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EXTENDING THE RANGE OF AMPEROMETRIC SENSORS

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Received: December 17, 2013 / Revised: January 12, 2014 / Accepted: April 02, 2014

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Abstract. It was experimentally and theoretically shown that the upper range limit of a chlorine sensor is limited by the component of chlorine mass transfer in the liquid phase of the electrolyte solution. To extend the range, it was proposed to enhance absorption of chlorine by the electrolyte through increasing its pH.

Keywords: chlorine sensor, amperometric type, measurement range, upper limit, electrolyte pH.

1. Introduction

Amperometric-type electrochemical gas sensors are widely used in gas analysers for monitoring the atmosphere within an area due to their high resolution, selectivity, precision (reproducibility), stability in time, functional simplicity and low energy consumption. The current signal within the range of amperometric sensors (AS) is described by the equation [1]:

$$I = K \cdot C + I_0 \quad (1)$$

where K is the conversion efficiency, C is the concentration of the target component of gas mixture, I_0 is the ground current (the signal at zero concentration of the target component).

The range is limited by the minimum (C_{\min}) and maximum (C_{\max}) concentrations reliably determined by AS. The maximum concentration is determined from the linear range of nominal statistical characteristic, where the conversion efficiency is constant (Fig. 1).

The problems of decreasing the lower range limit at the expense of increasing the conversion efficiency or decreasing the ground current have already been dealt with in Ukraine [2] as well as in other countries [3]. However, the problem of increasing the upper range limit without deliberately decreasing the conversion efficiency but through introducing additional diffusion barriers to the sensor's design has not been considered yet.

The limitation in the upper range limit of an amperometric sensor in Fig. 1 is due to the decreased

conversion efficiency in Eq. (1). Studies of factors determining the conversion efficiency [1, 3] show that the decrease in K is connected with the increased total reduced diffusion resistance R , which is the reciprocal value of the conversion efficiency K :

$$R = \frac{1}{K} = R_k + R_d + R_e \quad (2)$$

where the components of the reduced diffusion resistance have the following physical meaning: R_k is the convective mass-transfer resistance of the target component in the gas phase outside the sensor; R_d is the diffusion resistance in the gas phase inside the porous diaphragm (diffusion barrier) as a design element of the sensors; R_e is the reduced diffusion resistance of the sensing electrode.

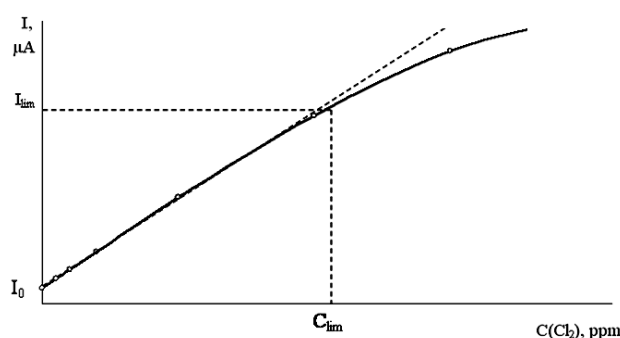


Fig. 1. Nominal statistical characteristic of amperometric sensors

Consequently, to extend the range at the expense of increasing its upper limit, the secondary component contributing to the total reduced diffusion resistance should be determined in conducting measurements within the linear range shown in Fig. 1, the primary one being the diffusion in the gas phase. This component will take up the first place in terms of the value at exceeding the upper range limit for the current signal I_{\lim} (Fig. 1).

Only the components of the total reduced diffusion resistance which will increase with the increase in the target

component concentration will cause a decrease in the conversion efficiency. Since the convective mass-transfer resistance of the target component in the gas phase outside the sensor R_k and the diffusion barrier resistance of the sensor R_d do not depend on the concentration of the target component, the causes of the decrease in the conversion efficiency should be sought in the reduced diffusion resistance of sensing electrode R_e .

A gas-diffusion sensing electrode is most commonly a solid current-conducting porous matrix soaked with electrolyte solution. The diffusion in the electrolyte solution being slowed down is indicated by an increased temperature coefficient for the sensor current signal, as diffusion activation energy in the liquid phase is by an order of magnitude higher than that for the gas phase. There is a possibility of lifting restrictions from the diffusion in the liquid phase by increasing the pH of the electrolyte due to the increased solubility of chlorine resulting from its disproportionation.

2. Experimental

The experiment was carried out using the chlorine sensors of the unified NTUU "KPI" series, which are characterized by $I_g = 0.02\text{--}0.05 \mu\text{A}$, and $K = (3 \pm 0.1) \mu\text{A} \cdot \text{mg}^{-1} \cdot \text{m}^3$. In long-duration operation of the chlorine sensor a linear dependence of current signal on chlorine concentration is observed at concentrations up to $C_{\text{max}} \leq 25 \text{ mg} \cdot \text{m}^{-3}$.

Dosing of the air-chlorine mixture was conducted with a coulometric doser [5], which regulated both the concentration of chlorine and the consumption of the mixture carried to an adapter and thermostat.

To study the effect of temperature on the performance of the chlorine gas sensors, a unit shown in Fig. 2 was used. The sensor under study (1) was connected to a potentiometer with a digital-analog converter (2) and placed in a tight vessel (3), where the temperature was controlled with the help of a water thermostat (8) with a heater (7). The temperature of the gas mixture in the vessel was read on a thermometer (6). The reference air-gas mixture with a set concentration of chlorine was produced with a generator consisting of a microcompressor (9), a manostat (10), a varying differential pressure flow-meter (11), a coulometric doser (12), a direct current source (14) and a milliammeter (13). The air-gas mixture was carried to and out of the vessel through glass tubes (4). To prevent the air from getting to the vessel, a water seal (5) was used. A three-way valve (15) redirects the gas mixture to the sensor, which is in a vessel with another temperature inside it.

The studies were carried out at temperatures of 293 ± 0.5 and 313 ± 2 K. At the given flow rates of the

gas mixture from the coulometric doser and chlorine concentrations the error in reproduction of current signals did not exceed $\pm 1\%$, with other conditions being equal.

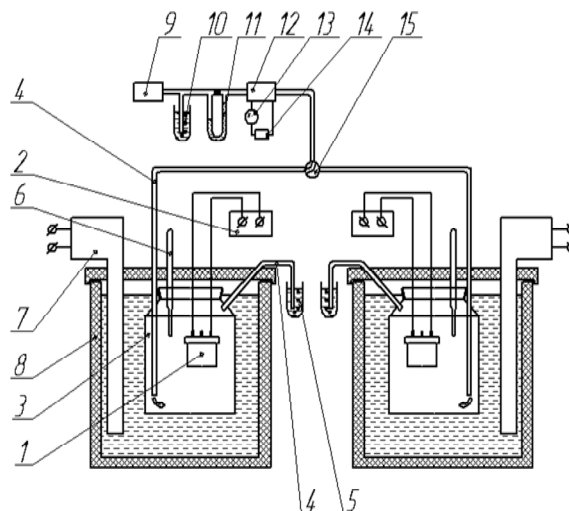


Fig. 2. Diagram of the experimental unit for studying the effect of temperature on the upper range limit: sensor (1); potentiometer (2); tight vessel (3); glass tubes (4); water seal (5); thermometer (6); electric heater (7); thermostat (8); gas compressor (9); manostat (10); manometer (11); coulometric chlorine doser (12); milliammeter (13); direct current source (14) and three-way valve (15)

The effect of pH electrolyte on the kinetics of chlorine reduction at a titanium electrode was investigated in a three-electrode cell with a LiCl-based electrolyte solution to which sodium hypochlorite was added. The sensing and auxiliary electrodes were made of compact titanium. A silver-chloride electrode was used as a reference one. Electrolyte pH was controlled with a pH-meter having a glass electrode. pH was changed by adding sodium hydroxide and hydrochloric acid solutions.

3. Results and Discussion

It is proposed in this work to split the reduced diffusion resistance of the sensing electrode into two components: the resistance of the target component to absorption by the electrolyte solution and following diffusion through the liquid phase layer R_L , and the resistance to the electrochemical reaction occurring at the sensing electrode, which is, as a matter of fact, polarization resistance R_p :

$$R_e = R_L + R_p \quad (3)$$

Theoretically, each of the above components of the reduced diffusion resistance of sensing electrode can change with increasing the concentration of the target component and therefore the current signal. However, the

change in R_p can be ignored, because the sensor generating a signal of about 10 μA at total resistance of the circuit of up to 100 Ohm results in polarization of the sensing electrode within 1 mV, which provides its stability according to the concept of polarization resistance [7]. Consequently, the changes occur in the R_L component in Eq. (3).

A number of experiments were carried out to determine the nominal statistical characteristic of the gas sensors at different temperatures. The results given in Fig. 3 show that within the linear dependence of current signal on concentration the increase in temperature from 293 to 313 K speeds up the current-producing process with a temperature coefficient of less than 0.5 % signal per 1 K. At signals exceeding the upper linearity limit at 293 K the temperature coefficient increases as the magnitude of current produced by the sensor is stepped

up. After the signals exceeding the upper linearity limit at 313 K the temperature coefficient reaches 5 % signal per 1 K.

According to the literature on kinetics of electrochemical reactions [8, 9], such temperature coefficients definitely point to the slowed-down diffusion in gas within the linear range of nominal statistical characteristic and a gradual growth of diffusion control in the liquid phase on reaching the upper linearity limit. At currents higher than those at which the temperature coefficient reaches 5 % signal per 1 K the current-producing process is controlled by chlorine diffusion through the film of the electrolyte in its meniscus zone in the sensing electrode pore. A somewhat extended linear range with increasing temperature in Fig. 3 is due to a greater effect of temperature on the diffusion coefficient in the liquid phase than that for the gas phase.

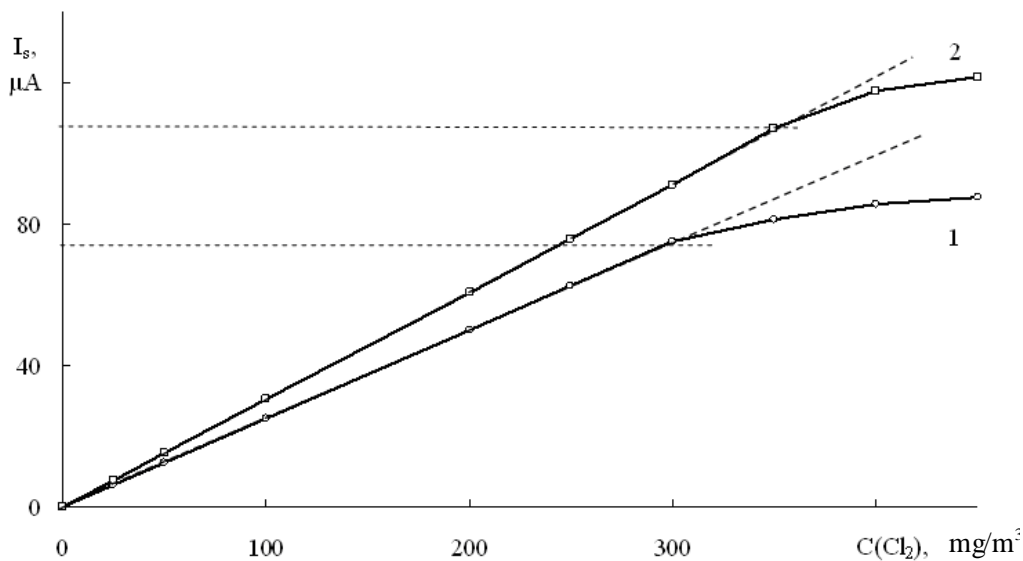
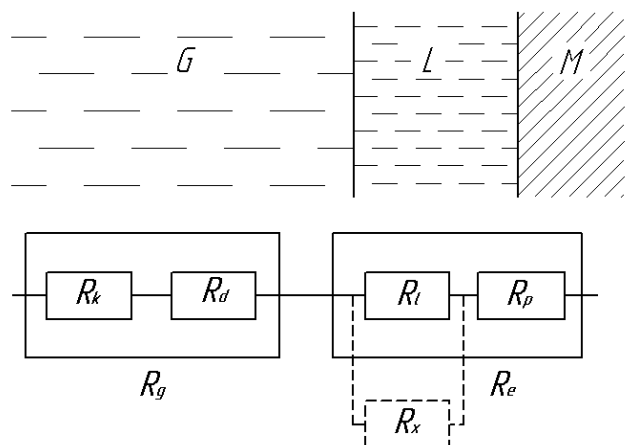


Fig. 3. Nominal statistical characteristic of chlorine sensors at different temperatures, K: 293 (1) and 313 (2)

Fig. 4. A scheme of total reduced diffusion resistance for the chlorine sensor: G – gas phase; L – electrolyte solution; M – electrode. Reduced resistances to the current-producing process: R_g – resistance in the gas phase; R_k – convective mass-transfer resistance outside the sensor; R_d – resistance in the diffusion barrier as a design element; R_L – diffusion resistance in the liquid phase; R_x – resistance of independent mechanism of the chlorine transport through the electrolyte; R_e – total resistance of the sensing electrode; R_p – polarization resistance of the electrochemical reaction at the “solid electrode-electrolyte” interface



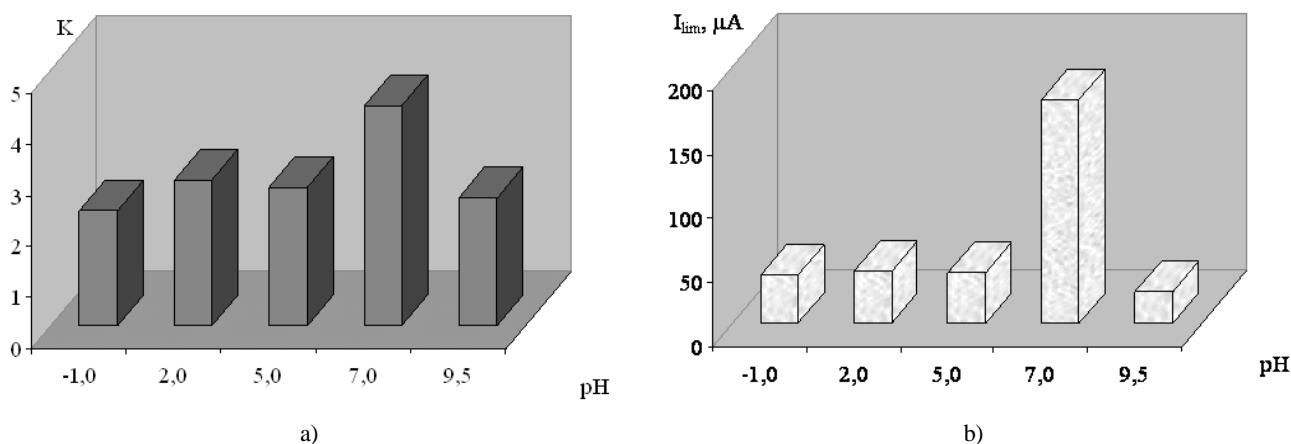
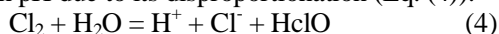


Fig. 5. Conversion efficiency (a) and the upper linearity limit of nominal statistical characteristic (b) vs. pH of electrolyte based on 6 m LiCl for the chlorine sensor

In terms of the results given in Fig. 3 and considering Eqs. (2) and (3) as an electric circuit of resistors connected in series (Fig. 4), the following way of increasing the upper range limit can be proposed. A parallel resistor of additional independent mechanism of the chlorine transport through the solution R_X , can be connected to the resistor of transport through the liquid phase R_L .

It is known that chlorine solubility in electrolytes increases with pH due to its disproportionation (Eq. (4)):



The increasing of pH shifts the equilibrium to the right and increases the content of oxidizing agents in soluble form. Hypochlorite ions exhibit greater solubility than molecular chlorine and are capable of diffusing independently through the film of electrolyte solution to the surface of the solid phase of the electrode, which provides implementation of the scheme in Fig. 4 with additional chlorine transport through the solution.

Tests of the chlorine sensors soaked with electrolytes having different pH showed that an increase in pH from pH 1 to pH 7 is accompanied by a considerable increase in both the conversion efficiency within the linear range of nominal statistical characteristic (Fig. 5a) and the upper range limit (Fig. 5b). However, a further increase in pH makes them drop sharply.

To find out the causes of the decrease in K and the upper range limit within the linear range of nominal statistical characteristic, the cathode reduction of sodium hypochlorite added to the supporting solution of lithium chloride on the surface of polished titanium foil according to a three-electrode scheme was studied. It follows from the results presented in Fig. 6 that at $\text{pH} > 7$ the rate of hypochlorite cathode reduction decreases dramatically, with the potential being unchanged. This correlates with stabilization of the hypochlorite and its decreasing reverse disproportionation to chlorine. Consequently, it is not

hypochlorite itself that is reduced at the solid phase of the electrode, but chlorine made in this disproportionation. Thus, the decrease in K in Fig. 5a at $\text{pH} > 7$ is due to the stabilization of hypochlorite and the absence of the final stage in the independent chlorine transport, namely a shift in the hypochlorite-chlorine equilibrium towards chlorine formation at the electrode-electrolyte interface. With increasing pH up to more than pH 9 the current-producing process is slowed down by almost complete conversion of chlorine into hypochlorite (Fig. 6).

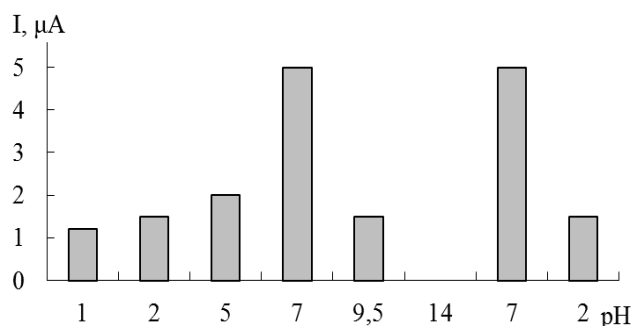


Fig. 6. The rate of chlorine reduction vs pH of electrolyte (pH values are displayed along the category axis from the left to the right in the chronological order of their change during the experiment)

Thus, a new method was proposed and implemented for increasing the upper range limit of AS. The method is based on overcoming the diffusion limitations in the electrolyte solution by using an additional mechanism of the target component transport from the gas-electrolyte interface to the solution-solid phase interface, which is realized through the chemical conversion of the target component due to its interaction with the solvent.

4. Conclusions

It has been established in this paper that the slowed down transport of the target component through the film of the electrolyte solution on the sensing electrode is responsible for the departure of nominal statistical characteristic in chlorine AS on reaching a certain current signal upper limit.

A method has been proposed for increasing the upper range limit and therefore extending AS range. The method does not imply decreasing the conversion efficiency and increasing the lower range limit of the sensor due to introduction of additional diffusion barriers in the sensor design, but is realized by using additional independent transport of the target component through the film of the solution due to its increased solubility.

Our findings show that the range of the chlorine sensor can be extended by increasing pH up to pH 7 owing to additional chlorine transport in the form of hypochlorite.

It has been determined that hypochlorite cannot be reduced on a titanium sensing electrode directly, but only after its reverse disproportionation to chlorine, due to which increasing pH up to more than pH 7 causes the cathode reduction to slow-down and to terminate.

Presumably, the implementation of this method for increasing the conversion efficiency K , and the upper range limit will require special attention to buffering pH of the electrolyte.

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РОЗШИРЕННЯ ДІАПАЗОНУ ВИМІРЮВАНЬ АМПЕРОМЕТРИЧНИХ СЕНСОРІВ

Анотація. Приведено теоретичні та експериментальні докази, що верхня межа діапазону вимірювань сенсора хлору обмежується складовою масопереносу хлору в рідкій фазі електроліту. Для розширення діапазону вимірювань запропоновано збільшити абсорбцію хлору електролітом внаслідок підвищення його рН.

Ключові слова: сенсор хлору, амперметричний тип, діапазон вимірювань, верхня межа, рН електроліту.

