

[54] OXYGEN SENSOR

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204/195 M

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[58] Field of Search. 204/195 R, 1 T, 195 M, 195 P

[56] References Cited

UNITED STATES PATENTS

3,296,113	1/1967	Hansen	204/195 R
3,594,233	7/1971	Charkey et al.	136/86 A
3,149,921	9/1964	Warner	23/232
3,328,204	6/1967	Grubb	136/86
3,647,641	3/1972	Grubb et al.	204/1 T

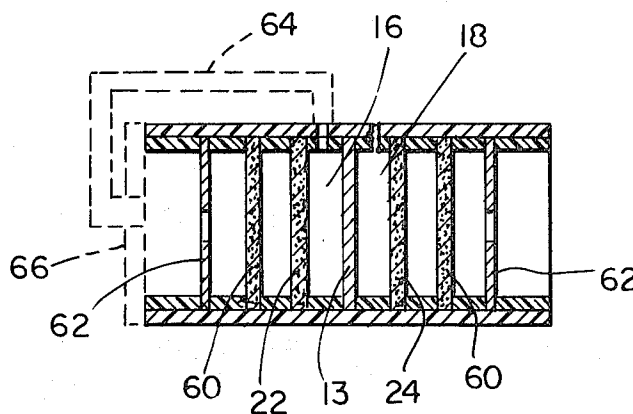
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ABSTRACT

A comparator element for gaseous oxygen comprises a first and a second oxygen-inert metal electrochemical cell. The first cell is fed with an oxygen containing gas of known oxygen content and the second cell is fed with a gas of unknown oxygen content. The design of the electrochemical cells is such that their electrical resistance when current is passed therethrough is inversely proportional to the oxygen content of the feed gas over a useful range. By comparing the resistances of the two cells, an accurate determination of the oxygen content of the unknown gas may be made with self compensation for ambient temperature. The range of the instrument may be increased by restricting the flow of gas to the oxygen electrodes. This may be accomplished by flowing the gas through a diffusion membrane and an orifice. Oxygen evolved from the metal electrode of the standard cell may be used to feed the oxygen electrode of the same cell thus providing a self sustaining standard atmosphere. The comparator may be compensated for pressure by providing pressure equalizing means between the gas feed to the first cell and the gas feed to the second.

20 Claims, 6 Drawing Figures



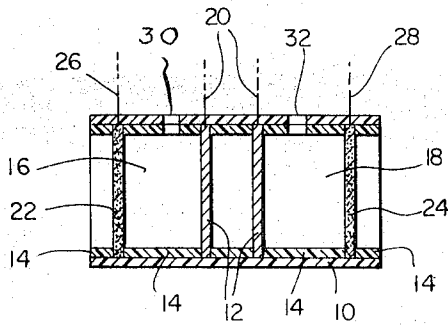


Fig. 1

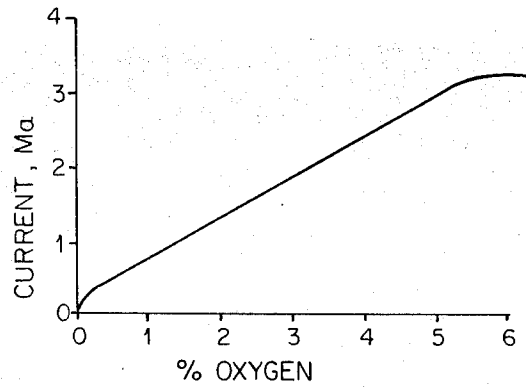


Fig. 3

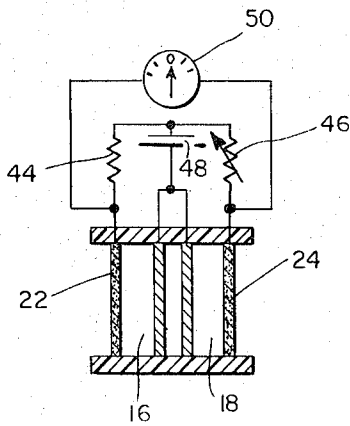


Fig. 2

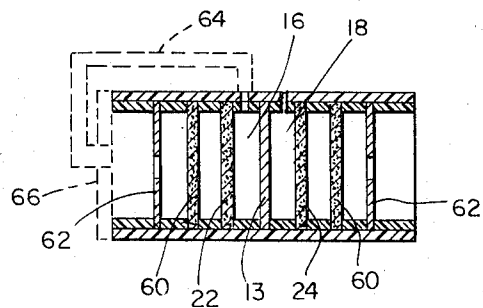


Fig. 4

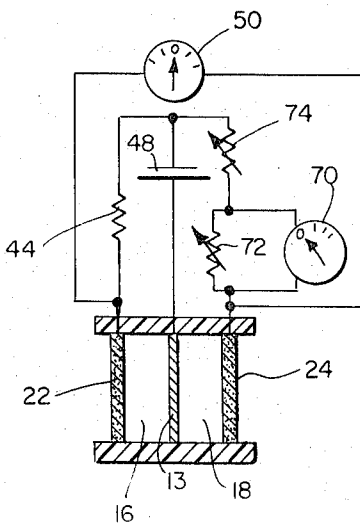


Fig. 5

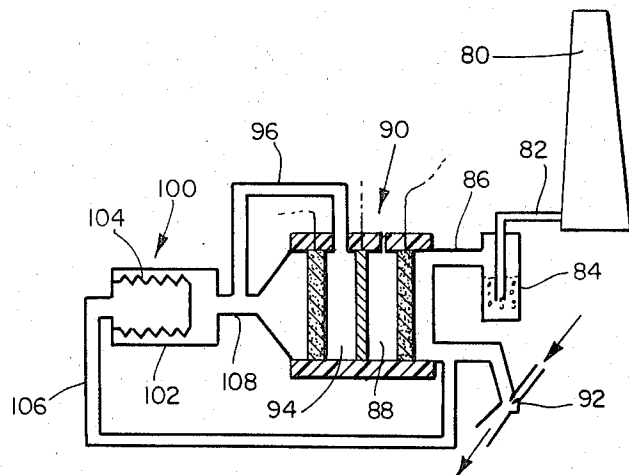


Fig. 6

1 OXYGEN SENSOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to gas monitoring and analysis devices. In particular it relates to devices for monitoring or analyzing the oxygen in a gas.

2. Description of the Prior Art

The science of determining the oxygen concentration in a gas has undergone a considerable evolution. One of the first oxygen deficiency sensors was the mine canary. A more scientific classical method is by chemical absorption such as is performed in an Orsat gas analyzer. This is slow and not easily adapted to continuous reading. Devices for measuring the thermal conductivity of gas have been perfected. These provide continuous readings but require a considerable volume of gas for proper functioning.

Oxygen deficiency indicating devices are required when men must work in confined spaces such as mines, vats, tanks, etc. Oxygen determination apparatus is also a requisite in such diverse application as space ships and capsules, submarines for military and civilian use as well as combustion control and other environmental studies. In spite of the many devices available, there is still a need for a small reliable oxygen sensor and analyzer operable by unskilled people and capable of reading a wide range of oxygen concentration. The gas chromatograph is useful for analyzing the composition of even very minute gas samples. However, the chromatograph is a large and delicate instrument suitable for laboratory work but not adapted to everyday use in industry. Small chemical absorption tubes have been perfected to measure oxygen, but these are of limited usefulness. Most recently fuel cell art has been utilized to provide a device which measures the oxygen content of a gas by the output of an oxygen-fuel electrochemical cell. Such cells can be made small in size, so that they may be carried about by a worker without inconvenience. However, they are subjected to loss of calibration due to the inconsistencies of the fuel cell.

SUMMARY OF THE INVENTION

A comparator element for gaseous oxygen comprises a first and a second oxygen-inert metal electrochemical cell. The first cell is fed gas containing oxygen of known concentration and the second cell is fed gas containing an unknown concentration of oxygen. When current is passed through the cells, the polarization resistance provides a measure of the comparative concentration of oxygen in the feeds. The range of the device is extended by constricting the flow of gas to the cells. Oxygen evolved at the anode of the companion cell may be used to feed the cathode thereof thus providing a self sustained reference. Compensation for ambient pressure may be provided by introducing pressure equalizing means between the two cells. The cells may be made quite small, of the order of 1 sq. cm. electrode area and requiring a feed in the order of 1/10 cc gas per second. A simple electrical bridge circuit fed from a single dry cell is sufficient for most applications. This can be arranged to provide low or high level oxygen alarms or may be used to directly read the percentage of oxygen present.

It will be seen from this description that the device of the invention can be made small in size, low in cost,

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rugged and portable. It is ideally suited to wear by workers such as miners, divers astronauts, etc. The self compensation provided by the use of two cells removes all problems usually associated with temperature, age, etc., while the use of a gassing cathode rather than a fuel cathode as used in certain presently available devices removes the uncertainty associated with the fuel electrode such as loss of catalytic power, poisoning, as well as the need to carry a fuel supply.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts in cross section a simplified sensor-reference cell of the invention;

FIG. 2 depicts the reference cell of FIG. 1 connected in a bridge circuit for an oxygen sensor or alarm;

FIG. 3 depicts a performance curve of the sensor relating current flow through the cell with the content of oxygen fed to it;

FIG. 4 depicts a second embodiment of the sensor-reference cell of the invention;

FIG. 5 depicts a second form of electrical circuit for use with the sensor-reference cell of the invention; and

FIG. 6 depicts the sensor of the invention connected for measuring gases from a chimney stack.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1, 10 represents in cross section a cylindrical housing enclosing two electrochemical cell means. The housing might be made from insulated metal or from one of the common structural plastics such as methacrylate, styrene, etc. It must be non-reactive with the strongly alkaline electrolyte. If a cemented construction is used, it should be a cementable material, and it should be dimensionally stable. There are four electrodes located in the housing, two to each cell means. The first two of these, 12, are gassing electrodes made from an impervious sheet of inert metal such as nickel. They are held tightly in housing 10 by ring 14 and are also sealed in position by a cement compatible with the material of the housing 10. The two electrodes separate the two cell compartments 16 and 18. An electrical lead 20 is attached to each electrode 12. Two identical oxygen electrodes 22 and 24 form the end walls of the compartments 16 and 18. Electrical leads 26 and 28 are attached to electrode 22 and 24. The electrodes can be any of the known oxygen consuming electrode structures. An oxygen consuming electrode that has been found particularly suitable can be made as follows: carbon powder and Teflon (polytetrafluoroethylene) in the ratio of about four to one by weight are mixed and formed into a porous sheet on rolls. The sheet so formed is pressed onto an expanded nickel sheet or other grid structure. A sheet of microporous non-wetting material such as Teflon (polytetrafluoroethylene) is then adhered by heat and pressure to one side of the above structure to form a triple laminate. In this electrode of the microporous sheet side faces the gas to provide microporosity to the electrode and to provide an hydrophobic surface to prevent leakage of electrolyte therethrough. The carbon particles provide catalytic sites and the screen serves as a current collector.

The two cell compartments 16 and 18 are filled with a suitable alkaline electrolyte such as potassium hy-

dioxide solution. Covered vents 30 and 32 provide access to the two compartments.

FIG. 2 shows a typical bridge circuit using the sensor of FIG. 1. 16 and 18 represent the two cell compartments and the two cell means. Resistors 44 and 46 connect the two air electrodes 22 and 24 to the negative of battery 48. Battery 48 need be only a single cell as 1.3 volts has been found to be ample for driving the circuit. For convenience, one or both resistors 44 and 46 may be adjustable. The adjustable feature is useful in calibrating the instrument. To complete the bridge circuit a signalling device such as the meter 50 is connected to the electrical leads of the gas electrodes. Other signaling devices include means such as a light or bell. Alternately an activator for a valve or damper may be caused to operate from the bridge circuit.

It is to be noted that when a direct current power source of fixed voltage is connected to cell means such as shown in FIG. 2 with the positive of the source connected to the nickel electrode and the negative of the source connected to the gas electrode, the current flow through the cell will be directly proportional to the oxygen available at the gas electrode. FIG. 3 shows a typical current oxygen curve for such a cell. Above about 5 percent oxygen the cell becomes saturated with oxygen and the proportionality relationship no longer holds. The cell can be likened to a variable resistor whose resistance value within the operating range is inversely proportioned to the oxygen content.

To use the sensor in the bridge circuit of FIG. 2, one of the cells, say, 22, is exposed to an oxygen source of a known concentration and the other cell, 24 is exposed to a source of unknown or varying oxygen content. When the concentration of oxygen of the unknown is equal to that of the known source, the bridge will be balanced; otherwise it will be out of balance. The device described will only be useful for measuring or comparing oxygen concentration below about 5 percent. Above this, the cell becomes insensitive as shown in curve FIG. 3. As a means to overcome this limitation, a constriction can be put in the line feeding the known and unknown gasses to the cell. Although various forms of orifice could be used, it has been found preferably to use a combination of an orifice and a diffusion membrane. The diffusion membrane should be a true diffusion membrane rather than a porous screen. Thin sections (5 to 25 mils thick) of such materials as natural and silicone rubber, polytetrafluoroethylene, fluorinated ethylene-propylene co-polymer, polybutadiene, poly(butadiene-styrene) ethyl cellulose, cellulose acetate and protein enriched triacetate cellulose make excellent membranes. Excellent results have been found when the membrane is chosen from such materials as silicone rubber, or protein enriched triacetate cellulose in thin sections. By the use of the orifice and diffusion membrane, the range of the oxygen sensing cells can be extended to cover the entire range of zero to 100 percent oxygen. FIG. 4 shows a cell design having diffusion membranes 60 and orifices 62 located in the passage feeding the gas electrodes 22 and 24. This cell also uses a single anode 13 for simplicity.

A further refinement of the reference cell is shown in dotted lines in FIG. 4. It has been noted that oxygen is produced from the electrode 13. The amount of oxygen given off in each cell must be exactly equal to the oxygen consumed by the oxygen electrodes. A conduit 64 is shown carrying oxygen from the cell compartment 16

to a chamber 66 feeding orifice 62, diffusion membrane 60 and gas electrode 22. With this construction the oxygen concentration in the cell defined by compartment 16 and electrode 22 will remain constant and at the value which was present when the cell is put in operation. Thus the cell means with the oxygen return conduit becomes an excellent reference cell. It is self contained and can be operated in any environment without affecting its output.

Another feature of the sensor is that by providing a means for equalizing the pressure between compartments 66 and 64, the sensor becomes self compensating for pressure. When the sensor is to be used in the open, i.e., with the complete device immersed in the gas of unknown oxygen content, a simple pressure equalizing means is to have a flexible gas bag attached to the feed-back tube 64. Where cell 24 is fed from a closed system, an enclosed bellows device may be used. Because both cells are closely associated and can be made conveniently small, the sensor has an automatic compensation for temperature.

The electrical circuit of FIG. 2 is very convenient when the sensor is used for an oxygen level control or alarm. For such use, the bridge balance point is adjusted by means of a variable resistance 46 so that the null point of the bridge is at the oxygen level which it is desired to monitor. As long as the oxygen level stays on the safe side of the null point, the polarity of the electric potential at meter 50 will be in one direction. However, if the level crosses into the danger area, the potential will reverse. Means for converting the reverse signal into a control or alarm signal are well known; for example a reverse voltage relay or an operational amplifier could be placed at 50 to give a power signal capable of operating a valve or energizing a light bulb or horn.

Because of the linearity of the cell potential with respect to oxygen content of the sensed gas, the sensor cell may be used as a direct reading oxygen meter. A possible circuit for this purpose is shown in FIG. 5. This circuit is similar to the circuit of FIG. 2 except that a meter 70 calibrated in percent oxygen having a paralleled variable resistance shunt 72 and a variable resistor 74 make up the resistor of the bridge indicated by 46 of FIG. 2. To operate the oxygen meter, the two sides of the sensor are fed from the same gas supply of known oxygen content. A convenient reference gas is air of 21 percent oxygen. The bridge is then balanced by combined adjustment of resistors 72 and 74. When balanced, meter 50 will be at its null point and meter 70 will point to the percent oxygen in the standard gas. To measure a gas of unknown oxygen content, cell 18 is fed the unknown gas and cell 16 is fed with the standard gas. The percent oxygen will be proportional to the current flow through the cell 18.

It will be observed that the oxygen sensor of this invention is capable of being built in a small size and in fact by making it small the lag time required to reach equilibrium will be made small; the electrical circuiting can likewise be made small. It is self contained and can be energized by a single dry cell. It is also rugged and truly portable. Thus it differs considerably from the classical oxygen sensing and measuring devices such as the orsat, the thermal cell and the gas chromatograph. These features make it particularly adaptable as a personal oxygen detector for miners, rescue workers and people working in enclosed spaces. Because of its built-

in pressure compensation, it is suitable for deep diving work where a small simple direct reading device is of extreme importance. For the same reason it is suitable for aerospace applications where pressures are below atmospheric. The device is useful in the process and other industries where control or measurement of oxygen content is required. Unfortunately, the electrolyte of the cell of the invention is a reactive to a gas such as carbon dioxide. Thus where such gasses may be present as in a flue gas it is necessary to pass the gas through a carbon dioxide absorption column prior to feeding it to the sensor cell.

When an unknown gas is fed to the sensor via a tube, it is necessary that the atmosphere to which the sensor is exposed is not materially changed by the oxygen consumed by the sensor. To achieve this, it is desirable to have a flow of gas across the sensor area. As an example, FIG. 6 shows chimney 80 connected by tube 82 to carbon dioxide absorption tube 84. Tube 86 feeds the washed gas to the sensor side 88 of gas analyzer means 90. A continuous flow of flue gas through the system is provided by a gas pump as for instance the aspirator 92. The standard side 94 of the analyzer 90 receives a continuous supply of oxygen from its gassing electrode via the feed back tube 96. A pressure equalizer 100 comprising a sealed vessel 102 with an internal flexible wall 104 is provided to equalize the gas pressures between cell means 88 and 94 by means of tubes 106 and 108 respectively.

Other uses of the device of the invention will be obvious to those skilled in the art of gas sensing and analysis.

Having fully described our invention and given examples of its embodiment as well as pointing out numerous sites where it will be of use, we claim:

1. A comparator for comparing the oxygen concentration of a gas of unknown oxygen content with the oxygen concentration of a gas of known oxygen content which comprises:

- a. a first electrochemical resistance cell comprising a first oxygen consuming cathode receiving a first gas of known oxygen concentration, a first electrolyte and an inert metallic gassing anode;
- b. a second electrochemical resistance cell comprising a second oxygen consuming cathode receiving a second gas of unknown oxygen concentration, a second electrolyte and an inert metallic gassing anode;
- c. a housing containing the first electrochemical cell and the second electrochemical cell;
- d. means for supplying a positive current to the cathode of the first electrochemical cell to produce a first resistive drop across the first electrochemical cell the first drop being dependent upon the oxygen concentration of the first gas;
- e. means for supplying a positive current to the cathode of the second electrochemical cell to produce a second resistive drop across the second electrochemical cell the second drop being dependent upon the oxygen concentration of the second gas; and
- f. means for comparing the resistance defined by the second resistive drop with the resistance defined by the first resistive drop so that the oxygen concentration of the unknown gas can be compared to the oxygen concentration of the known gas.

2. A comparator as defined in claim 1 including a first and a second means for restricting gas flow, the first means for restricting gas flow restricting the flow of gas to the cathode of the first electrochemical cell and the second means for restricting gas flow restricting the flow of gas to the cathode and the second electrochemical cell.

3. A comparator as defined in claim 2 wherein the first means for restricting the flow of gas to the first cathode includes a first diffusion membrane and the second means for restricting the flow of gas to the second cathode includes a second diffusion membrane.

4. A comparator as defined in claim 3 wherein the material from which the first and the second diffusion membranes are made is selected from the group which consists of natural rubber, silicone rubber, polytetrafluoroethylene, fluorinated ethylene-propylene copolymer, polybutadiene, poly(butadiene-styrene), ethyl cellulose, cellulose acetate, and protein enriched triacetate cellulose.

5. A comparator as defined in claim 2 wherein the first means for restricting the flow of gas to the first cathode includes a first orifice and the second means for restricting the flow of gas to the second cathode includes a second orifice.

6. A comparator as defined in claim 1 including conduit means for conducting oxygen gas given off by the anode of the first electrochemical cell to the cathode thereof.

7. A comparator as defined in claim 6 including means equalizing the pressure within the first electrochemical resistance cell to the pressure within the second electrochemical resistance cell.

8. A comparator as defined in claim 1 wherein each oxygen gas consuming cathode comprises a laminate of metallic grid, a porous sheet of carbon and polytetrafluoroethylene, and a sheet of microporous polytetrafluoroethylene, the side of the laminate bearing the grid being exposed to the electrolyte of the cell and the side of the laminate bearing the microporous sheet being exposable to an oxygen containing gas.

9. A comparator as defined in claim 1 wherein the means for comparing the resistance defined by the second drop with the resistance defined by the first drop comprises a four armed electrical bridge circuit.

10. A comparator element as defined in claim 1 wherein the inert metallic anode of the first electrochemical cell is a first side of a metallic anode and the inert metallic anode of the second electrochemical cell is in the second side of said metallic anode.

11. An oxygen meter for determining the oxygen concentration of a gas of unknown oxygen content which comprises:

- a. first electrochemical resistance cell comprising a first oxygen consuming cathode receiving a first gas of known oxygen concentration, a first electrolyte and an inert metallic gassing anode;
- b. a second electrochemical resistance cell comprising a second oxygen consuming cathode receiving a second gas of unknown oxygen concentration, a second electrolyte and an inert metallic gassing anode;
- c. a housing containing the first electrochemical cell and the second electrochemical cell;
- d. means for supplying a positive current to the cathode of the first electrochemical cell to produce a first resistive drop across the first electrochemical

cell the first drop being dependent upon the oxygen concentration of the first gas;

- e. means for supplying a positive current to the cathode of the second electrochemical cell to produce a second resistive drop across the second electrochemical cell the second drop being dependent upon the oxygen concentration of the second gas;
- f. means for supplying an equal and predetermined positive potential to the cathode of the first electrochemical cell and to the cathode of the second electrochemical cell;
- g. means for measuring the flow of current to the cathode of the second electrochemical cell; and
- h. calibration means for directly relating the magnitude of the flow of current to the oxygen concentration of the gas of unknown oxygen content.

12. An oxygen meter as defined in claim 11 including a first and a second means for restricting gas flow, the first means for restricting gas flow restricting the flow of gas to the cathode of the first electrochemical cell and the second means for restricting gas flow restricting the flow of gas to the cathode of the second electrochemical cell.

13. An oxygen meter as defined in claim 12 wherein the first means for restricting the flow of gas to the first cathode includes a first diffusion membrane and the second means for restricting the flow of gas to the second cathode includes a second diffusion membrane.

14. An oxygen meter as defined in claim 13 wherein the material from which the first and the second diffusion membranes are made is selected from the group which consists of natural rubber, silicone rubber, polytetrafluoroethylene, fluorinated ethylene-propylene co-polymer, polybutadiene, poly(butadiene-styrene),

ethyl cellulose, cellulose acetate, and protein enriched triacetate cellulose.

15. An oxygen meter as defined in claim 12 wherein the first means for restricting the flow of gas to the first cathode includes a first orifice and the second means for restricting the flow of gas to the second cathode includes a second orifice.

16. An oxygen meter as defined in claim 11 including conduit means for conducting oxygen gas given off by the anode of the first electrochemical cell to the cathode thereof.

17. An oxygen meter as defined in claim 16 including means equalizing the pressure within the first electrochemical resistance cell to the pressure within the second electrochemical resistance cell.

18. An oxygen meter as defined in claim 11 wherein each oxygen gas consuming cathode comprises a laminate of a metallic grid, a porous sheet of carbon and polytetrafluoroethylene, and a sheet of microporous polytetrafluoroethylene, the side of the laminate bearing the grid being exposed to the electrolyte of the cell and the side of the laminate bearing the microporous sheet being exposable to an oxygen containing gas.

19. An oxygen meter as defined in claim 11 wherein the means for supplying a positive potential includes an electrochemical battery, and the means for measuring the current flow including a four armed electrical bridge circuit.

20. An oxygen meter as defined in claim 11 wherein the inert metallic anode of the first electrochemical cell is a first side of a metallic anode and the inert metallic anode of the second electrochemical cell is the second side of said metallic anode.

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