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METHOD AND MEANS FOR OXYGEN ANALYSIS OF GASES

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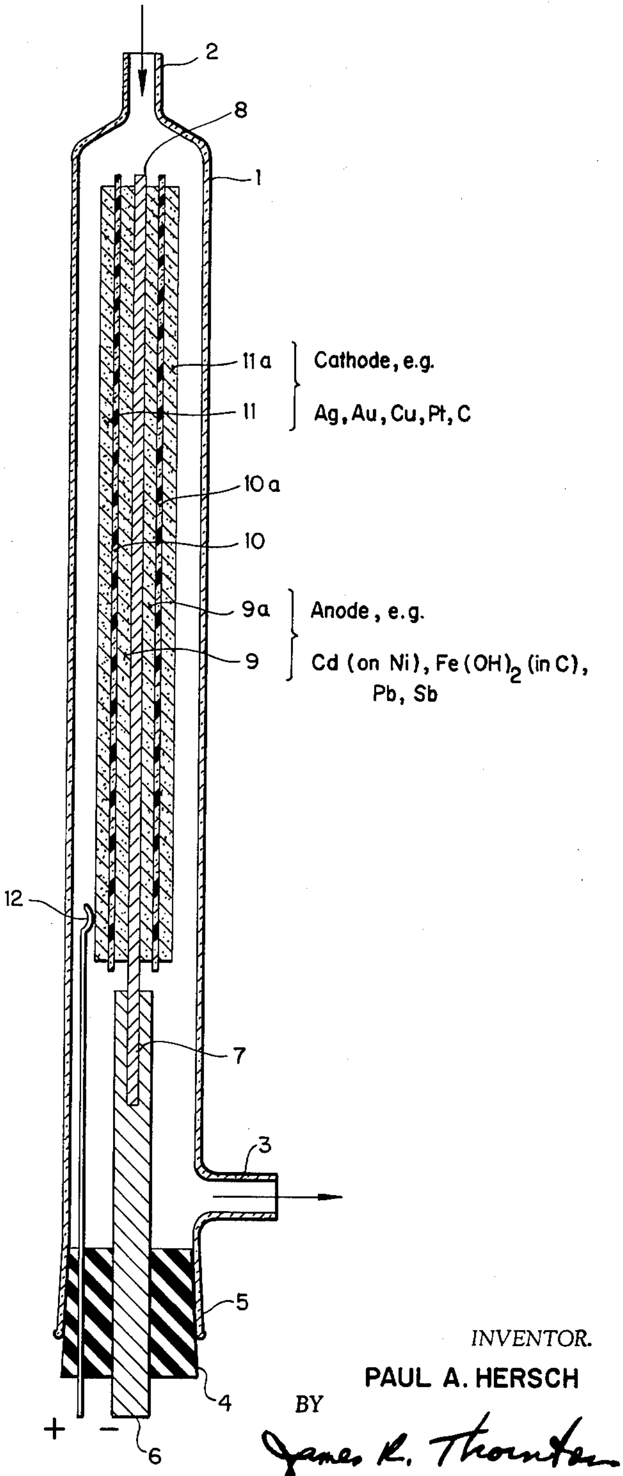

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METHOD AND MEANS FOR OXYGEN ANALYSIS OF GASES

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The present invention relates to the detection and measurement of oxygen and has particular reference to an improved apparatus and method for the detection and measurement of trace amounts of oxygen in other gases.

There has long been a need for an accurate method for the continuous determination of oxygen contained in other gases. Over the years there have been many methods proposed for measuring oxygen in terms of physical properties such as heat conductivity, electrolytic conductivity, heat of combustion, para-magnetism, electrode potentials and many others. It is well known to those skilled in the art that gaseous oxygen can be produced by the electrolysis of a suitable electrolyte and that the amount of gas evolved is proportional to the current flowing in the cell. It is also well known that oxygen can be absorbed into such a system at one of the electrodes so as to produce current. Various instruments have been described in which oxygen from a gas stream is reduced at an inert cathode while at the same time a base metal undergoes anodic oxidation. The galvanic current accompanying this double process is taken as a measure of the concentration of the oxygen in the gas stream or gas sample.

Early in the development of galvanic sensors for oxygen is was recognized that porous carbon or porous metal electrodes, wherein part of the cathode was exposed to the gaseous oxygen, were the most desirable type. However, these electrodes had disappointingly low sensitivities in that they could not detect extremely small amounts of oxygen, on the order of several parts per million, and they were unable to utilize for conversion into current more than a minute fraction of the oxygen offered.

The present invention provides a simple and effective means for utilizing the high capabilities of a porous cathode. The crux of the present invention is based upon the use of a porous cathode in combination with a carefully controlled amount of electrolyte. It have discovered that by the controlled use of a minimal quantity of electrolyte, not only is the cathode prevented from becoming inundated, but even more surprisingly the controlled quantities of electrolyte leads to cells operating coulometrically at convenient flow rates, such as 100 cu. cm./min. and under these conditions they need no calibration, no temperature compensation, no thermostating, and they have a cell constant predictable from Faraday's law (268 ma. min./cu. cm. O_2 at 20° C., 1 atm.).

In addition to achieving the above desirable characteristics, the present electrode sysems can also be operated non-coulometrically under conditions offering one advantage which coulometry cannot provide. At a sufficiently high rate of gas flow, easily attainable owing to the negligible flow resistance of the present cell, it is no longer necessary to measure the gas flow, nor to keep it stable and constant. This is possible because at high flow rates the signal for a given concentration of oxygen becomes independent of the flow rates, while in coulometric operation the signal is proportionally dependent on it. The operator can conveniently switch from conditions of flow independence to flow proportionality. The older electrochemical cells for oxygen measurement exhibit in practice either one or the other type of behavior, but not both.

Thus the present invention provides a simple and effective means for taking advantage of porous cathodes in absorbing oxygen electrochemically. In the systems according to the present invention the gas gives up its oxygen freely at convenient and readily manageable flow rates, and it does so with the gas sample flowing over the porous cathode rather than being forced through the cathode.

It is, therefore, the principal object of the present invention to provide an apparatus for the accurate detection and measurement of oxygen present in other gases.

Another object of the invention is to provide a relatively simple method for measuring small quantities of oxygen in gases which is predictable, reproducible and accurate.

A still further object of this invention is to provide a relatively simple apparatus for measuring oxygen in gases which is not subject to inaccuracies in measurement due to drift, generation of local current, insensitivity, etc.

Other objects will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the ways in which the principle of the invention may be employed.

Broadly stated, the present invention comprises an electrode assembly capable of detecting and measuring small amounts of oxygen in a gas, comprising in combination a chemically reducing anode, a non-conductive thin porous electrolyte-retentive diaphragm in intimate contact with at least one surface of said anode, a cathode comprising a thin porous conductive sheet in intimate contact with the surface of said diaphragm opposite to the surface in contact with said anode, an aqueous electrolyte contained in said porous diaphragm, the total volume of said electrolyte being less than the combined pore volume of the cathode, diaphragm and anode, whereby the pores of said cathode are only partially filled with electrolyte, said cathode being chemically non-reactive to said electrolyte and said anode being incapable of evolving hydrogen upon being circuited with said cathode.

Thus, from the foregoing broadly stated paragraph, it will be seen that the present electrode assembly can comprise a three-layered structure with the thin porous diaphragm in the center contacted by a cathode and anode on either side, or the electrode can be a five-membered assembly comprising an anode having a diaphragm on each surface and a cathode in contact with each free surface of the diaphragm; representing a double assembly with a common anode. The entire assembly is tied or clamped together and can be positioned with suitable supports in a tubular envelope with electrical connections and gas inlet and outlet means.

It must again be emphasized that the crux of the present invention is based entirely on the quantity of electrolyte used in conjnction with the porous cathode. It will be noted that the foregoing broadly stated paragraph explicitly states that the total volume of electrolyte must be less than the combined total pore volume of the cathode, diaphragm and anode (if the anode is also porous). With this arrangement, the electrolyte is so restricted in volume that only a minor portion of the pores of the cathode become wetted while a major portion of the pores of the cathode never become "swamped" or filled. Or to put it in other words, by observing this restriction I have been able to produce an electrode assembly whereby only the urface of the cathode which is in intimate contact with the diaphragm is wetted, and the top surface and major portion of the pores of the cathode remain substantially dry.

The combination of the nonconducting porous diaphragm incompletely filled with electrolyte avoids creepage of liquid farther into the cathode, but at the same time allows a minor portion of the pores of the cathode to be partially filled with electrolyte. By preventing such creepage I have been able to produce an electrode having superior stability and longer life than in prior art cells which have also used porous cathodes. Still further, with this arrangement a sensitivity is achieved which is much higher than has been accomplished from earlier cells used; for example, porous carbon electrodes where the volume of electrolyte was not a carefully controlled minimal quantity.

A further point of importance is that in the foregoing broadly stated paragraph the cathode is defined as a substantially thin porous sheet, having a thickness on the order of from about 0.5 to about 5 mm. It is to be clearly understood that the electrode is in sheet form and is not to be confused with cylindrical plugs, wire gauze or other reticulated structures. The present porous cathode differs from a wire cloth or gauze not merely in grade. I have found that if a cathode made from silver wire gauze having 60 mesh per inch is replaced by silver wire gauze with 200 mesh per inch, the sensitivity of the electrode is reduced or even destroyed. However, if the silver wire gauze having 60 mesh per inch is replaced as by a porous sheet of silver, with microscopic openings below about 100 microns in diameter, the sensitivity is enhanced far beyond that obtained by the use of any wire cloth. Still further, I have found that by the use of the porous metal sheet in conjunction with the limited quantity of caustic potash electrolyte, I have been able to obtain substantially coulometric conditions, i.e., conditions under which all of the oxygen which is offered to the cell is reduced. Where coulometric conditions can be obtained, temperature fluctuations and aging of the cathode surface no longer affect the strip.

The cathode while being capable of absorbing oxygen should not be of a material liable to chemical attack of its surface by the electrolyte. Silver, gold, carbon or graphite, platinum, and iridium are suitable cathode materials. The cathode may be composed entirely of the suitable cathode materials or the cathode may carry a deposit of such metals.

In the preferred embodiment of my invention I use as a cathode a sheet of silver having a thickness of about 1–2 mm., with about at least a 20% porosity and an average pore diameter below about 100 microns. Copper, carbon, or graphite with similar dimensions and pore structures may also be used. Porous carbon may be also coated with silver, copper, mercury, gold, platinum and iridium. Additionally porous polymeric materials having their pores coated with one of the foregoing metals may also be used as a cathode.

As noted previously, the present anode may be porous or non-porous. The only factor to remember in regard to the porosity of the anode is that when considering the amount of electrolyte to be used, the total volume of electrolyte is less than the total pore volume of the combined elements. A suitable anode material is a nickel grid onto which nickel powder has been sintered. The porous sheet so obtained is then impregnated with cadmium hydrate, and the cadmium hydrate is then reduced to metal, as for example, by submerging the entire assembly in caustic solution and "charging" against a separate inert auxiliary electrode not forming a part of the assembly. Other anode materials comprise lead sheet or foil, steel plated with a layer of antimony or arsenic, porous carbon impregnated with cadmium, lead or antimony, or with ferrous hydrate or other oxidizable material. Thus any porous inert conducting material coated with an oxidizable material can be used as the anode. Neither the anode metal nor any oxidizable material used as the depolarizer should cause hydrogen to evolve at the cathode when the assembly is circuited. This would give rise to parasitic currents, high zero readings, etc.

The preferred electrolyte is a strongly alkaline solution, for example, a 24% solution of caustic potash in water, but this concentration is not critical. Additionally, nonalkaline solutes may also be used. Saturated potassium bicarbonate is suitable for use with gases carrying carbon dioxide, and acidic electrolytes such as sulfuric acid can be used in combination with a porous cathode with a noble metal amalgam. The high over-potential on this latter surface discourages undesirable evolution of hydrogen.

As for the nonconductive porous diaphragm used in the present electrode assembly, this can be any chemically resistant resinous polymeric material, or porous ceramic material such as magnesium oxide.

In the preferred embodiment of my invention I use a sheet (on the order of from about 30–40 mils in thickness) of a porous non-conducting polymeric or ceramic material wherein the pores of such diaphragm material are smaller or more retentive of the electrolyte than the pores of the cathode material. By using such diaphragm material I have found that it is easier, even though using a severely limited amount of electrolyte, to prevent the cathode from drawnig up the electrolyte through its portes. Thus, by using such a diaphragm material one has one more controlling factor in allowing the surface of the cathode, which is in contact with the diaphragm, to be wetted while at the same time preventing the opposed top surface and a major portion of the pores from becoming swamped with the electrolyte.

Thus, the present electrode assembly rigidly defines and preserves the relative position of gas, cathode and electrolyte. One other feature which is to be noted is the fact that in the broadly stated paragraph the diaphragm can be in intimate contact with at least one surface of the anode. This means that, if desired, one can use a diaphragm on each surface of the anode and apply a sheet of cathode material to each diaphragm, thus constructing a sandwich-type electrode comprising 5 component parts. The substantially thin porous polymeric diaphragm can be any of the well-known plastic materials which come in sheet form, such as polyvinyl chloride, polyethylene, cellophane, etc., and it is immaterial to the present invention which of the well-known plastics are used as long as the material chosen is porous and resistant to the electrolyte. To give an example, the anode may consist of a strip of steel plated with antimony, lined on either side with a 40 mil thick sheet of a porous polyvinyl chloride, and a 1.25 mm. thick sheet of porous silver having pore openings on the order of below 100 microns in size. This electrode can be made to contain a caustic potash solution comprising about 30 grams of caustic potash to 100 grams of water. The 5 units of the electrode can be held together as by suitable clamps with electrical connections to the silver sheets and the antimony plated steel strip. Instead of antimony, the anode, if desired, can comprise a strip of steel coated with bismuth.

The gas sample should be prehumidified, especially in a prolonged continuous monitoring application. A 24% KOH solution of 20° C. neither loses nor gains water when the relative humidity of the sample is 72%. However, in the above-described system the concentration of KOH may be allowed to vary within wide limits without harming the performance. As a consequence the humidity of the gas sample may also vary and need not be controlled precisely. There is no need to encumber the equipment, and hold up response, with elaborate scrubbers for ensuring an exact match of sample moisture with the water vapor pressure of the cell electrolyte. The relative insensitivity to changes in the humidity of the sample gas is another advantage of this type of analyzer.

Cells made according to the present invention are superior to those produced according to prior art teachings, such as disclosed in U.S. Patent 2,805,191, where the cathode is a wire coil, screen, or expanded metal, with an undefined volume of electrolyte. These prior structures left a substantial portion of the oxygen, 30% and more, unreduced, a percentage which varied from cell to cell and with time. Merely increasing the surface area of the metal, e.g., by replacing a 60 mesh silver gauze by a 200 mesh gauze does not result in an increase but in a decrease of the rate of electroabsorption of oxygen. Nor do multiple layers of metal screen produce a corresponding multiplication in this rate.

The figure is a longitudinal cross-section of a cell embodying the present invention.

The cell assembly is contained in housing **1** which is provided with gas inlet **2**, gas outlet **3** and opening **5** through which the cell assembly is inserted into housing **1**. After the cell assembly has been inserted in housing **1** it is held in place as by stopper **4** which can be rubber, elastic, etc. Negative terminal **6**, which, for example, can be stainless steel, is inserted into housing **1** through an opening provided in stopper **4** and contacts the cell assembly through a flat metal strip **8**, which is of the same metal as terminal **6**, fits into slot **7** provided in negative terminal **6**. The cell assembly itself comprises the flat metal strip **8**, the opposite faces of strip **8** are lined with negative electrodes **9** and **9***a* which, for example, can be commercially available "Jungner" type batteries which consist of porous nickel sintered onto a nickel wire grid and are impregnated with cadmium hydroxide. Two strips of porous plastic **10** and **10***a* are applied to the outer surfaces of **9** and **9***a*, respectively. Finally two metal strips **11** and **11***a*, which, for example, can be porous sheets of silver, are applied to the outer surfaces of **10** and **10***a*, respectively. The cell assembly then consists of seven layers in the sequence **11**, **10**, **9**, **8**, **9***a*, **10**, and **11***a*, and the entire structure is held together as with several loops of nylon thread and one loop of silver wire to connect **11** and **11***a* (avoiding contact with **8**, **9** and **9***a*). The assembly is impregnated with an electrolyte and the volume of electrolyte adjusted as described in the following description. A spring contact **12** as for example stainless steel contacts **11** and comprises the positive terminal of the cell. Positive terminal **12** and negative terminal **6** are connected to the respective terminals of a microamperemeter or other current measuring device. On passing an inert gas containing traces of oxygen on the order of parts per million, through the cell, the meter reads the theoretical maximum number of microamperes allowed by Faraday's Law.

Thus the present cell provides a simplicity of construction, and performance which could only be obtained in prior cells by the use of a pressure differential on the order of 10 p.s.i.g. or more.

The following will give a practical example of an assembly in accordance with the invention:

The negative of a commercially obtainable alkaline battery of the layered Jungner type (consisting of porous nickel sintered onto a nickel grid and impregnated with cadmium) is sandwiched between two layers of commercially obtainable porous polymer battery separator sheet. The two outer faces of the polymer are lined with two sheets of porous silver, with about a 50% porosity having an average pore diameter of 30 microns, and being about 1½ mm. in thickness. The five layers are tied together with nylon thread. Wires are attached (not soldered), to the cadmium bearing central anode, and to the external pair of porous cathodes. This assembly is then submerged, in 5 N.KOH solution for impregnation, in a vessel of stainless steel. Rectified current is passed between the steel and the cadmium electrode to convert all cadmium hydroxide to metal. The cadmium is thus temporarily a cathode, the steel of the vessel is the anode and oxygen is evolved at the anode. The silver should not be connected to either of the electrodes during charging. The assembly is now withdrawn from the bath and excess electrolyte removed, first by gravity, then by carefully pressing the electrode system between sheets of highly bibulous paper. This should be repeated until no further trace of electrolyte passes from the porous sheets to the paper; the electrode can now be checked by weighing. The quantity of caustic solution still retained in the assembly should be substantially less than the combined volume capacity of the five layers. The porosity of the three materials and the dry weight of the five components must of course be known beforehand. The retentive power of both battery separator material and battery negative for the alkaline solution is sufficient to ensure the desired dryness of the silver.

By way of a further example, the anode may consist of a rod of stainless steel plated with antimony, then wrapped in a 1 mm. thick sheet of porous polyvinyl chloride. This in turn carries porous copper sheet, 2 mm. thick, bent to form a cylindrical outer envelope. The diaphragm and copper are kept in place by O-rings. This assembly is then axially positioned in a stainless steel tube stoppered at either end, with inlet and outlet tubuli for the gas. The electrolyte, the procedure of impregnation (without charging), and the eventual partial removal of liquid so as to leave at least half the pore voids of the copper empty, are as in the previous example.

Obviously, numerous variants of design and material will occur to those skilled in the art after these disclosures. For example, a disc-shaped, five-layered assembly may be positioned in a housing the shape of a flat cylinder, with an axial entrance for the gas facing one disc cathode, and an axial outlet facing the opposite disc cathode. Instead of adjusting the liquid volume in the way described above, the assembly may be mounted dry and the electrolyte may be introduced with a graduated hypodermic syringe.

Cells built in accordance with this invention are directly applicable to batchwise, intermittent and continuous analysis. In noncontinuous operation the sample is transferred into the cell housing, which is then closed and the current is recorded as it decays. The current-time integral under the curve represents the total amount of oxygen the housing has received. A limited sample may also be injected into an inert gas stream carrying the oxygen to the cathode. In this case a current pulse is observed, the height of which, or, more precisely, the area of which measures the oxygen. It is known that such pulses can be integrated directly by using a ballistic galvanometer. In continuous operation the measured or recorded current indicates the rate of supply of oxygen to the cell if this works coulometrically, and the concentration of oxygen in the gas if the operation is noncoulometric, at sufficiently high flow rates.

Although the immediate environment of the electrode assembly is as a rule very dilute in oxygen, the application of the cells is not limited to trace analysis. Using suitable dilution methods, the batchwise, intermittent or continuous analysis of samples is possible in which oxygen is a major constitutent. Nor need the original source of the oxygen be a gas. It may be a limited volume or stream of a fluid. The oxygen may even originate from a solid body. In these cases the sample is caused, by diffusion, or thermally, or by other means, to surrender all or part of its oxygen to a stagnant, stirred, flowing, or recirculating gas delivering it to the sensor. The same cell is applicable to measuring the oxygen from a drop of blood and to monitoring the oxygen content in a stream of boiler feed water. Oxygen dissolved in beverages, culture media, industrial effluents, and natural waters can be determined as well as oxygen generated by chemical reactions, such as the decomposition of peroxides, photosynthesis, or oxygen metabolized biochemically, or emerging in such physical processes as diffusion and desorption. The sensors can be applied to warn audibly of air leakages, or to operate controls in industrial processes when critical concentration limits are trespassed, one example being the polymerization of ethylene. Moreover, combustible gases and vapors can be analyzed indirectly by determining the oxygen consumed in their combustion. This again can be carried out batchwise, intermittently, or continuously, with traces as well as with major constituents, with gaseous samples or with dissolved, absorbed or adsorbed material, or with combustible substances emerging or vanishing in chemical reactions or physical separation processes.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features in any of the following claims or the equivalent of such be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. In an electrode assembly for detecting and measuring small amounts of oxygen in a gas, comprising in combination, a cell housing having a gas inlet and gas outlet, a consumable anode incapable of evolving hydrogen at the cathode upon being circuited with a cathode, a nonconductive, thin porous electrolyte-retentive diaphragm in intimate contact with at least one surface of said anode, a cathode in intimate contact with the surface of said diaphragm opposite to the surface in contact with said anode, and means for measuring current across said anode and cathode, said cathode comprising a porous, nonreticulated sheet having pores of an average diameter of less than about 100 microns.

2. In an electrode assembly capable of detecting and measuring small amounts of oxygen in a gas, comprising in combination, a cell housing having a gas inlet and gas outlet, a consumable anode incapable of evolving hydrogen at the cathode upon being circuited with a cathode, a non-conductive, thin porous electrolyte-containing diaphragm in intimate contact with at least one surface of said anode, a cathode in intimate contact with the surface of said diaphragm opposite to the surface in contact with said anode, and means for measuring current across said anode and cathode, said cathode comprising a porous, non-reticulated sheet in which said pores are partially filled with aqueous electrolyte.

3. An electrode assembly according to claim 2 in which said cathode is a sheet of silver having a thickness of about 1–2 mm. with at least about 20% porosity and an average pore diameter of less than about 100 microns.

4. An electrode assembly according to claim 2 in which said cathode is a porous sheet having a thickness of from about 0.5 mm. to about 5 mm.

5. An electrode assembly according to claim 2 in which the pores of said porous diaphragm are smaller than the pores of said porous cathode, whereby said diaphragm is more retentive of aqueous electrolyte than said cathode.

6. In an electrode assembly for detecting and measuring small amounts of oxygen in a gas, comprising in combination, a cell housing having a gas inlet and gas outlet, an anode material selected from the group consisting of ferrous hydrate, lead, cadmium, arsenic, bismuth and antimony, a nonconductive diaphragm consisting of a thin sheet of a porous polymeric material in intimate contact with at least one surface of said anode, a cathode in intimate contact with the surface of said diaphragm opposite to the surface in contact with said anode, and means for measuring current across said anode and cathode, said cathode comprising a porous, nonreticulated sheet having a thickness of from about 0.5 mm. to about 5 mm. and having pores of an average diameter of less than about 100 microns, said cathode selected from the group consisting of silver, gold, platinum, copper, iridium and carbon.

7. In the method for detecting and measuring small amounts of oxygen in a gas by contacting said gas with a cathode separated from a consumable anode by a porous electrolyte-containing diaphragm and measuring the current across said anode and cathode, said anode being incapable of evolving hydrogen at said cathode when circuited with said cathode, the improvement which comprises employing as said cathode a porous, nonreticulated, electrically conducting sheet having microscopic pores of an average diameter of less than about 100 microns, whereby the face of said cathode in contact with said diaphragm is wetted with aqueous electrolyte and the remaining face of said cathode is substantially dry.

8. In the method for detecting and measuring small amounts of oxygen in a gas by contacting a stream of said gas with a cathode separated from a consumable anode by a porous, electrolyte-containing diaphragm and measuring the current across said anode and cathode, said anode being incapable of evolving hydrogen at said cathode when circuited with said cathode, the improvement which comprises employing as said cathode a porous, nonreticulated, electrically conducting sheet in which said pores are partially filled with aqueous electrolyte.

9. In the method for detecting and measuring small amounts of oxygen in a gas by conducting a stream of said gas over a cathode separated from a consumable anode by a porous, polymeric electrolyte-containing diaphragm and measuring the current across said anode and cathode, said anode material being selected from the group consisting of ferrous hydrate, lead, cadmium, arsenic, bismuth and antimony, the improvement which comprises employing as said cathode a porous, nonreticulated sheet of silver having a thickness of from about 0.5 mm. to about 5 mm. and having pores of an average diameter of less than about 100 microns which are partially filled with aqueous electrolyte.

10. The electrode assembly of claim 2 where said porous cathode sheet is silver, said diaphragm is polyvinyl chloride, and said anode material is cadmium.

11. The electrode assembly of claim 2 where said porous cathode sheet is copper, said diaphragm is polyvinyl chloride, and said anode material is cadmium.

12. The electrode assembly of claim 2 where said porous cathode sheet is carbon, said diaphragm is polyvinyl chloride, and said anode material is cadmium.

13. The electrode assembly of claim 2 where said porous cathode sheet is carbon coated with a metal selected from the group consisting of silver, copper, mercury, gold, platinum and iridium, said diaphragm is polyvinyl chloride, and said anode material is cadmium.

14. In the method for detecting and measuring small amounts of oxygen in a gas by contacting a stream of said gas with a cathode separated from a consumable anode by a porous, electrolyte-containing diaphragm and measuring the current across said anode and cathode, said anode being incapable of evolving hydrogen at said cathode when circuited with said cathode, the improvement which comprises employing as said cathode a porous, nonreticulated, electrically conducting sheet in which the pores are partially filled with aqueous electrolyte, said cathode being selected from the group consisting of silver, gold, platinum, copper, iridium and carbon.

15. In the method for detecting and measuring small amounts of oxygen in a gas by contacting a stream of said gas with a cathode separated from a consumable anode by a porous, electrolyte-containing diaphragm and measuring the current across said anode and cathode, said anode being incapable of evolving hydrogen at said cathode when circuited with said cathode, the improvement which comprises employing as said cathode a porous, nonreticulated, electrically conducting sheet in which the pores are partially filled with aqueous electrolyte, said cathode being carbon coated with a member of the group consisting of silver, gold, copper, mercury, platinum and iridium.

16. An electrode assembly according to claim 6 in which

the pores of said cathode are partially filled with aqueous electrolyte.

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