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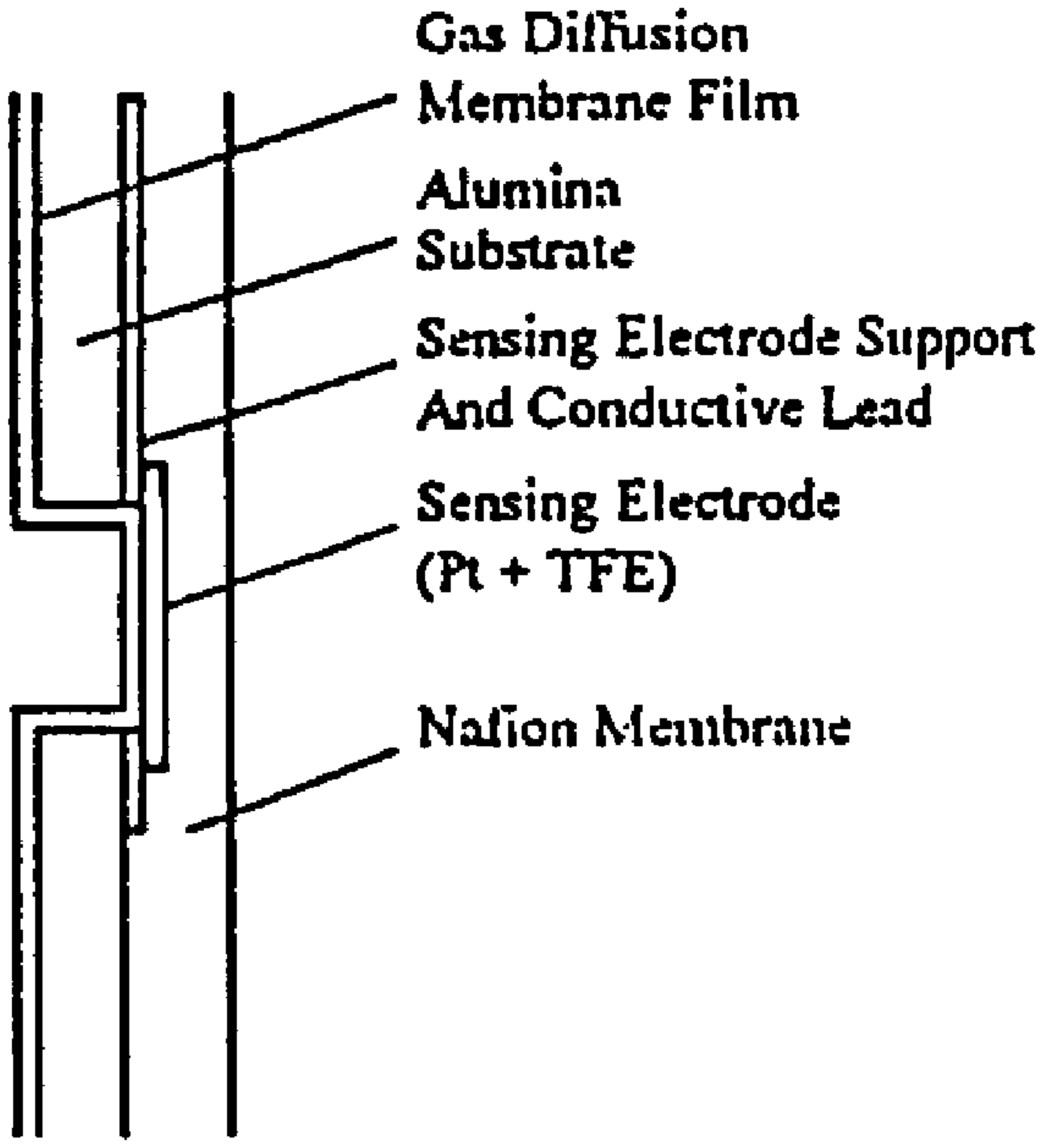
(54) **Titre :** CAPTEUR DE TYPE FILM HYBRIDE
(54) **Title:** HYBRID FILM TYPE SENSOR



(57) **Abrégé/Abstract:**

A miniaturized gas sensor comprises a thick-or-thin type electrodes, on a non-conductive supportive susbtrate (1), and in contact with a solid ionomer electrolyte (8), for the detection of toxic gases, i.e., carbon monoxide, and other oxidizable or reducible gases and vapors is described. The all-solid planar sensor cell has two or more film type electrodes (4, 5, 7) arranged on a non-conductive planar surface of a supportive substrate. The electrodes are discret and in intimate contact with the same solid polymer ionomer membrane. The sensor cell contains no liquid electrolyte and is operated in a constant-voltage, potentiostatic or potentiodynamic mode. A high sensitivity to a select gas or vapor is achieved by a novel three-phase contact area design for a sensing electrode which provides contact with the solid ionomer electrolyte, as well as the gas sample via diffusion openings or holes (2) that penetrate through the supportive substrate.

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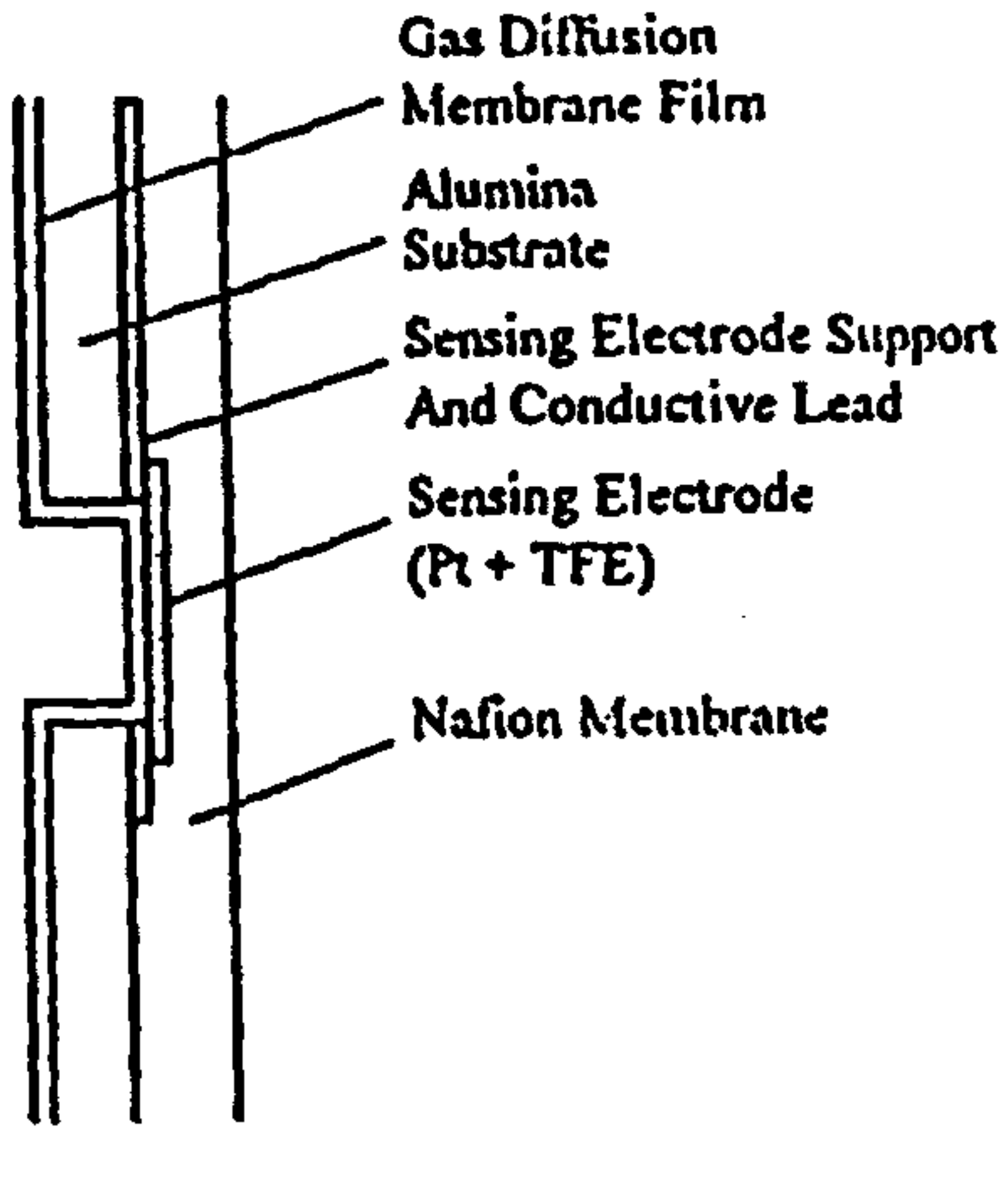
(54) Title: HYBRID FILM TYPE SENSOR



(57) Abstract: A miniaturized gas sensor comprises a thick-or-thin type electrodes, on a non-conductive supportive susbtrate (1), and in contact with a solid ionomer electrolyte (8), for the detection of toxic gases, i.e., carbon monoxide, and other oxidizable or reducible gases and vapors is described. The all-solid planar sensor cell has two or more film type electrodes (4, 5, 7) arranged on a non-conductive planar surface of a supportive substrate. The electrodes are discret and in intimate contact with the same solid polymer ionomer membrane. The sensor cell contains no liquid electrolyte and is operated in a constant-voltage, potentiostatic or potentiodynamic mode. A high sensitivity to a select gas or vapor is achieved by a novel three-phase contact area design for a sensing electrode which provides contact with the solid ionomer electrolyte, as well as the gas sample via diffusion openings or holes (2) that penetrate through the supportive substrate.

HYBRID FILM TYPE SENSOR

FIELD OF THE INVENTION

The invention is directed toward a sensor with thick or thin film electrodes on a non-conductive substrate.

BACKGROUND OF THE INVENTION

Film based techniques have been investigated for a wide variety of sensors, as reported by Wenyi et al., 1997; Hughes et al., 1997; Staley, 1996; Agbor et al., 1995; Tan and Tan, 1995; Menil et al., 1994; Kunnecke et al., 1994; Creasey and Varney, 1994; Geistlinger, 1993; Ishiji et al., 1993; Najafi et al., 1992; Hampp et al., 1992; Nakano and Ogawa, 1994; Yamazoe and Miura, 1994; and, Madou and Otagawa, 1989. While solid-state gas sensors have the advantage of being able to operate at elevated temperatures, they also have the disadvantages of slow response and recovery time and a high internal operating temperature as reported by Liu et al., 1993; and Narducci et al., 1993. More recent literature (Schwebel et al., 1997; Sheng et al., 1997; Micocci et al., 1997) details the substantial development work yet to be done before this type of sensor is applicable for use in battery-powered instruments.

A Nafion®-coated metal oxide pH sensor has been reported (Kinlen et al., 1994) with sputtered iridium oxide sensing and silver/silver chloride reference electrodes on alumina ceramic substrates. Nafion was used as a cation-selective ionomer coating in order to decrease the oxidation-reduction error generally affecting the performance of metal oxide pH electrodes. The use of Nafion as polymer-electrolyte for a thin-film CO sensor is described (Yasuda et al., 1994) with macro-sized, sputtered Pt sensing and counter electrodes and a smaller, sputtered Au electrode as reference electrode. A 5 wt% n-propyl alcohol solution of Nafion

(DuPont, 1100 EW) is used to form the polymer electrolyte film over the electrodes by casting. The polymer is washed and protonated in aqueous sulfuric acid prior to casting. The reported lifetime of this sensor is reported to be less than one month. During this time, the CO oxidation current decreases steadily down to a few percent of its original value without any period of stable measurement signal. The lifetime of the device may be extended up to three years by laminating the polymer electrolyte layer with a cast perfluorocycloether-polymer film in order to keep the CO permeability coefficient through Nafion constant; theoretical calculations showed that the drift rate of the signal could be significantly reduced under these conditions.

A description of typical state-of-the-art hydrated solid polymer electrolyte or ionomer sensors and sensor cells is described by Kosek et al. U.S. Patent 5,527,446; LaConti and Griffith, U.S. Patent 4,820,386; Shen et al., U.S. Patent 5,573,648; and, Stetter and Pan, U.S. Patent 5,331,310. These sensor cells, based on hydrated solid polymer electrolyte or ionomer technology, have several advantages over conventional electrochemical sensor cells. The catalytic electrodes are bonded directly to both sides of a proton conducting solid polymer ionomer membrane providing a stable electrode to electrolyte interface. One side of the electrolyte membrane is flooded with distilled water, making the sensor cell self-humidifying and independent of external humidity. Since no corrosive acids or bases are used in the sensor cell, a lifetime of over 10 years has been demonstrated for solid polymer ionomer sensor cells. Finally, the sensor cells are easy to maintain, and so are ideal for use in remote, unattended environments. Regular addition of water to the reservoir in the sensor housing every several months and monthly calibration checks are the only requirements.

A disadvantage of the state-of-the-art sensors described above is that the signal-to-noise ratio may not be conducive to detection of very low concentrations (parts per billion, ppb) of important environmental and biomedical gases and vapors. Also, response time may be relatively slow, and reproducibility between sensors and sensor cells may be difficult to achieve. Also, they are relatively costly.

Recently, miniaturized thick- and thin-film type sensors have been developed where the solid ionomer membrane acts as a conduit between the gas to be detected (sample gas) and the sensing electrode (Yasuda et al., 1994). The sample gas permeates through the membrane itself where a 3-phase contact area is established. A disadvantage with this configuration is that the solid ionomer membrane water content may control the gas permeation rate as well as proton conductivity. As the humidity increases, the membrane water content increases. This causes an increase in the gas diffusion rate as well as proton conductivity and sensor signal response. The best method of controlling or fixing the water content of the membrane is to have a water reservoir on the back side of the membrane, directly opposite to where the film type electrodes and non-conductive supportive substrate are located. Unfortunately in the above configuration the back side of the membrane is required to be free of liquid so that the sample gas can diffuse through the membrane to the sensing electrode.

The present invention overcomes the limitations of the state-of-the-art in miniaturized electrochemical sensors stated above by uniquely combining an advanced solid polymer ionomer membrane configuration with a film type electrode on a non-conductive supportive substrate. The substrate has diffusion openings or holes having a known area which permit easy access of the sample gas to a sensing electrode contact area. The sensor configuration provides a three phase contact area which serves as an interface for the membrane, the electrodes, and the gas being detected. This design utilizes the precision of solid-state device fabrication techniques to yield inexpensive, low maintenance, highly sensitive, rapidly responsive, and reproducible sensor devices for environmental, industrial, and biomedical monitoring.

SUMMARY OF THE INVENTION

This invention is directed toward a controllable and reproducible gas sensor configuration having a three-phase contact area, whereby the sample gas diffuses to the sensing electrode and membrane through openings, holes or slits that extend through the non-conductive supportive substrate.

This invention is further directed toward a gas sensor where the gas diffusion process is decoupled from the proton conduction process. The gas diffusion is controlled only by through openings of known area in the substrate or in the substrate and an additional rate limiting gas diffusion barrier film, eg: polyethlene, while proton conduction takes place only through an electrolyte layer, e.g., a Nafion® membrane.

The invention is also directed toward utilizing a method of mass producing film type gas sensors by stacking a number of component layers to form a series of adjacent sensors which are subsequently separated into individual sensors.

The invention is still further directed toward a gas sensor utilized in conjunction with a gas sensor control circuit.

The invention is also directed toward a gas sensor utilized in a gas sensing instrument.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic top view of the non-conductive supportive substrate.
Figure 2 shows a film type electrochemical sensor cell with Pt/Air (O_2) reference.
Figure 3 shows a film type electrochemical sensor cell with a polymeric gas-diffusion layer over the sensing electrode membrane.
Figure 4a shows a top view of a thick-film type electrochemical sensor cell.
Figure 4b shows a cross-section A-A'.

Figure 4c shows a cross-sectional view of sensor cell assembly.

Figure 5 shows a gas sensor control circuit.

Figure 6 shows a gas sensor utilized in a gas sensing instrument.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows the top view of a ceramic film type substrate *(1)* (e.g., alumina) having holes *(2)* uniformly distributed in parallel rows. The distance between the holes in the parallel rows and the distance between the rows determine the dimensions of the sensor. The holes are ideally punched in a single step, while the alumina plate is still soft, in the "green" stage of substrate fabrication, prior to high-temperature sintering. Other techniques to create the holes include laser ablation or use of soluble fillers.

Using screen printing or lithographic techniques, conducting leads *(3)* and thick- and thin-film electrodes are formed on the non-conductive substrate *(1)* for multiple electrodes. A typical sensor design utilizing this method is shown in **Figure 2**, which has a single reference electrode *(4)* (e.g., Pt/Air (O_2) electrode) and a Pt counter electrode *(5)*. The contact for the sensing electrode *(6)* is a ring concentric to the hole. This ring can be made of smooth, rough or platinized platinum. Some platinization may provide better contact. Simultaneous platinization of electrodes can be performed by customized electrolytic plating on properly masked multi-sensor plates.

The sensing or working electrode *(7)* may be a disc of Teflon®-bonded or Nafion-bonded platinum or other electrocatalyst. A number of discs are deposited on an ionomer film, such as Nafion electrolyte membrane *(8)* at uniform distances from each other, for instance, by decal transfer, silk printing, spray painting, artist brush lettering, or by any approach which lends itself to uniform deposition of a design on a transfer substrate without waste. The discs' distances from center to center are the same as for the holes of **Figure 1**. The diameter of the sensing or working electrode disc is somewhat larger than the diameter of the hole in **Figure 1** to allow for contact between the disc and the sensing electrode support ring of **Figure 2.** Instead of a single large hole per sensor of **Figure 1** (which requires the use of the substrate to control diffusion of the analyte), a series of smaller openings may be used, with small enough diameters to control diffusion independently of the analyte flow. The areas of the openings are chosen so as to control diffusion of the sample gas toward the sensor and to maintain a constant diffusion rate independent of any changes in the sample gas flow rate. By using a number of these diffusion-controlling orifices, a reasonably large signal may be maintained.

Over the empty alumina surface (the surface with no printed leads and electrodes) a gas-permeable diffusion film *(9)* is deposited in one configuration of the invention. This film is made to conform to the sensor electrode over the holes (as shown in **Figure 3**), or hangs loose over the (sensor) sensing electrode *(7)*. The substrate (with multiple arrays of printed conductors), the Nafion membrane (with multiple sensing electrode discs), and the gas-permeable film are arranged as shown in the schematic representation of **Figure 3**. After all the components are unitized, the resulting structure is cut in individual sensor units.

An additional advantage of this structure is that it allows for a water reservoir over the Nafion membrane on the opposite, or back side from where the sensing electrode is located as shown in **Figure 4c.**

A schematic drawing of the sensor cell assembly of this invention is shown in **Figure 4**. In a preferred embodiment of this invention a hole of approximately 80 mils (0.080 in) is formed in a film type substrate and sensing electrode contacts *(6)*, and Pt counter *(5)* and reference electrodes *(4)* are then deposited on the substrate *(1)* surface as shown in **Figure 4a**. In an alternative embodiment of this invention the hole *(2)* is drilled directly through the non-conductive substrate and integral sensing electrode contact structure. As a result the sample gas has direct contact through the substrate hole with the sensing electrode as shown in **Figure**

4b. This film type substrate structure is mounted in a sensor housing *(10)* as shown in **Figure 4c** with a solid ionomer membrane (Nafion 117). The Pt sensing electrode (with hole in center) and solid counter and reference electrodes are compressed tightly against the Nafion membrane. The fixture as shown in **Figure 4** has a water reservoir *(11)* on the opposite side of the membrane from where the electrodes are located. The reservoir *(11)* is filled with distilled water and wets the membrane, thus fixing and controlling the water content of the membrane and electrode assemblies. The reservoir *(11)* is sealed with a cap *(20)*.

The film type sensor configuration from above is integrated with a potentiostat and a voltage of approximately +0.1 V is applied to the Pt sensing electrode with respect to a Pt/Air (O_2) reference. This corresponds to an applied potentiostatic voltage of approximately 1.16 V with respect to a normal hydrogen electrode (NHE).

Gas samples of air and 7.4 ppm SO_2 in air are introduced into the sampling port of the fixture described above. The gas flow is approximately 60 cm^3/min and temperature is approximately 25°C. The sample gas diffuses through the 80-mil hole in the non-conductive substrate and electrochemically reactes at the exposed sensing electrode/solid ionomer electrolyte surface. Humidification is provided by the liquid water in the reservoir which soaks the opposite, or back side of the membrane as to where the electrode structures are located.

The background response signal with air is 30 nanoamps (nA). The response signal with 7.4 ppm SO_2 in air is 135 nA. This corresponds to a net response signal for 7.4 ppm SO_2 in air of 105 nA or 14.2 nA/ppm per 80-mil hole. It is possible to increase the magnitude of signal and signal-to-noise ratio by increasing the number of holes in the substrate above the integral sensing electrode structure.

It is also possible, with this configuration, to detect other oxidizable or reducible gases such as CO, NO, NO_2, H_2S, ozone, CO_2, hydrogen, hydrazine, ammonia, HCl, alcohols and acetone.

Referring to **Figures 5** and **6**, a block diagram of the sensor control circuit *(13)* is shown. The sensor control circuit *(13)* is designed to: 1) control the potential of the sensing electrode *(7)* at a predetermined voltage (the "potentiostatic voltage", or "E_{pot}"); 2) measure the temperature; 3) convert the gas concentration-related current to a temperature-compensated voltage signal; and 4) provide properly amplified voltage to the data acquisition/storage microprocessor *(14)*. An on-board micro power-regulated power supply *(16)* uses the microprocessor's *(14)* power supply to provide the required ±3.9 volts for the sensor circuitry. The DC power can be supplied by a 6-V battery *(16d)* or an AC adaptor *(16e)*.

The control amplifier portion *(17b)* of the sensor control circuit *(13)* consists of a micro power operational amplifier (e.g., MAX407 or LM6062). The sensing *(7)*, counter *(5)* and reference *(4)* electrode portions of the sensor assembly *(1)* are in the feedback loop of the control amplifier *(17b)* as shown in **Figure 5**, a standard configuration for potentiostat circuits. An adjustable voltage divider *(17a)* allows the polarizing voltage (E_{pot}) to be set at a predetermined voltage range such as 0 to 50 mV. This signal is compared to the reference electrode *(7)* voltage (which appears with it at the summing junction) by the control amplifier *(17b)* of the sensor control circuit *(13)*. The latter adjusts the current through the sensor cell *(10)* to minimize the difference between the E_{pot} and the reference electrode *(4)* voltages.

The resulting sensor cell assembly *(19)* current (flow of electrons from sensing electrode *(7)* to counting electrode *(5)*), which is linearly related to the concentration of gas, is transformed into a voltage signal by the current-to-voltage converter *(15a)*. Temperature compensation of the sensor signal is effected in the next stage of amplification *(15b)* using a thermistor *(18a)* which is positioned in the gas sensor housing *(10)*. The last stage of amplification *(15c)* provides the necessary inversion of the voltage signal as well as gain adjustment, to permit calibration for normal variations in sensitivity among sensors. The same type of micro power operational amplifier is used for these stages *(15a), (15b), (15c)* as for the control amplifier *(15b)*. The transformed current signal is directed to an A/D channel on the data acquisition board of the microprocessor *(14)*.

Power for the sensor control circuit *(13)* is provided by a Duracell 6-V battery *(16d)* (PX 28A or 28L) through a micro power-regulated power supply *(16)*. The power supply *(16)* utilizes a voltage inverter (e.g., ICL 7660) *(16a)* to convert the positive battery voltage to a negative voltage of the same magnitude, and a positive voltage regulator (e.g., MAX663) *(16c)* and negative voltage regulator (e.g., MAX 664) *(16b)* to provide a stable ±3.9 volts.

The film type gas or vapor sensing instrument *(12)*, as shown in **Figure 6**, includes the sensor cell assembly *(19)*, potential-control circuitry *(13)*, and the microprocessor *(14)* with the data acquisition-recording unit. The sensing instrument *(12)* is preferably battery operated, and has the ability to sample the gas or vapor and temperature signals at intervals and store in the random access memory (RAM) on the data acquisition board days to weeks of data. The data acquisition circuit microprocessor is programmed to sample and store the gas concentration signals at preset intervals. Data are off-loaded to a personal computer by accessing the microprocessor through an RS232 port.

The sensor cell assembly *(19)* and its potential-control circuit *(13)* are integrated with a battery-operated microprocessor *(14)* of 32K memory, which samples the sensor signal as well as temperature and other signals at 10-, 20-, or 30-second intervals and stores an average value at intervals of 2, 5, or 10 minutes according to a programmable protocol. The data acquisition/storage unit in the microprocessor *(14)* can record 8 days of data, storing at 2-minute intervals, or up to 40 days storing at 10-minute intervals. In clinical testing to date, a 2-minute interval is suitable for one-day clinical studies and a 10-minute interval is appropriate for extended use. The microprocessor *(14)* with data acquisition/logic circuit can be programmed to sample more than one analog signal from the control circuit *(13)*, and to convert these to digital signals and store them (i.e., gas concentration and temperature) at preset intervals together with real-time data. Data are off-loaded to a personal computer by accessing the microprocessor *(14)* through an RS232 port. After downloading, the digital data are converted to engineering units of gas concentration and temperature, and can be graphed by a menu-driven Lotus® 123 spreadsheet. Through a potentiometer in the gain amplifier circuit *(15c)*, the device can be calibrated with calibrated gas samples, to indicate gas concentrations in the ambient. The potential-control circuit *(13)* shown in **Figure 5** is powered, in a preferred embodiment, by six 1½ volt AA-size batteries *(16d)*. A typical microprocessor *(14)* with data acquisition-recording capability that has been successfully used is sold by ONSET Computers, Falmouth, MA, under the product name of "Tattletale Lite®." The sensor cell assembly *(19)* with its control circuit *(13)* is also designed to yield a current or voltage signal proportional to gas flux that could be used to continuously transmit the data to a remote receiving device or central monitoring station or unit.

The sensing electrodes can be organized in multiple arrays or sets containing a necessary number of counter or reference electrodes. Reference electrodes such as Pt/air (O_2), PtO_2, or dynamic hydrogen electrode as described by Giner (1964) may be employed. Electrically driven 3- or 2-electrode film type configurations may be employed using potentiostatic, potentiodynamic or potential control. Two-electrode configurations require a reversible or stable counter-reference electrode such as Pt/air (O_2), PtO_2 or Pt/H_2 which has a higher BET (Brunauer, Emmett, Teller) surface area (25 m^2/g or larger) and/or larger geometric surface areas than the sensing lectrode.

Electrochemically reversible electrodes may be used in 3 or 2 electrode configurations, but especially in a 2 electrode arrangement where the counter electrode also acts as a reference electrode. Electrochemically reversible electrodes are constructed of stable catalyst materials and usually have a relatively large electrochemical active surface area so that they remain stable and their potential is not perturbed by small current flow. Examples include PtO_2 and Ag/AgCl electrodes.

CLAIMS

1. A sensor cell for detecting gases comprising:
a substrate;
a sensing electrode; a counter electrode; and a reference electrode, said sensing, counter and reference electrodes in contact with said substrate;
an ionomer membrane in contact with said substrate and said sensing, counter and reference electrodes;
an open three-phase area in said substrate, proximate to said sensing electrode, said area providing contact among said gases to be detected, said sensing electrode, and said ionomer membrane; and
a diffusion opening proximate to said sensing electrode.

2. The apparatus of claim 1 whereby said diffusion opening comprises at least one opening in said substrate, said opening in close contact with said sensing electrode.

3. The apparatus of claim 1 whereby at least one of said sensing, counter, or reference electrodes contains a fluorocarbon-bonded particulate catalyst which is bonded to said ionomer membrane.

4. The apparatus of claim 3 whereby said fluorocarbon-bonded particulate catalyst is coated with a polymeric thin gas-permeable diffusion layer film.

5. The apparatus of claim 1 whereby at least one of said sensing, counter, or reference electrodes contains an ionomer-bonded particulate catalyst which is bonded to said ionomer membrane.

6. The apparatus of claim 5 whereby said ionomer-bonded particulate catalyst is coated with a polymeric thin gas-permeable diffusion layer film.

7. The apparatus of claim 1 whereby said sensing, counter and reference electrodes are in contact with said ionomer membrane.

8. The apparatus in claim 1 whereby said ionomer membrane is a proton exchange membrane.

9. The apparatus in claim 1 whereby said ionomer membrane is an anion, hydroxide ion exchange membrane.

10. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are formed by deposition on said ionomer membrane.

11. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are formed by deposition on said substrate.

12. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are metallic.

13. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes comprise a material selected from the group consisting of Pt, Au, C, platinized Pt, and platinized Au.

14. The apparatus of claim 1 wherein said ionomer membrane, substrate, and said electrodes are brought into contact by bonding techniques.

15. The apparatus of claim 1 whereby said ionomer membrane is humidified by an aqueous material.

16. The apparatus of claim 1 wherein said sensor cell is electronically controlled in a 2 electrode sensor configuration.

17. The apparatus of claim 1 wherein said sensor cell is electronically controlled in a 3 electrode sensor configuration.

18. The apparatus of claim 1 wherein said sensor cell is electronically controlled by a potentiostatic circuit connected to said sensing, counter and reference electrodes.

19. The apparatus of claim 1 wherein said sensor cell is electronically controlled by a potentiodynamic circuit connected to said sensing, counter and reference electrodes.

20. The apparatus of claim 1 wherein said sensor cell is electronically controlled by a constant voltage source connected to said sensing electrode and an electrochemically reversible counter electrode acting as a reference electrode.

21. The apparatus of claim 1 further comprising a microprocessor for real time data readout, data storage and retrieval, and remote data transmission.

22. The apparatus of claim 1 incorporated into a gas sensing instrument.

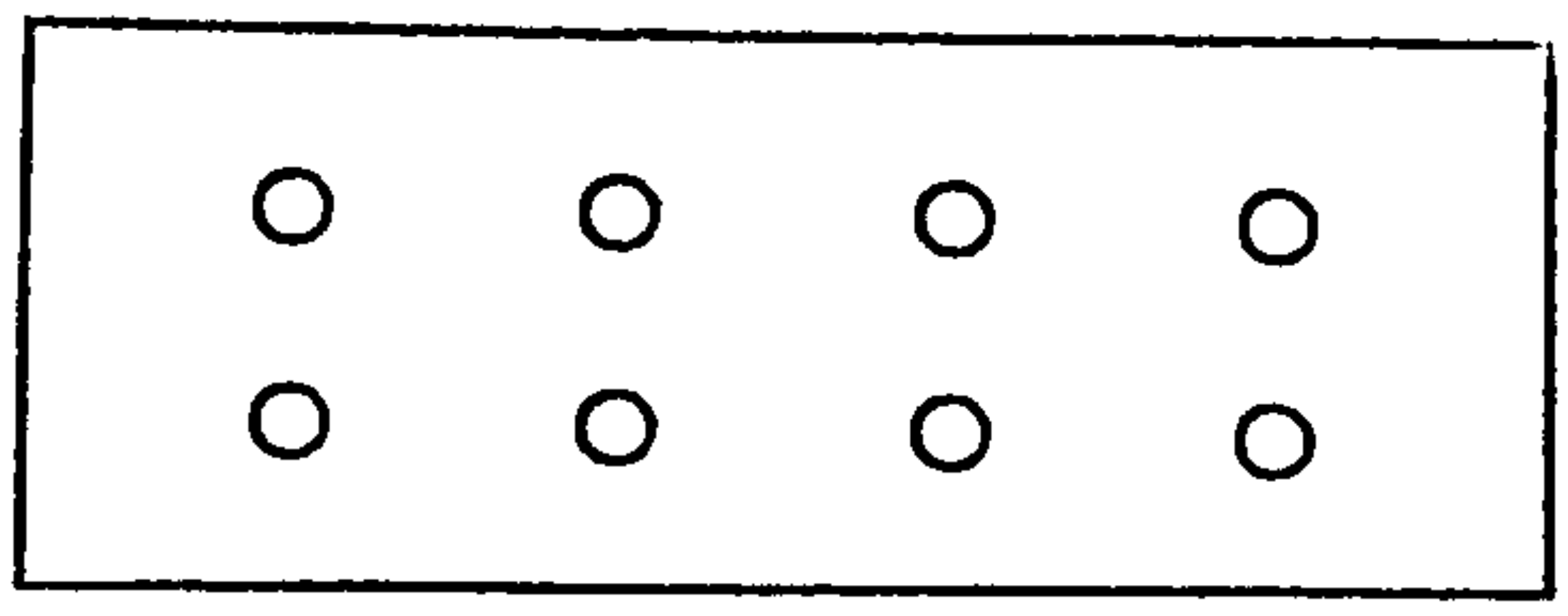


Figure 1

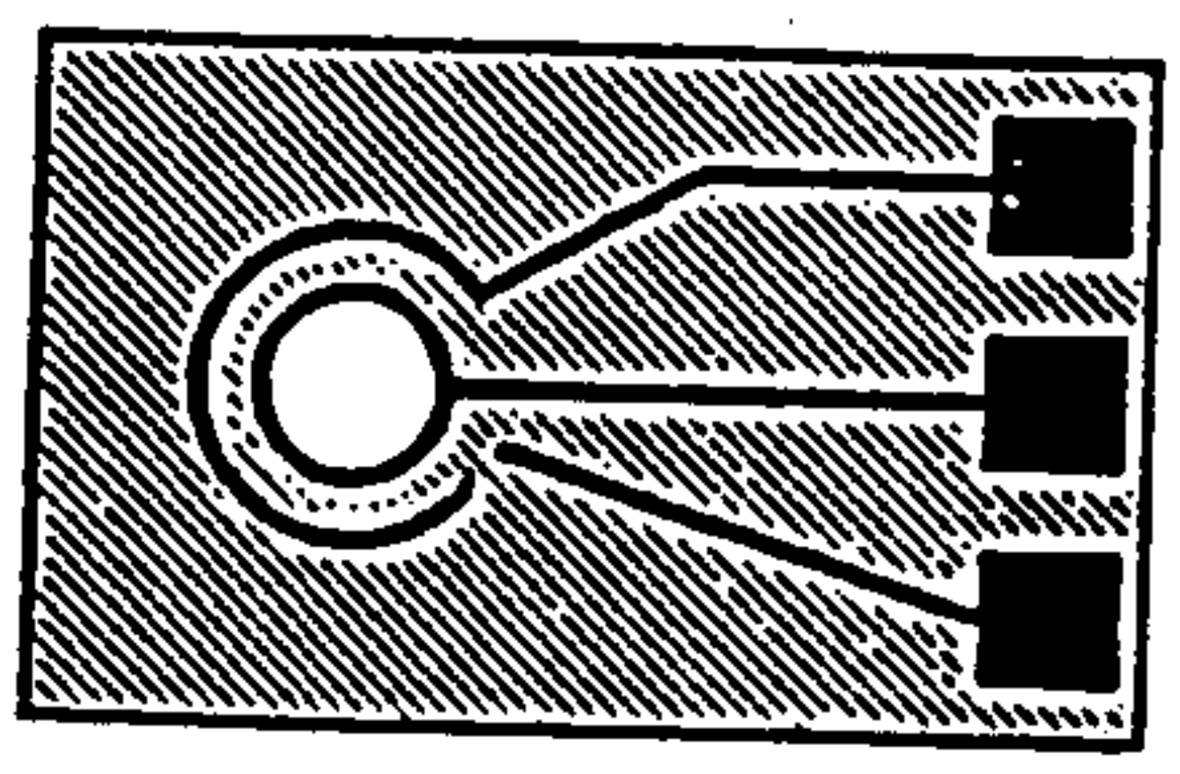


Figure 2

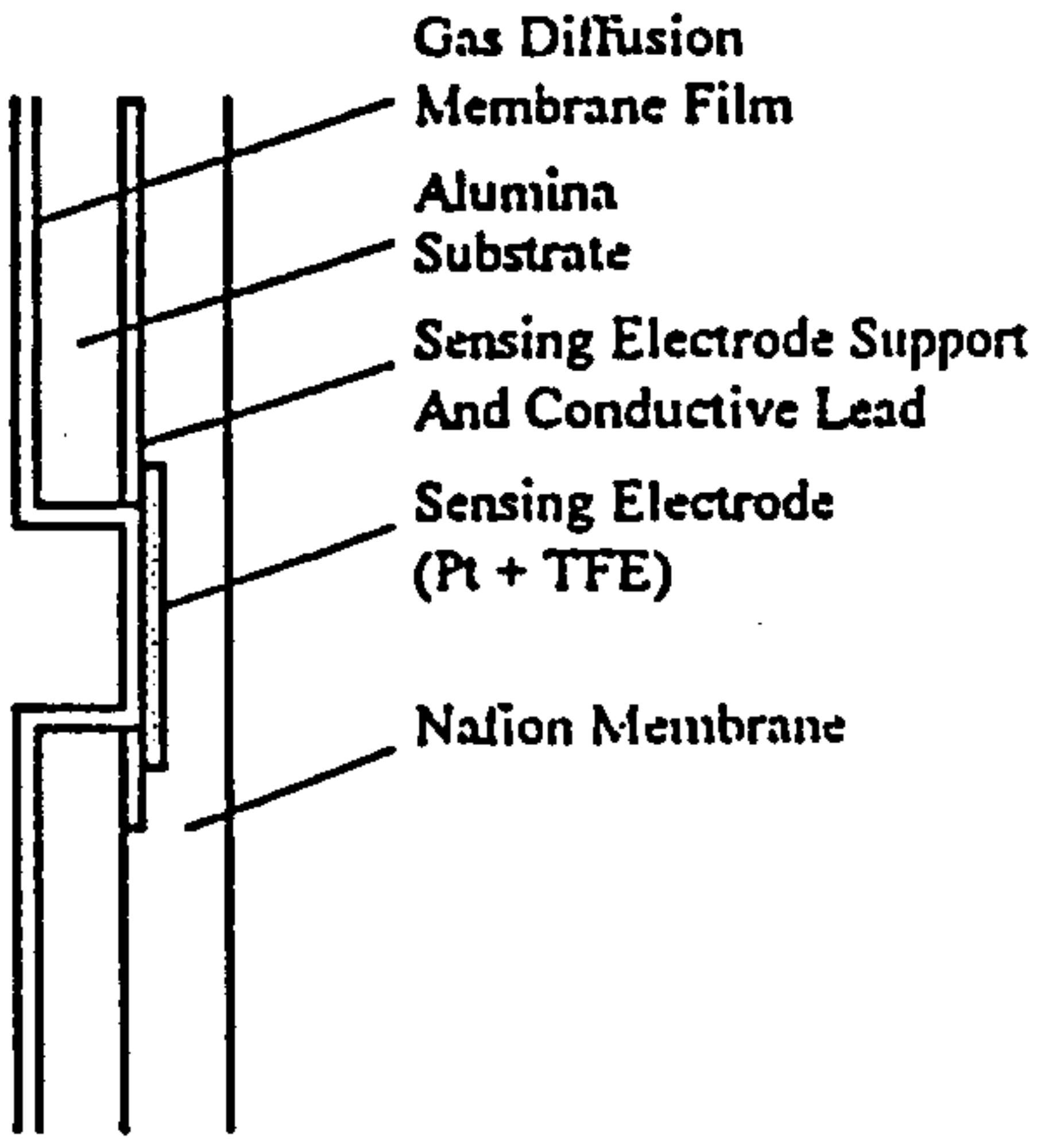


Figure 3

FIGURE 4(a)

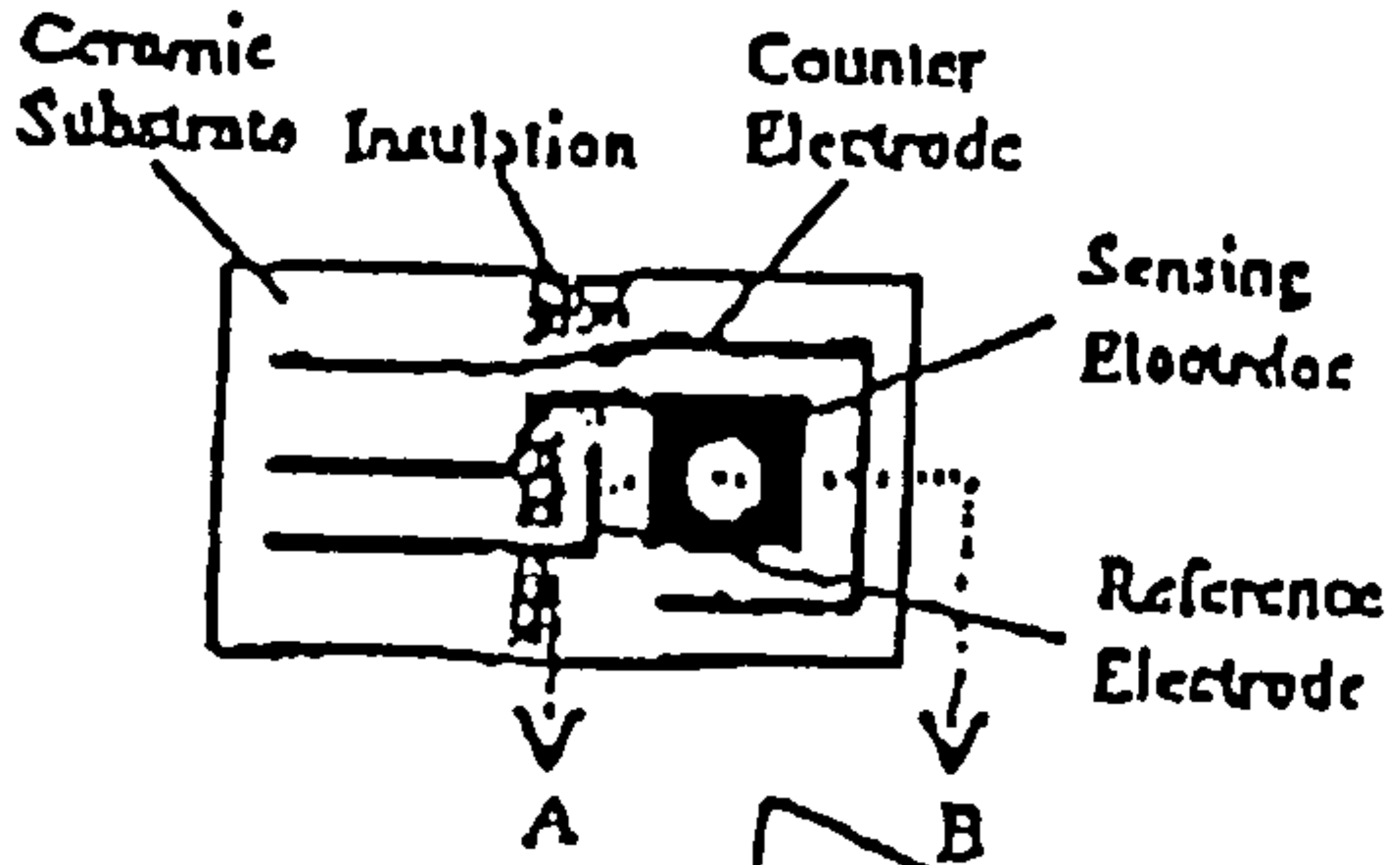
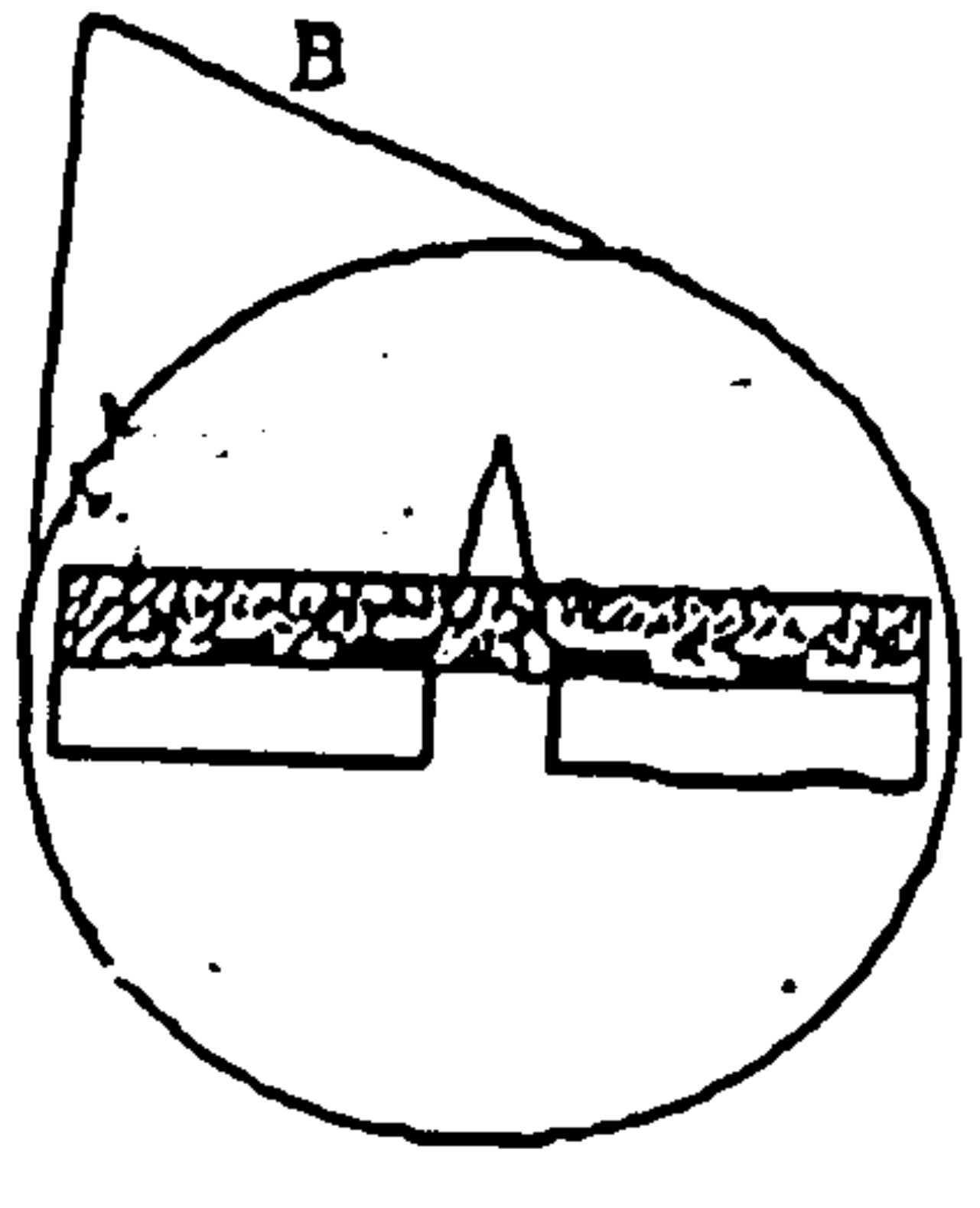


FIGURE 4(b)



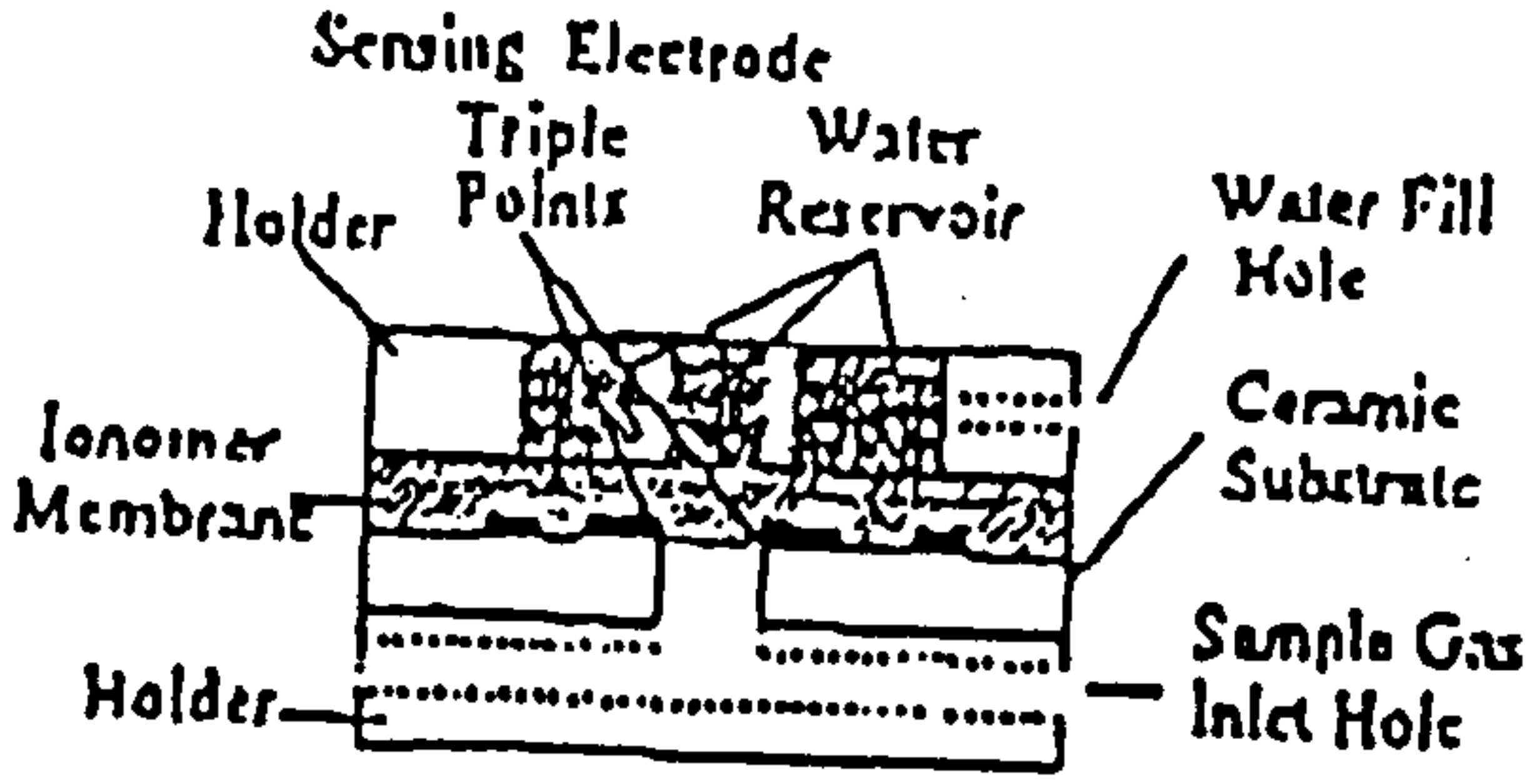


FIGURE 4(c)

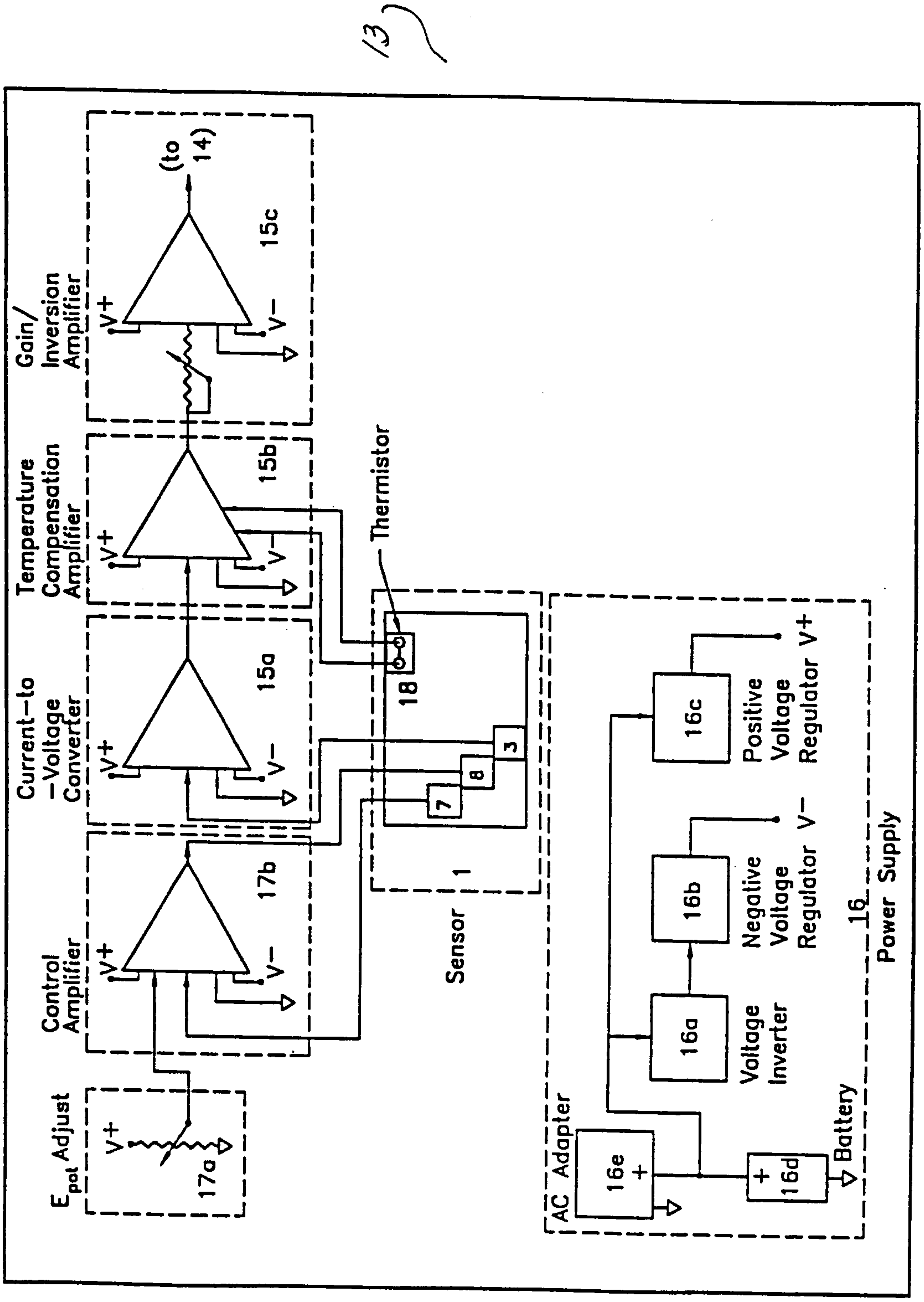

13
E_{pot} Adjust
V+
17a
Control Amplifier
V+
V−
17b
Current-to-Voltage Converter
V+
V−
15a
Temperature Compensation Amplifier
V+
V−
15b
Gain/Inversion Amplifier
V+
V−
15c
(to 14)
Thermistor
18
7
8
3
1
Sensor
AC Adapter
16e
+
Battery
+
16d
16a
Voltage Inverter
16b
Negative Voltage Regulator V−
16c
Positive Voltage Regulator V+
16
Power Supply

FIGURE 5

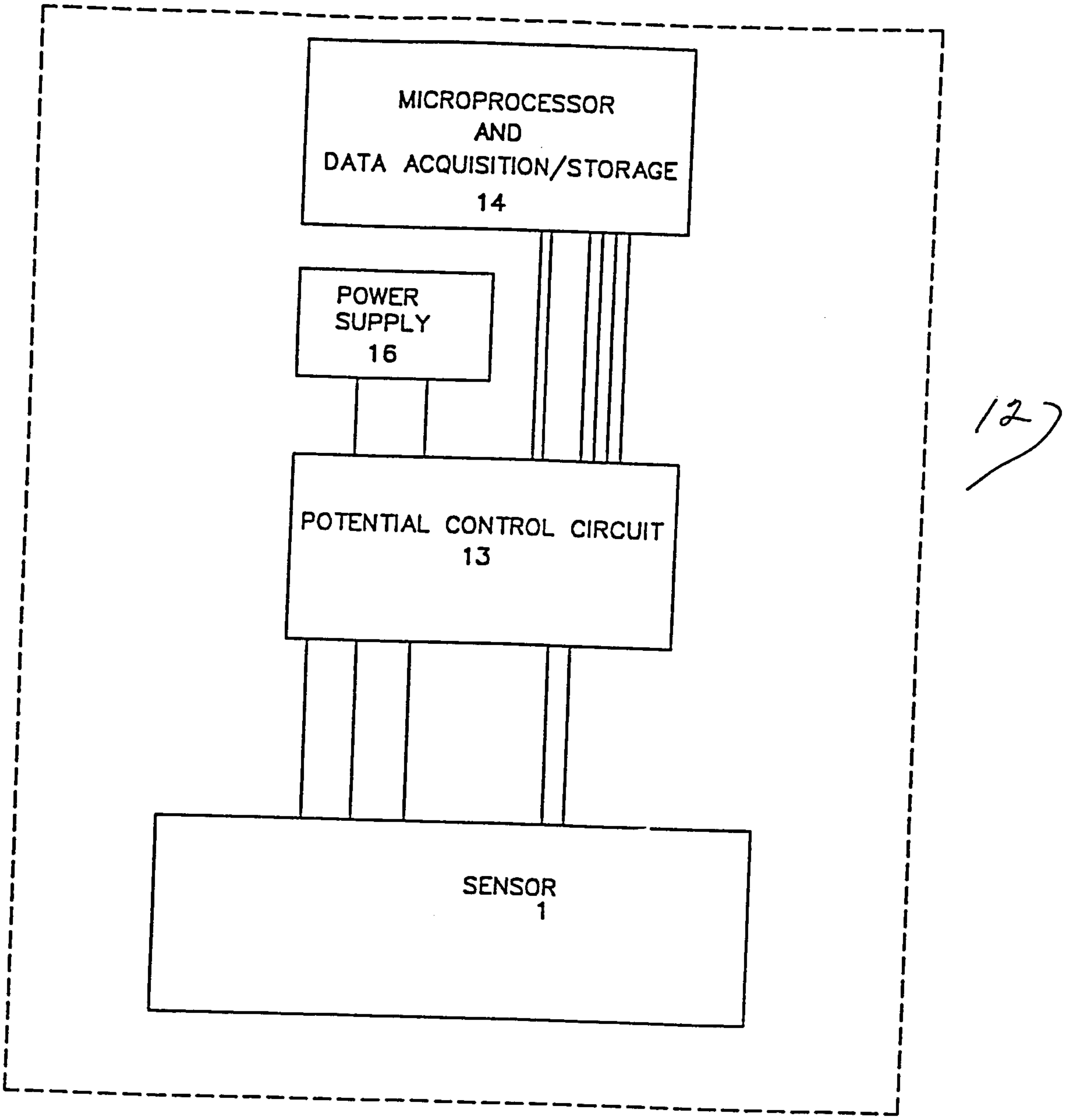
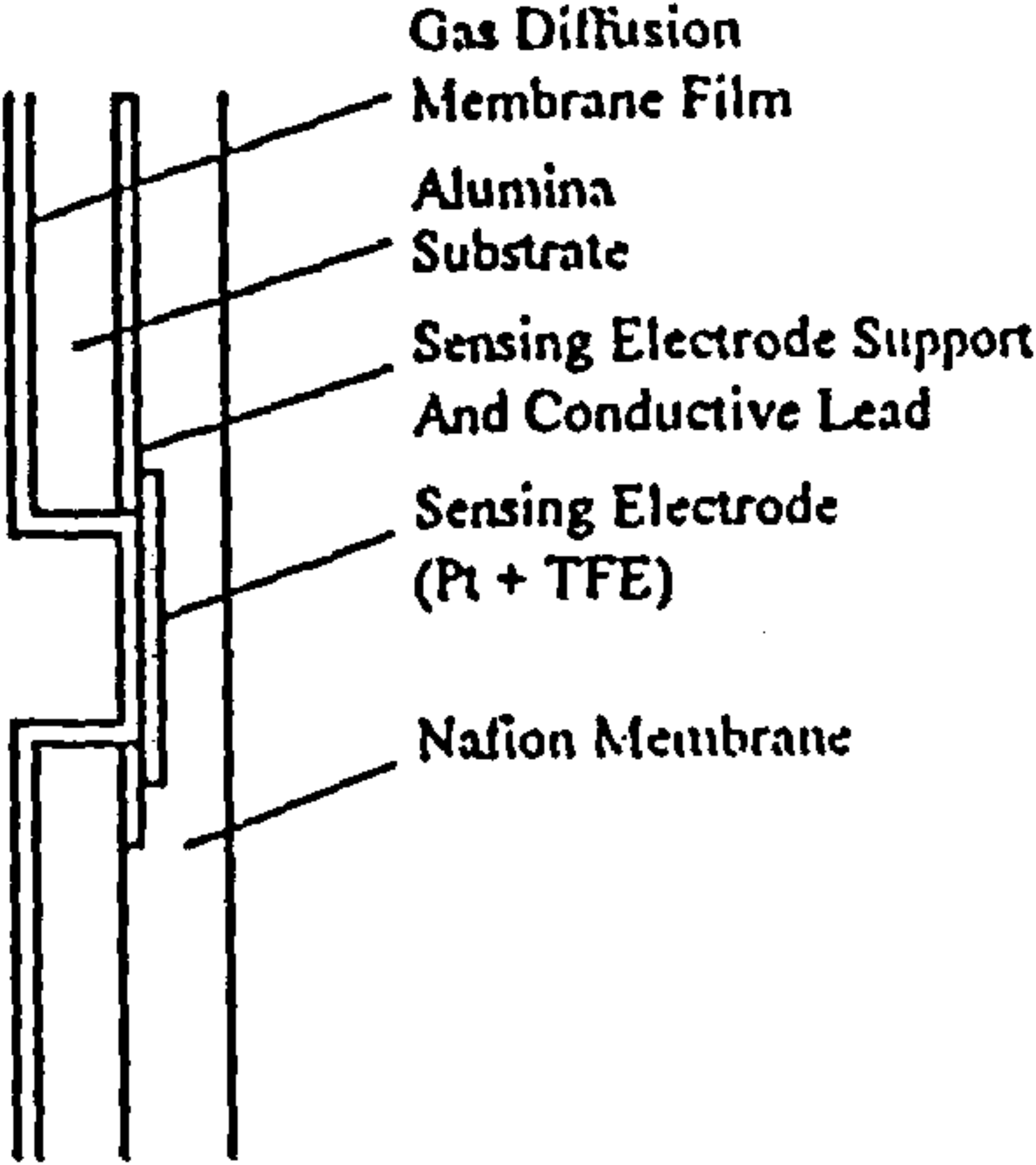

MICROPROCESSOR
AND
DATA ACQUISITION/STORAGE
14
POWER
SUPPLY
16
POTENTIAL CONTROL CIRCUIT
13
SENSOR
1
12

FIGURE 6


Gas Diffusion
Membrane Film
Alumina
Substrate
Sensing Electrode Support
And Conductive Lead
Sensing Electrode
(Pt + TFE)
Nafion Membrane