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(71) **Applicant** *(for all designated States except US)*: **RHOCRAFT RESEARCH AND DEVELOPMENT LTD.** [CA/CA]; 1950 Cochrane Street, Victoria, British Columbia V8R 3H5 (CA).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **ROWE, Robert, Donald** [CA/CA]; 1950 Cochrane Street, Victoria, British Columbia V8R 3H5 (CA). **FYLES, Thomas, Murray** [CA/CA]; 3478 Cardiff Place, Victoria, British Columbia V8P 4Z1 (CA). **ROBERTSON, George, David** [CA/CA]; 1279 Queensbury Avenue, Victoria, British Columbia V8P 2E1 (CA).

(74) **Agents: BAILEY, Thomas, W.** et al.; Oyen Wiggs Green & Mutala, 480 - The Station, 601 West Cordova Street, Vancouver, British Columbia V6B 1G1 (CA).

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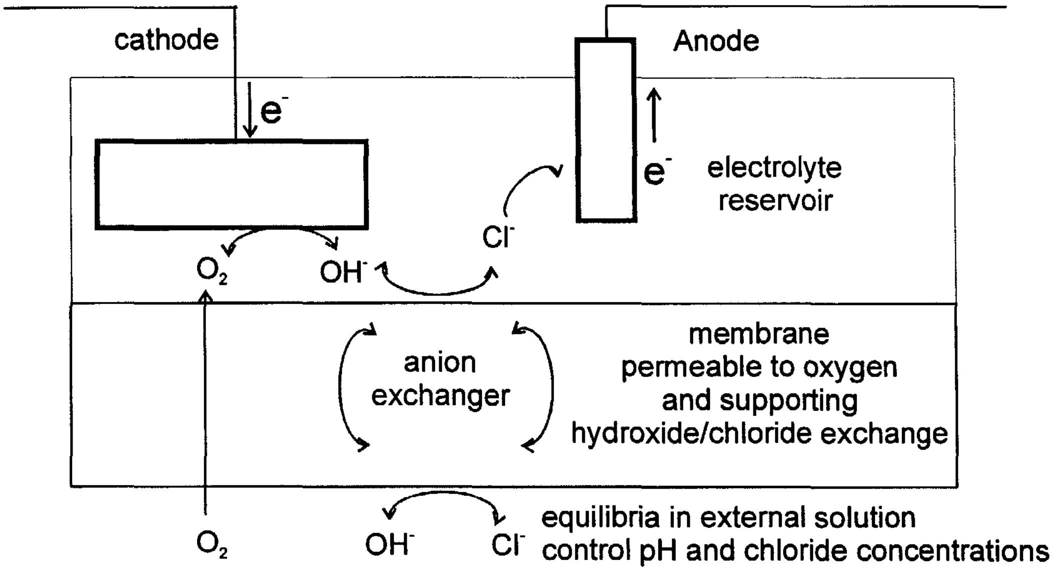
(54) **Title:** ION EXCHANGE MEMBRANES AND DISSOLVED GAS SENSORS



(57) **Abstract:** Ion exchange membranes for use in sensors that measure dissolved gases are described. Sensors constructed using the disclosed membranes are able to maintain electrolyte conditions within the electrolyte volume so as to have greatly extended and more stable lifetimes than sensors of similar construction and electrolyte volume constructed with standard membranes.

ION EXCHANGE MEMBRANES AND DISSOLVED GAS SENSORS

FIELD

The invention relates to ion exchange membranes and dissolved gas sensors.

BACKGROUND

Measurement of dissolved gases is important in many fields, including medicine, food science and environmental science. One type of sensor developed to measure dissolved gases is the Clark cell. Clark cells are used to detect gases that are readily reduced or oxidized, such as hydrogen sulfide, NO, NO_2, CO, Cl_2 and O_2. These sensors consist of a gas permeable membrane enclosing an electrolyte and working and reference electrodes in contact with the electrolyte (see, for example, Janata, J., *Principles of Chemical Sensors*, Plenum Publishing, 1991 and *Polarographic Oxygen Sensors*, Chapter 4,Gnaiger, E. and Forstner, H. (Eds.), Springer-Verlag, 1983). Gases pass through the membrane by diffusion, and are reduced or oxidized at the working electrode to create a detectable current flow.

The stability and reliability of Clark cells depends on many factors, but in particular there is a limitation on sensor lifetime imposed by the amount of electrolyte within the Clark cell. This problem has been central to Clark cells since their inception and is mentioned in many earlier patents (see, for example, US Patent No. 5,212,050). Since oxidation and reduction processes consume components of the electrolyte, Clark cells are inherently prone to instability and limited lifetime due to exhaustion of the electrolyte. This problem is particularly acute for small electrodes (microelectrodes) and there have been many attempts in the past to address this shortcoming mechanically. For example, increasing the electrolyte volume and providing a means to replenish the electrolyte are two approaches. Mechanical solutions, however, tend to increase the complexity of the sensor (see, for example, European Patent No. EP 0496521). For these reasons, Clark cells are typically expensive to construct and require frequent maintenance and calibration.

SUMMARY

Gas-permeable membranes comprising an anion exchanger, such as a guanidinium salt, and sensors made with such membranes are described. The membranes exhibit selective permeability for the gas to be analyzed and an ion exchange capacity that allows discharge of the ionic products of the redox reaction used to detect the gas and replenishment of electrolyte components consumed in the redox reaction from the sample being measured. The membranes alleviate problems associated with exhaustion of the sensor electrolyte and allow amperometric sensors to function in a stable manner for a much longer period of time than a sensor that must rely on only the ions present in the original electrolyte volume. The disclosed membranes therefore permit construction of very small and long lived, stable sensors.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing one embodiment of an oxygen sensor illustrating a method for replenishing the interior electrolyte and preventing build-up of redox products using ion exchange membranes.

FIG. 2 is a graph showing the output of a disclosed sensor as a function of the current measured by a commercial dissolved oxygen meter.

FIG. 3 is a graph showing the response of a disclosed sensor in response to an abrupt change in dissolved oxygen concentration.

FIG. 4 is a graph showing the output current of a disclosed sensor over a six-hour period.

FIG. 5 is a graph showing the output current of a matched pair of sensors under forcing conditions as a function of time, one sensor having a membrane according to the disclosure, the other without.

FIG. 6 is a graph showing the output current of a matched pair of sensors under forcing conditions as a function of the total charge transferred, one sensor having a membrane according to the disclosure, the other without.

FIG. 7 is a cross-sectional schematic diagram showing one embodiment of a disclosed dissolved gas sensor constructed on a printed circuit board.

FIG. 8 is a schematic diagram showing a top-view of one embodiment of a disclosed dissolved gas sensor constructed on a printed circuit board.

FIG. 9 is a graph showing the sensor output versus dissolved oxygen concentration for a printed circuit board sensor according to one embodiment of the disclosure.

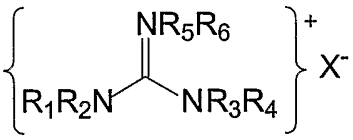
FIG. 10 is a graph showing the response characteristics of a printed circuit board sensor according to one embodiment of the disclosure in comparison to a commercial Clark cell sensor.

DETAILED DESCRIPTION

Although the performance of sensors for all readily reducible and oxidizable gases may be improved using the disclosed membranes and the principle on which they operate, the following description focuses on dissolved oxygen sensors. A Clark cell for oxygen detection consists of an inert cathode, typically gold or platinum, and a reversible anode, such as silver/silver chloride, within an electrolyte volume that is separated from the sample by an oxygen permeable membrane. As oxygen diffuses into the electrolyte volume, oxygen reduction at the cathode produces hydroxide ions that increase in concentration in the vicinity of the cathode. As current flows, there is a concomitant depletion of chloride ions in the vicinity of the anode. These concentration changes alter the stability of the sensor and, as the electrolyte is consumed, will ultimately inactivate the sensor.

The disclosed membranes alleviate these problems as diagrammed in FIG. 1. An anion exchanger is included within the gas-permeable membrane to remove hydroxide ions from and transport chloride ions into the electrolyte volume of the cell, ensuring a longer working lifetime and greater stability of the sensor over time. The external solution being analyzed acts as a sink for hydroxide ions and a source of chloride ions in this system. Thus, the medium in which the gas is being measured need only have sufficient chloride ions for the exchange mechanism to operate and sufficient capacity to absorb hydroxide ions. Examples of such media include seawater, foodstuffs, and biological fluids.

For oxygen sensors, any anion exchanger that can shuttle hydroxide and chloride ions through the gas permeable membrane may be utilized (for example, cationic species such as cationic metal complexes, guanidinium salts and ammonium salts, including quaternary ammonium salts). However, in particular embodiments the ion exchanger is a guanidinium salt having the formula:



In general, R_1, R_2, R_3, R_4, R_5, and R_6 may be independently chosen to impart an affinity of the guanidinium salt for the membrane phase and X^- is any anion, for example, any type of halide ion. In particular disclosed embodiments, R_1, R_2, R_3, R_4, R_5, and R_6 may be independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, alkenyl, substituted alkenyl, cycloalkenyl, substituted cycloalkenyl, alkynyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl. More particularly R_1, R_2, R_3, R_4, R_5, and R_6 may be independently selected from the group consisting of hydrogen, C1-30 alkyl, and aryl (for example, phenyl or napthyl). In particular embodiments X^- may be selected from the group consisting of chloride, bromide, fluoride, iodide, hydroxide, acetate, carbonate, sulfate, and nitrate and combinations thereof.

The gas permeable membrane may be any one of several types. One type of membrane is a supported liquid membrane (SLM) (see, for example, *Liquid Membranes: Theory and Applications*, Noble and Way (Eds.), ACS Symposium Series 347, American Chemical Society, 1987). In such membranes, a porous polymer support, such as microporous polyalkylene, including polytetrafluoroethylene, polyethylene or polypropylene, is imbibed with a solvent containing the ion exchanger. Suitable solvents include high-boiling solvents such as *ortho*-nitrophenyl ether, dioctyl adipate and others described below.

Another type of gas-permeable membrane is a polymer, such as high molecular weight poly(vinyl chloride) (PVC), silicon rubber or a cellulose ester (e.g. cellulose acetate), that is plasticized with a solvent that also serves to dissolve the ion exchanger. Suitable solvents include, without limitations, adipate esters (e.g. dioctyl adipate and diisononyladipate), sebacate esters (e.g. dioctyl sebacate and bis(2-ethylhexyl)sebacate), phthalate esters (e.g. dioctylphthalate, bis(2-

ethylhexyl)phthalate, and butyl hexyl phthalate), glycol esters (e.g. diethyleneglycol dibenzoate and dipropyleneglycol dibenzoate), low volatility ethers (e.g. *ortho*-nitrophenyl octyl ether), trimellitic acid esters (e.g. tris(2-ethylhexyl)trimellitate), phosphate triesters (e.g. isodecyl diphenylphosphate, and tert-butylphenyl diphenylphosphate), chlorinated paraffins (e.g. chlorowax and flexchlor), and mixtures thereof. Plasticized polymer membranes may be cast as a solution of the polymer and plasticizer in a volatile solvent such as tetrahydrofuran or trifluoroethanol.

Yet another type of gas-permeable membrane can be formed by modification of a polymer backbone to provide ion exchange groups directly linked to the polymer backbone. Any of the types of membranes described above may be fabricated with 0.1-10 wt%, for example, 1-5 wt%, of an added ion exchanger (e.g. the guanidinium salts described above). Other types of gas-permeable membranes, known or yet to be discovered, may benefit from adding ion exchangers as described herein.

The disclosed membranes can be used with a variety of construction methods to provide amperometric sensors with any number of geometries. In addition, the disclosed membranes may be applied in place of existing gas-permeable membranes to improve the lifetime and stability of an existing sensor. In one embodiment, the disclosed membranes are applied to "solid state" micro-fabricated sensor systems to more fully take advantage of the low electrolyte volumes required (for example, electrolyte volumes of less than 50 μL, less than 25 μL, less than 10 μL, less than 5 μL or less than 1 μL are possible). Working embodiments typically included about 5 μL. For instance, the membrane may be cast in place over a suitable dry salt such as NaCl or KCl that has been placed over a pair of electrodes so as to form a "solid state" sensor. Such a sensor may be stored "dry" and "wetted" before use (see, for example, US Pat. No. 4,933,048).

Suitable inert cathode materials for sensors incorporating the membranes of the disclosure may be selected from the group consisting of gold, platinum, silver, palladium, iridium, rhodium, ruthenium, osmium and alloys thereof. Suitable reversible anode materials may be selected from the group consisting of silver/silver halide (e.g. silver/silver chloride, silver/silver bromide, silver/silver fluoride, and silver/silver iodide), lead/lead sulfate, silver/silver oxide-hydroxide and lead/lead oxide-hydroxide. Suitable electrolyte salts may be selected from the group consisting of water-soluble cation/anion pairs formed from the cations of Na, K, Cs, Rb, Li, Mg, Ca, Ag, Zn, and Pb and mixtures thereof, and the anions of F, Cl, Br and I and mixtures thereof. The following anions also can be used in combination with the listed cations: acetate, perchlorate, hydroxide, carbonate, sulfate, and nitrate and mixtures thereof. In working embodiments, the electrolyte salts used have been alkali metal halides and mixtures thereof, such as KCl and NaCl and mixtures thereof.

Suitable insulating substrates for making sensors include ceramics (e.g. alumina) and glass. Plastics may also be used as substrates for making sensors, provided the plastic is impervious to the gas being measured by the sensor.

The disclosed membranes offer advantages in addition to improved longevity and stability. For example, because the membranes permit construction of Clark-type sensors with very small electrolyte volumes, the sensors are able to withstand cycling between low and high pressure because gases apparently diffuse out of the sensors faster than forming bubbles. In some embodiments, the sensors are able to withstand steam sterilization and are thus suitable for use in the food industry.

The following examples are provided to aid in the understanding of the disclosure and are not meant to limit the scope of the invention.

Example 1 - Amperometric sensors with a solid electrolyte salt.

The membranes described herein may be used to construct a sensor with a solid electrolyte. Such sensors may be constructed as follows:

1) An anode and cathode are placed upon a gas-impervious, electrically insulating substrate using standard printed circuit board techniques (see, for example, U.S. Pat No. 4,534,356). In some embodiments a third electrode or “guard ring” also may be formed on the substrate in the same manner as the other electrodes. For example, the electrodes may be formed using an appropriate mask (e.g. photoresist) and metal slurries (e.g. metal slurries provided by

Englehard, E.I. duPont de Nemours, or Johnson Matthey). If one of the electrodes is to be a silver/silver halide electrode it may be formed by depositing silver on the surface of the substrate and then halogenating the silver electrode by electrochemical techniques. For example, the silver electrode may be halogenated by chloridation using a solution of 1% sodium chloride. Chloridation can be achieved, for example, at 3.5 V at low current for a short period of time, such as 10 minutes. Electrodes may also be formed by sputter coating or applied as a thick or thin film. Any method, which places the electrodes of the appropriate materials in the appropriate position and proportion on a gas-impervious electrically insulating surface, will suffice. Provision is made to connect the electrodes to an electronics circuit capable of providing the correct bias voltage and amplifying the resulting signal. The electronics may be manufactured directly on the same substrate as the electrodes to produce a "chip scale" (sensor on a chip) sensor. The substrate also may be a flexible material, provided the rest of the components are constructed in a fashion that allows for flexion of the substrate.

2) A small quantity of electrolyte solution (for example 5 microlitres) is applied over the two electrodes and the solvent is allowed to evaporate, leaving a coating of dry salt over the surface of the electrodes.
3) Over this assembly a gas-permeable membrane of a formulation described herein is applied such that it covers both electrodes and the salt and is sealed on its outer edges to prevent communication between the inner electrolyte and the outer medium except by way of the membrane itself. The membrane may be "cast" in place in liquid form and allowed to polymerize or it may be pre-cast and applied to the substrate using a sealant or mechanical device to seal the outer edges from the outside medium.

4) Before operation, the sensor is placed in the liquid medium in which gas readings are to be taken and allowed to "hydrate" for a period of time. The hydration time varies depending upon several factors, including temperature, pressure and the chemical constituents of the medium. Working embodiments achieved hydration in about 10 to 20 minutes. Once the sensor has come into equilibrium with the environment, stable gas concentration readings may be taken.

Any number of gas sensors may be constructed on a single substrate, along with additional sensors, such as pH sensors and temperature sensors, to provide a compact sensor array.

Example 2-Characterization of a Gas-permeable Membrane Containing an Ion Exchanger

This example demonstrates the ion-exchange capacity of the disclosed membranes and its implications for making stable, low-volume dissolved oxygen (DO) electrodes. The advantage of the DO electrode is best seen under "forcing" conditions in which electrode failure occurs in a relatively brief period (<24 hours). This can be achieved using a limited amount of electrolyte: an electrode producing a 0.2μA current will consume the available chloride ions in 3μL of 0.01M NaCl in about 4 hours.

A PVC/dioctyl adipate membrane comprising tetradecylguanidinium chloride was tested with an experimental system that uses a measurement volume of 0.35M NaCl at 12 ± 0.5 °C and a set potential of 0.500 ± 0.001V. The system was stirred from below and the solutions were open to the atmosphere, so daily pressure variations could be seen in the longer data records. The probe uses a Pt cathode (~0.5 mm diameter) at the center of a silver ring anode (4 mm diameter, 1 mm thickness). The electrodes are bedded in epoxy and ground flat. The membranes mount directly on the flat surface holding the drop of electrolyte in place. Comparisons are based on matched probes and parallel circuitry. The calibration, response time, and stability criteria are established with "unlimited" electrolyte, typically 5μL of 0.1 M NaCl to give a working lifetime before electrolyte exhaustion of at least 48 hours. The lifetime criterion is established using "forcing" conditions of limited electrolyte, typically 5 μL of <0.01 M NaCl.

1) *Calibration*: For a thin membrane layer, the calibration will be linear in dissolved oxygen concentration with a zero intercept (one-point calibration). Conventional "thin" membranes on the probe produce ~0.05 μA / mgL^{-1} DO or about 0.5 μA for an oxygen saturated solution at the salinity and temperature noted above. The disclosed membranes will produce similar amounts of current at the same thickness. The fabrication procedures used for a long-lived electrode produce a membrane *ca.* 150 μm thick. Hence, the saturation current is somewhat lower (0.2 μA). FIG. 2 shows that the test electrode with the guanidinium salt as ion exchanger shows a slightly curved calibration response and a non-zero intercept with respect to a commercial Orion model 810. The Orion meter loses its internal calibration (cell current converted to ppm DO) after a period of *ca.* 20 minutes, but the "raw" current values continue to be reported by the Orion system).
2) *Response time*: This is defined as a time to respond to an abrupt change from an oxygen saturated solution to another at about 20% saturation and back again. The response time is usually in terms of >95% total change in a certain number (x) minutes. For a "thick" and aged electrode (beyond 1 equivalent of electrolyte) this will typically be <5 minutes. Thinner membranes respond more quickly. FIG. 3 shows the response time function for a 2-day old electrode having a membrane according to the disclosure.
3) *Stability*: This is the change, or drift, in the output signal for a period where the calibration applies for an electrode which is not electrolyte limited. It is usually set in terms of drift per time e.g. <2% per hour measured over a time certain, such as a 3-hour period. FIG. 4 shows a 6-hour period in which the drift in the output signal is less than 0.06%. The variation in the signal could be due to atmospheric variation in this period. The digital noise is evident.

4) *Lifetime*: A conventional electrode will consume the available electrolyte and eventually fail. The long-lived electrodes allow ion exchange and therefore do not fail when the electrolyte runs out. They do however, shift to a new current level which balances the oxygen consumption and the anion exchange processes. This is demonstrated by measuring the output signal as a function of total charge transferred. FIG. 5 shows the time-course for matched electrodes with and without ion exchanger in the membrane. The same output data are given as a function of total charge transferred in FIG. 6. Both electrodes contain sufficient electrolyte to consume 4.8 mC of charge. However, the conventional cell expires before this theoretical limit. The long-lived cell of the disclosure achieves a relatively steady current about the theoretical limit of 5 mC and thereafter maintains the oxygen consumption and ion exchange in balance for a 3-day period.

Example 3 - Construction and Characterization of a Printed Circuit Board Dissolved Oxygen Sensor

The components of a printed circuit board (PCB) sensor constructed using the techniques described in Example 1 is shown in FIG. 7. FIG. 7 shows a cross-section of sensor (10) that includes substrate (20), cathode (30), such as a gold cathode, an anode (40), such as a silver/silver chloride reversible anode, optional guard ring (50), such as a silver guard ring, solid electrolyte (e.g. NaCl) layer (60), and gas-permeable membrane (70), such as a PVC/dioctyl adipate membrane comprising tetradecylguanidinium chloride as the anion exchanger. FIG. 8 shows a top view of a PCB dissolved oxygen sensor (without the optional guard ring) having a gold cathode (100), silver/silver chloride reversible anode (110), and electrical contacts (120).

Briefly, the printed circuit board (PCB) sensor was produced from computer Gerber plots using gold plated traces and pads. The PCB sensor was also selectively plated with silver. It was then immersed in a salt solution (NaCl) and a potential of 3.5V applied to plate a small amount of silver chloride on the surface of one electrode. A small amount of electrolyte (5uL) was placed drop-wise by syringe over the two electrodes and allowed to dry completely. Next, a thin membrane layer was cast over the entire sensor and allowed to polymerize. Once the membrane dried the sensor was placed in a thermostatically controlled water chamber that was open to the atmosphere and allowed to hydrate. Once hydration was complete the unit stabilized and was is ready to be used.

A calibration curve for the PCB sensor is shown in FIG. 9 and shows that it has a linear response to oxygen concentration. FIG. 10 shows a comparison of the response characteristics of a commercial Clark cell based unit and the PCB sensor according to the disclosure. The sensor shows excellent stability and lifetimes, far exceeding those attainable for a Clark cell of equivalent volume. A working embodiment with a 5 μL electrolyte volume was stable and functional for one month of continuous use. In fact, the commercial unit, with an electrolyte volume of about 1 mL, that was used to provide calibration curves proved far less stable over the same period of time. Response times vary with membrane thickness and easily matched those of a commercial unit tested alongside.

As discussed before, a number of different electrode arrangements may be produced. For example, the PCB oxygen sensors also may be used to form sensor arrays, such as including sensor pads for other sensors, such as are useful for pH and temperature measurements.

Example 4- Alternative Construction Techniques for PCB Sensors

Other construction techniques have been developed to ensure a good seal and prevent membrane lifting from the PCB surface. One such technique for producing a PCB sensor includes the following steps:

1) a clean set of PCB sensor electrodes was first cleaned with acetone and allowed to dry.
2) a section of double sided laminating material (3M, St. Paul, MN) was cut and provided with a small (~10 mm) hole.
3) The laminating material was placed on the PCB sensor such that the hole was over the electrode portion of the sensor.
4) A small amount of electrolyte (NaCL, ~5 uL) was placed dropwise onto the centre of the electode area, inside the laminating adhesive cut-out.
5) The electrolyte was allowed to dry.

6) A small piece of microporous cellulose acetate, cut to size, was placed over the electrode area and pressed firmly into the adhesive.
7) The PVC membrane material containing the ion exchanger dissolved in a volatile solvent was added dropwise onto the cellulose acetate material and allowed to dry.
8) The resulting sensor was then hydrated and "conditioned" by applying a voltage of –0.5V until stabilized.
9) The sensor was then calibrated.

Sensors using this construction method have been tested for over 30 days with excellent results. These same sensors have been allowed to dry out and then rehydrated, with little degredation in performance.

It should be recognized that the illustrated embodiments are only particular examples of the inventions and should not be taken as a limitation on the scope of the inventions. Rather, the inventions include all that comes within the scope an spirit of the following claims.

Claims

We Claim:

1. A gas permeable membrane comprising a guanidinium salt.

2. The membrane of claim 1 comprising a supported liquid membrane.

3. The membrane of claim 2 where the supported liquid membrane comprises a porous polytetrafluoroethylene membrane.

4. The membrane of claim 1 comprising a plasticized polymer.

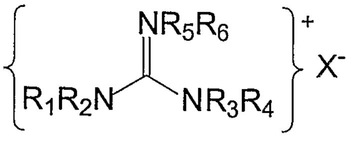
5. The membrane of claim 4 where the plasticized polymer comprises poly(vinyl chloride).

6. The membrane of claim 4 where the plasticized polymer is high molecular weight poly(vinyl chloride) plasticized with a solvent selected from the group consisting adipate esters, sebacate esters, phthalate esters, glycol esters, low volatility ethers, trimellitic acid esters, phosphate triesters, chlorinated paraffins, and mixtures thereof.

7. The membrane of claim 1 comprising from 0.1% to 10% by weight of the guanidinium salt.

8. The membrane of claim 7 comprising 1% to 5% by weight of the guanidinium salt.

9. The membrane of claim 1 where the guanidinium salt has the formula



$$\left\{ (R_1R_2N)(NR_3R_4)C{=}NR_5R_6 \right\}^{+} X^{-}$$

where R_1, R_2, R_3, R_4, R_5, and R_6 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, alkenyl, substituted alkenyl, cycloalkenyl, substituted cycloalkenyl, alkynyl, aryl, substituted aryl, heteroaryl and substituted heteroaryl, and X^- is an anion.

10. The membrane of claim 9 where R_1, R_2, R_3, R_4, R_5, and R_6 are independently selected from the group consisting of hydrogen, C1-30 alkyl, and aryl, and X^- is selected from the group consisting of chloride, bromide, fluoride, iodide, hydroxide, acetate, carbonate, sulfate and nitrate and combinations thereof.

11. An amperometric gas sensor comprising a gas-permeable membrane comprising a guanidinium salt.

12. The sensor of claim 11 further comprising an inert cathode and a reversible anode.

13. The sensor of claim 12 where the inert cathode is selected from the group consisting of gold, platinum, silver, palladium, iridium, rhodium, ruthenium, osmium and alloys thereof and the reversible anode is selected from the group consisting of silver/silver halide, lead/lead sulfate, sliver/silver oxide-hydroxide and lead/lead oxide-hydroxide.

14. The sensor of claim 13 where the inert cathode is gold and the reversible anode is a silver/silver chloride electrode.

15. The sensor of claim 11 where the gas permeable membrane is a supported liquid membrane.

16. The sensor of claim 11 where the gas permeable membrane comprises a plasticized polymer.

17. The sensor of claim 11 where the guanidinium salt removes an ionic product of an electrode reaction from an electrolyte volume and transports an ion consumed in the electrode reaction from the sample into the electrolyte volume.

18. The sensor of claim 17 where the ionic product is hydroxide ion and the ion consumed in the electrode reaction is chloride.

19. A solid state amperometric gas sensor, comprising:
a gas-permeable membrane comprising a guanidinium salt;
an electrolyte salt in contact with the gas-permeable liquid membrane through a first surface of the electrolyte salt; and
a pair of electrodes in contact with a second, opposite surface of the electrolyte salt.

20. The sensor of claim 19 where the gas-permeable membrane is a supported liquid membrane.

21. The sensor of claim 19 where the gas-permeable membrane comprises a plasticized polymer.

22. The sensor of claim 19 where the electrolyte salt is selected from the group consisting of Group I metal halides.

23. The sensor of claim 22 where the electrolyte salt is selected from KCl and NaCl and mixtures thereof.

24. A dissolved oxygen sensor, comprising:
a gas permeable membrane comprising a guanidinium salt;
an inert cathode; and
a reversible anode.

25. The dissolved oxygen sensor of claim 24 further comprising an electrolyte volume of less than 50 μL.

26. The dissolved oxygen sensor of claim 24 further comprising an electrolyte where the cathode and anode are imprinted on an oxygen impervious, insulating substrate, the electrolyte is in contact with the cathode and anode and the gas-permeable membrane prevents communication between the electrolyte and an external medium.

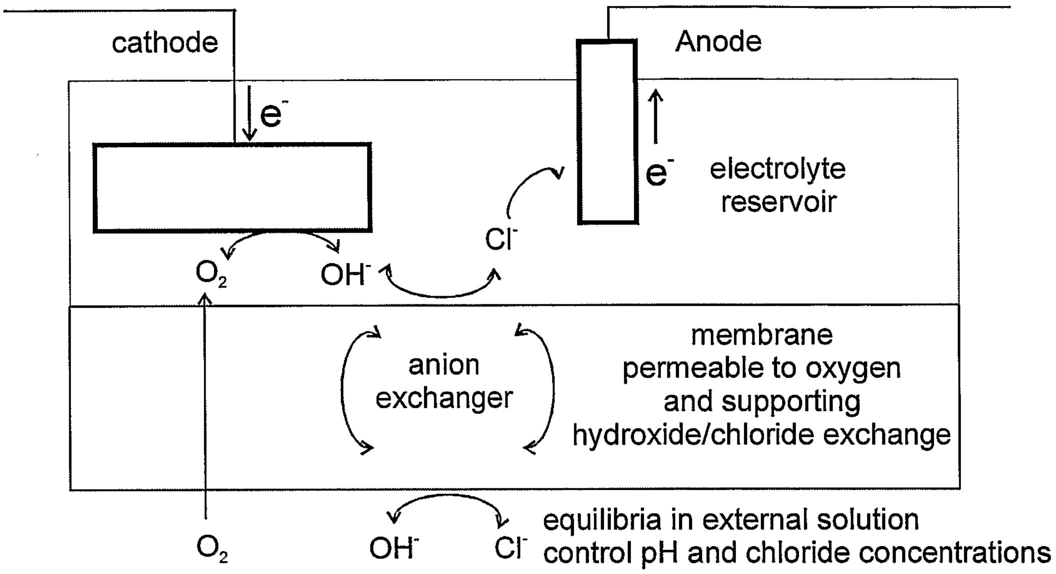

cathode
Anode
e⁻
e⁻
electrolyte reservoir
Cl⁻
O₂
OH⁻
anion exchanger
membrane permeable to oxygen and supporting hydroxide/chloride exchange
O₂
OH⁻
Cl⁻
equilibria in external solution control pH and chloride concentrations

FIG. 1

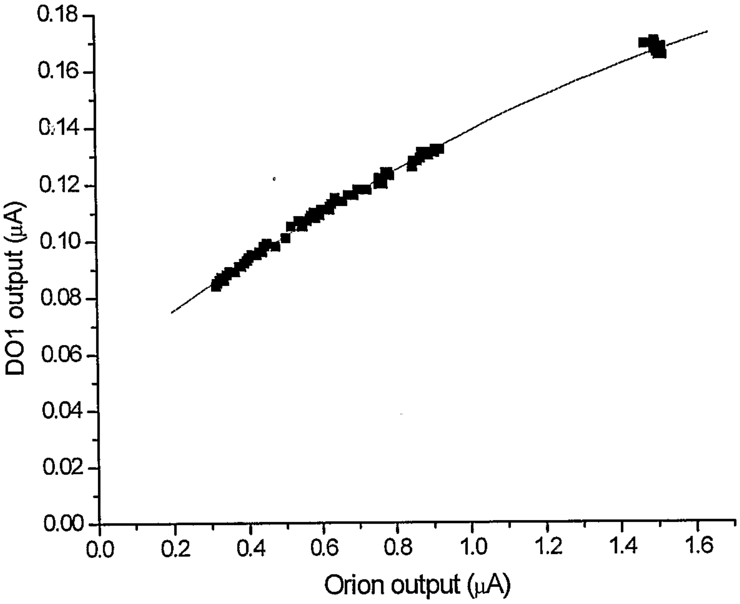

0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
DO1 output (μA)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Orion output (μA)

FIG. 2

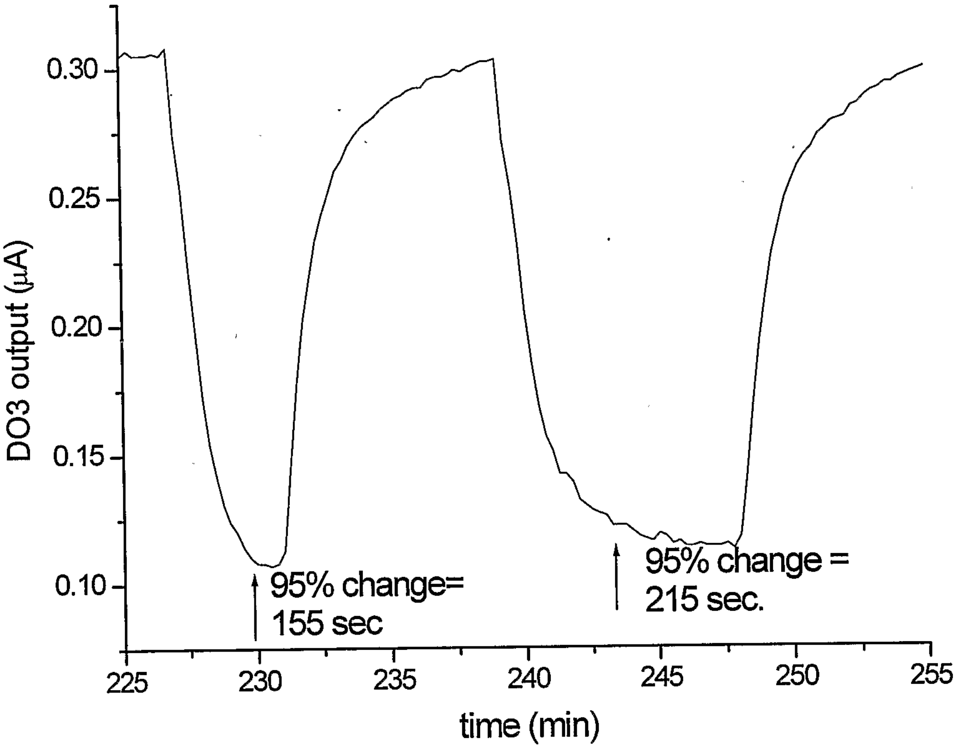

DO3 output (μA)
0.30
0.25
0.20
0.15
0.10
95% change= 155 sec
95% change = 215 sec.
225
230
235
240
245
250
255
time (min)

FIG. 3

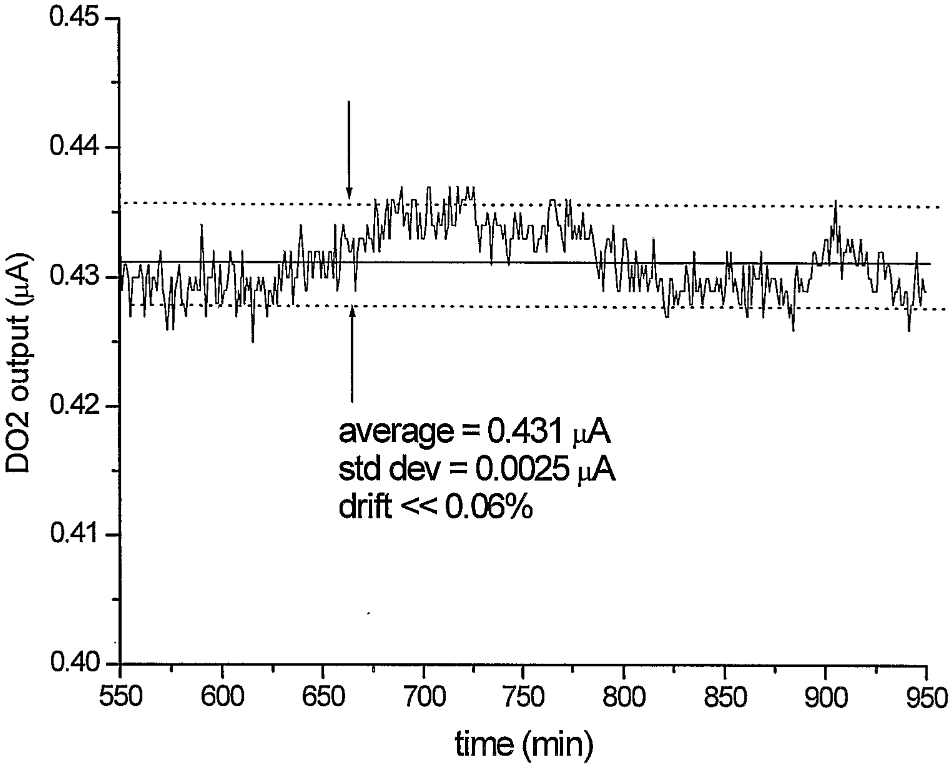

0.45
0.44
0.43
0.42
0.41
0.40
DO2 output (μA)
550
600
650
700
750
800
850
900
950
time (min)
average = 0.431 μA
std dev = 0.0025 μA
drift << 0.06%

FIG. 4

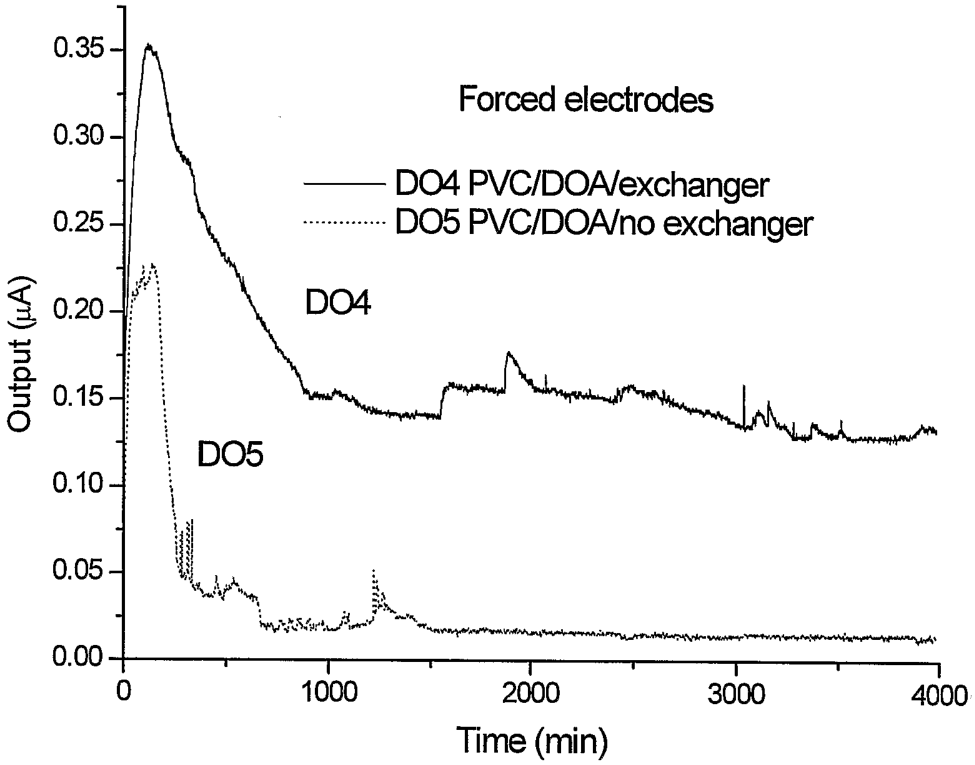

Forced electrodes
DO4 PVC/DOA/exchanger
DO5 PVC/DOA/no exchanger
DO4
DO5
Output (μA)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1000
2000
3000
4000
Time (min)

FIG. 5

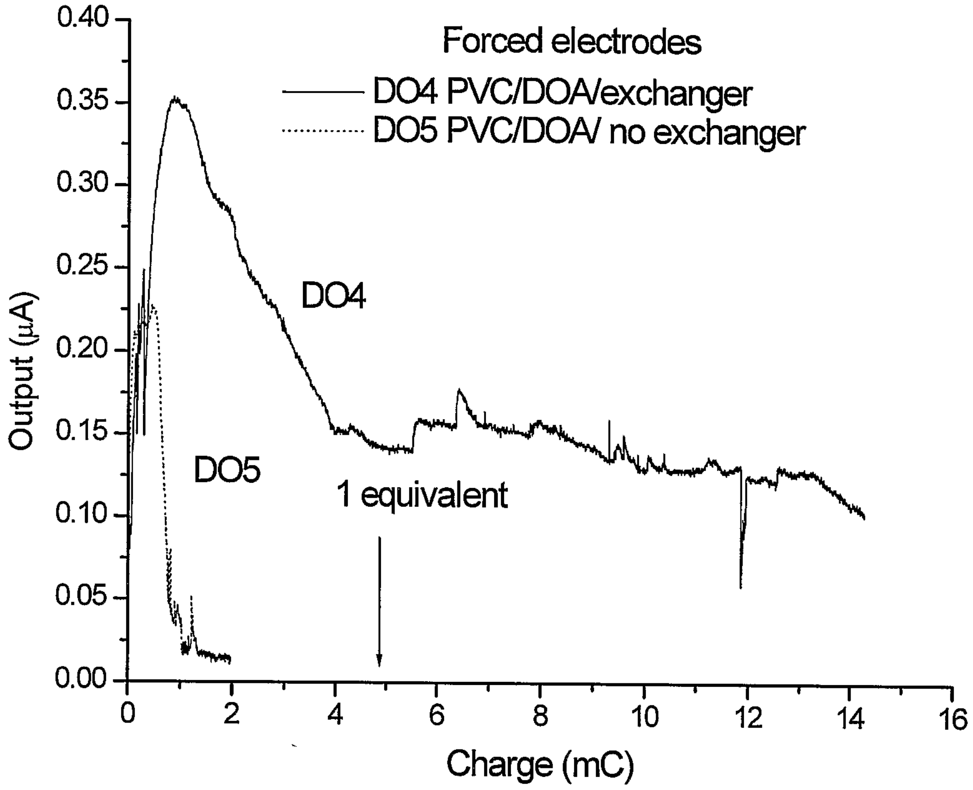

Forced electrodes
DO4 PVC/DOA/exchanger
DO5 PVC/DOA/ no exchanger
DO4
DO5
1 equivalent
Output (μA)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Charge (mC)
0
2
4
6
8
10
12
14
16

FIG. 6

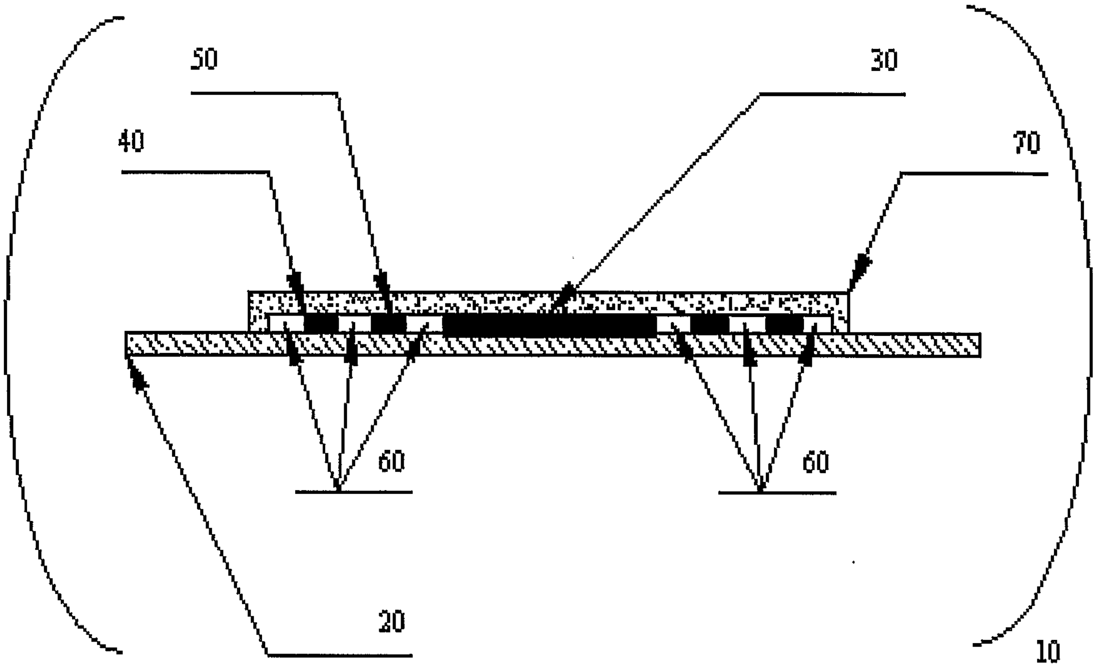


FIG. 7

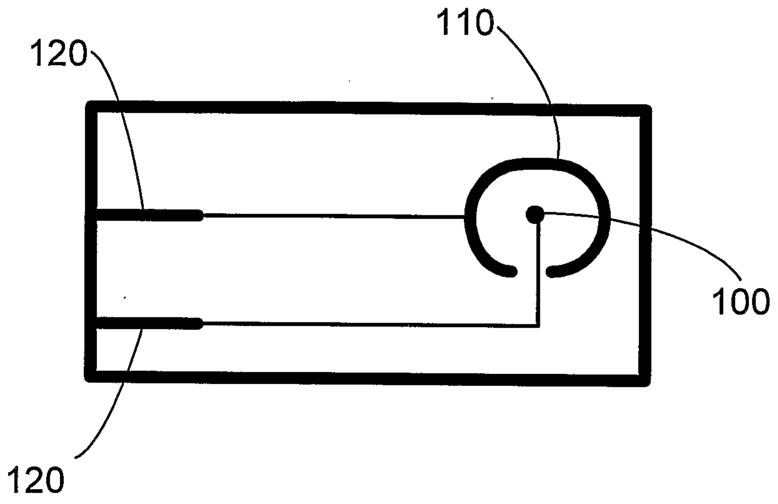


FIG. 8

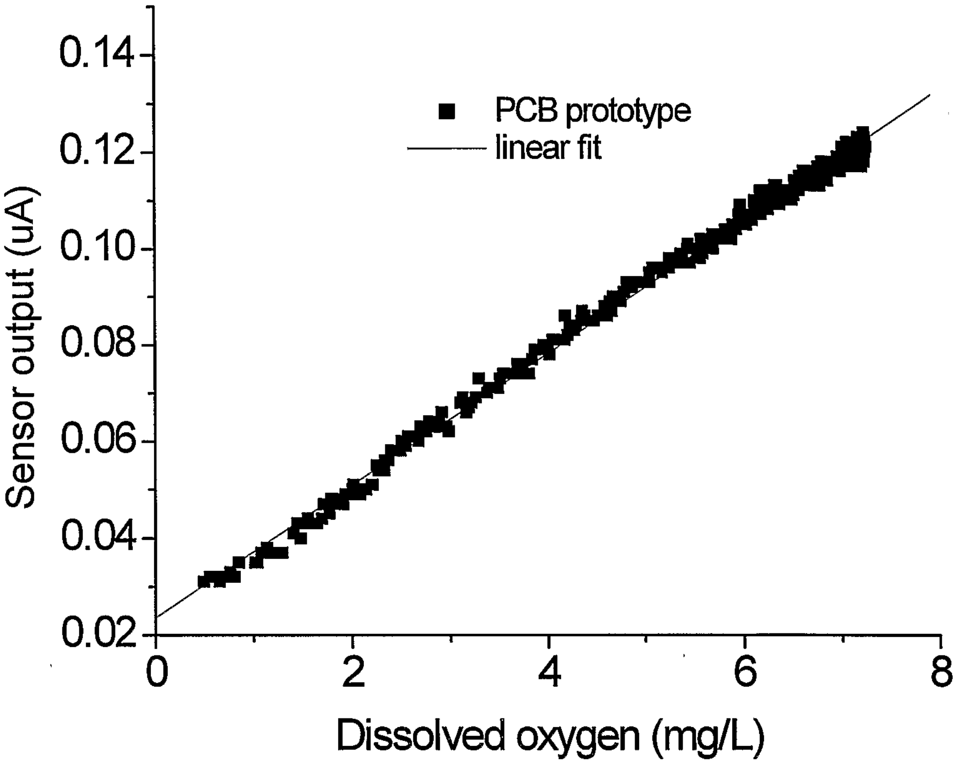

■ PCB prototype
linear fit
Sensor output (uA)
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0
2
4
6
8
Dissolved oxygen (mg/L)

FIG. 9

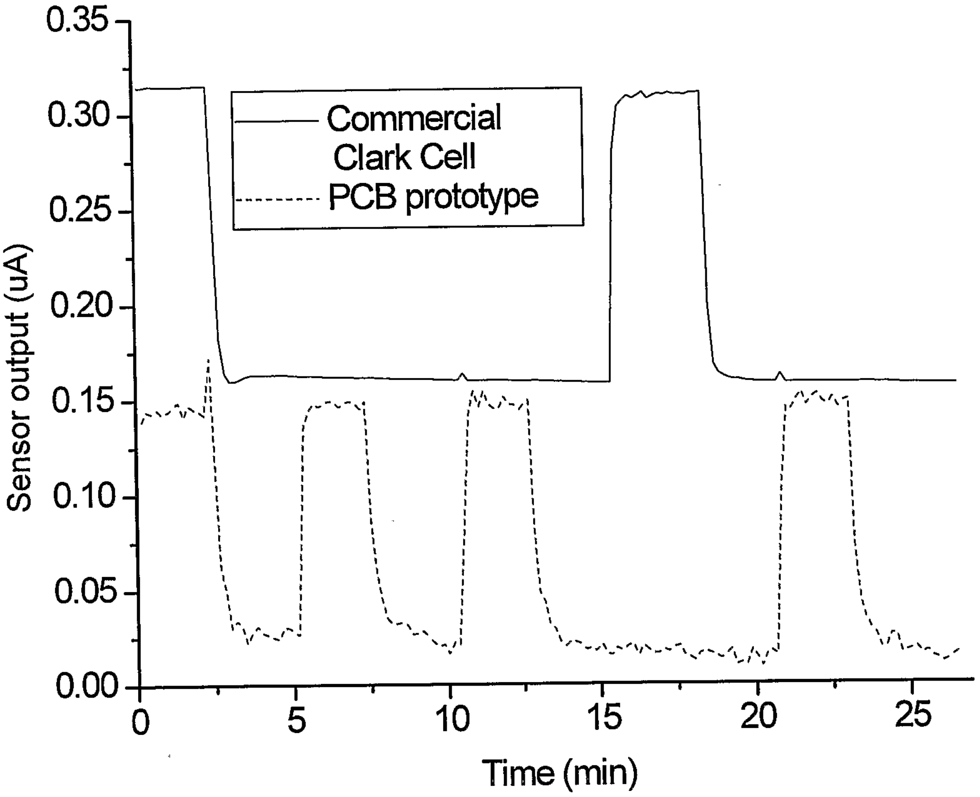

0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Sensor output (uA)
0
5
10
15
20
25
Time (min)
Commercial Clark Cell
PCB prototype

FIG. 10

In nal Application No
PCT/CA 02/00750

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/49 G01N27/40 G01N27/333 B01D69/10 B01D69/14
B01D53/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search
13 March 2003

Date of mailing of the international search report
27/03/2003

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL – 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer
Cordero Alvarez, M

INTERNATIONAL SEARCH REPORT

Int ›nal Application No
PCT/CA 02/00750

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/CA 02/00750

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