ELECTROCHEMICAL METHOD
FOR CONTINUOUS DETERMINATION
WITH FAST RESPONSE OF OXYGEN IN GASES*

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

An electrochemical method is described for a continuous determination with fast response of oxygen in gases. The electrochemical cell consists of two reference, reversible, non-polarizable electrodes and an indication, hollow, graphite electrode. All the electrodes are immersed in the same electrolyte consisting of sulphuric acid for storage batteries. A scheme of a simple electrical circuit and characteristics of the cell are given. The linear dependence of the electric signal on the partial pressure of oxygen is discussed.

The continuous determination of oxygen with fast response is of great significance in the industry as well as in the research work[1,2]. The review of different methods for oxygen determination is given by Hobbs[3]. Some types of analysers are evaluated by Váňa[4] from the point of view of their practical applications.

In a study of kinetics between the diluted gaseous sulphur dioxide and solid alkaline carbonates we had to follow continuously and with fast response the concentration of oxygen in a gas mixture the composition of which approached the flue-gases. The following conditions were to be fulfilled: *a*) an instantaneous information on the right concentration of oxygen, *b*) continuous measurement, and *c*) the insensitivity with respects to carbon dioxide which is contained in flue-gases at higher concentrations and elimination of its effect on the life-time of the sensor. Similarly the other possible admixtures in flue-gases must not interfere with the determination.

The electrochemical method has been investigated partially because of its great selectivity to oxygen partially because it renders possible an eventual automatization.

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* The method described is the object of the following patents: Czechoslov. Pat. 123 256; French Pat. 1 441 603; Brit. Pat. 1 066 513; Us-Pat. 3 432 404, and Japan Pat. 537 466.

EXPERIMENTAL

Electrochemical Cell

We have proposed and investigated a cell in which the effect of carbon dioxide is eliminated in the whole concentration range by using an electrolyte with the pH value lower than one, in contrast to Kordesch and Marko[6] and to Jacobson[7] who proposed cells for determination of oxygen in a flowing gas where the carbon dioxide is interfering.

The electrochemical measuring cell[5] consists of a commercial lead storage battery and an indication electrode. The lead storage battery represents a system of two reference, reversible, and non-polarizable electrodes which render possible to branch off an optimum potential for the indication electrode. In praxis, one cell of the lead storage battery of capacity 14 Ah has been used from which one negative and one positive plate have been removed so as to get the space necessary for the indication electrode. The remaining negative electrode situated in front of the indication electrode has been provided with a separator which prevented the penetrating of bubbles into the space of the indication electrode. An opening has been drilled into the battery casing into which the indication electrode has been inserted. The packing ring has been made from silicone rubber which has been sealed into the casing by means of picein. This packing exhibited the sufficient elasticity and prevented the leaking and creeping of the electrolyte. The cell adapted in this way has been sufficient for 175 hours of operation without charging with a potentiometer resistance R_3 of 50 ohms. The discharging of reference electrodes can be prevented by setting a potential from an external source to reference electrodes so that the operation time is not limited by the capacity of the reference electrodes.

Indication Electrode

The indication electrode in the cell mentioned above has been a porous graphite electrode depolarizable by oxygen which consisted of a glass tube closed at one end by a hollow graphite cone. On the other end the inlet and outlet tube were situated. The inlet tube leads into the hollow graphite cone and, in this way, a thorough and rapid washing out of the electrode with the gas to be analysed is ensured and the dead spaces are eliminated (Fig. 1). A sealed-in silver wire forms an electrical contact. The inner walls of the electrode are silvered. The hydrophobization of the electrode has been carried out with substances on the base of silicones dissolved in benzene.

Thermostat

The electrochemical cell has been kept at a constant temperature in a thermostat formed by an aluminium block provided with a heating wire on the external walls and with a resistance thermometer on a part of its internal surface. The heating input amounted to 50 W. It has been possible to vary the temperature in the range of 25—35°C and the fluctuation of the temperature did not exceed the value of ± 0.05°C.

Scheme of Electrical Circuit

The electrical circuit into which the electrochemical measuring cell is inserted is given in the Fig. 2. The reference electrodes of the lead storage battery B are connected to potentiometer R_3 with a total resistance of 50 ohms which is divided in the ratio 1 : 9. Thus the branched off voltage is by 200 mV lower than the potential of the negative electrode. The most advantageous range for the measurements has been found by experiment from 175 to 200 mV. The indication electrode E is connected to the branched off voltage through the variable loading resistances R_1 and R_2.

The variable loading resistances have been made from laboratory decades Metra XL 6. For current measurements it is sufficient to use only one loading resistance. The circuit described above has been selected so that it were possible to measure the characteristic properties of indication electrodes at variable current intensity. The voltage on the resistance R_1 has been measured with an electronic compensation millivoltmeter with a range of $0-2$ mV.

Measuring Procedure

The calibration gas mixtures of different oxygen concentrations have been prepared so that the nitrogen has been continuously fed into the air and the flow rate of individual components has been measured by means of calibrated flowmeters. To achieve a thorough mixing of both components the glass tubing of internal diameter of 3 mm has been provided with a glass jet and with a bed of glass beads of diameter from 0·4 to 0·5 mm which has been fixed by sealed-in platinum gauze.

It is necessary to emphasize that the cells with different indication electrodes didn't yield the same values of the electromotive force and of internal resistance, however, certain characteristic properties of the cell remained the same. The observed dispersion of these values has been caused in the first place by the fact that in preparing the indication electrodes it is not possible to keep the exactly same value of the surface area of the graphite part of the electrode which affects significantly the current output even though the preparation procedure has been standardized. Equally the porosity of the indication electrode may be altered in the course of its preparation. The calibration of the cell has been carried out with a gas of known composition. Because of the linear dependence a single check-point is sufficient and, therefore, the simplest way of calibration is the calibration with the air. In the calibration the resistance R_1 is adjusted so that the recorder indicates 21% of oxygen (1·68 mV) with the air passing through the indication electrode (in current measurements the resistance R_2 is omitted). In this way it is possible to adjust an arbitrary range, however, for ranges smaller than 21% of oxygen it is necessary to use calibration mixtures with a corresponding concentration of oxygen.

For a possible automatization of this method, the range is of interest in which it is necessary to vary the loading resistance with individual electrode so as to get a convenient constant voltage
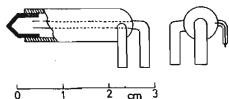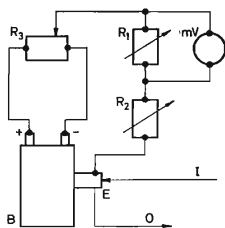

FIG. 1

Indication Electrode

FIG. 2

Electrical Scheme

I Inlet of the analysed gas; O outlet, the remaining symbols are expained in the text.

on the loading resistance R_1 with the air passing through the indication electrode. For a great number of electrodes the value of the loading resistance ranged within the limits of $2-25$ ohms.

The electromotive force of the cell has been determined by measuring the voltage at various current intensities on passing the air through the indication electrode. The value extrapolated to zero current represents the electromotive force (Fig. 3). In a great number of measured cells the value of EMF varied within the limits $310-330$ mV. The values of internal resistance of the cells R_i varied within broader limits from 500 ohms up to 3000 ohms and has been evaluated from the equation

$$\text{EMS} = J(R_e + R_i), \qquad (1)$$

where R_e is the resistance of the external circuit and J is the current intensity.

The dependence of the depolarization current (which is given by the voltage on the resistance R_1) on the partial pressure of oxygen at various current intensity is vizualized in Fig. 4. This characteristic dependence has been shown with all the cells measured even though the values of loading resistances diferred greatly. The values are given for one of the electrode hydrophobized with a 2% solution of the paraffin in benzene.
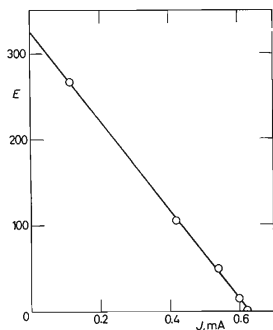

Fig. 3

Dependence of the Cell Voltage (in mV) on the Current Intensity at the Partial Pressure of O_2 of 0·21 atm

DISCUSSION

From the experimental data it follows that the cells at high current intensities exhibit a linear dependence of the voltage E on the partial pressure of oxygen. This linear dependence has been found in the whole concentration range. In contrary to this the cells at low current intensity exhibit a logarithmic dependence which can be explained by the fact that at low intensities the measurement of electromotive force is approached, and, consequently, the effect of partial pressure will follow the Nernst equation.

At high current intensities the rate of the generating reaction will depend on the kinetics and mechanism of the reaction. The mechanism of the generating reaction and the effect of separation of the electrolyte from the gas to be analysed may be explained in the following way. The electrochemical cell consists of two reference,

reversible, and non-polarizable electrodes, and of a hollow, porous, graphite indication electrode activated with silver. All the electrodes are immersed in the same electrolyte which is formed by the sulphuric acid of the density 1·24. The indication electrode forms a three-phase boundary electrolyte–electrode–gas. The electrolyte penetrates into the pores of the porous graphite electrode only partially and owing to the hydrophobization it cannot penetrate to the other side of the electrode which is in contact with the gas. Under the influence of the inserted potential which is by 200 mV lower than the potential of the negative electrode with respect to hydrogen[8], the hydrogen ions from the solution begin to be discharged and the formed hydrogen remains adsorbed in that part of pores which is not filled up with the electrolyte. If this adsorbed hydrogen is not exhausted in the chemical reaction with oxygen a stationary and practically currentless state is established since the molecular gaseous hydrogen can't be set free at the potential given owing to the existing hydrogen overvoltage on the material of the indication electrode[9]. If the oxygen is present in the gas to be analysed it begins to react with the hydrogen adsorbed on the wall of pores on the side of the electrode exposed to the gas. The stationary state is disturbed by this decrease of the adsorbed hydrogen, and the adsorbed hydrogen begins to migrate quickly on the surface of the pores to the gas side of the electrode. In this way the stationary adsorbed amount in the immediate vicinity of the electrolyte decreases and consequently additional hydrogen ions begin to be discharged from the electrolyte and the discharging current formed in this way represents the measure of exhausting the hydrogen, and also the measure of oxygen concentration in the gas to be analysed. In this arrangement it is not necessary for the oxygen to get to the three-phase boundary electrolyte–electrodes–gas and, therefore, a direct contact of the analysed gas with the electrolyte need not occur, since the transport is realized by a fast surface migration of the adsorbed hydrogen and not by dissolution and diffusion of oxygen in the liquid phase, which are relatively slow processes as it is generally known. Thus the unusually great response rate may be explained in this way by a very quick transition from one stationary state into another. For illustration sake the record is given in the Fig. 5 of a sudden change of oxygen concentration *viz.* from the air to nitrogen and conversely. The value τ_{95} denotes the time necessary for reaching 95% of the final deflection.

The typical behaviour of the electrochemical cell under different partial pressures and at different current intensities may be explained by the following consideration. The electromotive force of the cell is determined by the relation

$$\text{EMS} = JR_i + E = J(R_i + R_e),\qquad(2)$$

where E is the terminal voltage. Let us assume in agreement with experiments that the electromotive force is a function of the temperature only. Further let us assume that the internal resistance R_i is a function of the partial pressure of oxygen and of the temperature. In the place of the internal resistance it is more adequate to consider

the internal conductance defined by the relation

$$G_i = 1/R_i . \qquad (3)$$

Finally let us assume that in the first approximation the internal conductance will be directly proportional to the partial pressure of oxygen, i.e.

$$G_i = k . p_{O_2} , \qquad (4)$$

where the proportionality constant k will be a function of temperature only. From the equations (2), (3), and (4) we obtain a relation for the current intensity

$$J = \text{EMS} . p_{O_2}/(a + R_e . p_{O_2}) . \qquad (5)$$

where

$$a = 1/k = R_i . p_{O_2} \qquad (6)$$

In the case mentioned above (Fig. 3), the electromotive force has been calculated by the method of averages and amounted to 322·0 mV. From the equation (2) we obtain for the internal resistance a value of 509·3 ohms, and, therefore, for the constant a from the equation (6) we obtain the value of 106·6 ohms atm.
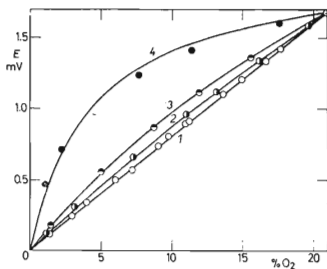

FIG. 4

Dependence of the Cell Voltage on the Partial Pressure of Oxygen at Different Current Intensities.

1 $R_e = 2\cdot7$; *2* $R_e = 92\cdot6$; *3* $R_e = 252\cdot3$; *4* $R_e = 2383\cdot0$; the full line denotes the calculated values.
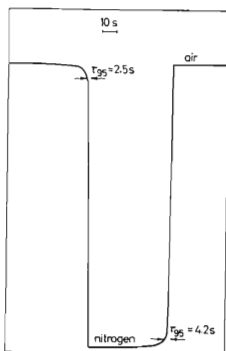
FIG. 5

Record of the Sudden Change in Oxygen Concentration from the Air to Nitrogen and Conversely

As it is evident from the electrical circuit (Fig. 2) the current has been measured as a voltage on the resistance divider and for different current intensities it has been necessary to adjust the air point so that the voltage V in mV read off on the measuring millivoltmeter at different current intensities has been recalculated according to the relation

$$V = 1.68 . J/J_{0.2093} , \qquad (7)$$

where $J_{0.2093}$ indicates the current which flows through the resistance R_1 and produces on this resistance the standardized voltage of 1.68 mV, with the air passing through the indication electrode. The current J is then determined by the equation (5). By combining the equations (5) and (7) we obtain a relation expressing the dependence of the voltage measured across the resistance R_1 on the oxygen partial pressure at different external resistances R_e

$$V = B . p_{O_2}/(a + R_e . p_{O_2}) , \qquad (8)$$

where

$$B = 1.68 . \text{EMS}/J_{0.2093} .$$

For the case mentioned above the following values of the constant B have been found at different external resistances

R_e, Ω	2.7	92.6	252.3	2 383.0
B	860.0	1 011.1	1 279.6	4 860.3

The values calculated from the relation (8) are vizualized in the Fig. 4 by full lines. The simple and reasonable assumption that the internal conductance is directly proportional to the oxygen partial pressure reproduces the measured data with a sufficient accuracy.

CONCLUSIONS

The method described above makes possible to determine the oxygen concentration in a streaming gas in a simple way and its advantages may be summarized as follows:

1. The determination is continuous and in a wide range independent of the flow rate through the indication electrode. No effect has been observed in the range

of flow rates from 50 up to 500 ml/min. At low oxygen concentrations and at flow rates below 10 ml/min only, it may be assumed that the change in the flow rate would have an observable effect. *2.* The short response time makes possible to follow quickly the changes of oxygen concentration in the gas to be analysed. *3.* The carbon dioxide at an arbitrary concentration does not interfere with the determination nor affects the life-time of the sensor. Similarly the hydrogen, the carbon monoxide, the saturated and unsaturated hydrocarbons, water vapour (up to a concentration at which no condensation takes place inside the indication electrode) do not interfere. *4.* The long life-time of the sensor which is achieved by the continuous regeneration of the reference electrodes during the measurement. The life-time of the indication electrode under laboratory conditions varied within the limits from four up to six months. Under heavy industry conditions where the flue-gases from the air preheaters were analysed and were purified by means of a filter filled up with sodium hydrogen carbonate only, the electrodes exhibited the life-time from one to four months. *5.* The explosive mixture can be analysed safely. *6.* The presence of solid aerosols in the analysed gas does not interfere. *7.* The calibration can be achieved by a single check point owing to the linear dependence of the electric signal on the partial pressure of oxygen. *8.* The measuring range can be varied arbitrarily and simply.

Further on, the method described possesses the prerequisites for a complete automatization the calibration including, and it has been applied in praxis already. A fully automatic instrument[10] has been designed on the principle described above which has been tested for the analysis of flue-gases and proved to be a useful apparatus[11].

LIST OF SYMBOLS

EMS	electromotive force
J	current
R_i	internal resistance of the cell
R_e	resistance of the external circuit
G_i	internal conductance
E	terminal voltage
V	voltage in mV measured on the resistance R_1
p_{O_2}	partial pressure of oxygen

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