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ARTICLES

Determination of Oxygen in Gas Media Using a Gas-Diffusion Electrode Based on Manganese Dioxide

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Abstract—It was shown that manganese dioxide isolated from a fluoride-containing electrolyte can be used as an electrode material for determining oxygen in gas media.

The control of biochemical processes, monitoring of gas media, development of special medical equipment, and modernization of defensive arms are closely related to the development of chemical sensors [1, 2]. Sensor technology is being actively developed in Japan, Germany, United States, and Great Britain. It is noteworthy that the control of process gases, workplace air, and air basins is one of the most important problems. Most of commercial electrochemical sensors are based on chemically active electrode materials and liquid or solid electrolytes [3, 4]. The main advantage of electrochemical sensors based on gas-diffusion electrodes is that the analyte is involved into the current-generating reaction. This ensures a high sensitivity and 100% selectivity of the sensor. The selectivity of an electrochemical sensor depends on the electrode material acting as a current diverter; therefore, the electrode must possess high electric conductivity and chemical, thermal, and mechanical stability. These properties are inherent to some metal oxides and their compositions.

Sensors based on SnO, ZnO, TiO_2, and NiO oxides [5] and manganese-containing spinels have found wide application. Inexpensive electrode materials with high catalytic and electrochemical activity are searched for. A similar problem arises with electrodes for fuel cells. In both cases, peroxide and hydroxide ions should rapidly form in aqueous solution in the presence of a catalyst. The catalyst should promote the decomposition of hydrogen peroxide [6]. It was found that catalytic activity enhances when the catalyst structure is disordered [6]; therefore, manganese dioxide with the general formula MnO_x ($1.7 < x < 2$) [7] offers promise. This is a common and inexpensive oxide, whose structure and properties are determined by the preparation procedure [7, 8].

The aim of this work was to study manganese dioxide [7] as an electrode material for an oxygen sensor.

EXPERIMENTAL

Manganese dioxide prepared from a fluoride-containing electrolyte [7] was studied. A two-layer porous gas-diffusion electrode (which represents a three-phase electrode–electrolyte–oxygen system) was used as an indicator electrode. The analyte gas diffused through a hydrophobic layer and entered into the current-generating reaction in the current generation zone at the three-phase interface. The electrode (d = 30 mm) was prepared by pressing. The hydrophobic layer contained 0.3 g of acetylene soot and 25% polytetrafluorethylene as a binding agent; the active layer contained 0.3 g of manganese dioxide. Its composition is given in the table. The electrolyte was a solution of 5 M NH_4Cl and 2 M $ZnCl_2$ in distilled water. The auxiliary electrode was fabricated from metallic zinc (S = 15 cm^2). The cell operated like a zinc–air chemical battery. All potentials are given against the Ag/AgCl reference electrode. The voltage–current characteristics of the detector were measured using a three-electrode cell; current was generated with a high-resistance voltmeter and a microampermeter in the cell for testing the air electrode (Fig. 1). The sensitivity of determining oxygen in a gas mixture was estimated by comparing the currents measured at the same electrode potential in different gas media. The potential was recorded at the maximum load and minimum background current under an argon atmosphere. The measurements were conducted under an argon atmosphere (0% oxygen), in air (21% oxygen), and in a stream of pure oxygen (100%), beginning with the oxygen-free atmosphere. Before measure-

Composition of electrolytic manganese dioxide isolated from a fluoride-containing electrolyte

Mn(IV), %	Mn(III), %	Mn(II), %	H_2O_{total} (%)	OH^-, %	x in MnO_x
50.8	5.4	0.3	9.9	2.2	1.95

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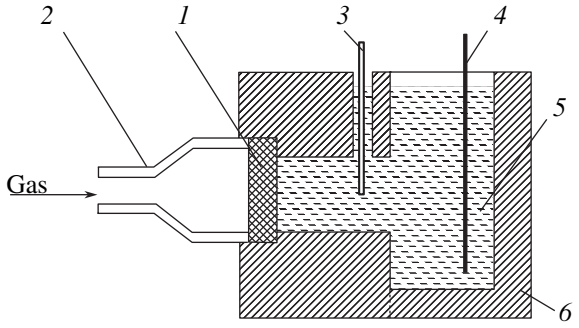

Fig. 1. Schematic diagram of an electrochemical cell: (*1*) indicator electrode; (*2*) gas supply chamber; (*3*) reference electrode; (*4*) auxiliary zinc electrode; (*5*) electrolyte; (*6*) cell case.

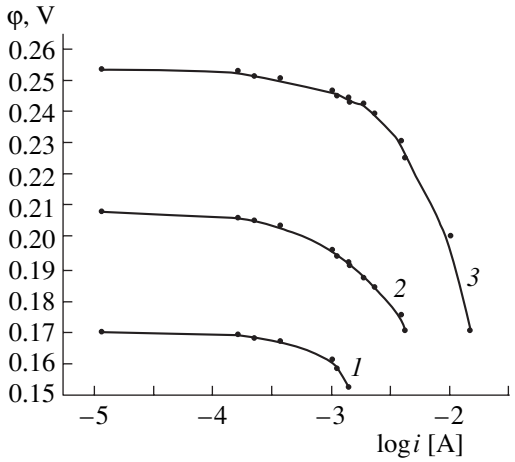

Fig. 2. Potential–current plots in different gas media: (*1*) argon; (*2*) air; (*3*) oxygen.

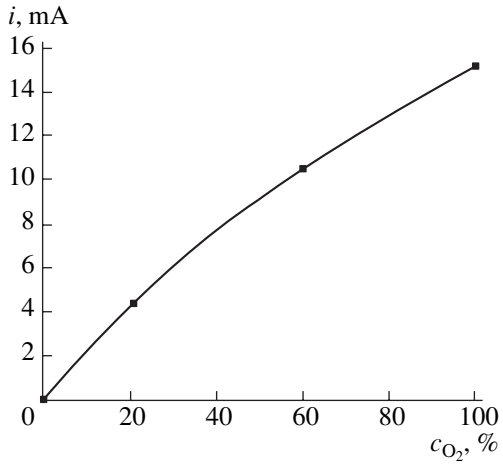

Fig. 3. Current as a function of oxygen concentration.

ments, the electrode was kept in the corresponding medium for 1 h under a small positive pressure created with a rubber cushion and controlled with a manometer. Under a load of 1×10^5 Ω, the electrode potential was measured and the voltage–current characteristic was recorded under an argon atmosphere. Next, the gas mixtures were successively changed, and the voltage–current characteristics were recorded after 15 min (when the electrode potential was stabilized).

In each medium, measurements were conducted while gradually decreasing the load until the potential of the indicator electrode became equal to that in an argon atmosphere; the characteristics obtained were compared. The voltage–current characteristics of the electrode based on manganese dioxide in different gas media are shown in Fig. 2.

RESULTS AND DISCUSSION

From the experimental results it follows that potentials equal to those established in an argon atmosphere were attained in the gas media at minimum loads. It should be noted that, after unloading, the electrode potential returned to its initial value; therefore, no irreversible changes in the composition of the gas-diffusion electrode took place during measurements.

The results of sensitivity measurements of the manganese dioxide–based indicator electrode are shown in Fig. 3. The sensitivity of the indicator electrode was estimated from the relationship between the current and oxygen concentration in the studied gas media.

As oxygen concentration in the gas media increased from 0 to 21%, the current increased by 370 times, which is indicative of the high chemical and catalytic activity of the manganese dioxide studied. This is also confirmed by the higher constant of hydrogen peroxide decomposition (2.17×10^{-4} s^{-1}), which is due to the significant disordering of this manganese dioxide species [8] compared to that of manganese dioxide isolated from the EDM-2 sulfate electrolyte (1×10^{-4} s^{-1}).

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