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A SURVEY OF CONCEPTS/TECHNIQUES FOR SENSING OXYGEN IN AIRCRAFT OXYGEN-GENERATING SYSTEMS

W. A. Porter, Ph.D.
D. A. Dietrich, Ph.D.
H. K. Lesser, Captain, USA
J. D. Brand, Ph.D.
Texas A&M Research Foundation
Faculty Exchange Box H
College Station, Texas 77843

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Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

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This technical report has been reviewed and is approved for publication.

Kenneth G. Ikels
KENNETH G. IKELS, Ph.D.
Project Scientist

RICHARD L. MILLER, Ph.D.
Supervisor

Lawrence J Enders
LAWRENCE J. ENDERS
Colonel, USAF, MC
Commander

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This survey has shown that the commercial market has concentrated mainly on chemical-type oxygen sensors. We believe that industry in general is "on top" of the opportunities for improving chemical-type oxygen sensors, and that new developments in chemical sensors will most likely come from industry. Most work in the solid-state sensor area has been very fundamental, and oxygen sensor development has not been pursued by industry. The solid-state area is believed to offer good promise for the development of improved

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20. **ABSTRACT** (Continued)

oxygen sensors, and further research should be conducted, particularly in the thin-film oxide area. The area of fluidics also warrants further investigation. An approach using fluidic oscillators should be considered. A modified sound separation probe should also be considered as a possible acoustic approach. Questions of measurement sensitivity are of the greatest concern here however. Of all of the recommendations given above, we believe that the solid-state area holds the best promise for immediate improvement.

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A SURVEY OF CONCEPTS/TECHNIQUES FOR SENSING OXYGEN IN AIRCRAFT OXYGEN-GENERATING SYSTEMS

INTRODUCTION

The U.S. Air Force School of Aerospace Medicine (USAFSAM) is currently conducting programs to develop on-board, in-flight generation of aviator's breathing oxygen to replace the use of stored liquid oxygen as a source. As a part of this effort, USAFSAM requested a survey of oxygen-sensing concepts/techniques. This report provides information on such concepts/techniques that could lead to the development of a real-time, on-board oxygen sensor for the breathing gas in high-performance aircraft. Basic criteria for such a sensor are:

1) low in weight
2) small in size
3) unaffected by pressure changes (760-50 mm Hg)
4) orientation insensitive
5) capable of presenting the oxygen concentration 20-100% ± 2% in real time
6) reliable.

The 1954 National Bureau of Standards (NBS) Report 3130, "Survey of Methods for the Determination of Oxygen in Oxygen-Enriched Air" (4), was used as the starting point for the research covered by our report. We concentrated on the three basic areas of investigation: chemical-electrochemical, acousto-mechanical, and solid-state methods for determining the oxygen content of an ambient gas. We conducted extensive computer-aided library and patent searches to locate applicable references, and contacted manufacturers of existing oxygen sensors for information and data concerning their products. The information that follows does not cover all materials collected or researched but rather is limited to those particular concepts, techniques, or already existing sensors which are believed to have the potential for satisfying the above-listed Air Force criteria.

COMMERCIALLY AVAILABLE OXYGEN MONITORS

We conducted a search for commercially available devices that could be used to measure or monitor oxygen concentration or partial pressure in a mixture of gases, requesting information from more than 100 companies about manufactured devices. Requirements stated in the requests were:

1) Application: Monitor level of oxygen in respiratory gases supplied to pilots on aircraft
2) Measurement: Concentration or partial pressure of oxygen
3) Oxygen Concentrations: 20-100%
4) Other Gases: Nitrogen and argon
5) Accuracy: ±2% of concentration
6) Readout: Digital, real time in terms of being updated every 5 seconds (approximately)

7) Additional Considerations:

- low weight
- small size
- unaffected by changes in barometric pressure (760-50 mm Hg)
- unaffected by orientation
- unaffected by vibration
- reliable
- reasonable lifetime

In addition, a required temperature range of -50° to +120°F (-46--49°C) was included at a later date.

In all, we received approximately 40 responses and screened them to determine the most appropriate. The companies listed in Table 1 offer devices most closely meeting the specified requirements; however, none of the devices appear to satisfy the requirements completely. Table 2 is included as a convenient cross-reference of the various devices, although it does not give a complete description of any one device. In fact, some data in the table are not comparable from one device to another. Care should be taken, therefore, to check the conditions or qualifications of each entry. Table 3 lists additional companies that manufacture oxygen monitors or gas-analysis devices. These companies have not responded to the inquiry or produce devices which do not now meet the requirements.

TABLE 1. OXYGEN MONITOR MANUFACTURERS

Ambac/Bacharach
Bacharach Instrument Company
Division of Ambac Industries, Inc.
625 Alpha Drive
Pittsburgh PA 15238
Contact: W. H. Milon

Astro Resources Corporation
POB 58159
Houston TX 77058
Contact: Raymond L. Haak

Beckman Instruments, Inc.
Advanced Technology Operations
1630 S. State College Blvd.
Anaheim CA 92806
Contact: John Burgess

Catalyst Research Corporation
1421 Clarkview Road
Baltimore MD 21209
Contact: J. D. Olson

Comsip Delphi, Inc.
Engineers and Contractors
10650 E. Ruch St.
S. El Monte CA 91733
Contact: Denise Robinson

Horiba Instruments, Inc.
1021 Duryea Avenue
Irvine CA 92714
Contact: Robert D. Gafford

Sybron/Taylor
4930 Cranswick Rd.
POB 40466
Houston TX 77040
Contact: John Burkland

Teledyne Analytical
Instruments
333 W. Mission Dr.
POB 70
San Gabriel CA 91776
Contact: Dennis M. Antieau

TABLE 2. OXYGEN MONITORING DEVICES

Manufacturer	Technique	Range	Accuracy	Pressure range	Temperature range °F/°C	Response time	Service time	Comments
Ambac	Polarographic (electrochem)	0-100%	3%	Low-pressure sensitive	32-100/ 0-38	<10 s (90%)	4-6 mo	Orientation sensitive
Astro	Zirconium oxide electrolyte	0-100%	--	Low-pressure sensitive	--	3 s	--	
Beckman	(OMII) Polarographic	0-100%	±.5%	--	60-104/ 16-40	.2 s (90%)	--	Developing another device for US navy
Catalyst Res.	Electrochemical	0-100%	--	--	32-104/ 0-40 (-40--150/-40--65 storage)	<20 s (97%)	6-9 mo	Under development
Comsip Delphi	Paramagnetic	0-100%	±1%	1-50 psig	30-120/ -1--49	10 s (90%)	--	
Horiba	Polarographic	0-25%	--	1 psi-10 psig	41-105/ 5-41	<1 s (90%)	--	
Sybron/ Taylor	Paramagnetic	0-100%	--	1/3-10 psi	32-120/ 0-48 (-4--140/-20--60 storage)	--	--	
Teledyne	Electrochemical	0-25%	2%	--	--	5 s	2 yr	

TABLE 3. ADDITIONAL MANUFACTURERS OF GAS-ANALYSIS DEVICES

Anacon, Inc.
30 Main St.
POB 267
Ashland MA 01721

Corning Glass Works
Medical Products Div.
Scientific Instruments Dept.
Medfield Industrial Park
Medfield MA 02052

Edmont-Wilson
Coshocton OH 43812
(see Energetics Science, Inc.)

Gam Rad, Inc.
46101 Grand River
Novi MI 48050

Lazar Research Labs Inc.
731 S. La Brea Ave.
Los Angeles CA 90036

London Co.
811 Sharon Dr.
Cleveland OH 44145
(The London Company is US Representative for Radiometer, Copenhagen, Denmark)

Milton Roy Co.
Hays-Republic Div.
742 E. 8th St.
Michigan City IN 46360

Sensors, Inc.
3908 Varsity Dr.
POB 1383
Ann Arbor MI 48106

Transidyne General Corporation
903 Airport Dr.
Ann Arbor MI 48106

Yellow Springs Instruments Co.
Box 279
Yellow Springs OH 45387

Babcock & Wilcox Co.
Bailey Meter Co.
29801 Euclid Ave.
Wickliffe OH 44092

Critikon
2620 McGraw Ave.
Irvine CA 92713

Dynatron Inc.
Barnes Industrial Park
Wallingford CT 06492

Energetics Science, Inc.
85 Executive Blvd.
Elmsford NY 10523

Instrumentation Laboratory Inc.
113 Hartwell Ave.
Lexington MA 02173

Litton Medical Electronics
777 Nicholas Blvd.
Elk Grove IL 60007

Lumidor Safety Products
5364 Northwest 167th St.
Miami FL 33014

Orion Research Inc.
380 Putnam Ave.
Cambridge MA 02139

Perkin-Elmer Corp.
Coleman Instruments Div.
2000 York Rd.
Oak Brook IL 60521

Technicon Instruments Corp.
511 Benedict Ave.
Tarrytown NY 10591

Weston and Stack Inc.
446 Lancaster Ave.
Malvern PA 19355

Rexnord
Instrument Products
30 Great Valley Parkway
Malvern PA 19355

A few of the manufacturers supplied some additional information. The Advanced Technology Operations (ATO) of Beckman Instruments, Inc. is currently under contract to provide the Oxygen Monitoring/Alarm System for the U.S. Navy's high-performance-aircraft on-board oxygen-generating system (OBOGS). According to the manufacturer, the system continuously monitors the OBOGS output over a wide range of temperature and altitude variations, sounding an alarm should the oxygen fall below a preset level. Both Astro Resources Corporation and Ambac/Bacharach Instrument Company produce devices which they believe meet all criteria except the large barometric-pressure range (760-50 mm Hg).

A letter from Teledyne Analytical Instruments best summarized currently available devices:

> "It is our understanding the equipment would need to meet the following basic requirements:
>
> a. Light weight and small in size.
> b. Operable in approximately 2-5 minutes.
> c. Low power consumption.
> d. Unaffected by motion and vibration.
> e. Capable of withstanding up to 6 Gs.
> f. Maintenance scheduled once per year.
> g. Storage temperature: -50°F.
>
> If the above requirements are indeed valid, it is TAI's firm belief that none of the known and accepted methods for the detection of gaseous oxygen would be accepted for this application in the present form. In an effort to assist you in your endeavor, we are listing below most of the basic principles of oxygen detection, as we understand them, and their limitations related to this application.

Principle	Limitations
Thermomagnetic; wind	Vibration, flow sensitive, weight
Paramagnetic	Vibration, flow sensitive, orientation, G forces
High temperature ceramic	Warm-up time approximately 1-2 hours, power requirements comparatively high
Polarographic (Electrochemical)	Minimum storage temperature: -20°F maintenance - 6 months, adversely affected by low barometric pressure
Galvanic (Electrochemical)	Minimum storage temperature: 30°F, adversely affected by low barometric pressure
Coulometric (Electrochemical)	Minimum storage temperature: 30°F flow sensitive, adversely affected by low barometric pressure

The technical staff of TAI, armed with its 25 years of experience in the development of oxygen transducers, believes a number of the above principles may lend themselves to this application, namely, the high temperature ceramic and electrochemical techniques appear to be the most likely candidates."

CHEMICAL-ELECTROCHEMICAL TECHNIQUES

Electrochemical sensors for measuring oxygen are without exception based on oxidation-reduction (redox) reactions. Although a variety of such reactions have been used historically, only two are important in contemporary oxygen analyzers:

- Reduction of dissolved oxygen in solution at a metal cathode

  $O_2 + 2H_2O + 4e \rightleftarrows 4\ OH^-$

- Gas phase catalytic reduction at a noble metal cathode

  $O_2 + 4e \rightleftarrows 2\ O^{2-}$

A variety of electroanalytical methodologies have utilized these reactions for the quantitative measurement of oxygen. Sensors based on electrochemical reduction of oxygen in solution commonly are amperometric (measurement of current at fixed potential), although coulometric and potentiometric systems also have been described. Sensors using the gas phase reaction depend on the fact that certain metal oxides (notably zirconia, ZrO_2) become permeable to the superoxide ion (O^{2-}) at sufficiently high temperatures and can thus be used as solid electrolytes in concentration cells.

The nomenclature applied to electrochemical sensors, particularly by manufacturers, is often confused and confusing. Terms such as "polarographic," "electrolytic," "galvanic," and "fuel cell" are applied indiscriminately without regard to their accepted definitions. In this report we will attempt to apply consistent and accurate terminology, with explanations where appropriate.

Most electrochemical sensors for oxygen measure the partial pressure of the gas (PO_2). If a readout in percent oxygen is required, the total gas pressure must be measured in addition to PO_2; miniature integrated-circuit pressure transducers are commercially available and will not be further considered here. Certain coulometric oxygen sensors are designed to measure the total oxygen content in a gas stream and provide a direct measurement of percent oxygen.

The Clark Electrode

Among the earliest practical electrochemical sensors for oxygen is that first described by Clark (3). Although design and construction materials have changed some, this sensor is now used in essentially unaltered form in all commercially available biomedical oxygen analyzers including those for blood gas analysis and for the transdermal measurement of PO_2.

Lakshminarayanaiah (9) has given a reasonably straightforward account of the operation of the Clark electrode, which will be summarized here. More advanced discussions have been given by Buckles et al. (2). The Clark electrode is illustrated diagrammatically in Figure 1. It comprises a microcathode, generally a platinum wire, and a silver/silver chloride anode which also serves as a reference electrode. The electrolyte solution is normally a dilute aqueous solution of potassium chloride. A thin membrane of Teflon or polypropylene is stretched across the cathode. In some designs a "spacer" such as tissue paper or nylon net is placed between the cathode and the plastic membrane. Other designs eliminate this spacer and rely on a slight "roughness" in the end of the glass surrounding the cathode to maintain electrolyte continuity between cathode and anode; this approach results in faster response times.

If the voltage applied across the cell is increased, the rate at which oxygen is reduced

$$O_2 + 2H_2O + 4e \rightleftarrows 4\ OH^-$$

increases, resulting in an increase in current. Figure 2 shows a current-voltage curve, or voltammogram. Eventually a point is reached at which the rate of oxygen reduction is equal to the rate at which oxygen diffused through the plastic membrane and electrolyte solution to reach the cathode. Further increase in applied voltage results in little increase in current and gives rise to a "diffusion controlled wave." At extreme applied voltages, a further increase in current is observed resulting from electrochemical reduction of the solvent (water). The magnitude of the current on the diffusion-controlled plateau is proportional to the PO_2 of the sample surrounding the sensor. If the applied voltage is fixed at a value corresponding to the diffusion plateau, measurement of the cell current allows determination of PO_2; this is an amperometric* sensor. The necessary voltage depends on the choice of reference electrode; -0.7 V is commonly used for a Ag/AgCl reference. The current measured is typically of the order of 75 nA (nanoamps) for the dimensions of microelectrodes used in commercial sensors. Calibration of the sensor requires at least two points in practice. Although zero current would be expected at zero PO_2, some reduction of water may occur at the applied voltage and give rise to nonzero "residual" currents. After correction for residual currents, the measured current is proportional to PO_2:

$$i = k\ PO_2.$$

For a given electrode, the constant k depends on temperature.

---

*Amperometry is a technique in which electrode current (I) is measured at a fixed applied voltage (V). Voltammetry is the process of defining a complete I-V curve by measuring current at a series of applied voltages. Polarography is voltammetry applied to a mercury microelectrode with a periodically renewed surface (dropping mercury electrode).

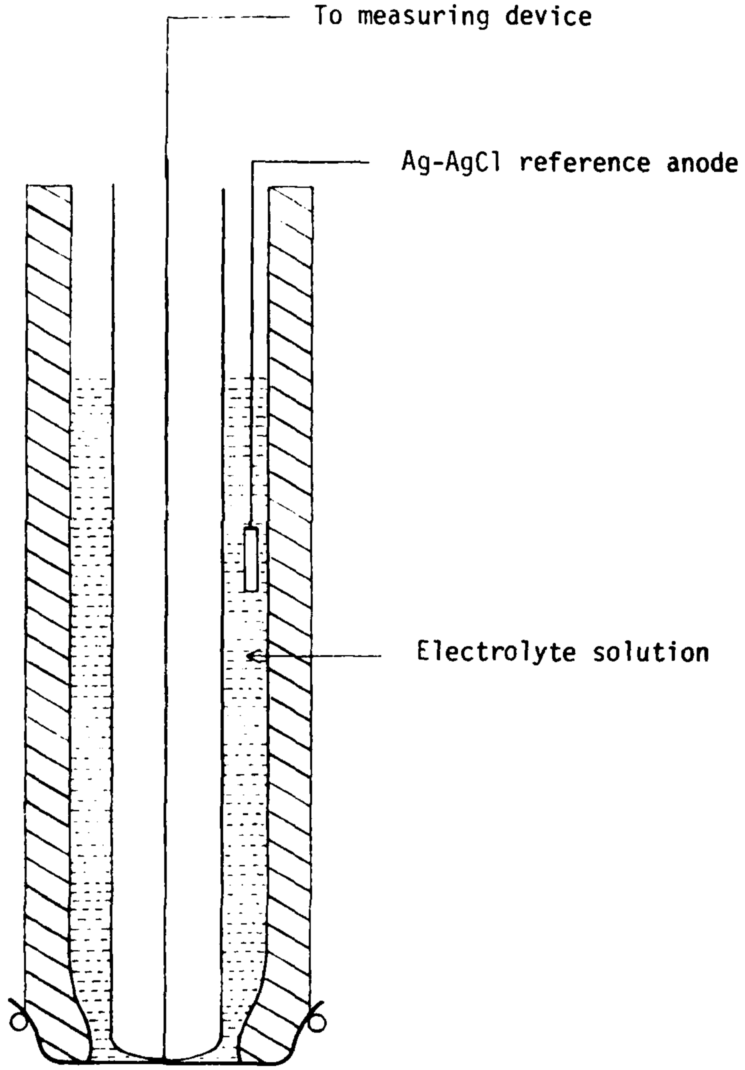


Figure 1. Clark type of oxygen electrode.

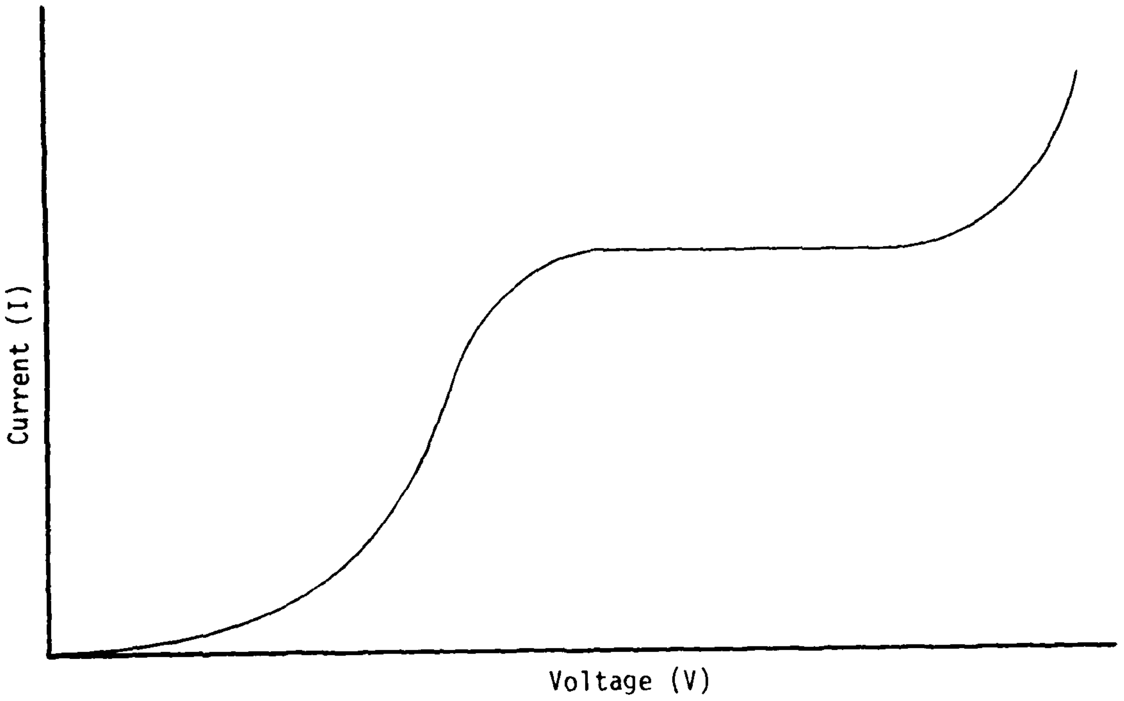


Figure 2. Current-voltage curve for the reduction of oxygen at a constant concentration of oxygen.

Amperometric Sensors with Lead Anodes

The applied voltage in a Clark electrode was noted to depend on the choice of reference electrode. Appropriate choice of the reference anode half-cell reaction allows the potential of the cathode to be maintained on the diffusion current plateau at zero applied volts.

The voltage applied to the cell is equal to the sum of the cathode and anode potentials:

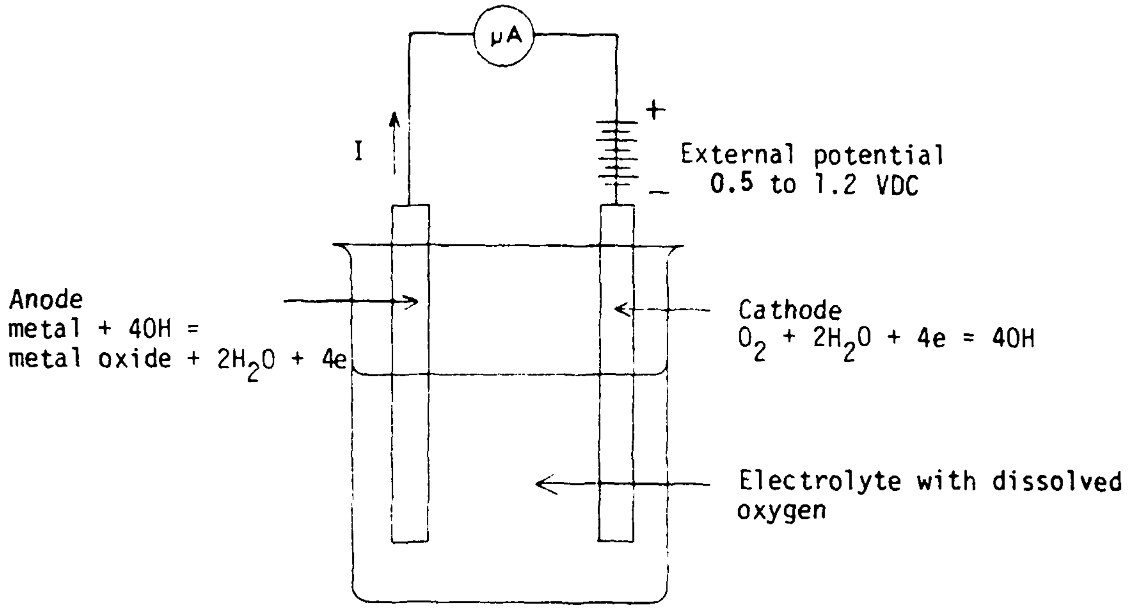
$$E\ app = Ec + Ea.$$

Thus for a Clark electrode

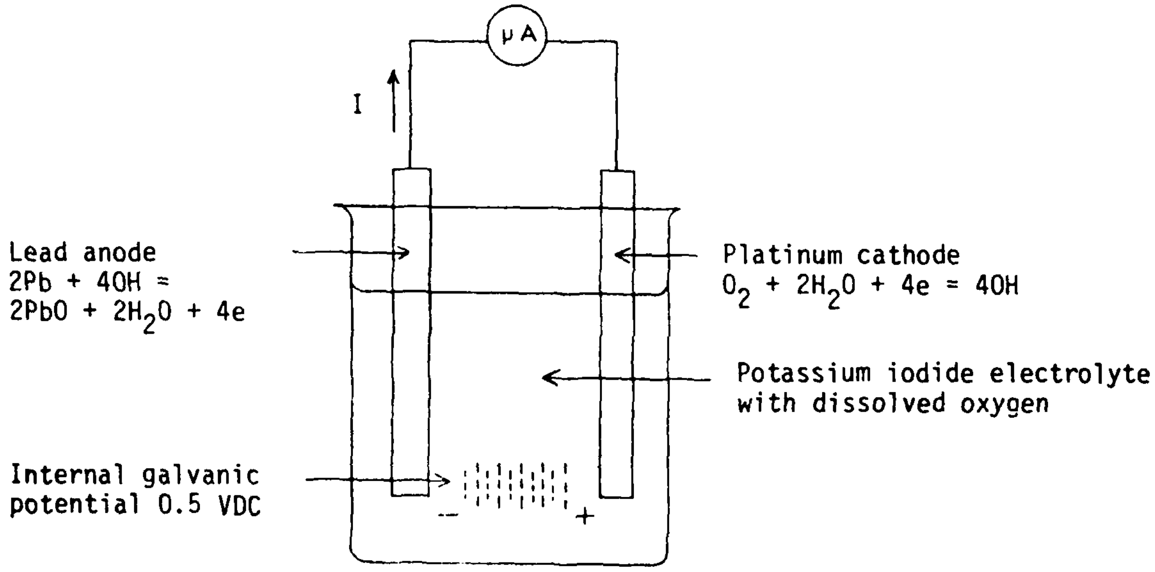
$$-0.7 = Ec + E_{AgCl}$$

or $$Ec = -(0.7 + E_{AgCl}).$$

Ec can be obtained by using a reference electrode having a potential 0.7 volts more negative than a silver/silver chloride electrode. The lead/lead oxide electrode meets this requirement and has commonly been used. The essential difference between the Clark electrode and cells using lead anodes is shown in Figure 3. From a practical standpoint, the only difference lies in the measuring circuit; the Clark electrode requires an external applied voltage, the lead anode cell does not. It has been customary to term the Clark cell "electrolytic" and the lead anode cell "galvanic." Although this



(A) Molecular-type oxygen probe



(B) Weston & Stack oxygen probe

Figure 3. Principle of molecular oxygen probe.

distinction became a key issue in a legal suit (1), it is more semantic than real. Electrolysis occurs in both cells and both are galvanic cells.

Solid Electrolyte Cells

When certain metal oxides are heated to a high enough temperature, they become electrically conductive. For example, at temperatures above 700-800°C (1300-1475°F), zirconia dissociates into zirconium and superoxide ions:

$$ZrO_2 \rightleftarrows Zr^{4+} + 2\ O^{2-}.$$

Within the solid-phase crystal lattice, the superoxide ion is mobile. Furthermore, the concentration of O^{2-} ions can be sensed by a platinum electrode, at which the half-cell reaction occurs:

$$O_2 \rightleftarrows 2\ O^{2-} + 4e$$

Consider now an electrochemical cell which comprises two platinum electrodes and a solid zirconia electrolyte; the platinum/zirconia interfaces are exposed to two different gas mixtures having oxygen partial pressures P_1 and P_2:

$$Pt\ \Big|\ O_2\ (P_1)\ \Big|\ ZrO_2\ \Big|\ O_2\ (P_2)\ \Big|\ Pt$$

A potential difference exists between the two platinum electrodes. If the electrodes were short circuited, electrons would flow in the shorting wire and oxygen would be transported through the electrolyte (as O^{2-} ions) until the partial pressure of oxygen was equal on both sides of the zirconia electrolyte. The open circuit potential difference between the two platinum electrodes is a measure of the tendency of this reaction to occur. The cell is a concentration cell (its potential depends on a concentration gradient of oxygen), and the open circuit potential is given by the Nernst equation

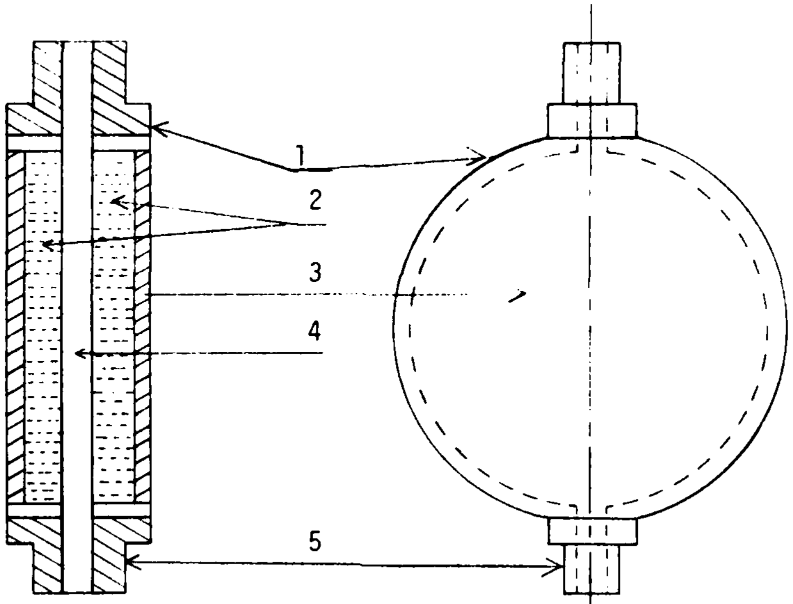
$$E = 0.0496\ T\ \log_{10}\left\{\frac{P_1}{P_2}\right\} + \text{constant}$$

where E is the open circuit potential in millivolts, and
T is the temperature in absolute K.

If the partial pressure of oxygen on one side of the cell is fixed, then measurement of the cell potential provides a measure of the PO_2 on the other side. This principle is utilized in solid electrolyte sensors for measurement of oxygen. Further details of different forms of solid electrolyte cells are given by Rossotti (12) in her chapter "Cell with Solid Electrolytes."

Coulometric Analyzer

Fleet and Tenygl (5,14) have described the use of a porous catalytic silver cathode for determining oxygen. This cathode, which is in fact a fuel-cell electrode, offers a very large surface area for the interface between gas, electrolyte, and electrode. The structure of the electrode is shown in Figure 4; it has a diameter of about 5 cm.



(A) Cross-sectional view (B) External planar view

(1) Nickel frame
(2) Catalytic operating layers
(3) Protective layers
(4) Annular space
(5) Gas inlet and outlet tubes

Figure 4. Porous silver electrode.

The electrode is immersed in a potassium hydroxide electrolyte and forms the cathode in a three-electrode cell connected to a potentiostat. Gas is pumped through the cathode at a slight positive pressure. Because of the very large effective surface area of the cathode, all oxygen in the gas is reduced to hydroxide ions. If the current is integrated over a known time period during which a measured quantity of gas flows through the cell, the percent oxygen can be obtained from Faraday's Law

$$\int I . dt = 4 F N$$

where F is Faraday's constant, and
N is the number of moles of O_2 in the gas sample.

This analytical approach is termed coulometry at controlled potential; further details of the principles are given in texts on instrumental analysis (e.g., ref. 10). The particular advantage offered by the technique is that it eliminates the need for calibration. Coulometry is an absolute method for reactions like the electrochemical reduction of oxygen which can have 100% current efficiency and is made to proceed quantitatively.

The Thallium Electrode

Hahn (7) has described a thallium electrode for the potentiometric measurement of oxygen. The thallium electrode is surrounded by potassium chloride solution, into which is dipped a calomel reference electrode. A gas permeable membrane covers the thallium electrode in a configuration similar to that of the Clark sensor. Figure 5 shows the geometrical arrangement.

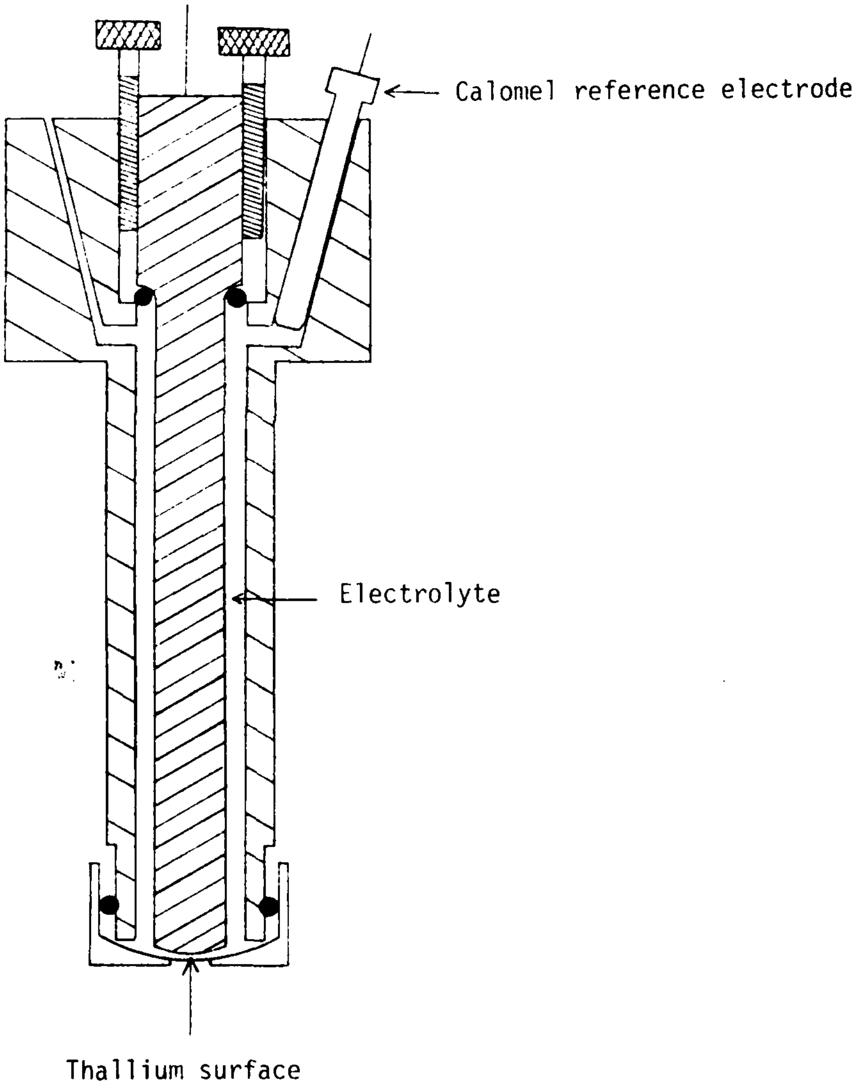


Figure 5. Cross-section of thallium electrode together with calomel reference electrode and electrode-holder assembly.

Oxygen in the electrolyte solution is reduced by thallium to hydroxide ions, while the thallium metal is itself oxidized to thallous ions (Tl^+):

$$O_2 + 4H^+ + 4e \rightleftarrows 2\ H_2O$$

$$Tl^+ \quad + e \rightleftarrows Tl$$

These two half-cell reactions can be combined to give the overall reaction:

$$O_2 + 4\ Tl + 4H^+ \rightleftarrows 4\ Tl^+ + 2\ H_2O.$$

The thalleous ions in solution participate in some fairly complex equilibria, involving higher oxidation states of thallium, hydroxide complexes, and chloride complexes. For simplicity, however, we can assume that the potential of the thallium electrode is determined by the thallous ion concentration in solution through the Nernst equation

$$E = \text{const} + 0.199\ T \log\ [Tl^+]$$

where E is the potential in millivolts, and
T is the temperature in absolute K.

The thallous ion concentration is in turn determined by the oxygen partial pressure in the sample, and thus the electrode potential is related to PO_2. In this approach, the cell potential is measured at zero current. It should be noted, however, that the thallium electrode slowly dissolves on contact with the oxygen.

ACOUSTOMECHANICAL TECHNIQUES

The NBS report 3130 limited the number of recommended approaches to three (4). One of the recommended approaches was by "acoustical methods in which the % oxygen is indicated by a frequency measurement." However, there have been no approaches of a new fundamental nature using an acoustic or mechanical approach since the NBS report. This has been surprising since the basic phenomenon of the acoustic techniques (i.e., the speed of sound) is so well known. A few approaches, though, have used the basic phenomenon of the NBS report along with more recently developed measurement techniques and instrumentation.

Fluidic Sensors

Woods (15,16) has described an attempt to develop a fluidic oxygen partial pressure sensor. This work was sponsored by USAFSAM, Brooks Air Force Base. The device consists of a fluidic bridge circuit with both sides of the bridge containing a linear fluidic resistor (orifice) and a nonlinear fluidic resistor (capillary). A reference gas of known composition flows through one side of the bridge. The gas flowing through the other side has an unknown percentage of oxygen. The method used to determine oxygen content relies on measuring the pressure differential between the two sides of the bridge at a location between the fluidic resistances of each side. The pressure differential is a linear function of the partial pressure of the oxygen if the suction or back pressure on the entire bridge is directly proportional to the ambient pressure.

A low downstream pressure and ambient inlet pressure provide the pressure drop across the fluidic bridge. A fluidic aspirator provides the suction and maintains the suction pressure directly proportional to the ambient pressure. However, the pressure upstream of the aspirator, which is used to drive the aspirator, is at an elevated pressure (above ambient), and the downstream pressure is again the ambient pressure. An alternate approach would have been to provide the bridge flow by means of some mechanical device, but every effort was made to minimize the mechanical components.

Some alternate possibilities exist for the fluidic bridge technique. Rather than fluidic resistance devices, fluidic oscillators may be used. Then basically, the difference in composition of the reference and sample gases can be determined by the difference, or beat frequency, of the two oscillators. Still another approach is the use of a vortex-type sensor. In this case the reference gas and the sample gases flow into a vortex chamber and establish a swirling motion. The swirl angle of the flow is proportional to the gas concentration. Much of the vortex-sensor work was done at the Harry Diamond Laboratories.

In the case of the fluidic resistance bridge, the sensor is much less sensitive to mixtures of oxygen and nitrogen than to other mixtures. To increase the signal strength used to determine the oxygen partial pressure, a fluidic amplifier is used. This does amplify the desired signal, but it also increases the noise and nonlinearity within the system. In addition, the capability of the system decreases significantly as the pressure of the sample gas decreases, so such a device would not work satisfactorily at the low pressures specified for this study. However, the device would not be damaged by low pressures.

Houben and Pabst (8) have described another fluidic device for determining the mixing ratio of binary gases. The basic approach of this device, which has a wall-attachment fluidic oscillator as the central element in the sensor, is similar to the approach discussed previously where two fluidic oscillators were used. In this case only one oscillator (rather than two) is used. The frequency of the oscillator depends on the speed of sound in the gas. The speed of sound in turn depends on the temperature and composition of the gas mixture. The oscillator-frequency and gas-temperature measurements are used to determine the composition of binary gases. The information derived from the fluidic oscillator can be used in a control system to maintain a specified mixture. However, the device was not demonstrated for mixtures of oxygen and nitrogen, which are of primary concern in this study.

Sound Separation Probe

Sound separation probes have been developed recently to study acoustic characteristics internally for gas turbine fan-jet engines. The probe consists of at least two high-response pressure transducers separated by a small distance. Each transducer can detect acoustic signals or acoustic-like signals over a wide range of amplitude and frequency. When the signals of the two transducers are processed properly, the flow turbulence, the downstream radiated noise, and the upstream radiated noise can be separated and analyzed. This is a detailed procedure, but using a similar technique to determine the speed of sound in a mixture is a much simpler task. A sound separation probe has not been used in determining the composition of a mixture of gases, but the development of high-response transducers and advanced electronic devices may make this approach feasible.

Acoustic Phase Shift

Ringwall and Keltz (11) have described another technique that depends on the acoustic characteristics of oxygen. The partial pressure of oxygen depends on the phase shift of an acoustic signal, which may also be used to maintain the partial pressure within required limits. This system utilizes the acoustic transmission properties of a mixture of gases. The central elements of the device are two small piezoelectric elements which are separated by a small distance. One of these elements transmits an acoustic signal of some predetermined frequency through the gas mixture to be analyzed. The other element receives the acoustic signal which is processed electronically to determine the phase relationship between transmitted and received signals. The phase relationship is a function of the distance between the piezoelectric surfaces, the temperature of the gas, and the percentage of oxygen. An additional feature in the device is pressure-sensitive response mechanisms that automatically vary the distance between the transmitting and receiving elements. The device is described as being capable of measuring and controlling the partial pressure of oxygen; however, the technique was developed to work for a helium-oxygen mixture and not an oxygen-nitrogen mixture. It is doubtful that the difference in the acoustic transmission characteristics of oxygen and nitrogen is sufficient to make this approach feasible.

SOLID-STATE OXYGEN-DETECTION TECHNIQUES

The possibility of using semiconductor oxides such as ZnO, SnO, TiO_2, CdO, CoO, ZrO_2, etc., to detect oxygen in various gases has been studied in recent years in an attempt to develop an oxygen sensor relatively insensitive to changes in ambient pressure, flow rate, and concentration and to the position of the sensor itself. Examination of such studies indicates that these devices can be divided into two types, bulk phase and surface adsorption (6).

The operation of bulk-phase detectors is based on the fact that the equilibrium chemical potential of the oxide changes on contact with the oxygen and greatly influences the resistance of the wires or strips of the corresponding oxidized metals. These detectors operate at temperatures of about 1000°C (1830°F) and so are not likely candidates for use in an aircraft oxygen-generating system.

The action of surface adsorption devices is based on the influence of the chemisorption of molecular oxygen (an electron acceptor) on the conductivity of sintered bars or thin films of semiconductor oxides. Oxygen present at even very low concentrations in various gases and mixtures has a significant influence on the conductivity of the semiconductor, similar to the effect on electron-accepting species--such as free radicals on the electrophysical properties of semiconductor films. An equilibrium is reached between the oxygen in the gas phase and the oxygen adsorbed on the semiconductor surface. These detectors can operate at temperatures in the range of 20-500°C (68-930°F) but seem to work best in the 300-400°C (575-750°F) range. Extensive work performed by Wortman et al. (13,17), at Research Triangle Institute under NASA contract on ZnO thin-film oxygen partial pressure sensors, indicates that such devices are feasible.

One main feature of Wortman's work is the demonstration of the practically linear variation of the logarithm of film resistance with reciprocal temperature at constant oxygen pressure in the range from about room temperature to 400°C. The resistance can be represented by

$$R = R_o \exp (E_R/kT)$$

where R_o is a temperature-independent constant, and
E_R is the activation energy of the process.

The value of R_o and E_R depend upon the oxygen content in the gas ambient of the ZnO films; both parameters increase with increasing oxygen content. The following model was developed to explain this behavior and assumes that the increase in resistance is due to the trapping of conduction-band electrons at the surface of the ZnO by adsorbed oxygen.

The resistance at pressure p for oxygen and temperature T is given by

$$R(p,T) = R(O,T) + \Delta R(p,T)$$

$$= R_o + \Delta R.$$

For $\Delta R >> R_o$,

$$R(p,T) \approx \Delta R.$$

If it is assumed that the change in resistance at a constant temperature T is due only to a change in the number of carriers free to move in the material under the influence of an electric field, then

$$R_o = K_R/n_o$$

$$R = K_R n = K_R/n_o - \Delta n$$

$$\Delta R = R - R_o = K_R(1/(n_o - \Delta n) - 1/n_o)$$

$$= K_R \Delta n/(n_o - \Delta n)n_o$$

$$\Delta R/R_o = \Delta n/(n_o - \Delta n) = \Delta n/n_o \div (1 - \Delta n/n_o)$$

$$\Delta n/n_o = \Delta R/R_o \div (1 + \Delta R/R_o)$$

where n_o represents the initial free carrier density, and
Δn, the change in free carrier density.

The constant K_R depends upon the geometry of the sample, the charge per carrier, and the mobility of the carriers. The quantity $\ln(\Delta R/R_o)$ has a slope proportional to the difference in the activation energies associated with R and R_o; i.e., $E_R - E_{R_o}$. Defining $V = E_R - E_{R_o}$, the resistance equation becomes

$$\Delta R/R_o = A_o \exp (V/kT)$$

and

$$\Delta n/n_o = A_o \exp (V/kT) \div (1 + A_o \exp (V/kT))$$

$$= (1 + 1/A_o \exp (-V/kT))^{-1}.$$

The ratio of the change in carrier concentration at temperature T and pressure p to the carrier concentration at T with $p = 0$, is given by the probability of an equilibrium surface coverage at p and T, which is represented by the right-hand side of the last equation. The energy V can be interpreted as an interaction energy between adsorbed oxygen species. If these adsorbed molecules or atoms are mobile, there is a tendency to depopulate the surface as T increases, due to repulsive forces developed as the adsorbed species approach each other. At low pressure the surface population is low enough so that such encounters are infrequent. Raising the pressure raises the adsorbate density and increases the possibility of encounter as T increases. The surface population is assumed to be identical with the number of carriers depleted from the conduction band. The factor exp (-V/kT) may be regarded as a crowding factor. The factor $1/A_o$ depends upon the surface when crowding is ignored.

Unless it is intentionally doped, ZnO is usually found to be an n-type semiconductor, with the donors assumed to be interstitial zinc atoms, Zn_i. At elevated temperatures the interstitial zinc near the oxygen-rich surface in contact with the gas phase is combined with adsorbed oxygen. This creates a concentration gradient which promotes the diffusion of Zn_i to the surface. Because it is highly probable that adsorbed oxygen traps an electron, the electric field created by adsorbed oxygen would be apt to enhance diffusion of ionized zinc interstitial atoms, Zn_i^+, toward the surface.

The reaction taking place at the surface is assumed to be

$$Zn_i^+ + e + 1/2\ O_2 \rightleftarrows ZnO.$$

The equilibrium constant for this reaction is

$$K_1 = (ZnO)/(Zn_i^+)(e)[(O_2)]^{1/2}$$

where the brackets indicate the surface concentrations of the reactant species. The surface concentration of oxygen is determined by the partial pressure of oxygen in the ambient gas, PO_2, the gas temperature, T_G, and the surface temperature, T_S. It is also influenced by the presence of other gases and their adsorption characteristics because molecules of other gases are in competition for surface sites.

The amount of ZnO at the surface is given by

$$(ZnO) = K_1(Zn_i^+)(e)(O_2)^{1/2}.$$

If there is a high concentration of electrons, due perhaps to donor species other than zinc interstitials, the tendency is to increase the surface concentration of ZnO and deplete the Zn_i concentration until equilibrium is reached. If Zn_i is the only donor source, the equilibrium equation

$$(Zn_i) = K_2(Zn_i^+)(e)$$

must hold, and the preceding equation may be written as

$$(ZnO)/(Zn_i) = K_1/K_2 \times (O_2)^{1/2}.$$

The equilibrium constants K_1 and K_2 depend on the change in free energy of the respective reactions and on the temperature in the form

$$K = \exp\ (\Delta\mu/kT)$$

where $\Delta\mu$ is the change in free energy. Then

$$(ZnO)/(Zn_i) = (O_2)^{1/2}\ \exp\ (\Delta\mu/kT)$$

which states that at equilibrium there is a fixed ratio of the concentrations of oxygen, hence the ambient oxygen partial pressure, and of the temperature.

If the temperature and oxygen partial pressure are sufficiently large, the number of remaining Zn_i should be small. Then the bulk donor concentration no longer dominates the electrical behavior, and the donor species is assumed to be located at the ZnO surface. This is most likely due to the disruption of the Zn-O bond, which is the inverse reaction of that leading to the formation of ZnO at the surface. This bond disruption permits oxygen to leave the surface and enter the gas phase, leaving behind free zinc to ionize and free an electron into the conduction band. The ionization energy of the zinc is small compared to the bond disruption energy that dominates the process. The ionized zinc tends to diffuse away from the surface, but at a slow enough rate so that if the oxygen partial pressure of the ambient gas is increased, the electrons can be retrapped at the surface and the zinc and oxygen recombined.

From the last equation, the ratio of $(ZnO)/(Zn_i)$ is dependent upon the square root of the surface concentration of oxygen. Thus the number of disrupted Zn-O bonds at the surface and number of free electrons should decrease as the square root of the oxygen surface concentration, which is directly proportional to the ambient oxygen partial pressure. Therefore,

$$(O_2)\text{surface} = A_oPO_2$$

where A_o is a proportionality constant.

An oxygen-partial-pressure sensor made of sputtered ZnO thin films over a silicon-bar heater element was constructed and tested by Wortman (Fig. 6). Circuits for temperature control and signal conditioning were also designed and tested (Figs. 7 and 8). The sensor was relatively inert to nitrogen, carbon dioxide, and argon gases, but water vapor changed the characteristics to an important degree. About 2.5-W power consumption was required to maintain the sensor at the operating temperature of about 400°C required for optimum response. By using 4-ohm-cm p-type silicon, reliable high-temperature contacts could be made to the heater bar and the ZnO film, and the current required could be kept at levels on the order of 100 mA. Film thickness was an important factor in the response but not in the sensitivity to changes in the conductance. Film thickness of about 900 Å exhibited 10-90% response times of 20-30 seconds to step changes in oxygen partial pressure.

Based upon the results achieved by Wortman (17) and upon other reported work, construction of oxygen partial pressure sensors from semiconductor oxide thin films that meet the requirements for use in aircraft oxygen-generating systems appears to be feasible and offers the possibility of further development.

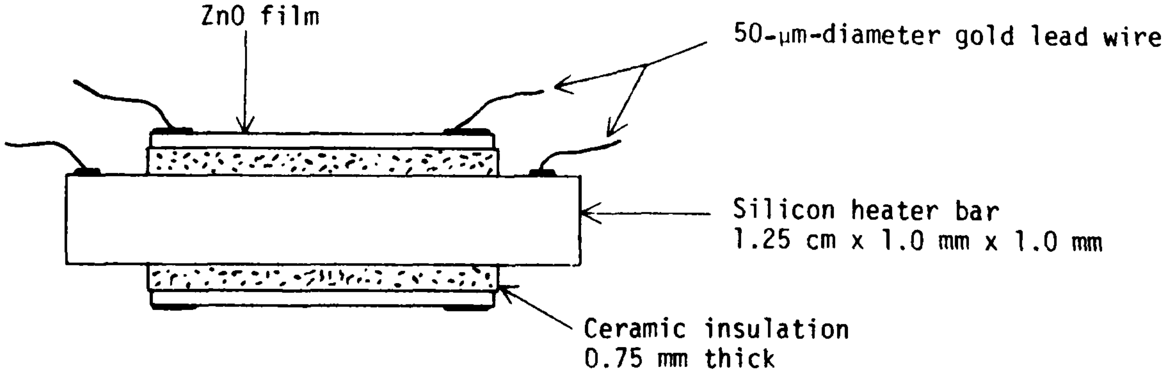


Figure 6. Cross-section of thin-film oxygen sensor.

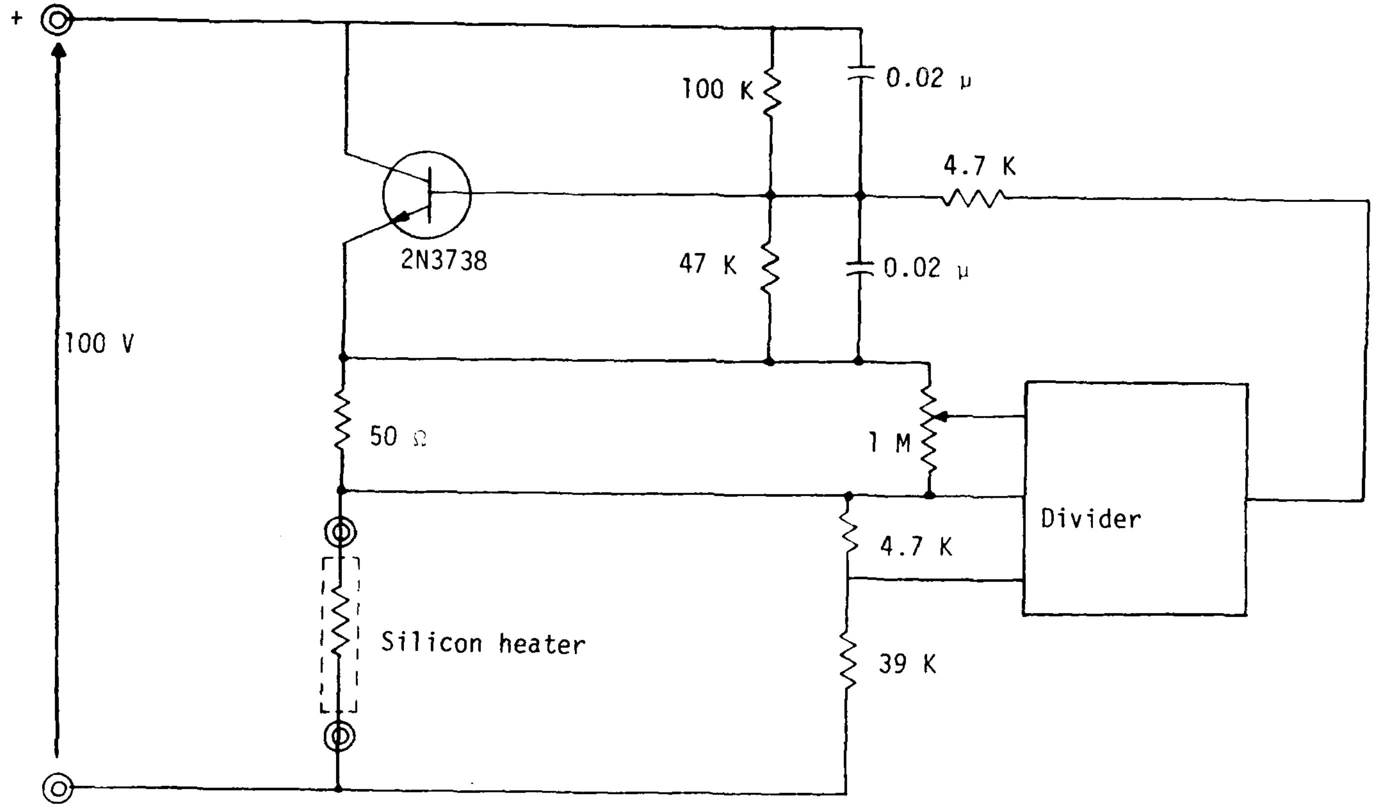


Figure 7. Schematic diagram of heater controller using divider network.

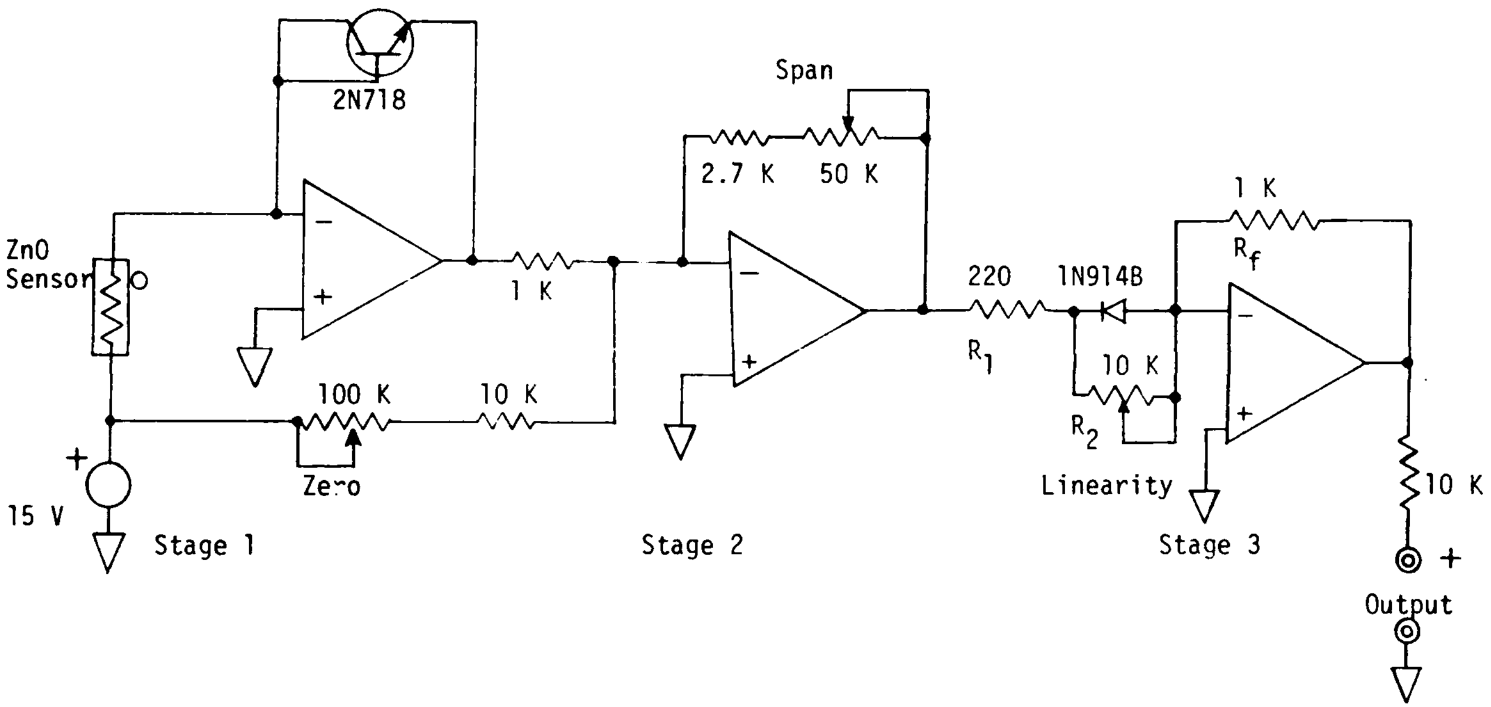


Figure 8. Signal-conditioning circuit.

CONCLUSIONS

The commercial market has concentrated mainly on chemical-type oxygen sensors. We believe that industry in general is "on top" of the opportunities for improving chemical-type oxygen sensors and that new developments in these sensors will therefore most likely come from that area. In the solid-state sensor area, however, most of the work has been very fundamental, and oxygen-sensor development has not been pursued by industry. The thin-film semiconductor oxide sensor described in this report has certain shortcomings (e.g., long response time, poor sensitivity at low temperatures, and individual calibration required for each device), but the principles on which it is based are sound. Further investigation and research concerning this device, to include different semiconductor oxides and different device configurations, could well result in the development of an oxygen sensor that satisfies the requirements.

Our survey related to acoustomechanical techniques for determining the oxygen content in a mixture of gases has shown no recent developments of a fundamental nature other than the introduction of fluidic devices. However, work has been done to apply the basic phenomenon, and descriptions of the devices have been included in this report. Other approaches applicable to pollutant monitoring or that require a combustion process in the device have not been included in this report since their application to an oxygen monitor for respiratory gases seems unlikely. The basic recommendation by the 1954 NBS report remains valid. Acoustic phenomena and the speed of sound are well-known physical effects related to gases and gas-mixture composition. Further work in the area of acoustomechanical techniques appears possible, as suggested in the recommendations section of this report.

Measuring the speed of sound in a mixture of gases by any one of a number of techniques is an example of such a phenomenon. Although the measurement of acoustomechanical phenomena appears relatively simple, no commercial devices are available that use acoustomechanical techniques. The acoustomechanical approaches have apparently not met with complete success in the past; however, an acoustomechanical device (if developed) might be much less susceptible than available devices in adverse operating conditions such as low temperatures or pressures.

RECOMMENDATIONS

We believe that the solid-state area offers good promise for the development of improved oxygen sensors and that further research should be conducted. The thin-film semiconductor oxide sensor should be seriously considered as a viable approach to meet the stated requirements for an on-board, real-time sensor for high-performance aircraft.

The area of fluidics also warrants further investigation. A fluidic-oscillator approach similar to that described in this report should be considered. The modified sound-separation probe should also be considered as a possible acoustic approach. Questions of measurement sensitivity are of the greatest concern here.

Of the recommendations given, we believe that the solid-state area holds the best promise for immediate improvement. Research efforts should initially be concentrated to eliminate the calibration problems associated with the thin-film oxide solid-state sensor.

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