July 12, 1966 J. W. ROSS, JR 3,260,656

METHOD AND APPARATUS FOR ELECTROLYTICALLY DETERMINING A SPECIES IN A FLUID

Filed Sept. 27, 1962 2 Sheets-Sheet 1

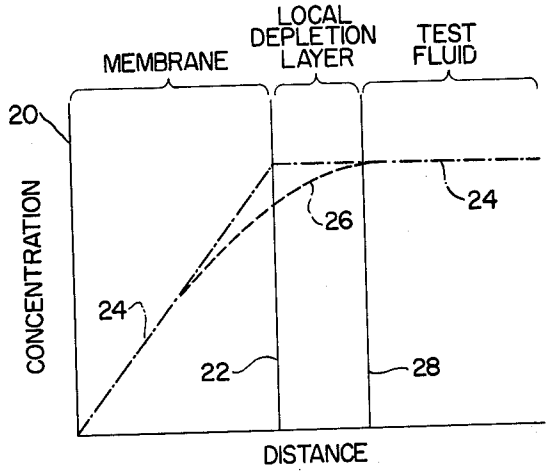

FIG. 1 (PRIOR ART)

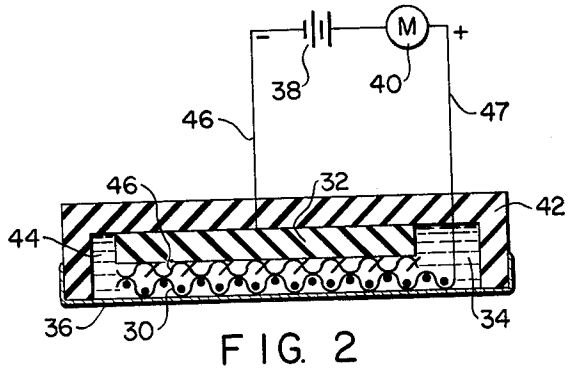

FIG. 2

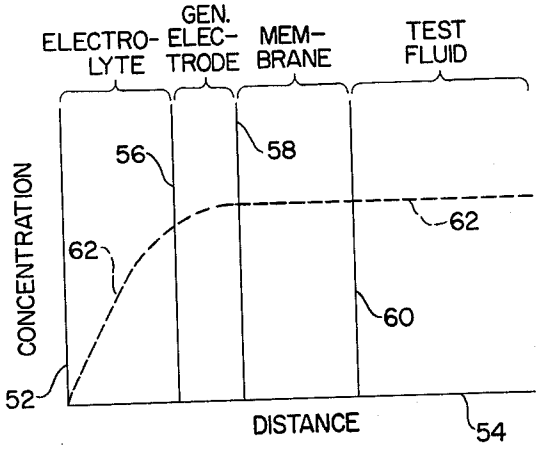

FIG. 3

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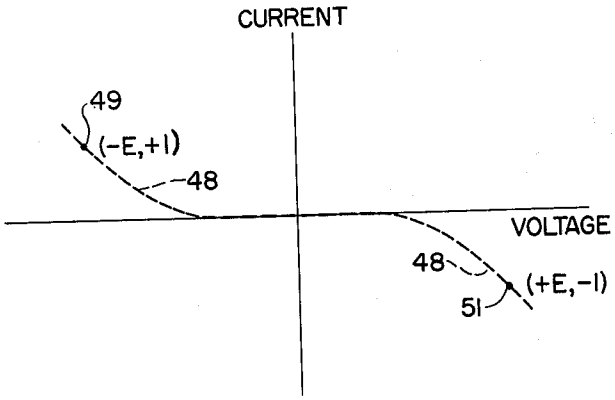

FIG. 4

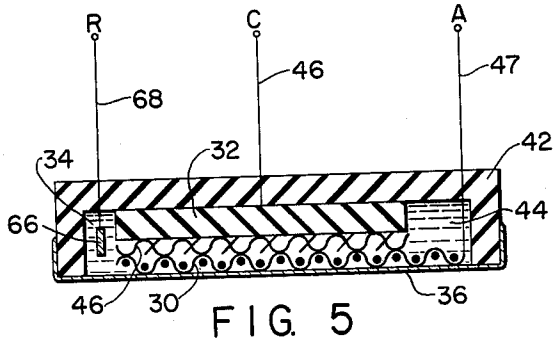

FIG. 5

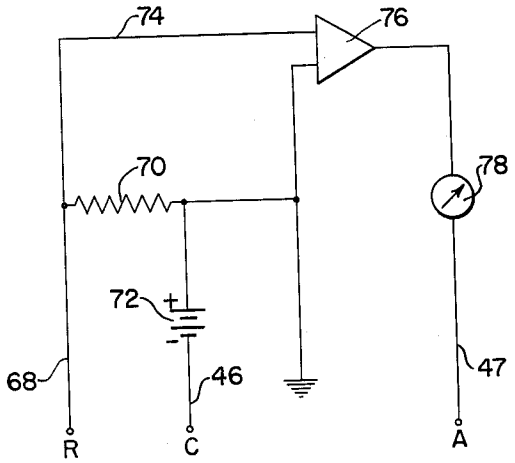

FIG. 6

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United States Patent Office 3,260,656 Patented July 12, 1966

3,260,656

METHOD AND APPARATUS FOR ELECTROLYTICALLY DETERMINING A SPECIES IN A FLUID

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Filed Sept. 27, 1962, Ser. No. 226,533
19 Claims. (Cl. 204—1)

This invention relates to electrochemical apparatus and more particularly to improved devices for electrically measuring the concentration of electrochemically active materials in fluids.

The term "fluids" as used herein is intended to include gases, liquids, vapors and mixtures thereof. Heretofore, in the determination of the concentration in fluids of an electrochemically active species (i.e. a substance such as an ion which is capable of being either reduced or oxidized at an electrode), electrochemical devices have been used in which an electrical characteristic of the species is measured and correlated with the concentration. Polarographic devices, for example, usually measure a characteristic potential at which such a species is reduced, and a diffusion current proportional to the concentration. An improvement on the basic polarographic apparatus is the well-known Clark apparatus as disclosed in U.S. Patent No. 2,913,386 issued November 17, 1959. The latter employs a dual electrode structure immersed in an electrolyte and encased at least in part in a membrane which is permeable to a predetermined species, for instance, gaseous oxygen. Typically, when used for oxygen analysis, the cathode is formed of platinum and is located closely adjacent the membrane; the anode is formed of silver-silver chloride; and the electrolyte is an aqueous alkali halide solution. In operation of such a device, oxygen in a test fluid outside of the membrane permeates the latter and is presumably reduced at the cathode to water in accordance with the overall equation

$$2H^+ + \tfrac{1}{2}O_2 + 2e \rightarrow H_2O$$

It will be apparent that the Clark device is intended to completely reduce the oxygen permeating the membrane. The current ($2e$) necessary to effect this reduction is a measure then of the oxygen concentration in the test fluid. In determining oxygen concentration this device typically employs the Ag-AgCl anode with a KCl electrolytic solution. Hence, the anode reaction is

$$Ag + Cl^- \rightarrow AgCl + e$$

As the electrode operates, H^+ is consumed at the cathode, changing the pH of the electrolyte in time. For prolonged operation, a buffer is therefore required.

While devices of this type have proved satisfactory for many purposes, certain problems arise in some applications. For instance, referring to FIG. 1, there is shown graphically a concentration diagram for such devices. In this diagram, the ordinate **20** is the scale from zero of the relative concentration of oxygen, and the abscissa represents distance from the cathode-membrane interface toward a test fluid. The position of the cathode-membrane interface (neglecting any small displacement between the two) is at line **20**. Line **22**, parallel to the ordinate, then represents the membrane-test fluid interface. The distance between lines **20** and **22** is representative of the membrane thickness. Now it may be assumed that the concentration of oxygen in the test fluid adjacent the outer face of the membrane is constant, as shown by the horizontal portion of broken line **24**, and that the consumption of oxygen at the cathode is complete so that the concentration of oxygen at the cathode-membrane interface is substantially zero. Under such circumstances,

the concentration gradient, represented by the remainder of broken line **24**, across the membrane is approximately linear and its slope is an inverse function of the membrane thickness.

However, during actual operation of the device, as oxygen is consumed at the cathode, there is a continual flow of the gas from the test fluid through the membrane to replenish the oxygen supply being consumed or reduced. If the oxygen in the test fluid adjacent the outer surface of the membrane is not continually replenished so as to be maintained at a constant level, the concentration gradient will then extend out into the test fluid, and its slope will become non-linear and reduced as shown at broken line **26** in FIG. 1, due to the local depletion of oxygen in a layer shown between lines **22** and **28**. With continued operation of the device and no replenishment of oxygen, the local depletion layer will continue to expand further out into the test fluid, distorting the concentration gradient more and more. The distortion of concentration gradient reduces the measurement sensitivity and changes the mass flow rate of oxygen through the membrane to the cathode, making measurement uncertain and even spurious over a period of time. In order to avoid such occurrence, it is customary to provide means for breaking up any depletion layer, as for instance by stirring.

Further, if the fluid under measurement is a minute sample to which access is restricted, as in biological cells for example, depletion will continue until all of the oxygen is consumed. Because access to the fluid is restricted by the cell walls which act as barriers, the consumed oxygen cannot readily be renewed; the measurements in a short time become inconclusive. Additionally, even assuming that local depletion layers on the outer membrane surface can be avoided, in order to maintain the gas concentration at the cathode substantially at zero with reasonable current consumption the input flow rate of the oxygen must be controlled. This is usually done by providing a relatively thick membrane which, however, acts to slow the response time of the device to changes in oxygen concentration in the test fluid.

Accordingly, the present invention contemplates the provision of improvements in electrochemical analytic devices by virtue of which the sensitivity and response time are enhanced, and which improvements minimize material changes in the concentration of the species in the fluid under measurement during the measurement time. A principal object of the present invention is therefore to prove an improved electrochemical analytical device.

Further objects of the present invention are to provide an electrochemical device including enclosure means for an electrolytic medium, at least a portion of the enclosure means being formed of barrier means selectively permeable to a predetermined spaced relation to one another within the enclosure means, means for impressing a predetermined potential difference across the electrode, the electrolytic medium being one from which the electro-active species can be liberated by passage of electrical current between said electrodes, the electrolytic medium bridging the electrodes and being in contact with the barrier means; to provide such a device in which one electrode is adapted to consume said species and the other electrode is adapted to generate said species; to provide such a device in which the cathode is adapted for reduction of said species and the anode is adapted to generate said species; to provide such a device in which the cathode is adapted for reduction of said species and the anode is adapted to generate said species in dependence upon said reduction, said anode being adjacent the barrier means and between the latter and the cathode; to provide such a device in which

the anodic current flow is maintained at the same absolute value as the cathodic current flow; and to provide such a device in which the cathodic current is dependent upon the equilibrium between the species generated at the appropriate electrode and the concentration of the species which is outside of the enclosure means and free to permeate the barrier means.

Other objects are to provide such a device including a reference electrode which is in contact with the electrolytic medium and provides a high stability to the potential at the consuming electrode; to provide such a device which does not substantially affect or deplete the concentration of the electro-active species outside of the enclosure means except (briefly, if at all, during transient changes in said concentration) for appreciable time periods and in restricted samples of fluid; and to provide such a device in which the sensitivity and response time to changes in the concentration of electro-active species in the test fluid are markedly improved. Yet other objects of the present invention are to provide an electrical circuit for use with an electrochemical analytic device of the type described; and to provide such an electrical circuit which includes a negative feedback loop for stabilizing the potential between a reference electrode and a consuming electrode.

Other objects of the invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the apparatus possessing the construction, combination of elements and arrangement of parts which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims. For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a graphical representation of the concentration gradient across the selectively permeable membrane in prior art devices as hereinbefore described;

FIG. 2 is a diagrammatic cross-sectional view of one embodiment of the present invention;

FIG. 3 is a graphical representation of a concentration gradient across a portion of the electrode-membrane structure of the embodiment shown in FIG. 2;.

FIG. 4 is a graphical representation of the current-voltage relationship at the electrodes in the structure of FIG. 2;

FIG. 5 is a diagrammatic cross-sectional representation of another embodiment of the present invention; and

FIG. 6 is a diagram of an electrical measuring circuit particularly adapted for use with the electrode structure of FIG. 5.

To effect the objects heretofore set forth the present invention generally comprises a pair of electrodes electrically coupled through an electrolytic medium of predetermined fixed characteristics. The medium is isolated from the test fluid under measurement by barrier means selectively permeable to the electro-active species which is to be detected and measured in the test fluid. A first electrode is adapted to consume the desired electro-active species, while the other electrode is adapted to produce or generate said species in dependence on the consumption activity of the first electrode. Thus, in operation, there is a steady state equality established between consumption and generation within the electrolyte. The electrode-membrane structure is such that this steady state equality is in turn responsive to an equilibrium between relative concentrations of the species on both sides of the barrier means. It will be seen, therefore, that in the present invention, during steady state conditions, there is no net transfer of species through the barrier means; only during transient changes in the concentration of the species in the test fluid will there be a small net transfer which rapidly decays as an internal steady state is reestablished. Consequently, the consumption of the electro-active species is minimized and changes in the concentration of the species in the fluid under measurement which may be ascribed to the analytical activity of the apparatus, are minute and quickly and automatically compensated.

The term "electro-active species" as used herein is intended to mean any group of identical chemical entities such as ions, molecules, atoms, etc., which are capable of being electrically oxidized or reduced. Where the species is a gas e.g. oxygen, chlorine or the like, which is dissolved in or mixed with another fluid, rather than referring to concentration, it is perhaps more accurate to refer to the equilibrium partial pressure. This is so because a gas may exhibit different solubilities with respect to different fluids. Hence, although the equilibrium partial pressure (hereinafter referred to as the tension) of the gas in one fluid may be precisely equal to the tension of the same gas in another fluid, the concentrations of gas with respect to each of the fluids are not necessarily the same. However, where the gas tensions on opposite sides of a gas-permeable membrane are in equilibrium, the tension on one side is proportional to the concentration on the other side.

Referring now to FIG. 2, there will be seen one embodiment of the present invention in which there is shown a structure comprising a first electrode or anode **30**, a second electrode or cathode **32**, an electrolytic medium **34** which electrolytically coupled the anode and cathode, and selectively permeable barrier means, such as membrane **36**. Means, such as battery **38**, are provided for applying an appropriate potential across the cathode and anode through respective leads **46** and **47**. The invention also may include means shown schematically as meter **40**, for measuring current flow in the cathode-anode circuit. In order to encase the electrodes and the electrolytic medium there is provided enclosure means **42** which preferably incorporates membrane **36** as a wall portion thereof.

Enclosure means **42** is preferably formed with a substantially hollow chamber **44** interiorly thereof, the chamber having at least one opening to the outside of the enclosure means. Membrane **36** is so disposed as to completely cover the opening in chamber **44**. The electrolytic medium (i.e. a medium capable of providing both positive and negative ionic charge transport as by ions provided from a disassociatable compound in a polar solvent, or by ions provided by a molten salt or the like), for example an aqueous electrolyte, is disposed within the chamber in sufficient quantity to maintain a continuous electrical contract between electrodes. The enclosure means preferably then is formed as a liquid-tight container so that the electrolyte cannot leak out. The electrolyte is preferably selected to be one whose ions require a more negative potential for reduction than does hydrogen and require a more positive potential for oxidation than does water or hydroxyl ion. The difference between these more negative and positive potentials is generally termed the decomposition voltage of the electrolyte.

The walls of chamber **44**, other than membrane **36**, are preferably made of a material, such as glass, ceramic, solid polymer or the like, which is substantially impermeable to fluids, is a high resistance material (i.e. an electrical insulator) and is substantially chemically inert to the electrolyte and decomposition products of the latter. Membrane **36**, in the form of a sheet with a substantially uniform thickness, for example, not more than approximately 5 mils, is selected from materials which exhibit selective permeability to the electro-active species which one desires to measure. For instance, where the species is gaseous oxygen, membrane **36** may be of a polymer such as polyethylene, polyvinyl chloride, rubber, or other known substances which provide a solid barrier selectively pervious to the gas. Barrier materials are known which are selectively permeable to other electro-active species. Appropriate means (not shown) are provided for sealing the membrane across the opening to chamber **44**, for instance, adhesives which are insoluble in the

electrolyte and test fluid, an O-ring, or other known techniques or structures.

Anode **30** is formed as a substantially sheet-like element typically having a thickness of about 3 mils and being porous to both the electrolyte and electro-active species. The anode is made of an electrically conductive material, preferably a noble metal such as platinum, gold or the like. To provide porosity, the anode may be provided as a mesh or screen as shown, as a spongy mass, or in other known configurations. In the form shown, anode **30** is disposed within electrolyte **34** and is superposed adjacent membrane **36**, i.e. arranged either in face-to-face contact with the latter, or, if the anode and membrane are in separated condition, then there is approximate parallelism of the adjacent surfaces of the anode and membrane with a stratum of electrolyte between them.

Cathode **32**, in the form shown, is also a substantially sheet-like element which may be either porous or solid, preferably the latter, and its thickness is determined by cost and considerations of structural strength. The cathode is also preferably made of a noble metal, for instance the same metal used as the anode. Cathode **32** is also disposed within electrolyte **34** and is disposed in approximately parallel face-to-face relationship to the anode, but separated from the latter a short distance by appropriate means such as spacer **46**.

In the preferred form, spacer **46** is a substantially sheet-like porous element, such as a woven fabric. The spacer is preferably formed of material which is electrically nonconductive, relatively chemically inert to the electrolyte and its decomposition products, and exhibits good dimensional stability with respect to variables such as temperature, pressure, solvents and the like, whereby the spacing between the anode and the cathode is maintained at a substantially constant value. Typical materials from which such spacer may be made are nylon, polytetrafluorethylene, and the like. It will be seen then that the electrode structure of FIG. 2 is that of a sandwich in which the anode is spaced from the cathode and retained in between the latter and the membrane, other portions of the volume between the membrane and cathode being substantially filled with electrolyte.

In describing the operation of the embodiment of FIG. 2, it will be exemplary to consider oxygen as the electroactive species. In such case, the electrolyte is preferably an aqueous solution of a base, such as KOH, because in the operation of the device it is desired to avoid evolution of gaseous hydrogen at the anode. Hence, the pH of the electrolyte should preferably be basic and generally not less than approximately pH 2 or 3. In selecting the cathode and anode in this instance, it is preferred to use materials which will respectively reduce oxygen and generate oxygen with maximum current efficiencies. Because of their low oxygen over-voltages and relative chemical inertness, the noble metals are thus preferred and both anode and cathode can be made of, for example, platinum. If the potential applied across the anode and cathode is established well below the decomposition voltage of the electrolyte, and there is no oxygen available in the electrolyte (as from diffusion into the electrolyte through the membrane, or from being dissolved in the latter), only a virtually constant, minute, residual current will flow in the cathode-anode circuit. If, however, a supply of oxygen is presented to the outer surface of membrane **36**, as for instance, by contacting the latter with a liquid having a dissolved oxygen content or by contacting the latter with a gas which comprises oxygen, because of the selective permeability of the membrane some oxygen will diffuse through the latter to its inner face and thence into the electrolyte to the cathode. If the potential across the electrodes is above the reduction potential of oxygen, although below the decomposition potential of the electrolyte, oxygen present at the cathode will be reduced. The reduction process is believed to be according to the same equation heretofore used in describing the cathodic reduction in the Clark apparatus.

Referring now to FIG. 4 there is graphically shown the general current-voltage relationship in the present invention during operation. The ordinate is shown as the current axis, the voltage axis being the abscissa. While the curve **48** is shown as being symmetrical about the origin, this is only for purposes of illustration and is not actually the case. At a point where there is a predetermined negative voltage $-E$, the oxygen at the cathode is electrically reduced. This produces a current I whose amplitude is a function of the concentration of gaseous oxygen present in the electrolyte. With a negative current $-I$, equal in magnitude to I, now flowing at the anode, the latter is at a positive voltage $+E$, shown at point **51**, predetermined by the nature of the anode material and electrolyte. With proper choice of parameters in the example described above, at the anode the current oxidizes the water in the electrolyte, generating oxygen according to the following:

$$H_2O - 2e \rightarrow \tfrac{1}{2}O^2 + 2H^+$$

Hence the system consumes the species at one electrode and tends to generate a like quantity thereof at the other electrode, without changing the electrolyte pH. This leads rapidly to an internal or interelectrode steady state condition between the consumption and generation of the species, and the current flow is therefore a measure of the O_2 present in the system. The steady state equality between generation and consumption is, however, responsive to any change in concentration of the oxygen outside of the membrane. This is largely because of the geometry of the system wherein the generating electrode lies between the consuming electrode and membrane. The gas tensions on both sides of the membrane will tend to reach an equilibrium with one another inasmuch as a high tension outside the membrane will result in net diffusion of the gas throughout the latter toward the anode, and conversely a higher tension inside the membrane would result in net gaseous diffusion through the membrane from the anode to the test fluid. Thus, any change in gas tension outside the membrane will upset the internal steady state of the system, forcing it to a new steady state by either increase or decreased consumption of gas and a corresponding increase or decrease in gas generation. Each change in gas generation is thus in a direction tending to establish equilibrium between the gas tensions on opposite sides of and across the membrane. Every change in the internal steady state is, of course, accompanied by a chance in the current flowing between the electrodes. It will thus be seen that in the equilibrium condition of gas tension across the membrane, the current flow is constant and there is no net transfer of gas through the membrane. On the other hand, if the gas tension in the test fluid should change, a transient condition will exist until a new steady state is established internally which again provides a gas tension equivalency on both faces of the membrane. Hence, depletion of oxygen is minimized at points adjacent the outside surface of the membrane i.e. the surface contacting the test fluid.

Referring now to FIG. 3, there is shown graphically a concentration diagram taken across the electrode-membrane structure of the embodiment of FIG. 2. As in FIG. 1, the ordinate **52** represents the relative concentration of the particular electroactive species. The absicca **54** represents distance from the cathode-electrolyte interface which is at the origin of the graph and hence, in a sense, the latter interface is line **52**. Lines **56** and **58** then represent the respective surfaces of the anode facing the cathode and the membrane; and line **60** is the outer surface of the membrane in contact with the test fluid. For the sake of clarity, no displacement between anode and membrane is shown, hence line **58** can also be considered the anode-membrane interface. The

distance between the various lines is representative of the thickness of the various elements but is not to be considered as necessarily showing the actual proper proportions. Using again the example of oxygen and assuming for simplicity, that the oxygen exhibits the same tension in both electrolyte and test fluid and the concentration of oxygen in the test fluid is constant, the latter concentration is indicated by the horizontal portion of broken line **62** which extends from the test fluid into the membrane. The concentration gradient, represented by the remainder of broken line **62**, extends from the anode-membrane interface to the cathode-electrolyte interface. The slope and position of line **62** will not change during steady state operation because of the equilibria established as heretofore described which results in no net transfer of oxygen across the membrane. However, during a transient change in oxygen concentration in the test fluid, although the horizontal portion of line **62** extending into the test fluid from membrane surface **60** will shift its level, this only results in a temporaray departure from a zero slope of the concentration level across the membrane. This zero slope is quickly re-established by the corresponding change in generation of oxygen at the anode. Hence, substantially no depletion layer will be created in the test fluid.

If the membrane is made very thin, for example, in the nature of 0.5 mils, the response time is considerably reduced inasmuch as diffusion time through the membrane in enhanced. Presupposing constant diffusion coefficients for the membrane, electrolyte and anode, the steady state current is approximately

$$-I=\frac{KC}{(H+L)}$$

where K is a constant depending, inter alia, on the diffusion coefficients, C is the concentration of the species in the test fluid and H and L are respectively the anode (generating here) thickness and inter-electrode spacing.

It is apparent that the spacing between the cathode and anode affects the sensitivity and response time, hence should be as small as possible without creating a dead short circuit. Typically, a spacing of 1 to 10 mils has proved quite satisfactory. Similarly, the spacing between the anode and membrane, if any, will also affect the response time and can be minimized without concern for short circuits.

Referring now to FIG. 5 there will be seen another embodiment of the present invention similar in many respects to the embodiment of FIG. 2, and wherein like numerals denote like parts. The device shown in FIG. 5 also includes, in a configuration similar to FIG. 2, enclosure means **42** having a hollow **44** therein open to the outside of the enclosure means, the opening being sealed by membrane **36**. A generating electrode, such as anode **30**, is disposed inside hollow **44** against the membrane. A consuming electrode, such as cathode **32**, is also disposed within hollow **44** and separated, as by separator **46**, from the anode **36**. Appropriately fluid-sealed electrically conductive leads **46** and **47** are respectively attached to cathode **32** and anode **30** to provide electrical connection to the electrodes from the exterior of the enclosure means. An electrolytic medium, such as a fluid electrolyte **34**, substantially occupies the remaining space within hollow **44**. Contacting the electrolyte and spaced from the other electrodes and membrane is a third or reference electrode **66** to which another electrically conductive lead **68** is attached to provide an electrical connection between electrode **66** and the exterior of the enclosure means.

Where this latter embodiment is intended to measure concentration of, for example, oxygen, the elements thereof can be selected and formed in the manner and of the materials heretofore described in connection with the embodiment of FIG. 2, except that electrode **66** is preferably an Ag-AgO electrode.

Referring now to FIG. 6 there will be seen an electronic circuit for use with the embodiment of FIG. 5 to determine the current flow between anode and cathode as well as to provide high stability to the operation of the system. The circuit of FIG. 6 comprises means for electrically connecting the circuit to electrodes of FIG. 5, and such means may comprise leads **68**, **46** and **47** respectively adapted to be connected to reference electrode **66**, cathode **32** and anode **30**. Lead **68** is also connected to lead **46** through a series resistor **70** and an electrical power source, such as battery **72**, the latter being poled so that lead **46** is negative. A point intermediate resistor **70** and the reference electrode is connected, as by lead **74**, to the input of D.C. voltage amplifying device or amplifier **76**, the output of the latter being coupled to the anode through lead **47**. A measuring instrument such as ammeter **78** is located preferably in the circuit between the amplifier and anode. The amplifier and positive side of the battery should be appropriately grounded in order to avoid transient from extraneous phenomena.

In operation of the device shown in connection with FIGS. 5 and 6, the presence of a species in the electrolyte permits current flow between the cathode and reference electrode, creating a potential across resistor **70** due to the IR drop therein. The voltage across resistor **70** is amplified by the gain of amplifier **76** and applied to anode **30**. It will thus be apparent that amplifier **76** is a D.C. inverting amplifier which preferably exhibits high gain (in the order of thousands) and is also preferably stabilized as by internal negative feedback, chopper-stabilization or the like, all as well known in the art. Thus the reference electrode is positive with respect to cathode **32**, but negative with respect to anode **30**. If the gain of amplifier **76** is sufficiently high, the coupling of its output through anode **30** to reference electrode **66** constitutes a negative feedback loop which will tend to create a virtual ground at the input of the amplifier. The potential of the reference electrode is therefore fixed at the virtual ground, and the potential between cathode **32** and the reference electrode is consequently maintained at a very stable level at which only oxgen will be reduced at the cathode.

The following example is illustrative of the construction and operation of a device of the type shown in connection with FIGS. 5 and 6. A hollow container was formed of polymethylmethacrylate. In the container was placed a cathode formed of 1 mil platinum metal foil of approximately 0.3 square centimeter per surface. a platinum metal anode formed of 80 mesh gauze, 3 mil diameter wire, and having a mean thickness of 5 mils, was placed in the container and spaced from the cathode with a nylon fabric spacer having a thickness of approximately 5 mils. In contact with the electrolyte there was also installed an Ag-AgO reference electrode in the form of a very short piece of No. 16 gauge wire. The remainder of the container was filled with a 1M KOH aqueous solution, and the opening into the container was capped with a polytetrafluoroethylene membrane having a thickness of 0.5 mil. In operation, the cathode potential was set at −0.7 volt with respect to the Ag-AgO electrode, and the device was operated at a temperature of 20° C.

In order to establish the backgriund current, the device was first operated with pure helium disposed against the surface of the membrane opposite the surface contacting the electrolyte, and a steady state current of 4.3 microamperes was obtained. Subsequently the outer surface of the membrane of the device was exposed to a number of various oxygen-containing fluids in samples of 0.2 cc. each, with the following results:

Sample:	Current in microamperes
Air saturated water	17.3
Air	17.3
90% O_2	59.6

All readings reached a constant level within a maximum of one minute after exposure to the sample. Each reading stayed constant for more than 3 hours after the initial transient. Despite the different mobilities of the oxygen in water and in air, the readings achieved with respect to air and air saturated water were nevertheless identical and remarkably stable, indicating that in fact there was no net oxygen diffusion through the membrane during steady state operation.

If one uses a similarly constructed apparatus in which however the electrolyte is aqueous KCl and the cathode is Ag-AgCl (thereby ensuring that no oxygen generation would occur within the apparatus), after 40 minutes the concentration of oxygen in a sample of similar size will be reduced approximately 70%. On the other hand, in the present invention, when operated for the same period of time there was no detectable change in oxygen concentration in the test sample.

It will be apparent to those skilled in the art that many modifications of the invention as thus described can be made. For example, a large number of electrolytes may be used. Indeed, under some circumstances the electrolyte may be a molten salt, and the enclosure means a membrane selected accordingly to have appropriate temperature resistant characteristics. While the anode and cathode of the present invention have been shown as substantially flat plates, of course other configurations which preserve the relative positioning of the electrodes and membrane may also be used. For example, the device may be constructed with the anode and cathode as concentric cylinders, the membrane lying along a portion of the exterior cylindrical surface of the anode. It will also be apparent that where the species to be measured is reducible, the generating electrode is an anode and the consuming electrode is a cathode. However, if the species to be measured is oxidizable, the generating electrode will be a negative electrode placed adjacent the membrane and the consuming electrode will be an anode or positive electrode.

Since certain changes may be made in the above apparatus without departing from the scope of the invention herein involved it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. An electrode assembly for measuring the concentration of a specific electro-chemically active species in a fluid, said assembly comprising in combination:

a liquid electrolyte;

first electrode means of a material electrochemically inert to both said electrolyte and said species and in contact with said medium;

barrier means for separating said electrolyte from said fluid, and being selectively permeable to said species, and in contact with said medium;

an electrical power source connected for biasing said first electrode means at a potential at which said species in said electrolyte will be consumed at said first electrode means;

second electrode means of a material electrochemically inert to both said electrolyte and said species, said second electrode means being in contact with said medium and connected to said power source for completing a circuit in which a current from said source can flow through both said electrode means at a level which is a function of such consumption;

said electrolyte being one from which substantially only said species is electrolytically generable at said second electrode means at said current level, said second electrode means being biased by said power source at a potential at which said species is generable from said medium; and

said second electrode means being so positioned with respect to said first electrode means and said barrier means that said species as generated at said second electrode means is available for consumption at said first electrode means in quantity dependent upon a tendency of said species to establish an equilibrium condition across said barrier means between concentration of said species respectively in said electrolyte and in said fluid.

2. An assembly as defined in claim 1 including means for measuring said current.

3. An assembly as defined in claim 1 including container means enclosing said electrolyte and said electrode means, said container means having said barrier means as a wall portion thereof.

4. An assembly as defined in claim 1 wherein said barrier means comprises a membrane having opposite surfaces, one of which is in contact with said electrolyte and the other of which is adapted to contact said fluid.

5. An electrode assembly for measuring the concentration of a specific electrochemically reducible gas in a fluid, said assembly comprising, in combination:

a cathode of an electrochemically inert material;

an anode of an electrochemically inert material;

an electrolytic medium in contact with both said cathode and anode;

barrier means for separating said fluid and said medium, said barrier means being selectively permeable to said gas, and in contact with said medium;

an electrical power source connected to said cathode for establishing a cathodic potential at said first electrode, said cathode being adapted for reducing said gas in said medium at said cathodic potential, said source providing an electrical current flow at said cathode at a level which is a function of such reduction;

said medium being a medium from which only said gas is electrolytically generable at said anode at said current level, said anode being adapted for generating said gas from said medium at said current level and connected to said power source so as to complete a circuit between said anode and cathode and bias said anode at an anodic potential at which said gas can be generated from said medium;

said anode and cathode being positioned in spaced relation to one another and to said barrier means, and said potentials being established at magnitudes, such that said current flow tends to substantially steady state condition responsively to a tendency for an equilibrium condition to become established across said barrier means between the partial pressures of said gas in said medium and said fluid.

6. An assembly as defined in claim 5 including means for maintaining the magnitude of said cathodic potential at said cathode at a substantially constant value.

7. An assembly as defined in claim 5 wherein said electrolytic medium comprises a first material from which said gas can be generated at said anode at said current level and anodic potential, and a second material which provides ionic charge transport;

said source being connected for maintaining the magnitude of said anodic potential below the decomposition potential of said second material and above the potential at which said gas can be generated at said current level.

8. An electrode assembly for measuring the concentration of a specific electrochemically active gas in a fluid according to the level of electrical current flowing at a polarographic cathode responsively to the availability at said cathode of said gas; said assembly comprising in combination;

a liquid medium electrolytically and anodically decomposable to generate only said gas;

barrier means for separating said fluid from said medium and being selectively permeable to said gas and in contact with said medium;

said polarographic cathode being of a material electrochemically inert to both said medium and said gas,

and having a surface in contact with said medium for electrolytically consuming said gas;

an anode in contact with said medium and being of a material electrochemically inert to both said medium and gas, said anode being positioned wholly between said surface of said polarographic cathode and said barrier means and capable of generating said gas from said medium with a current efficiency substantially the same as the current efficiency of consumption of said gas at said polarographic cathode, so that said gas as generated at said anode is available for consumption at said cathode in quantity dependent upon a tendency of said gas to establish across said barrier means an equilibrium condition between concentrations of said gas respectively in said medium and said fluid.

9. An assembly as defined in claim **8** wherein said second electrode is positioned in contact with said barrier means, said second electrode being porous to both said electrolytic medium and said gas.

10. An assembly as defined in claim **9** wherein said second electrode is a mesh.

11. An assembly as defined in claim **8** including means for impressing on said polarographic electrode, a first potential above the polarization potential for said gas, and means for impressing on said second electrode a second potential which is above the potential required for generation of said gas from said medium by electrolytic decomposition.

12. As assembly as defined in claim **11** including a third electrode contacting said medium and spaced from said polarographic and second electrode, and means for maintaining said third electrode at a reference potential between said first and second potentials and fixed with respect to said first potential.

13. An electrode assembly for measuring the concentration of a specific electrochemically active gas in a fluid according to the level of electrical current flowing at a polarographic cathode responsively to the availability at said cathode of said gas; said assembly comprising in combination:

a liquid medium electrolytically and anodically decomposable to generate only said gas;

barrier means for separating said fluid from said medium and being selectively permeable to said gas and in contact with said medium;

said polarographic cathode being of a material electrochemically inert to both said medium and said gas, and having a surface in contact with said medium for electrolytically consuming said gas;

an anode in contact with said medium and being of a material electrochemically inert to both said medium and gas, said anode being positioned wholly between said surface of said polarographic cathode and said barrier means, for electrolytically generating said gas;

a third electrode in contact with said medium;

means for impressing (1) at said polarographic cathode a first potential which is above the polarization potential for said gas, (2) at said anode, a second potential which is above the decomposition potential for said medium and (3) at said third electrode, a third potential between said first and second potentials, said first potential being fixed with respect to said third potential, said first and second potentials providing a current flow at said anode when said gas is present at said cathode, which current flow is equal and opposite to the current flow at said cathode, so that said gas as generated at said anode is available for consumption at said cathode in quantity dependent upon a tendency of said gas to establish an equilibrium condition, across said barrier means, between concentrations of said gas respectively in said medium and said fluid.

14. An assembly as defined in claim **13** wherein said means for impressing said potentials comprises an electrical power source connected through a series resistance between said polarographic and third electrodes, and a D.C. amplifier means having the potential drop across said resistance as the input signal thereto, the output of said amplifier being connected to said second electrode so as to tend to maintain said potential drop at a minimum.

15. An electrode assembly for measuring the concentration of gaseous oxygen in a fluid, said assembly comprising in combination:

means defining an electrolyte space and having as a wall portion thereof barrier means selectively permeable to oxygen and impermeable to said fluid;

a first electrode of an electrochemically inert material and adapted to polarographically reduce said oxygen and disposed within said space in contact with said medium;

a second electrode for electrolytically generating oxygen, and formed of an electrically conductive material substantially electrochemically inert to said medium and to oxygen, said second electrode being positioned between said first electrode and said barrier means;

an electrolytic medium disposed within said space in contact with said electrodes and said barrier means, said electrolytic medium comprising a material from which said oxygen can be generated at said second electrode by passage of an electrical current therethrough; and

means for effecting a current between said electrodes through said medium for simultaneous and substantially equal consumption and generation of oxygen at the respective electrodes in dependence upon establishment of an equilibrium between the partial pressures of oxygen at each side of said barrier means when the side of said barrier means opposite said electrolytic medium is in contact with said fluid.

16. An electrode assembly for measuring the concentration of an electrochemically reducible gas, said assembly comprising, in combination:

a hollow container of electrically insulating material having an opening therein, a membrane sealing said opening and being selectively permeable to said gas and impermeable to liquids, a cathode of electrochemically inert metal disposed within said hollow of said container for electrolytically reducing said gas, a porous anode of electrochemically inert metal disposed in said hollow between said cathode and said membrane adjacent the latter for electrolytically generating said gas;

means spacing said cathode from said anode, an electrolytic medium so disposed within said hollow as to form an ionically conductive path between said cathode and anode while in contact with said membrane, said electrolytic medium being capable of being so oxidized by an electrical current at said anode as to produce only said gas which is therefore available for reduction at said cathode in quantity dependent upon a tendency of said gas to establish across said barrier means an equilibrium condition between concentrations of said gas respectively in said medium and said fluid.

17. An electrode assembly as defined in claim **16** including means for impressing at said cathode, a potential above the polarization potential for said gas and means for impressing at said anode a potential above the potential necessary to produce said gas from said medium.

18. Method of measuring the concentration of an electrochemically active gas in a fluid comprising the steps of:

providing a body of electrolytic medium from which said gas can be electrolytically generated;

diffusing said gas between said fluid and said medium through barrier means selectively permeable to said gas, and impermeable to both said medium and fluid;

impressing a first potential on a first electrochemically inert metal electrode immersed in said medium and

a second potential on a second electrochemically inert metal electrode immersed in said medium so as to cause a flow of current at said electrodes;

positioning said electrodes in spaced relation to one another and to said barrier means, and maintaining said potentials at magnitude and values at which said current flow causes at said electrodes a redox reaction in said body so that there is electrolytic generation of said gas at one electrode tending to an equality with an electrolytic consumption of said gas at the other electrode according to a tendency of said gas to establish an equilibrium of the partial pressures of said gas on opposite sides of said barrier means and the net diffusion of said gas through said barrier means is minimized, and,

measuring the magnitude of said current flow.

19. Method of measuring the concentration of gaseous oxygen in a fluid, comprising the steps of:

providing a body of electrolytic medium from which oxygen can be electrolytically generated,

contacting opposite sides of a membrane, which is selectively permeable to oxygen, respectively with said fluid and said medium so as to permit oxygen diffusion through said membrane;

impressing first and second potentials respectively on an anode and cathode, both of electrochemically inert metals, in contact with said body, said anode being positioned in spaced-apart relation to and between said cathode and said membrane;

maintaining said potentials at values at which current

flows in said body between said anode and cathode to generate oxygen at said anode responsive to a simultaneous reduction of oxygen at said cathode, the rate of oxygen generation being responsive to a tendency of the partial pressures of oxygen in said fluid and medium to establish a substantially static equilibrium across said membrane; and

measuring said current flow.

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