermistor 26 in
10 accordance with the present invention is located in very close
proximity to the liquid electrolyte adjacent the expansion
membrane 22 in a substantially thermally insulated relationship
with the gas sensor body and the gases applied to the gas sensor
10' and thereby eliminates the prior art time delays involved
15 in tracking the temperatures of the gases applied to the gas
sensors during a change in the temperature of the gases.

To this end, the thermistor 26 is potted to the rear
side of the expansion membrane 22 with a heat sink compound 34,
such as a zinc oxide or silicone, as illustrated in Fig. 3. In
20 this manner, any change in temperature of the gases undergoing
analysis are not directly conveyed to the thermistor 26 to
produce erroneous signal outputs. The lead wires for the
thermistor 26 comprise an electrically insulated cable 26C of
approximately 3-4 inches in length having the individual lead
25 wires thereof secured to the printed circuit board 24 at the
points "4" on the board; see Figs. 4 and 6.

Another important feature of the assembly of the
thermistor 26 to the gas sensor 10' is the provision of thermal
insulative means arranged between the heat sink compound 34
30 and the tops of the circuit board devices on the printed circuit
board 24 as best illustrated in Figs. 3 and 5. The insulative
means, as illustrated, comprises three individual layers of
foam stacked upon one another between the heat sink 34 and the
printed circuit board 24. The individual layers of foam in-
35 sulation are each a different size and are identified in the



1 drawings as layers 36, 38 and 40 from the top to the bottom,
see Fig, 5, in particular. The top most insulative layer 36
is positioned below the thermistor 26 and the heat sink
compound 34 and is the smallest in size, diameter wise, of the
5 three insulative layers. The bottom insulative layer 40 is
the largest in diameter while the layer 38 is intermediate in
size between the diameters of layers 36 and 40. The thickness
of the three layers are essentially the same and in combination
occupy the volume between the heat sink compound 34 and the
10 printed circuit board 24. The three layers are arranged in a
staggered relationship as best seen in Fig. 5. The insulative
cable 26C for the thermistor 26 is spiraled or coiled between
the insulative layers 36, 38 and 40 between the stacked layers,
see Figs. 3 and 4, and the individual lead wires of the cable 26C
15 are connected to point "4" on the printed circuit board 24, as
best seen in Fig. 4 and 6.

In the above described manner of insulatively securing
the thermistor 26 any change in temperature of the gas mixtures
applied to the gas sensor 10' is not directly conveyed to the
20 thermistor 26 since the gas sensor container or body 18 both
experience the change in gas temperature at essentially the
same time. Therefore, the electrical output signals developed
by the gas sensor 10' and the thermistor 26 when combined,
correctly compensates the sensor generated electrical output
25 signals for the sensed temperature variations so that the
resulting temperature compensated electrical output signals are
true representations of the signals produced at the gas sensing
cathode electrode, without any erroneous increases or decreases
due to temperature changes.

30 The gas sensor 10' was tested in the identical manner
as the sensor 10 and plotted in Fig. 7 for a temperature change
in the sensor applied gas from 24 degrees C. to 40 degrees C.
In Fig. 7, the output signals for six gas sensors are illustrated
as coming to equilibrium right away, without any false increases
35 or decreases in electrical output signals as in the known prior



1 art devices.

It should now be appreciated by those skilled in the gas sensor art that the present disclosure has advanced the art for precisely tracking the temperature changes in the gas mixtures applied to the gas sensor so as to provide more sensitive and accurately compensated electrical output signals that better track temperature changes. This tracking results due to the thermistor being responsive to the temperature changes imparted to the liquid electrolyte and not the temperature changes of the sensor body.

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CLAIMS

1. . . An electrochemical gas sensor for sensing the concentration of an electrochemically active gas

in a gas mixture to be analyzed and providing sensor electrical output signals representative of the sensed concentrations, said gas sensor comprising

an insulative sensor container having an open end and adapted for storing a liquid electrolyte in the container, means for defining a gas sensing cathode electrode supported within the container adjacent said open end of the insulative sensor container,

a gas permeable, liquid impermeable membrane secured to said open end of said container in intimate contact with the cathode electrode and having a preselected thin thickness for limiting the diffusion of the gases to be sensed and to be conveyed to said cathode,

an expansion membrane mounted within said sensor container and being spaced a preselected distance from said open end and for storing an electrolyte in the volume between said gas permeable membrane and the expansion membrane,

a liquid electrolyte stored in the volume between said gas permeable membrane and the expansion membranes,

means for defining an anode electrode mounted in the electrolyte adjacent the expansion membrane, the improvement comprising thermistor means mounted adjacent to the expansion membrane in a substantially thermal isolated relationship with respect to the temperature of the gases to be sensed that are conveyed to said gas permeable membrane so that any change in the temperature of the gas to be sensed is not directly conveyed to the thermistor means whereby the sensor and the thermistor means both experience any change in temperature of the gas to be sensed at substantially the same time whereby said thermistor provides electrical output signals in response to the sensed temperature changes without any substantial time delays between the temperature changes and the

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1 thermistor electrical output signals useful for temperature
compensation of said sensor electrical output signals.

2. An electrochemical gas sensor of the type defined
5 in claim 1 wherein said thermistor means is secured to said
expansion membrane with a thermal insulator so as to be sub-
stantially sensitive only to temperature changes of
said electrolyte for providing temperature compensation signals
for the output signals generated by said gas sensor.

10

3. An electrochemical gas sensor of the type defined
in claim 2 wherein said thermistor means is secured to said
expansion membrane with heat sink means and further including a
printed circuit board for enclosing the end of said insulative
15 container opposite to said open end thereof, a plurality of
thermal insulators stacked between said thermistor means and said
printed circuit board for minimizing any direct heat transfer
from said gases to be sensed to the thermistor means, said
thermistor means having an insulated electrical cable spiraled
20 between said stacked thermal insulators and connected to said
circuit board.

4. An electrochemical gas sensor of the type defined
in claim 3 wherein said plurality of thermal insulators com-
25 prise individual insulators of different sizes that increase
in size from adjacent said thermistor means to said printed
circuit board.

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1 5. An electrochemical gas sensor of the type defined
in claim 3 wherein said plurality of thermal insulators com-
prise three thermal insulators stacked between said thermistor
means and the printed circuit board, the thermal insulator
5 adjacent said thermistor means being the smallest insulator and
the largest insulator being adjacent said circuit board, and
the third insulator being of a size larger than the smallest
insulator and smaller than the largest insulator and stacked
intermediate the small and large insulators, said insulated
10 thermistor having lead wires spiraled into coils of increasing
diameter between the small and third insulators and between the
large and third insulators and being electrically connected
to said circuit board.

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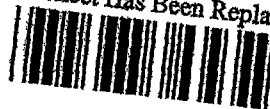
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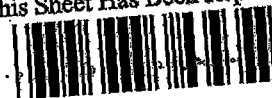


1 6. A method of compensating an electrochemical gas
sensor for sensing the concentration of an electrochemically
active gas ~~such as oxygen~~ in a gas mixture to be analyzed due
to changes in temperature of the gas mixture applied
5 to the electrochemical gas sensor, said gas sensor providing
electrical output signals representative of concentration of
the sensed, active gas due to the resulting cathodic reaction
that is compensated for any temperature changes in the applied
gas mixture,

10 the method including the steps of providing an
electrochemical gas sensor having a gas sensing cathode and
anode wet by an electrolyte and adapted to provide an electrical
output signal in response to the application of a gas mixture
having an electrochemically active gas to be sensed therein
15 to said gas sensing cathode due to the production of a cathodic
reaction whereby the electrical output signal is representative
of the concentration of the sensed electrochemically active gas,
said electrical output signal being further characterized as
varying with the variations in temperature of the gas mixture
20 applied to said sensor resulting in erroneous electrical output
signals due to the temperature variations,

 mounting thermistor means in the sensor in a pre-
selected thermal insulative manner for minimizing any direct
heat transfer to said thermistor means whereby said gas sensor
25 and said thermistor means are exposed to temperature changes
of the gas being sensed at essentially the same time permitting
compensation of the electrical output signals from said sensor
without time delay and thereby providing accurate temperature
compensation output signals with the temperature variations of
30 the gas undergoing sensing representative of the true sensed
gas concentrations.

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1 7. A method of compensating an electrochemical gas
sensor for sensing the concentration of an electrochemically
active gas ~~such as oxygen~~ in a gas mixture to be analyzed due
to changes in temperature of the gas mixture applied to the
5 electrochemical gas sensor, said gas sensor providing electrical
output signals representative of concentration of the sensed,
active gas due to the resulting cathodic reaction that is
compensated for any temperature changes in the applied gas
mixture, as defined in claim 6

10 the method including the steps of providing an
electrochemical gas sensor having an insulative container
storing a gas sensing cathode, an anode and an electrolyte
wetting the cathode and anode for producing a cathodic reaction
upon the application of an electrochemically active gas to
15 the gas sensing cathode arranged in the insulative sensor
container with a preselected volume of electrolyte,

 mounting a temperature sensitive resistor in the
insulative sensor container immediately adjacent the volume of
electrolyte for closely tracking the variations in temperature
20 of gases to be sensed for providing temperature compensation
signals in response to the temperature variations, without any
time delays, for combination with the electrical output signals
provided by the gas sensor whereby the combination of the
compensation signals and electrical output signals provide
25 compensated electrical output signals accurately representative
of the concentrations of the sensed active gases in the gas
mixture applied to the gas sensor.

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1 8. A method of compensating an electrochemical gas
sensor for sensing the concentration of an electrochemically
active gas in a gas mixture applied to the sensor for temp-
erature changes, the gas sensor providing electrical output
5 signals representative of the sensed electrochemically active
gas that vary with the temperature variations of the applied
gas mixture, the method includes the steps of providing an
electrochemical gas sensor having an insulative container
having a gas sensing cathode electrode and an anode electrode
10 mounted in the container with an electrolyte, said container
having an open end adjacent the cathode electrode for applying
the gas mixture to the cathode electrode and an expansion
membrane mounted to said container in a preselected spaced
relationship with said open end of the container and containing
15 the electrolyte,

 mounting thermistor means on the expansion membrane
to be responsive to temperature changes in the electrolyte,

 securing the thermistor means to the expansion
membrane with heat sink means so as to substantially prevent
20 any temperature changes from being directly transmitted to the
thermistor means so that said gas sensor and the thermistor
means both respond to any temperature changes at substantially
the same time,

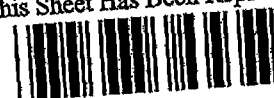
 mounting thermal insulative means on the opposite
25 side of the thermistor means from the side secured to the
expansion membrane,

 the thermistor means including insulated lead wires
extending therefrom for deriving temperature compensating
electrical signals from said gas sensor, and

30 arranging said leads with said thermal insulative
means so as to be contained within said insulative means to
prevent temperature changes to be conducted to said thermistor
means and to be accessible outside of the gas sensor.

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1 9. A method of compensating an electrochemical gas
sensor as defined in claim 8 wherein the step of mounting
thermal insulative means includes the steps of stacking a
plurality of thermal insulative means, each a different, pre-
5 selected size, for thermally insulating the thermistor means,
and spiralling said lead wires of the thermistor
means in an insulative relationship between each of the stacked,
plurality of insulative means and arranged to be accessible
externally of the gas sensor.

10

10. A method of compensating an electrochemical gas
sensor as defined in claim 9 wherein the step of spiralling
the lead wires comprises wrapping the lead wires in a coiled
configuration between the stacked insulative means.

15

11. An electrochemical gas sensor according to any
one of claims 1 to 5 wherein said electrochemically active
gas is oxygen.

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12. A method according to any one of claims 6 to 10
wherein said electrochemically active gas is oxygen.

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