PREVENTION OF CARBONIZATION IN THE ALKALINE ELECTROLYTE OF OXYGEN SENSOR

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Amperometric oxygen sensors are the basis for air quality monitoring systems to ensure its suitability for human breathing. The first sensors of this type were realized as a Clarke element with an alkaline electrolyte. Today, global manufacturers have abandoned such a system as a result of unresolved problems associated with the carbonization of KOH under the influence of carbon dioxide gas. This work shows that complete carbonization of the electrolyte in the Clarke element is fundamentally impossible due to the preferential formation of lead carbonate during the functioning of the lead anode of the sensor. In the presence of metallic lead in the electrochemical system, the electrolyte composition is spontaneously maintained as a mixture of KOH and K_2CO_3 with high osmotic properties (the solution does not dry out on contact with natural air) at a pH of 13.1. The phenomenon of blocking a part of the working electrode surface by $KHCO_3$ crystals is revealed under the condition that the sensor is stored without generating a current. This phenomenon is eliminated if the sensor generates a current of oxygen reduction in conditions of pulsating air pressure drops. The possibility of creating an amperometric oxygen sensor based on the Clarke system with three electrodes is shown. Such a sensor has an extended service life. Carbonization of the electrolyte of such sensor is eliminated by decomposition of $KHCO_3$ to K_2CO_3 at a high current density, reduces the pH of the solution at the surface of the auxiliary platinum electrode. Due to this, carbon dioxide is removed from the electrochemical system together with oxygen formed in the anodic decomposition reaction of water. The advantage of electrochemical systems based on the Clarke element is a lower consumption of electricity: in a two-electrode system, only the signal strength measurement circuit consumes energy, and in a three-electrode system, the cell voltage is reduced due to the replacement of sulfate anions (modern sulfuric acid-based sensors) with hydroxyl anions.

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for its suitability for human respiration. Electrochemical systems of oxygen sensors can contain two or three main electrodes. Two-electrode oxygen sensors were developed on the basis of the Clarke element [1] for a long time. This system consists of a platinum working and auxiliary lead electrodes, separated by a 30% KOH electrolyte solution. Famous manufacturers of amperometric sensors have refused to use the Clarke system due to some operational problems, which are explained by the propensity of this system to carbonization [2,3]. Indeed, KOH interacts with the carbon dioxide of air. This interaction leads to the formation first of K_2CO_3 and further to $KHCO_3$. The osmotic properties of these salts are weaker than in KOH, as a result of which the electrolyte solution begins to lose water. It is known that the K_2CO_3 solution completely dries out at relative humidity of atmospheric air, which corresponds to a range characteristic of natural conditions and also of workers and living spaces.

The problems caused by carbonization are radically solved by replacing the electrolyte of Clarke element (using acetate buffer based on ammonium acetate [2]) and using exclusively platinum electrodes and aqueous solution of sulfuric acid (mainly the production of three-electrode and four-electrode sensors [3]). The first solution causes a problem of very large background currents, and the second solution leads to large power outlays in portable devices.

This proceeding proves that the problem of carbonization of the electrolyte of Clarke element is not perceived correctly. It is also possible to significantly reduce energy spending when implementing three-electrode or four-electrode sensors based on 30% KOH.

Research methodology

The basis for the research was the thermodynamic calculations of the probability of parallel electrochemical reactions. The experiments were performed on a two-electrode (Fig. 1a) and a three-electrode (Fig. 1b) cells containing a working electrode 4 with 6 mg of platinum black. The auxiliary electrode 6 of the two-electrode sensor (Fig. 1a) was pressed from 18 g of lead granules. In a three-electrode sensor (Fig. 1b), a reference electrode 7 was made by pressing 5 g of lead granules, and an auxiliary electrode 6 was made of platinum wire with a diameter of 0.1 mm and a length of 10 mm. The electrodes are separated by a porous separator 5 which is impregnated with an aqueous solution of 30% KOH. The oxygen reduction current was limited by diffusion resistance 2 with a calibrated hole 3. The signal current of the two-electrode sensor was recorded with a potentiometer 9 (Fig. 1a) after the voltage drop across the resistor 8. The current of the signal of the three-electrode sensor was recorded by dint of the potentiostat ПИ-50-1.1 10 (Fig. 1b) with the potential of the working electrode equal to the potential of the reference electrode 7 (is approximately -0.60 V in the 30% KOH solution on the

hydrogen scale). Pressure drops for pulsed polarization of working electrodes were created by squeezing an elastic balloon in which the sensor was placed. The value of the difference was recorded with a U-tube manometer. The determination of the salt cation was carried out by the atomic absorption method. The carbonate anion was detected by gas evolution when reacted with a drop of sulfuric acid under a microscope. Resistance between electrodes of electrochemical cells was determined by an AC bridge at a frequency of 10 kHz.
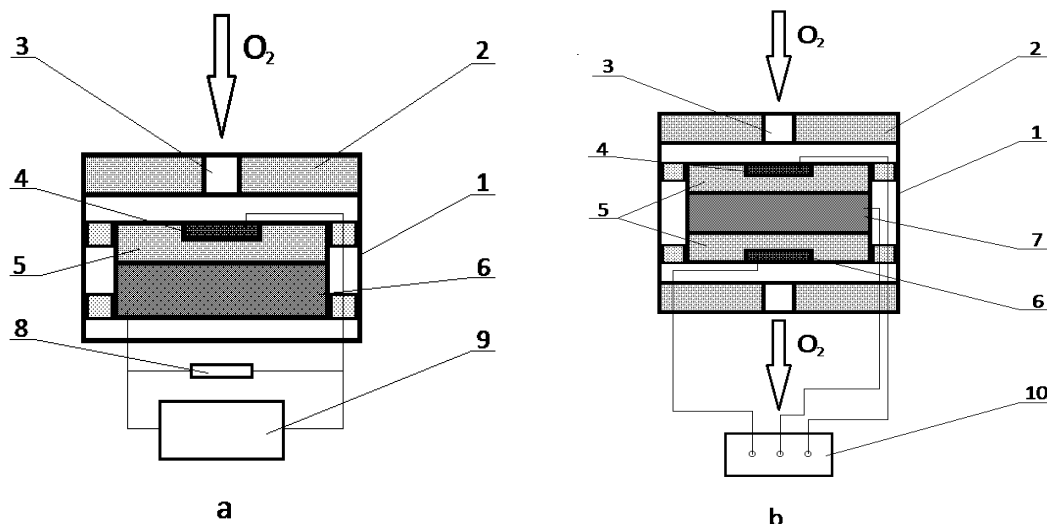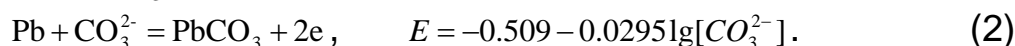

Fig. 1. Scheme of two-electrode a) and three-electrode b) oxygen sensor based on 30% KOH solution: 1 - case; 2 - diffusion resistance; 3 - calibrated hole; 4 - working electrode; 5 - separator; 6 - auxiliary electrode; 7 - reference electrode; 8 - the resistor; 9 - potentiometer; 10 - potentiostat.

Results and Discussion

Anodic oxidation of the lead electrode in KOH should proceed with the formation of PbO:

$$\mathrm{Pb + 2OH^- = PbO + H_2O + 2e}, \qquad E = 0.248 - 0.059\,pH, \qquad (1)$$

and/or PbCO$_3$

$$\mathrm{Pb + CO_3^{2-} = PbCO_3 + 2e}, \qquad E = -0.509 - 0.0295\lg[CO_3^{2-}]. \qquad (2)$$

Solutions system of equations (1) and (2) is an equation

$$25.7 = 2pH - \lg[CO_3^{2-}]. \qquad (3)$$

Total transformation 30% KOH gives a solution 5.0 mol/L K$_2$CO$_3$ with water activity 0.6 and activity factor of electrolyte about 0.7. Therefore, calculation in equation (3) gives pH 13.1. Below this pH value, carbonate accumulation in solution thermodynamically impossible because of preferred the reaction (2). That is, the total reaction in the sensor

$$\mathrm{Pb + O_2 + 2K_2CO_3 + 2H_2O = 2PbCO_3 + 4KOH} \qquad (4)$$

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maintains a pH not lower than pH 13.1 and counteracts complete carbonation and drying of the electrolyte.

The resistance of the sensor in fig. 1a increases from 30 to 55 Ohm as the electrolyte carbonizes from KOH to KOH + K_2CO_3. The sensor signal and the duration of the transient process of its stabilization do not change at the same time. The duration of the transient process grows only after the sensor is stored without generating an oxygen reduction current (when the electrodes are disconnected from the resistor 8 Fig. 1a) for several weeks. The duration of the transient process doubles after 2 months. Visual inspection of the working electrode surface showed the presence of small crystals of salts. Qualitative analysis of salts showed the main components - potassium and carbonate. That is, the crystals should consist of $KHCO_3$.

It is known that cathodic processes cause an increase in the pore filling of the electrolyte solution in porous electrodes due to electroosmosis. This phenomenon can be used to dissolve excess salts from the surface of the working electrode. To do this, it is necessary to periodically increase and decrease the current on the working electrode causing periodic renewal of the solution in the pores and the visible surface of the electrode. To conduct electrolysis of water on the sensor electrodes as in an electrolytic bath is inappropriate for this, since the electrolyte solution will irreversibly lose water. It is advisable to use an increase and decrease in the cathodic oxygen reduction current. Additional oxygen is proposed to be pumped to the working electrode through the hole 3 (Fig. 1) by a convective method. To do this, the sensor was placed in a 5 dm^3 elastic cylinder, which was sealed and connected to a differential pressure gauge to monitor the differential pressure. When the balloon was compressed for 5 seconds, the pressure increased by 50 mm of the water column. The removal of the mechanical load returned the pressure in the cylinder to atmospheric level. The sensor signal in this case changed in a jump from 40 µA steady-state value to almost 1 mA for 10 seconds, after which the current dropped almost to zero. After 15 minutes, the current returned to the previous value.

The procedure for dissolving potassium hydrogen carbonate crystals on the working electrode was checked after the transient process had increased from 20 seconds to 100 seconds for the sensor as a result of carbonation for 3 months. The sensor was pressurized in a sealed container for 10 seconds, followed by relaxation at atmospheric pressure for 1 minute. Cyclic treatment was carried out for an hour with a break for 15 minutes eight times during the working day. After that, the sensor was left for 20 hours connected to the resistor 8 Fig. 1. The next day tests showed the duration of the transient process of 30 seconds, which is a good result of restoring the properties of the sensor.

The three-electrode sensor shown in Fig. 1b, generates a current signal of 40 μA equal to the signal of a two-electrode sensor if an identical diffusion resistance 2 is used. However, the background signal of the three-electrode sensor was ~5 μA with the background signal of the two-electrode sensor 0.2 μA. The increased background current of the three-electrode cell consists mainly of the error of the potentiostat ~4 μA (determined on an equivalent circuit). The last 1 μA should include, among other things, the current of cathodic reduction of oxygen formed on the auxiliary electrode 6 and diffuses to the working electrode 4 through two separators 5 and a reference electrode 7 (Fig. 1b). It can be argued that the use of well-regulated electronic devices will reduce the background current of the three-electrode sensor to ~1 μA. Oxygen sensors are most often used to signal the decrease in oxygen concentration from 21 vol% to 15 vol.% (1 level of signaling) and 9 vol.% (2 signaling level). With a signal of 40 μA in the ambient air, the sensor has a relative additive signaling error at level 1

$$1 \mu A \cdot 21 vol.\% \cdot 100\% / (41 \mu A \cdot 15 vol.\%) \approx 4\% . \qquad (5)$$

Signaling at level 2 has a relative additive error

$$1 \mu A \cdot 21 vol.\% \cdot 100\% / (41 \mu A \cdot 9 vol.\%) \approx 6\% . \qquad (6)$$

The measurement error of the three-electrode sensor is permissible.

Tests of resistance to carbonization of a three-electrode sensor were carried out on two cells for 6 months. The first cell had an auxiliary platinum electrode 0.1 mm in diameter and 10 mm in length (area ~0.03 cm^2). The second cell had an auxiliary electrode made of platinum black with a diameter of 15 mm (a geometric surface of 1.8 cm^2, the true surface in several orders of magnitude higher). The cells were polarized by single-channel potentiostats devices without displacement of the working electrode potential relatively to the lead reference electrode for 8 hours 5 days a week. Power-off of the potentiostats unlink the sensor electrodes.

The cell resistance was 30 Ohm at the beginning of the experiment. In three weeks, the resistance of the first cell increased to 50 Ohm and during the next 5 months it slowly grew to 60 Ohm. The duration of the transient process was 25±5 seconds. The resistance of the second cell increased to 100 Ohm for 3 months, as a result of which the duration of the transient process increased to 120 seconds. For 6 months of the experiment the cell resistance increased to ~150 Ohm, and the duration of the transient process was ~600 sec. Experiments have shown that the release of oxygen on the auxiliary electrode with increased current density contributes to the removal of CO_2 from the electrolyte. The true current density at the auxiliary electrode is difficult to determine, since only part of the wire surface adjacent to the separator operates. Part of

the platinum surface is periodically overlapped by the gas phase, which is formed on the electrode.

The three-electrode sensor based on Clarke element with alkaline electrolyte has a potential difference between the working and auxiliary electrodes by ~300 mV less than the exact same sensor impregnated with sulfuric acid solution. This phenomenon is known from the processes of hydrogen production by the electrochemical method and is explained by the adsorption of sulfate anions on the anode. The effect of this adsorption predominates in the effect of reducing the electrical conductivity upon transition from sulfuric acid to the alkali solution and contributes to a reduction in the supply voltage on the three-electrode sensor. Therefore, a three-electrode sensor based on an alkaline electrolyte consumes less electricity, which extends the use of portable gas analyzers.

Conclusions

Thermodynamic calculations show and experiments confirm the absence of complete carbonization of the alkaline electrolyte of the oxygen sensor in the presence of metallic lead in the electrochemical system. The reason is the primary anodic oxidation of lead to lead carbonate. The sensor reaches a steady state, at which the ratio of KOH concentration and K_2CO_3 concentration at pH 13.1 is constant.

A three-electrode sensor based on 30% KOH with a lead reference electrode maintains a constant electrolyte composition if oxygen is released at a high current density on a platinum auxiliary electrode. Then the pH of the solution at the anode decreases, which contributes to the removal of carbon dioxide together with oxygen.

Crystallization of $KHCO_3$ on the visible surface of the working electrode reduces its effective surface area and leads to a deceleration of the transients and sensor failure. Eliminate this phenomenon by pulsed polarization of the cathode with periodic injection of air into the sensor under pressure (10 sec pressure and 1 min. Relaxation for 8 h).

In general, the use of oxygen sensors based on an alkaline solution of 30% KOH makes it possible to reduce energy consumption in comparison with sulfuric acid based sensors, contributing to the creation of portable gas analyzers.

References

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